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THE EFFECT OF SURFACTANTS ON HEAT AND MASS TRANSFER

TO WATER DROPS IN AIR

by

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Abstract

The temperatures and evaporation rates of surfactant-contaminated droplets were determined under controlled conditions. The surfactants used were sodium stearate, sodium palmitate, sodium myristate and sodium laurate. The drops were suspended on fine glass fibres or thermocouples in an environmental cell maintained at known temperature and humidity, and the evaporation rate was determined by optical measurement of the change of diameter with time.

The results showed an early evaporation following a "clean" model, with a relatively sharp transition to a regime of "contaminated" evaporation kinetics. Simultaneous measurements of temperature and evaporation rate showed that the contaminants had no effect on heat transfer, i.e. their effect was limited to forming an additional mass transfer resistance. This mass transfer resistance increased strongly with initial surfactant concentration. Surfactants with longer carbon chains produced higher resistances, but after a longer delay.

The partial differential equations describing surfactant diffusion within an evaporating drop were set up and solved, and an approximate analytical solution was shown to agree well with a numerical solution. By assuming that the surfactants retarded evaporation at the drop surface both by presenting a diffusional resistance to water transport and by vapour pressure lowering, a model was constructed to predict the evaporation behaviour of contaminated drops. It predicted the results obtained with sodium stearate well, but was unable to explain the results for shorter chain surfactants which were complicated by their adsorption behaviour at the surfactant-water interface.

This model of single drop evaporation was extended to describe the evaporation of contaminated aerosols and used in an attempt to explain the measurements of Raper et al. (1982). Their results could not be explained quantitatively by a surfactant contaminant (though a surfactant would have produced similar qualitative features) and were probably caused by experimental error.

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Nomenclature

A	Henry's law constant for the surfactant film.	-
a	Internal radius of spherical shell shaped region.	m
B	Dimensionless fibre length.	-
b	External radius of spherical shell shaped region.	m
C	Concentration of surfactant in water.	kg m ⁻³
C ₀	Concentration of surfactant at time zero.	kg m ⁻³
C _p	Specific heat.	J kg ⁻¹ K ⁻¹
C _R	Concentration of surfactant on the water side of the solution/film interface.	kg m ⁻³
C _ζ	Concentration of surfactant at the surface of a drop.	kg m ⁻³
D	1) Drop diameter;	m
	2) Diffusivity of surfactant in water.	m ² s ⁻¹
D ₀	1) Initial drop diameter;	m
	2) Diffusivity of surfactant at infinite dilution.	m ² s ⁻¹
D ₁	Diffusivity of surfactant in region 1.	m ² s ⁻¹
D ₂	Diffusivity of water in the surfactant film (region 2).	m ² s ⁻¹
D _g	Diffusivity of water vapour in air.	m ² s ⁻¹
D _ζ	Surfactant diffusivity at the surface of a drop.	m ² s ⁻¹
F	1) Actual drop evaporation rate divided by the rate for a single isolated drop in an infinite medium;	-
	2) $2(n^2+n+2) / (n+1)/n+2)/(n+3)$.	-
f	Dimensionless diffusivity of surfactant in water = D/D_0 .	-
g	Acceleration due to gravity.	m s ⁻²
h	Heat transfer coefficient.	W m ⁻² K ⁻¹
K ₅	Arbitrary constant.	s m ⁻²
K ₆	" "	m s
K _F	Dimensionless fibre conductivity = k_f/k_g .	-
k _B	Boltzmann's constant.	J K ⁻¹
k _C	Mass transfer coefficient.	m s ⁻¹
k _f	Thermal conductivity of a drop support (fibre).	W m ⁻¹ K ⁻¹
k _g	Thermal conductivity of air.	W m ⁻¹ K ⁻¹
M	Dimensionless coordinate based on equal quantities of solute ($dM = 3 U \rho^2 d\rho$).	-
N	Number of intervals in finite difference grid.	-
n	Index used in (H6).	-
Q _{cond}	Heat flow through the surrounding gas to an evaporating drop by conduction.	W

$Q_{\text{cond+conv}}$	Heat flow through the surrounding gas to an evaporating drop by conduction and convection.	W
Q_{fib}	Heat flow by conduction along the fibre supporting a drop.	W
Q_r	Ratio of the heat flow by conduction along a drop support to that conducted by the air.	—
Q_{rad}	Rate of heat transfer by radiation to an evaporating drop	W
q_i	Magnitude of image charge i .	C
R	1) Drop radius; 2) Monolayer evaporation resistance.	m s m^{-1}
R_0	1) Initial drop radius; 2) Radius of solute molecule.	m
r	Radial coordinate.	m
r_f	Radius of a drop support (fibre).	m
S	Dimensionless surfactant concentration at the drop surface = C_L/C_0 ;	—
T	Temperature.	K
T_0	Air temperature at the drop surface.	K
T_∞	Air temperature at an infinite distance from the drop.	K
T_f	Temperature at a point along a drop support (fibre).	K
T_y	Air temperature at a distance y from a drop support.	K
t	Time.	s
t_j	Time at finite difference level j .	—
U	Dimensionless surfactant concentration = C/C_0 .	—
$U_{i,j}$	U at finite difference grid point X_i and time level t_j .	—
$\hat{U}_{i,j}$	Average of $U_{i,j}$ over time levels $j-1$, j and $j+1$.	—
V	Electrical potential.	V
v	1) Root mean square velocity of gas molecules; 2) Drop terminal velocity.	m s^{-1} m s^{-1}
W_R	Water concentration in the surfactant film at radius R .	kg m^{-3}
$W_{R+\delta}$	Water concentration in the surfactant film at radius $R+\delta$.	kg m^{-3}
X	Dimensionless x coordinate = x/R .	—
X_f	Dimensionless fibre radius = r_f/R .	—
X_i	X at finite difference grid point i .	—
x	X coordinate.	m
Y	Dimensionless y coordinate = y/R .	—
y	Y coordinate.	m
Z	Dimensionless radial coordinate = r/R .	—
z	The fraction of a drop's surface covered by surfactant.	—

Greek symbols

α	1) Evaporation coefficient;	-
	2) Empirical constant = 6.1043.	-
α_m	Evaporation coefficient of a monolayer-covered surface.	-
α_w	Evaporation coefficient of a clean water surface.	-
β	Empirical constant = 2.8385.	-
Δt	Spacing between finite difference time levels = $t_{j+1} - t_j$.	-
ΔX	Spacing between finite difference grid points = $X_{i+1} - X_i$.	-
δ	Surfactant film thickness.	m
ϵ	1) Emissivity;	-
	2) Dimensionless x coordinate of drop centre.	-
ϵ_i	Dimensionless x coordinate of charge image i.	-
Γ	Mass of surfactant in the surface film.	kg
λ	Latent heat of evaporation.	J kg ⁻¹
μ	Viscosity.	N s m ⁻²
ρ	1) Water vapour concentration;	kg m ⁻³
	2) Dimensionless radial coordinate = r/R_0	-
ρ_f	Density of the surfactant film.	kg m ⁻³
ρ_g	Air density.	kg m ⁻³
ρ_l	Density of liquid water.	kg m ⁻³
ρ_o	Water vapour concentration in the air next to the surface of a pure water drop.	kg m ⁻³
$\rho_{R+\delta}$	Water vapour concentration in equilibrium with the outer surface of the surfactant film.	kg m ⁻³
ρ_∞	Water vapour concentration a large distance from a drop.	kg m ⁻³
θ	Dimensionless time = $(R_0/R)^3 - 1$.	-
τ	Dimensionless fibre temperature = $(T_f - T_\infty)/(T_0 - T_\infty)$.	-
τ_i	Dimensionless fibre temperature at X_i	-
σ	Stefan-Boltzmann constant = 5.67×10^{-8} .	W m ⁻² K ⁻⁴
Φ	Arbitrary function of X , t , U and $\partial U/\partial X$.	-
ϕ	The value of Φ at the grid point X_i, t_j .	-
Ψ	Arbitrary function of X , t , U and $\partial U/\partial X$.	-
ψ	The value of Ψ at the grid point X_i, t_j .	-
ω	$X_f^2 K_f \ln(Y/X_f) / 2 \Delta X^2$.	-
ω^+	The value of Ω at a point midway between X_{i+1} and X_i .	-
ω^-	The value of Ω at a point midway between X_i and X_{i-1} .	-
Ω	Arbitrary function of X , t and U .	-

Dimensionless numbers

Fo	Fourier number = $D_o t / R_o^2$
Gr	Grashof number = $D^3 g (\rho_o - \rho_w) \rho_g / \mu^2$
N _D	Best number = $4 D^3 g (\rho_l - \rho_g) \rho_g / 3 \mu^2$
Nu	Nusselt number = $h D / k_g$
Pe	Peclet number = $-\frac{R}{D_o} \frac{dR}{dt}$
Pr	Prandtl number = $C_p \mu / k_g$
Re	Reynolds number = $\rho_g v D / \mu$
Sc	Schmidt number = $\mu / \rho_g D_g$
Sh	Sherwood number = $k_c D / D_g$

Subscripts

o	1) At time zero; 2) At the drop surface; 3) At infinite dilution.
1	In region 1.
2	In region 2.
∞	At an infinite distance from the drop surface.
cond	Conduction.
cond+conv	Conduction and convection.
f, fib	Fibre.
g	Gas.
i	1) Image number; 2) Finite difference grid point.
l	Liquid.
m	Monolayer.
R	At radius R.
r	Dimensionless ratio.
rad	Radiation.
R ⁻	At a radius infinitesimally below R.
R+ δ	At radius R+ δ .
w	Water.
ζ	At the surface of a drop.

1 INTRODUCTION

1.1 Background

This thesis is concerned with the evaporation of contaminated aerosols. It was inspired by the work of Raper et al. (1982) at AERE Harwell who examined the evaporation of polydisperse aqueous aerosols. They measured the drop size distribution of an aerosol at various positions down a horizontal wind tunnel and then attempted to predict the size distribution from theory. Their simulation was based on the evaporation of single pure water drops which is well understood (see Section 2.1), and follows Maxwell's (1890) equation:

$$-\rho_l \frac{dD}{dt} = \frac{4 D_g (\rho_o - \rho_\infty)}{D}$$

(all symbols are defined in the nomenclature Section on page V). As the evaporation rate is inversely proportional to the drop diameter, small drops evaporate much faster than large drops. Accordingly, if an aerosol, initially containing drops with a wide range of diameters, is allowed to evaporate over a period of time, the small drops should rapidly evaporate to extinction while the large drops change little in size, consequently, the range of the drop size distribution should narrow as the number of small drops decreases. Experiment showed that the number of small drops actually rose over time.

The aerosol in these experiments was formed by atomising water of 'Analar' grade purity. The observed size distributions could therefore only be explained by a contaminant which was capable of retarding water evaporation when present in trace quantities. Since it is well known that small quantities of surface active agents (surfactants) can greatly reduce evaporation from plane surfaces (see Section 2.1), it was hypothesised that a surfactant was responsible for the size distributions observed. In order to test this theory, a sample of the water used to generate the aerosols was evaporated until its volume had been reduced by a factor of eight. Its surface tension was found to have nearly halved, confirming the presence of trace quantities of a surfactant. Since the water containers and much of the equipment used were plastic, and the distilled water used was in contact with it for long periods of time, it was hypothesised that

plasticiser was being leached out of the equipment walls so that when the aerosol evaporated this collected at the drop surface and hindered evaporation.

1.2 Objective

The objective of this thesis was to construct a model to describe the evaporation of a contaminated aerosol, and compare its predictions with the measurements obtained from the wet wind tunnel at AERE Harwell. To do this it was first necessary to study the influence of surfactants on the evaporation of single water drops.

Since the available literature on the evaporation of contaminated drops was very confused (see Section 2.3.1) and the extensive literature on the effect of surfactants on evaporation from plane surfaces was inapplicable (see Section 2.1), experimental work had to be performed to remedy these deficiencies. Experiments were performed with single water drops contaminated with known concentrations of a series of representative surfactants to determine the dependence of the heat and mass transfer resistances on experimental conditions. The relevant experimental conditions were obviously those which determine the evaporation of pure water drops (air temperature and relative humidity) and the surfactant type and concentration.

In a freshly formed drop, any surfactant present will be uniformly distributed throughout the drop. However surfactants, by their nature, have a strong tendency to adsorb at air-water interfaces and so a layer of surfactant will soon form at the drop surface. As the drop evaporates, the drop surface will recede, surfactant will start to accumulate at the surface and a concentration profile will build up as the accumulation is compensated for by surfactant molecules diffusing back into the drop bulk. So modelling the evaporation of contaminated drops requires some understanding of both the relationship between evaporation rate and the concentration of surfactant at the drop surface and also the diffusion of surfactant within the drop as evaporation proceeds.

Studying the effect of surfactants on drops rather than plane surfaces has advantages in that a drop-based system has fewer contamination problems, has simple boundary conditions and avoids some of the problems caused by convection currents which complicate work with plane surfaces.

1.3 Applications

The primary application of the work in this thesis is in the design of demisting systems for removing contaminated aerosols from gas streams.

The majority of workers who have investigated the effects of surfactants on the evaporation of water drops have been interested in modifying the properties of fogs. Interest, which began in earnest in the early sixties, has centered on two main applications.

The first concerns the dispersal of natural fogs whose economic costs in such effects as disruption to and accidents in transport systems are so large that any method of dispersing them, or even simply improving visibility, is obviously of considerable interest. The basic idea was to treat part of the fog with surfactant, thereby permitting some of the fog drops to grow at the expense of the others. In time the growing drops would become large enough to settle out under gravity, and so improve visibility. It was also thought that drops contaminated by surfactants, having a lower surface tension than that of pure water drops, would coalesce with other drops more easily, grow in size, settle out and again improve visibility. Unfortunately, despite considerable effort and interest (Elton, 1953; Pilpel, 1953; Jiusto, 1964; Prihot'ko, 1964; Pilie, 1966; Gernet et al., 1966; Bakhanova et al., 1969; Kocmond et al., 1972; Marchetti, 1972) the method has not yet been shown to work any better than seeding the fog with hygroscopic solutions of salts such as NaCl.

By contrast, the second application is concerned with generating long-lasting fogs. This is feasible as a mono-disperse aerosol is stable if all the drops have been treated with an equal quantity of surfactant. The ability to generate a durable screening fog is

obviously of considerable interest both to the military and for the protection of crops against frost. In world war II oil fogs were used for screening purposes (Dellicolli, 1973). However, because the quantity of surfactant needed to retard water evaporation is very small, and water is readily available in most places, surfactants enjoy a tremendous logistical advantage. They are also very much safer to generate and cause much less environmental damage. The same advantages also apply with regard to crop protection, and patents have been taken out on the idea (Mihara, 1967).

2 LITERATURE REVIEW

2.1 Introduction

Before examining the literature on the effect of surfactants on drop evaporation, it is first necessary to consider two closely related subjects - the evaporation of pure liquid drops and the effect of surfactants on the evaporation of water from plane surfaces.

The evaporation of pure liquid drops has been investigated by many workers both experimentally and theoretically and is well reviewed by Fuchs (1959), Hidy et al. (1970) and Davis (1983). It is beyond the scope of this thesis to review the extensive literature on this subject in detail, but a select bibliography is given in Table 2.1.

The effect of surfactants on evaporation from plane surfaces has received considerable attention, the primary aim being to reduce the rate of water loss from reservoirs. The subject has been reviewed by La Mer (1962), and a select bibliography is given in Table 2.2. Unfortunately the above work was primarily concerned with monolayers - single layers of surfactant molecules - while the geometry of an evaporating drop ensures that any monolayer formed would soon be crumpled by the shrinking of the drop surface and form a steadily thickening multilayer. Furthermore, the work on reservoirs used insoluble surfactants (since a long lasting film was desired) while, in looking at drop evaporation, it is necessary to look at soluble surfactants because the surfactant is initially uniformly dispersed throughout the drop. As a result, the work performed on plane surfaces is of little help in predicting the effect of surfactants on drop evaporation.

Attempts to predict the effects of surfactants on evaporation from first principles (Barnes et al., 1970; Barnes and Quickenden, 1971; Quickenden and Barnes, 1978; Blank, 1964, 1979; Dickinson, 1978) have so far had only limited success.

Table 2.1 Work on the evaporation of pure liquid drops

Sreznevskii (1882)	Nuzhnyi and Shimanskii (1965)
Maxwell (1890)	Nuzhnyi et al. (1965)
Houghton (1933)	Todes et al. (1966)
Zak (1936a,b)	Ro et al. (1968)
Tverskaya (1949,1950,1951)	Kolesnik (1968,1969)
Johnson (1950)	Pikkov and Siirde (1972)
Ranz and Marshall (1952)	Reiter et al. (1972a,b)
Bradley (1955)	Chang and Davis (1974)
Hoffman and Gauvin (1960)	Rakhmatulina (1981)
Schluender (1964)	

Table 2.2 Work on the effect of surfactants on the evaporation of water from plane surfaces

Hedestrand (1924)	Blank and Mussellwhite (1968)
Rideal (1925)	Macritchie (1968,1969)
Glazov (1938,1939a,b)	Bingham (1970)
Sklyarenko and Baranaev (1938)	Chalenko et al. (1970)
Zolin (1939,1961)	Navon and Fenn (1971a,b)
Sebba and Briscoe (1940)	Wu (1971)
Sklyarenko et al. (1940,1944)	Mansfield et al. (1972)
Langmuir and Schaefer (1943)	Cammenga et al. (1975)
Mansfield (1953,1955)	Costin and Barnes (1975)
Archer and La Mer (1955)	Turner et al. (1975)
Rosano and La Mer (1956)	O'Brian et al. (1976)
La Mer et al. (1963,1964)	Reiser and Ruhoff (1978)
La Mer and Healy (1965)	Wolf et al. (1979)
Barnes (1968)	Barnes et al. (1980a,b)

The experimental techniques required to obtain the extreme purity needed for work with surfactants are well documented (Miles and Shedlovsky, 1944; Clayfield and Matthews, 1957; Harrold, 1960; Costin and Barnes, 1967; Rosen, 1982).

2.2 Theoretical work

Almost all attempts to model the effect of surfactants on the evaporation of water drops have been based on Maxwell's (1890) equation for pure liquid drops. This can be arranged in two forms:

$$\left. \begin{aligned} -\rho_l \frac{dD^2}{dt} &= 8 D_g (\rho_o - \rho_\infty) & (a) \\ -\rho_l \frac{dD}{dt} &= \frac{2 (\rho_o - \rho_\infty)}{(D/2D_g)} & (b) \end{aligned} \right\} \quad [2.1]$$

Since the right hand side of form (a) is almost independent of diameter (see Section 4.1), dD^2/dt should be a constant for any given set of experimental conditions, and a graph of diameter squared as a function of time should be a straight line. The simplest way of extending this equation to represent the evaporation of contaminated drops is to assume that the surfactant retards evaporation by reducing the vapour pressure of water at the drop surface by a constant factor and so reduces the driving force for evaporation. According to this model, then, a surfactant simply changes the gradient of a graph of diameter squared against time but not its shape.

By analogy with Ohm's law, form (b) can be regarded as being of the form $\text{RATE} = \text{DRIVING FORCE} / \text{RESISTANCE}$. So an obvious way to extend this equation to represent the evaporation of contaminated drops is to include one or more extra resistance terms in the denominator. The models developed so far have all been intended to apply to drops contaminated by a surface monolayer of insoluble surfactant. Under these conditions, the resistance due to the monolayer will be nearly independent of drop diameter and very much larger than the diffusional resistance of the surrounding air. As a result, the total resistance is only a weak function of diameter, dD/dt should be a constant, and a graph of diameter versus time should be a straight line. So models of this type predict a more fundamental change in the evaporation behaviour. More generally, if the resistance due to the monolayer arose

some time after the drop was formed, the drop would initially follow the Maxwell equation and a transition should be seen from $D^2\alpha t$ to $D\alpha t$.

Bradley (1955) developed equation [2.2] on the assumption that an insoluble monolayer of surfactant retarded evaporation by reducing the size of the evaporation coefficient α ; i.e. the monolayer made the surface more attractive to water molecules:

$$-\rho_l \frac{dD}{dt} = \frac{2(\rho_o - \rho_\infty)}{(D/2D_g + 4/\alpha v)} \quad [2.2]$$

Deryagin et al. (1960a, b, 1961) and Deryagin and Kurgin (1964) extended this model to produce equation [2.3], arguing that, in addition to Bradley's reduction in α , there was also a resistance due to water molecules having to penetrate the monolayer:

$$-\rho_l \frac{dD}{dt} = \frac{2(\rho_o - \rho_\infty)}{(D/2D_g + 4/\alpha v + R)} \quad [2.3]$$

Kachurin and Morachevskii (1965) reviewed the early experimental work on the retardation of drop evaporation by surfactants and considered three possible mechanisms:

- 1 A layer of surfactant molecules acts as an energetic barrier, reducing the value of α ;
- 2 The surface concentration of surfactant lowers the vapour pressure of water in accordance with Raoult's law;
- 3 The surface concentration of surfactant lowers the vapour pressure of water by more than would be expected from Raoult's law.

They concluded that the third mechanism was the most probable, although it could not explain all the experimental evidence examined. A number of workers have measured the vapour-pressure of water above surfactant solutions (Randall et al., 1926; Smith and Robinson, 1942; McBain and Lee, 1943; Brady et al. 1951a, b; Altsibeeva et al., 1963; Vachnadze, 1972). As might be expected, they all agree that Raoult's law does not apply. Unfortunately, testing this third mechanism experimentally requires a reliable estimate of the surfactant concentration at the surface of the drop, which is difficult to obtain.

Shih and Coughanowr (1968) considered a drop covered by an insoluble layer of surface-active impurity. As the drop evaporated the layer increased in thickness. By assuming that the only resistance to evaporation was to the diffusion of water through the surface film, they obtained the following implicit equation for diameter:

$$t = K_5(D_0^2 - D^2) + K_6\left(\frac{1}{D} - \frac{1}{D_0}\right) \quad [2.4]$$

Borzilov et al. (1979) pointed out that equations [2.1] and [2.3] required a discontinuous change in α to explain the sharp change in evaporation rate observed experimentally. They removed this discontinuity by assuming a linear relationship between α and the fraction of the drop surface covered by surfactant z :

$$-\rho_l \frac{dD}{dt} = \frac{2(\rho_o - \rho_\infty)}{(D/2D_g + 4/(\alpha_w(1-z) + \alpha_m z)v + R)} \quad [2.5]$$

To sum up then, most workers have tried to describe the effect of surfactants on drop evaporation by extending the Maxwell equation in some way and, depending on the assumptions made, their equations predict either $D^2 \propto t$ or $D \propto t$. In principle, it should be a simple matter to decide experimentally between these two possibilities, but in practice this can only be done if the drop evaporation has been followed over a sufficiently wide range of diameters, as the two forms look very similar over a narrow range. Unfortunately, as Section 2.3.1 will show, this ideal has hitherto been rarely attained in practice.

2.3 Experimental work

2.3.1 Effect of surfactants on mass transfer from drops

A sizeable amount of experimental work has been performed on this subject, covering a wide range of experimental conditions (see Table 2.3). Unfortunately many workers failed to give full experimental details of their work. Uncertainties arise largely from the difficulty of coating a drop with a precise quantity of an insoluble surfactant. This, and the diversity of experimental conditions used, mean that few of the results obtained are readily comparable. Because few workers have followed the evaporation of individual drops over a sufficiently wide range of diameters, there is no agreement on the exact form of the

Table 2.3. Experimental details of previous work.

Author & year	Surfactant		Air ^{1,2}		Drop size measurement	
	Chemical composition ³	Concentration	Temperature	Relative humidity	Range of diameters	Experimental technique
		ppm	C	%	μm	
Pleteneva & Rehinder (1946a, b, 1947)	p-cresol. Sodium oleate.	16,000 100- 1000	225- 500	?	2900- 5700	The evaporation time of a drop of surfactant solution of known volume when placed on a hot metal plate was noted.
Eisner et al. (1958, 1960)	A mixture of cetyl, stearyl & myristyl alcohols.	20- 80,000	28.3	30-100	10-100	The size distribution of an aerosol falling under gravity was determined using sampling slides.
Kiryukhin et al. (1963)	Trimethyl- β -oxyethyl ammonium chloride. Two alkyl benzyl-sulphonates.	100- 10,000	15- 20	90-95	60-350	The mass of a drop suspended on a 40 μm hair was measured using a quartz torsional microbalance and checked using photomicroscopy.
Jiusto (1964)	Cetyl & stearyl alcohol, stearic acid, Sodium tetra & hepta decyl sulphates. Nonyl phenyl polyethylene glycol ether.	? ⁴	20- 25	40	10-500	The diameters of drops suspended on glass, quartz and spider's web filaments were measured using photomicroscopy.
Iyashev et al. (1965, 1966)	Tetra substituted ammonium bases with (a) 16-18 & (b) 18+ carbon atoms.	2,500	25	15	15-200	Drops suspended on 3-5 μm glass fibres were observed through a microscope.
Deryagin et al. (1966a, b)	Cetyl alcohol.	? ⁵	23-5	40-45	20-600	Drops suspended on 10 μm glass fibres were observed through a microscope.
Leonov & Prokhorov (1966, 1967)	Iso-amyl alcohol. Quatrolite. Choline chloride. n-Hexyl alcohol. n-heptyl - n-decyl alcohol.	100- 10,000 100-5,000 10,000	20	90	1-4	The diameters of drops suspended on 0.1 μm drawn organic glass fibres were determined using photomicroscopy.
Mihara (1966, 1967)	A mixture of $\text{C}_{22}\text{H}_{45}\text{OC}_2\text{H}_4\text{OH}$ & $\text{C}_{18}\text{H}_{37}\text{OC}_2\text{H}_4\text{OH}$.	20,000	3-25	72-90	5-30	The diameters of drops suspended on 0.5 μm spider's web were determined using photomicroscopy.
Ivanitskii & Shimanskii (1967)	A trimethyl alkyl ammonium chloride.	100-3,000	20	15-75	600-1700	The diameters of drops suspended on 70 μm quartz fibres were determined using photomicroscopy.
Shinyaev (1967)	Sodium laurate. Sodium palmitate. Iso-amyl alcohol.	10-1000	40	?	?	The weight difference between the flow of surfactant solution through a capillary and the cumulative weight of drops falling from the tip gave the evaporation rate.
Snead & Zung (1968)	n-decanol (dispersed by petroleum ether).	25,000- 100,000	24-25	0	1-5	The masses of charged drops suspended in a 'Millikan oil drop' type apparatus were determined from Stokes' law and the applied voltage.
Garrett (1971)	A total of 14 long chain fatty acids & alcohols.	? ⁴	25	30,50	50-500	Drops sprayed onto 5-10 μm spiders' web or 15 μm teflon fibres were observed through a microscope.
Hughes & Stampfer (1971)	Hexadecanol. Dodecanol.	? ⁵	29.9	96-99	6-18	The size distribution of an aerosol falling under gravity was determined using photography and Stokes' law.
May (1972)	Cetyl alcohol. $\text{C}_{18}-22\text{H}_{37}-45\text{OC}_2\text{H}_4\text{OH}$	2,000	2-25	0-80	10-150	Drops sprayed onto 0.1-0.02 μm spiders' web were observed through a microscope.
Morikawa et al. (1972)	Sodium dodecyl sulphate.	13-90	35-51	0	≈ 3000	Drops suspended from a 2.8 mm syringe tip were photographed periodically. A miniature thermocouple measured drop temperature.
Sokolov (1972a, b)	Potassium stearate. Polyoxyethylated dioctyl phenol. Sodium dodecyl sulphate. Dimethyldodecylamine hydrochloride.	1-1000	-10 - 0	90-98	950- 1100	Drops of surfactant solution and pure water were suspended side by side on small thermistors and their size measured using a travelling microscope.
Dellicolli (1973)	$\text{C}_{14}-\text{C}_{20}$ straight chain alcohols.	? ⁵	?	?	30-160	The diameters of charged drops suspended in an electrodynamic field were measured microscopically.
Davies (1978)	n-docosanol.	?	?	0	500-1000	Drops were suspended on fine glass spalls.
Kudritskii et al. (1981)	Potassium stearate. Potassium palmitate. Ammonium laurate.	30-400	5-25	3	150-720	The diameters of drops suspended on 20 μm glass filaments were determined using photomicroscopy.

¹ Two experimenters used sub-atmospheric pressures: Ivanitskii & Shimanskii (25-750 mmHg) and Shinyaev (32 mmHg).

² Several experimenters studied non-stationary drops: Eisner et al., Hughes & Stampfer and May examined drops moving at their terminal velocity relative to the surrounding air, Iyashev et al. blew air past their drops at a velocity of 0.06 m/s and Morikawa et al. did likewise with a velocity of ≈ 1 m/s.

³ Only two experimenters specially purified their surfactants. Morikawa et al. used Soxhlet extraction with diethyl ether followed by recrystallization from ethanol. Dellicolli used triple recrystallization from hexane.

⁴ Surfactant coated drops were obtained by agitating a plane water surface coated with surfactant.

⁵ The drop surfaces were coated with surfactant by exposing the drop to an atmosphere of surfactant vapour.

retardation, although most workers agree that surfactants retard drop evaporation. Deryagin et al. (1960a, b) have suggested the theoretical possibility that a surfactant may increase drop evaporation rates. However, there is no incontrovertible experimental evidence that surfactants can increase evaporation rates despite many claims (Izmailova et al., 1957; Tovbin and Savinova, 1957a,b; Savinova and Tovbin, 1962; Beredjick, 1965; O'Grady, 1971; Gorodetskii, 1977). Six workers concluded that $D^2 \propto t$:

Kiryukhin et al. (1963) interpreted their results in terms of Maxwell's (1890) equation for pure liquid drops with a correction for vapour-pressure lowering based on the surface concentration of surfactant. However their results must be treated with caution as the ratio of initial to final drop radii was often substantially less than two.

Leonov and Prokhorov (1966, 1967) only determined the relative evaporation rates of drops of pure water and surfactant solution because of the difficulty of measuring humidity in very small volumes. All the drops studied followed $D^2 \propto t$. Both soluble surfactants (iso-amyl alcohol, quartolite, choline chloride and hexanol) and insoluble surfactants (heptanol - decanol) reduced the rate of evaporation by approximately 50%. The evaporation rate decreased with increasing surfactant concentration.

Snead and Zung (1968) observed that all drops obeyed $D^2 \propto t$ initially; however, in some drops the evaporation rate then slowed dramatically. This effect did not appear to be reproducible. It has been noted (Garrett, 1971) that the evaporation rates measured were very close to those of pure n-decanol. Considering that pure water drops evaporated too fast for measurements with the equipment used, it seems likely that most of the evaporation process was missed.

Garrett (1971) found that $D^2 \propto t$ held for all the drops he observed, though some drops initially evaporated at the pure water rate, later switching to a lower evaporation rate. This was attributed to slow spreading of the films used to coat the drops. The evaporation rate of surfactant-coated drops was up to 20 times lower than that for pure

water with long straight-chain alcohols having the strongest effect. While Garrett stated the overall range of drop diameters studied, he did not state the range of diameters over which the behaviour of individual drops was observed. Since the measured evaporation rates had uncertainties of $\pm 5\%$ (pure water) to $\pm 14\%$ (surfactant), the range and number of drop size measurements cannot have been large. However his drops were suspended on spiders' webs and it has been suggested (May, 1972; Dellicolli, 1973) that water can spread along thick ($> 3 \mu\text{m}$) spiders' webs so giving artificially high evaporation rates and this may be a source of error in Garrett's work.

Sokolov (1972a, b), who suspended drops of surfactant solution and pure water side by side, concluded that all evaporating drops obeyed $D^2 \propto t$. Sodium dodecyl sulphate, polyoxyethylated dioctyl phenol and dimethyl dodecylamine hydrochloride concentrations of 0.01 and 0.001% reduced the rate of evaporation by approximately 60%, while strange as it may seem, concentrations of 0.1 and 0.0001% had no effect compared to pure water. Potassium stearate only reduced the evaporation rate at 0.1% concentration. However, the drop separation used was only of the order of one drop radius, and it can be shown (by using the method of images to solve Laplace's equation for the appropriate boundary conditions) that at such a separation a pair of drops will evaporate at approximately three quarters of the unhindered rate (see Appendix A). Furthermore the ratio of initial to final drop radii was only 1.05, so Sokolov's results must be treated with care.

Dellicolli (1973) found that all drops evaporated according to $D^2 \propto t$. However there were sudden changes in dD^2/dt when a drop passed through the Rayleigh stability limit (Doyle et al., 1964; Taylor, 1964). This occurred whenever the surface charge density became too high and the drop ejected several small highly charged drops to reduce it. The rate of evaporation after such an ejection was always lower than before. The resulting discontinuities in dD^2/dt made accurate determination of evaporation rates difficult because of the small change in diameter between ejections. The rates of evaporation measured ranged from 40% below to 160% above those of Garrett (1971). As expected, alcohols with longer carbon chains retarded evaporation most strongly. However, Dellicolli does not appear to have controlled or measured the

humidity of the drop environment and so his results are of limited value.

Eight workers concluded that $D \propto t$:

Eisner et al. (1958, 1960) determined the sizes of droplet which just evaporated on falling a fixed height (the 'cutoff' radius). These gave reasonable agreement with values predicted from [2.2]. The evaporation coefficient used in [2.2] was measured for a plane surface by a separate series of experiments. However, in view of the mounting evidence (Littlewood, 1956; Narusawa, 1971, 1975; Barnes, 1978; Hickman, 1978; Cammenga, 1980) that deviations of α from unity are due to either heat transfer limitations or contaminants, the significance of the values of α so determined must be in doubt.

Jiusto (1964) examined the effects of both soluble and insoluble surfactants. The soluble surfactants examined (sodium tetra- and hepta- decyl sulphates and nonyl phenyl polyethylene glycol ether) produced no effect on evaporation rate, while an insoluble surfactant (a mixture of hexadecanol and octadecanol) produced a marked reduction. The results were represented by equation [2.2] and were considered to be consistent with evaporation coefficients of 1.2×10^{-5} to 3.0×10^{-5} .

Lyashev et al. (1965, 1966) obtained results which initially followed the relationship $D^2 \propto t$, however, there was then an abrupt change and the relationship $D \propto t$ held thereafter. This change was explained by either a large increase in the monolayer resistance R or a large decrease in the evaporation coefficient. The dependence of D on t remained strictly linear as D tended to zero. Drops left to stand in a 100% saturated atmosphere changed to the second relationship earlier. The results were represented mathematically by [2.3]. However, it should be noted that as the drops were evaporating into a moving stream of air, their results are not strictly comparable with those of other experimenters.

Deryagin et al. (1966a, b) observed evaporation behaviour essentially identical to that observed by Lyashev et al. (1965, 1966). Longer exposure to alcohol vapour reduced the duration of the first

regime. The results were represented by [2.2].

Ivanitskii and Shimanskii (1967) observed that drops initially evaporated at the same rate as pure water following $D^2\alpha t$. The evaporation rate then fell sharply following $D\alpha t$ for the remainder of the experiment. Drops left to stand in saturated air changed to the second relationship earlier. When α was calculated from a single measurement of evaporation rate, equation [2.2] gave reasonable agreement with the experimental results. The evaporation rate decreased with increasing surfactant concentration, reaching a minimum for concentrations above 0.05% and remaining constant thereafter. It also fell with increasing humidity, but pressure had almost no effect in contrast to the evaporation rate of a pure water drop which, obeying [2.1], is inversely proportional to pressure.

May (1972) found that drops of a surfactant-water emulsion obeyed $D\alpha t$ right up to the point of formation of a solid residue. His results agreed well with those of Mihara (1966) with increases in drop lifetimes of 300 to 3000 times.

Davies (1978) interpreted his results in terms of [2.2] and measured α to be 2×10^{-6} for n-docosanol. In agreement with Garrett, he found that compounds with hydrophilic groups, double bonds or branches in their carbon chain had lower evaporation resistances than the straight chain alcohols. Proteins and cholesterol produced little retardation.

Kudritskii et al. (1981) observed that drops initially evaporated at the same rate as pure water following $D^2\alpha t$. The evaporation rate then fell sharply following $D\alpha t$ for the remainder of the experiment. Drops left to stand in saturated air changed to the second relationship earlier. The values of dD/dt in the second period were independent of initial surfactant concentration, temperature and the time the drop was maintained in a saturated environment. Sodium stearate, lithium palmitate and ammonium stearate, palmitate and laurate also retarded evaporation. However, the aluminium, lead, manganese and cobalt salts showed no effect.

Three other workers also concluded that surfactants decreased drop evaporation rates, but as they did not measure drop diameters continuously, it is not possible to decide whether their results fit [2.2], [2.3] or some other equation altogether:

Pleteneva and Reh binder (1946a,b, 1947) observed that drops of sodium oleate and p-cresol solutions took approximately 20% longer to evaporate than pure water drops although, because of the very high evaporation rates used, they were only able to measure drop lifetimes. Mihara (1966, 1967) presented his results as the time for the drop radius to decrease from 30 to 5 μm for pure water and for an emulsion of surfactant in water. The ratio of the two times rose from approximately 150 at 25°C to 3000 at 3°C.

Shinyaev (1967) measured the evaporation coefficient of drops of different surfactant solutions using the method of Alty (1935). In this method α is determined by comparing the evaporation rate of a pendant drop held in a vacuum with the rate predicted from kinetic theory. Shinyaev concluded that α decreased with increasing surfactant concentration down to a minimum of one third of the value for pure water.

Of the 19 workers who have examined the effects of surfactants on drop evaporation, only two failed to report a reduction in evaporation rate:

Hughes and Stampfer (1971) concluded that surfactants actually increased drop evaporation rates. While this seems improbable, it is difficult to discredit their results as they performed replicate experiments with coated and uncoated water drops under otherwise identical conditions.

Morikawa et al. (1972) examined the evaporation of pendant drops of sodium dodecyl sulphate solution suspended from the tip of a syringe, but observed no significant change in the evaporation rate compared to pure water drops. However, dust accidentally introduced into the drop showed the drop to be in violent motion, probably as a result of the air flow past the drop, and this may have prevented surfactant from

accumulating at the drop surface and forming an evaporation resistance.

2.3.2 Effect of surfactants on heat transfer to drops

It is difficult to study the effect of surfactants on heat transfer through the air-water interface on plane surfaces because most of the latent heat of evaporation is supplied by conduction and convection through the bulk liquid, and heat transfer through the air-water interface is small even without any additional resistance due to the presence of surfactant.

Some work (Jarvis, 1962; Jarvis and Kagarise, 1962; Seimiya and Sasaki, 1966; Navon and Fenn, 1971a, b; Barnes and Cammenga, 1979; Barnes and Feher, 1980; Barnes and Hunter, 1982) has been performed on the effect of surfactants on heat transfer through the bulk liquid; however, there is very little work in the literature which gives direct evidence of the effect of surfactants on heat transfer to drops.

Brady et al. (1951a, b) measured the temperature difference between two drops suspended side by side on thermistors. One drop was pure water, the other potassium laurate solution. They were primarily interested in determining the vapour pressure of water above the surfactant solution. However, since their results agreed well with vapour pressure data obtained from freezing point depressions, they concluded that the surfactant must have been affecting heat and mass transfer equally.

Morachevskii and Sokolov (1971, 1975) also measured the temperatures of a pair of drops suspended on thermistors. They were concerned with drop freezing temperatures and observed that drops of 0.01% sodium dodecyl sulphate solutions froze at $-13.1 \pm 0.2^\circ\text{C}$, while pure water drops froze at $-15.0 \pm 0.2^\circ\text{C}$. They concluded that this difference was due to heat transfer effects.

Morikawa et al. (1972) measured drop temperatures using a thermocouple; however, they made no attempt to analyse the effect of surfactants on heat transfer themselves, and presented insufficient information for any conclusions to be drawn from their data about any

such effect.

Kremnev et al. (1974) suspended drops of both a 0.05% trimethyl alkyl ammonium chloride solution and pure water on the junctions of a differential thermocouple and photographed the drops over a period of time. The temperature of the gas surrounding the drop was varied from 20°C to 200°C. Unfortunately few other experimental details were given. The results showed that below 50°C the surfactant approximately halved the evaporation rate, but above 50°C the retarding effect dropped rapidly to a negligible level. This was attributed to a change in the monolayer structure. The monolayer heat transfer resistance was also calculated and was found to be of the same order as the gas heat transfer resistance. This result is inexplicable in terms of a conventional resistance to conduction as it implies a thermal conductivity one million times lower than that of the bulk surfactant.

Kudritskii and Dmitrieva (1983) attempted to repeat Kremnev's work. They used potassium stearate or cetyl alcohol to retard the evaporation of water drops and compared their temperatures to those of pure water drops evaporating at the same rate. For both surfactants the temperature difference was less than experimental error indicating a negligible monolayer heat transfer resistance.

If a surfactant monolayer can display a significant heat transfer resistance, there are profound implications for the work on mass transfer described in Section 2.3.1. There a reduction in α was the most frequent explanation for a reduction in evaporation rate. However, if reductions in α are simply due to heat transfer limitations, then any analysis which fails to consider both heat and mass transfer will be incorrect.

2.4 Conclusions

Although a significant amount of work has been performed on the effect of surfactants on mass transfer as described above, much of it is of questionable validity especially in the theoretical interpretation of results. Confusion abounds to the extent that the reported

reductions in evaporation rates range from zero to several thousand times, while some workers have even reported increases in evaporation rates.

Part of the reason for this confusion is that many workers only studied the evaporation process over a narrow range of drop diameters. Under such conditions it can be very difficult to distinguish between $D^2\alpha t$ and $D\alpha t$. Almost all of the experimenters who studied a wide range of diameters saw the pattern observed by Lyashev et al. (1965, 1966) in outline, though there is some disagreement about the details (i.e. what effect the initial surfactant concentration has on the second period of evaporation). The most notable exceptions are Leonov and Prokhorov (1966, 1967) and Hughes and Stampfer (1971); however, they were using very small drops for which different factors may be controlling.

The small amount of work performed so far on the effect of surfactants on heat transfer is also contradictory, though most of the work performed to date suggests a strong retarding effect analogous to the well documented effect on mass transfer.

The theoretical models produced so far are restricted to insoluble surfactants and each involves several constants which have to be determined empirically. As a result they are of little predictive value. Zung (1969) has reached essentially the same conclusion. Existing models are unable to predict the time of change from $D^2\alpha t$ to $D\alpha t$ and give unrealistic limits for dB/dt as D tends to zero. Equations [2.2], [2.3] and [2.5] assume that the resistance to evaporation is always due to a monolayer, but as the drop shrinks, there must come a time when multilayers are formed with a correspondingly higher evaporation resistance. Equation [2.4] also predicts that evaporation will continue until $D=0$, ignoring the volume of the surfactant left when all the water has evaporated.

No attempt has yet been made to formulate a model including the effects of surfactants on both heat and mass transfer, or to take into account the effect of soluble surfactant diffusing into the drop bulk. This is attempted in succeeding chapters.

3 EXPERIMENTAL TECHNIQUE

3.1 Introduction

In order to determine the effect of surfactants on heat or mass transfer, it is necessary to measure both the transfer rate and the driving force for transfer with and without surfactant.

In the case of mass transfer from an evaporating drop, the driving force is the difference between the water vapour concentration at the drop surface and at an infinite distance from the drop, and the rate is the rate of change of drop mass with time. The water vapour concentration at large distances from an evaporating drop can easily be set to a known value by allowing the air in which the drop is suspended to equilibrate with a saturated solution of an inorganic salt. The water vapour concentration at the drop surface cannot be measured directly, but must be inferred from the drop temperature. The rate of change of drop mass with time can be measured directly by suspending a drop on a microbalance; however, in practice it is experimentally simpler and more accurate to measure the rate of change of drop diameter with time, and then calculate the drop mass.

In the case of heat transfer to an evaporating drop, the driving force is the difference between the temperature of the drop and of the air at large distances from the drop, and the rate is the rate of heat flow to the drop. The temperature of the air at infinite distance from the drop can easily be measured using a thermocouple, and the temperature of the drop can be measured by suspending the drop on a thermocouple, provided that appropriate measures are taken to reduce and correct for heat conduction along the thermocouple leads. The heat transfer rate can easily be inferred from the measured mass transfer rate and the latent heat of water.

So the technique used to measure the effect of surfactants on heat and mass transfer was to place drops of either pure water or surfactant solution in an environmental cell, where the temperature and humidity were kept at known constant values, and to measure the variation of drop diameter and temperature with time. The drops were suspended from

either fine glass fibres or thermocouples. Figure 3.1 shows an overview of the apparatus used.

3.2 Measurement of drop diameter

The drop was viewed through the front window of the environmental cell by a Meiji EMZ-2 zoom stereomicroscope fitted with a filar micrometer eyepiece (an eyepiece with a movable graticule connected to a micrometer). The microscope was mounted with its optical axis horizontal (see Figure 3.2) so that it could be focused on the drop by moving it back and forth along its focusing block. The cell was mounted on the front of a graduated mechanical microscope stage, which had been positioned vertically, so that a drop could be centered on the optical axis of the microscope. This facility for full X-Y-Z movement made it possible to use drop supports of slightly different sizes, a necessity when using drawn glass fibres.

The microscope provided a magnification of $\approx 10\times$, and since the filar micrometer scale had a resolution of 0.01 mm, the system as a whole provided a nominal resolution of 1 μm , which was quite acceptable. The exact magnification used was determined by calibrating the microscope/micrometer eyepiece combination against a stage micrometer, i.e. a microscope slide marked in divisions of 1, 0.1, and 0.01 mm.

The procedure used was to set a graticule line up against the left hand side of the drop, read the time from a stopwatch, read the micrometer scale, and then repeat the procedure as quickly as possible for the right hand side of the drop. The difference in the two micrometer readings gave the drop diameter at a time corresponding to the average of the two stopwatch readings.

Drop diameters were measured over the range 1.2 mm, the largest size of drop practicable for a 100 μm support, down to 0.3 mm, below which the support became significant in size relative to the drop and began to alter the drop's evaporation.

Because of the very fine supporting fibres used, the drop had a marked tendency to vibrate. As a result it was necessary to mount the

Figure 3.1 Apparatus overview

Figure 3.2 Viewing assembly

entire microscope and cell assembly on a vibration-proof support. This consisted of a paving stone laid on top of two foam rubber cushions and it greatly reduced the problem. However, it was also necessary to take three further precautions. Firstly, pressure pulses in the tubing carrying water to the environmental cell, caused by the circulating pump, had to be removed by passing the water through a constant head tank open to the atmosphere. Secondly, in measuring a diameter it was necessary to set a graticule line up against the side of a drop by turning the micrometer screw. Inevitably, this produced a certain amount of vibration, so the micrometer screw was covered with a layer of foam rubber to minimize this problem. Finally, the circulating pump was itself mounted on a foam rubber support to prevent it from transmitting vibrations to the rest of the equipment.

The drop was illuminated by a Schott KL1500 fibre optic cold light source. To ensure that the lighting was not significantly disturbing the system, care was taken that the lighting was not aimed directly at either the drop or cell thermocouple. In addition, thermocouple readings were taken with the lighting both on and off. The resulting difference in thermocouple readings was less than 0.1°C .

3.3 Measurement of drop temperature

To measure drop temperatures, a drop was suspended from a thermocouple instead of the normal glass fibre support. The type of thermocouple used was dictated by the overriding need to disturb the evaporation of the drop as little as possible. The main problem was that a thermocouple, consisting of two highly conductive metal wires, could significantly increase the heat flux to the drop from the surrounding air, raise the drop temperature, and so increase the drop's evaporation rate. Clearly then, the thermocouple wires had to be as thin as possible and have the minimum thermal conductivity to keep the extra heat flux to a minimum. Using such thin wires would also minimize the possibility of the drop's shape being distorted by their physical presence. In addition, because of the relatively small temperature differences between the drop and the surrounding air, it was obviously desirable to use the thermocouple which gave the highest e.m.f per $^{\circ}\text{C}$. Fortunately these requirements were not contradictory and

were best met by type E (chromel-constantan) thermocouples. The smallest type E thermocouples commercially available are made from 12 μm diameter wire and so these were the ones used. The drop was suspended from one thermocouple junction, while the other junction was at the cell temperature, so that the thermocouple measured the temperature difference between the drop and the surrounding air. The thermocouple e.m.f. was recorded either by a Philips PM8251 single pen chart recorder or (later) a Solartron 3530 Orion datalogger. Both instruments were sensitive to 1 μV .

Unfortunately, it was not possible to calibrate assembled thermocouples because the hot and cold thermocouple junctions were only 20 mm apart and it was physically impractical to generate two precisely known, but significantly different, temperatures so close together. As a result, it was necessary to assume that the e.m.f.-temperature relationship followed that given in British Standard 4937 (1973).

3.4 Drop containment and support

3.4.1 Environmental cell

The supported drops were mounted within an environmental cell, shown in Figure 3.3. It consisted of a jacketed glass cylinder with an optically flat glass window at the front through which the drop could be observed. In addition, two ports were provided. The support holding the drop under study was inserted through one, and the thermocouple used to measure the cell temperature through the other. Internally the cell was a 55mm long cylinder with a diameter of 50mm. The front glass window was removable to permit easy cleaning of the cell interior.

The temperature in the cell was kept constant by passing water at a known temperature through the cell jacket. The water was pumped from a temperature-controlled tank through the constant head tank, the cell jacket and back to the tank. The temperature of the water in the temperature-controlled tank was always within $\pm 0.1^\circ\text{C}$ of the desired temperature; however, because the room temperature varied slightly from day to day, the temperature of the environmental cell could vary

Figure 3.3 Environmental cell

by more than this, though it was essentially constant during the course of an experiment.

The humidity in the cell was controlled by a saturated salt solution placed in the bottom of the cell (see Table 3.1). Care was taken that both liquid and solid were always present to ensure that the solution was saturated. In addition, when using ZnCl_2 and MgCl_2 , replicate experiments were performed using salts from two different sources to confirm that the relative humidity in the cell was not dependent on any trace impurities present in the salt. Air was circulated through the cell before the start of an experiment to ensure that all the air was at the correct temperature and humidity. Because the pump was external to the cell, the circulating air was passed through a heat exchanger before it re-entered the cell to ensure that it was at the correct temperature. The water passing through the heat exchanger shell came from the same constant head tank as the water passing through the cell jacket.

Table 3.1 Relative humidity of saturated salt solutions (%)

Temperature °C	ZnCl_2	$\text{LiCl} \cdot \text{H}_2\text{O}$	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	$\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$	NaCl	KNO_3
10	—	13.3	34.2	57.9	75.2	95.5
15	—	12.8	33.9	56.6	75.3	94.4
20	—	12.4	33.6	55.2	75.5	93.2
25	3.0	12.0	33.2	53.8	75.8	92.0
30	—	11.8	32.8	52.5	75.6	90.7
35	—	11.7	32.5	51.2	75.5	89.3
40	—	11.6	32.1	49.8	75.4	87.9

All data are taken from Wexler and Hasegawa (1954) except for the value for ZnCl_2 which was taken from Kudritskii et al. (1981).

During an experiment, the temperature of the air in the cell was measured by a calibrated type K (chromel-alumel) thermocouple inserted through the cell's side port and connected to a digital multimeter

(Keithley model 160). The cold junction of the thermocouple was placed in a vacuum flask filled with a mixture of crushed ice and distilled water.

The atmospheric pressure in the cell was not controlled, but its value was read from a Fortin barometer every time an experiment was performed.

3.4.2 Positioning of a drop on a support

Because the drop supports used had such small diameters and were rendered hydrophobic, the force holding a drop to the support was very small. As a result it was not possible to generate drops of the required size on the end of a pipette, and transfer them by simply touching the drop to the support and then removing the pipette, as the drop would simply stick to the pipette unless it had as small a diameter as the support. A pipette of such a diameter would be incapable of generating a 1 mm drop within a reasonable time because of its very narrow bore.

To get around this problem, an intermediate stage was added. Water or surfactant solution was sprayed onto a pair of crossed glass fibres using a glass pipette with a fine drawn tip. When a drop of the required size had been obtained, it was transferred to a support by bringing the support (held in a micromanipulator) up to the drop, and then carefully withdrawing each of the crossed fibres in turn. Figure 3.4 shows a drop in the process of being transferred. The crossed fibres were mounted on a bar which could be rotated out of the way when not in use. It was found that best results were obtained when the tip of the pipette was at an angle of approximately 30 degrees to the horizontal, so the pipettes used were made with a bend in the stem to facilitate this (see Figure 3.5). This configuration also prevented drips of surfactant solution from running back down the pipette.

The support was moved into the cell using a combination of the micromanipulator and the vertical adjustment on the microscope stage. This was achieved by moving the cell down into its lowest position using the microscope stage's vertical adjustment, positioning the

Figure 3.4 Details of drop transfer

Figure 3.5

(a) Details of thermocouple circuit

(b) Glass fibre support

(c) Heating coil

(d) Pipette

support vertically above the top cell port using the micromanipulator, and then raising the cell using the microscope stage, taking care that the support did not collide with the cell and knock the drop off. When the drop support was safely seated in the socket joint of the cell port, it was disconnected from the micromanipulator so that the cell could be centered on the microscope's optical axis.

3.4.3 Construction of a glass fibre support

Constructing a drop support of this type involved drawing a thin, straight, uniform glass fibre in such a way that it was attached to a handleable support. An example of a completed support is shown in Figure 3.5.

A Quickfit B10 extended cone was sealed at the cone end and a 23 gm weight pushed onto the end of its shaft. The weight consisted of a 25 mm rubber bung with a hole bored through its centre to fit the B10 cone and an iron washer glued to its underside using epoxy adhesive.

A piece of glass rod was joined to the cone and drawn away to leave a column of glass approximately 0.5 mm in diameter and 3 cm long joining the two. The glass rod was then clamped in a retort stand with the cone hanging vertically below it.

The glass was melted by placing a small coil of nichrome resistance wire, heated by an electrical current, around it. The coil, a 15 mm long helix 0.5 mm in diameter, was bent round in the shape of a horseshoe to enclose the glass rod to be drawn. An AC voltage of approximately 7 V was applied across the coil via a variable voltage transformer. Since the wire's resistance was 7 ohm, it drew a current of 1 amp and the coil produced approximately 7 watts of heat. This heated the wire to orange heat and softened the glass enclosed within the coil. The glass then began to draw under the weight of the cone and bung. It fell a distance of approximately 10 cm onto a magnet which held the iron washer and prevented the cone from falling onto its side and breaking the freshly drawn fibre.

The fibre (typically $25 \pm 5 \mu\text{m}$ in diameter) was then nipped to the required length and a $100 \mu\text{m}$ bulb formed at the tip by touching the fibre to a bunsen flame. This was necessary because a $25 \mu\text{m}$ diameter fibre cannot support a drop as large as 1 mm . Finally the fibre was rendered hydrophobic by dipping it for approximately 10 seconds in a 2% solution of dichlorodimethylsilane in 1,1,1-trichloroethane. This was found to be necessary to stop drops climbing up their supports during the course of an experiment.

When fibres were needed for transferring drops, they were drawn in the same way, except that two glass rods were used instead of a rod and a cone, and the hydrophobisation stage was omitted.

The main problem encountered was that the cone/glass rod joint was relatively fragile because the B10 cone was made of pyrex while the glass rod was made of ordinary soda glass. It was not possible to use pyrex glass throughout because of the difficulty in obtaining a high enough temperature to soften the pyrex.

3.4.4 Construction of a thermocouple support

The thermocouples used were purchased as single junctions with one chromel wire and one constantan wire. The bead was approximately $50 \mu\text{m}$ in diameter which was too small to hold a 1 mm drop, so a glass fibre had to be added to support the drop. This had the advantage that the thermocouple could be positioned centrally in the drop.

A schematic diagram of the thermocouple circuit used is shown in Figure 3.5. The thermocouple was assembled on a piece of printed circuit board (p.c.b.) with a single copper strip on each side. Copper wires were soldered to the strips at one end of the p.c.b. and were then inserted into a Quickfit B10 cone which had had two 1 mm holes pierced on opposite sides halfway along its shaft. The wires were pulled through the holes, formed into terminals, and glued to the outside of the cone with epoxy adhesive.

The p.c.b. was also glued to the inside of the cone at the socket end. Sufficient glue was used to seal this end of the cone entirely.

The p.c.b. left outside was then trimmed to the right size and the copper strip removed from most of one side.

The final stage was fixing a thermocouple to the support. A metallic paint (DAG dispersion 915) was used both as glue and to make electrical connections. Needless to say, the size of the thermocouples used meant that the operation of transferring a thermocouple to the p.c.b. was very delicate requiring considerable care, and it was necessary to use the micromanipulator which had also been used in positioning drops as described above.

The glass fibre was made in the usual way (see Section 3.4.3), but was then broken off from the B10 cone and stuck to the rear of the p.c.b. with double sided adhesive tape. This method of fixing had the advantage that the tip of the fibre could easily be moved close to the thermocouple bead.

3.5 Double distilled water

All the water used for rinsing glassware or in making up surfactant solutions was obtained from a specially constructed still. Ordinary distilled water was redistilled over an alkaline permanganate solution in an all glass Quickfit still. Because of the large quantity of water needed, the still was adapted for semi-continuous operation.

Distilled water flowed under gravity from a two-litre bottle through a solenoid valve and into a three-armed one litre spherical flask. An electric mantle heated the flask to which 5 ml of saturated potassium permanganate solution and 5 ml of a 1 molar sodium hydroxide solution had been added to oxidise any surfactants present. Vapour rising through the central arm of the flask was condensed in a Liebig condenser and collected in a Winchester bottle.

The water level in the still was controlled by a simple on-off controller connected to the solenoid valve on the water inlet. The water level in the still was sensed by four tungsten wires inserted through the third arm of the flask. The wires were of different lengths and the resistance between any two wires indicated whether the

top wire was above or below the water surface. In order to prevent the still boiling dry when the feed bottle was empty, the controller was set to cut off the power to the heating mantle if the water level fell below that of the longest wire.

Dry ground glass joints were used everywhere except on the water feed line where the solenoid valve made this impractical. All the glassware was cleaned with chromic acid prior to starting up the still for the first time, and the system was run for several weeks before any of the product was used to ensure that it was fully purged of contaminants.

When fully operational, the still produced water with a conductivity of 3-4 $\mu\text{mho/cm}$.

3.6 Making up a surfactant solution

3.6.1 Surfactant synthesis

The majority of the surfactants used were purchased; however, some were not available commercially and so had to be synthesised. Table 3.2 lists the surfactants used, their chemical formulae, and the abbreviated codes used to refer to them.

Table 3.2 Surfactants used

Common name	Chemical formula	Code
Sodium stearate	$\text{CH}_3(\text{CH}_2)_{16}\text{COONa}$	NAST
Sodium palmitate*	$\text{CH}_3(\text{CH}_2)_{14}\text{COONa}$	NAPA
Sodium myristate*	$\text{CH}_3(\text{CH}_2)_{12}\text{COONa}$	NAMY
Sodium laurate*	$\text{CH}_3(\text{CH}_2)_{10}\text{COONa}$	NALA
Sodium lauryl sulphate	$\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4\text{Na}$	NALS
Cetyltrimethylammonium bromide	$\text{CH}_3(\text{CH}_2)_{15}(\text{CH}_3)_3\text{NBr}$	CTAB
Glycerol monostearate	$\text{CH}_3(\text{CH}_2)_{16}\text{COO}.\text{CH}_2\text{CHOHCH}_2\text{OH}$	GMST
Triton X-100	iso-octylphenoxypolyethoxyethanol	TRIN
(the polyethoxy chain contained approximately 10 ethoxy units)		

Those surfactants which could not be purchased (those marked * in the table) were prepared from equi-molar quantities of the appropriate fatty acid and sodium hydroxide. The reaction used was

where R- was $\text{C}_{11}\text{H}_{23}-$, $\text{C}_{13}\text{H}_{27}-$ or $\text{C}_{15}\text{H}_{31}-$. A quantity of analar grade acid was weighed into a beaker and immersed in hot water to melt the acid while minimizing the possibility of it being oxidised by excessive heating. The required amount of sodium hydroxide was dissolved in as little double-distilled water as possible (to minimize the amount of water to be removed later) and allowed to drip through a filter funnel into the melted acid. It was necessary to stir the mixture continuously throughout the reaction as the sodium salt precipitated out immediately. When the funnel was empty, it was refilled with double distilled water to rinse the residual sodium hydroxide through and complete the reaction. The final product, as expected, was a white soapy solid.

3.6.2 Surfactant purification

Archer and La Mer (1955) have shown that impurities can significantly modify the effects of surfactants on evaporation rates, so to obtain reproducible results it was necessary to ensure that all the surfactants used in experimental work were properly purified.

The surfactant was placed in the thimble of a Soxhlet extractor and refluxed with analar diethyl ether for several days. It was then removed from the thimble and the ether allowed to evaporate off in a desiccator. Finally the surfactant was recrystallized from hot absolute ethanol, dried again, and stored in a desiccator.

The fatty acids used in the syntheses referred to above were often visibly yellow when melted indicating the probable presence of oxidation products; however, it was noted that a brown residue collected in the bottom of the Soxhlet extractor indicating that the ether was successfully removing these contaminants, and the final surfactant produced was pure white in colour.

3.6.3 Preparation of a solution of known concentration

The surfactant solutions were all made up in a wide-necked 300 ml conical flask. The flask was cleaned in chromic acid overnight, rinsed thoroughly with double-distilled water, and allowed to drain before use.

The desired quantity of surfactant was weighed out onto a piece of fresh filter paper on a 0-0.1 gm microbalance (Stanton instruments model MC5). The filter paper was then carefully moved to the conical flask using tweezers and the surfactant gently shaken into the flask. The filter paper and residual surfactant were then reweighed, the difference between this and the previous weight giving the quantity of surfactant transferred to the flask.

The conical flask was weighed on an ordinary 0-1000 gm laboratory balance and double distilled water added until the weight of water needed to obtain the desired concentration had nearly been added. The mixture was heated (but not boiled) to dissolve the surfactant. The heating was kept to a minimum both to eliminate hydrolysis of the surfactant, and because boiling the solution could easily lead to loss of surfactant due to the solution boiling over. To minimize errors due to evaporation of water, the solution was cooled down to room temperature by bathing the flask in ice. Finally water was added to the solution until the desired concentration was reached, and the solution was then used immediately.

4 THE EVAPORATION OF PURE WATER DROPS

4.1 Theoretical model

To describe the evaporation of a pure liquid drop rigorously would entail solving the partial differential equations describing the transient diffusion of vapour away from the drop and conduction of heat towards the drop. The equations describing heat transfer must also be solved because the evaporation rate of a drop is determined by the concentration of water vapour in the air above the drop's surface which, in turn, is determined by the vapour pressure of water at the surface temperature of the drop. The temperature distribution inside the drop can be assumed spatially uniform because the thermal diffusivity of liquid water is much higher than that of air. The equations and associated boundary conditions describing the diffusion of water vapour from the drop are:

$$\frac{\partial \rho}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[D_g r^2 \frac{\partial \rho}{\partial r} \right], \quad [4.1]$$

$$\rho = \rho_{\infty} \quad \text{at} \quad t=0, \quad [4.2]$$

$$\rho = \rho_0 \quad \text{at} \quad r=R(t) \quad [4.3]$$

$$\text{and} \quad \rho = \rho_{\infty} \quad \text{at} \quad r=\infty. \quad [4.4]$$

The equations for the diffusion of heat to the drop are entirely analogous:

$$\rho_g C_p \frac{\partial T}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[k_g r^2 \frac{\partial T}{\partial r} \right], \quad [4.5]$$

$$T = T_{\infty} \quad \text{at} \quad t=0, \quad [4.6]$$

$$T = T_0 \quad \text{at} \quad r=R(t) \quad [4.7]$$

$$\text{and} \quad T = T_{\infty} \quad \text{at} \quad r=\infty. \quad [4.8]$$

Fortunately, since diffusion in the gas is relatively fast compared to the rate at which the drop shrinks, it is possible to assume that the drop is in a 'quasi-steady state' and treat the moving boundary condition [4.3] as if the drop were fixed in size. Chang and Davis (1974) have demonstrated that this assumption is reasonable at moderate evaporation rates, though for very high evaporation rates the equations must be solved rigorously.

In a quasi-steady state, all the time derivatives will be zero, so integrating [4.1] twice and substituting conditions [4.3] and [4.4], it is easy to show that the steady state concentration profile in the gas is

$$\rho = \rho_{\infty} + \frac{R}{r} (\rho_0 - \rho_{\infty}) \quad [4.9]$$

By Fick's first law of diffusion the total rate of mass transfer from the drop surface is

$$4\pi R^2 D_g \left. \frac{\partial \rho}{\partial r} \right|_R = -4\pi R (\rho_o - \rho_\infty) D_g.$$

Equating this with the rate of change of drop mass with time

$$\frac{\partial}{\partial t} \left[\frac{4}{3} \pi R^3 \rho_l \right]$$

and simplifying gives the well known Maxwell equation:

$$\frac{dR}{dt} = - \frac{D_g}{\rho_l R} (\rho_o - \rho_\infty) \quad [4.10]$$

Similarly, if thermal diffusion (conduction) is the only mechanism of heat transfer to the drop, the temperature profile in the gas is

$$T = T_\infty + \frac{R}{r} (T_o - T_\infty) \quad [4.11]$$

By applying Fick's first law again, it is easy to show that the total amount of heat transferred to an evaporating drop via conduction through the surrounding gas is

$$Q_{\text{cond}} = 4\pi R k_g (T_\infty - T_o)$$

For a drop surrounded by stagnant air, conduction will be the main mechanism by which heat is transferred to the drop; however, the other two possible mechanisms, convection and radiation, may also contribute to the heat flux depending on the conditions. For a drop placed in an enclosed cell whose walls are all radiating at a temperature T_∞ , elementary theory gives the radiative heat flux as

$$Q_{\text{rad}} = 4\pi R^2 \epsilon \sigma (T_\infty^4 - T_o^4)$$

Heat transfer to the drop by convection can be calculated from [4.16] (see Section 4.2) since

$$Q_{\text{cond+conv}} = Q_{\text{cond}} \cdot \frac{\text{Nu}}{2}$$

In the case of a drop supported on a fibre or thermocouple, it is also necessary to take account of the heat conducted down the support to the drop. It can be shown (see Appendix B) that this heat flow may be approximated by the following empirical equation:

$$Q_{\text{fib}} = Q_{\text{cond}} \cdot 0.178 \cdot \left[\frac{k_f}{k_g} \right]^{0.798} \cdot \left[\frac{r_f}{R} \right]^{1.74}$$

A heat balance can now be constructed for the drop by equating the rate of change of the drop's sensible heat to the difference between the latent heat of evaporation and the sum of the various flows of heat to the drop.

$$\frac{4}{3} \pi R^3 \rho_l C_p \frac{dT}{dt} = \lambda \frac{d}{dt} \left[\frac{4}{3} \pi R^3 \rho_l \right] + Q_{\text{cond+conv}} + Q_{\text{rad}} + Q_{\text{fib}} \quad [4.12]$$

As the main mechanism of heat transfer to a drop is conduction, the flow of heat to a drop will be approximately equal to Q_{cond} which is proportional to the drop radius. Since the latent heat of evaporation is also proportional to the radius, the variation of the two terms as the drop evaporates will cancel out and the drop temperature should be almost independent of drop radius. The quasi-steady temperature attained will be close to the wet-bulb temperature, though not exactly equal to it, as the various terms in the heat balance have different relative magnitudes for a wet-bulb thermometer.

Equations [4.10] and [4.12] form a pair of coupled ordinary differential equations which can be readily integrated numerically by standard methods to give the variation of drop diameter and temperature with time for any given set of environmental conditions. The FORTRAN program PUREWATER was written to do this. It is largely self-documented and a program listing is given in Appendix C. The fourth order Runge-Kutta method (Gerald, 1978) was used to integrate the differential equations. This method was chosen because it is accurate enough to permit the use of a large step size, and so use little computer time, without being unnecessarily complex to program. Obviously the solution obtained will be strongly dependent on the values assumed for the transport properties D and k . Unfortunately the diffusion coefficient of water vapour in air is the least certain parameter in the model. Figure 4.1 shows the published results of 17 experimenters obtained over a period of nearly a century. The solid line is a least squares fit to the data, ignoring the work of Ackermann and Petit which appear to be subject to large errors. The fitted equation is

$$D_g = 0.225 \times 10^{-4} (T/273.1)^{1.82} \quad [4.13]$$

As can be seen, almost all the data fall within a range of $\pm 10\%$ about equation [4.13]. The results of all experimenters were given equal weighting when performing the least squares fit, as it was not obvious

Figure 4.1 Diffusion of water vapour in air

Table 4.1 Key to Figure 4.1

Symbol	Source	Basis of measurement
A	Brown and Escombe (1900)	Diffusion through an aperture
B	Mache (1910)	Evaporation tube
C	Le Blanc and Wuppermann (1916)	Evaporation tube
D	Summerhays (1930)	Evaporation tube
E	Ackermann (1934)	Evaporation tube
F	Gilliland (1934)	Evaporation tube
G	Trautz and Muller (1935)	Evaporation tube
H	Schirmer (1938)	Evaporation tube
I	Brookfield et al. (1947)	Evaporation tube
J	Kimpton and Wall (1952)	Evaporation tube
K	Lee and Wilke (1954)	Evaporation tube
L	Bose and Chakraborty (1955)	Evaporation tube
M	Narsimhan (1955)	Evaporation tube
N	Nelson (1956)	Unsteady evaporation
O	Richardson (1959)	Evaporation tube
P	Petit (1965)	Unsteady evaporation
Q	Wilhelm and Battino (1972)	Evaporation tube

which results were the most reliable. In particular, and in contrast to what might be expected, no convergence of the values with time and with development of experimental technique is apparent.

Touloukian et al. (1970) reviewed the available experimental data on the thermal conductivity of air and air-water vapour mixtures. They examined over sixty sources and concluded that the majority of the data fell within a band of $\pm 3\%$ about their recommended values. For computational purposes, the following empirical equation was fitted to their values using the method of least squares.

$$k_g = 0.0241 (T/273.1)^{0.84} \quad [4.14]$$

It reproduces their recommended values to an accuracy of $\pm 0.1\%$.

Gruss and Schmick (1928) and later Dikjema et al. (1972) measured the thermal conductivity of wet air. However it is easy to show from their results that, for the water vapour concentrations encountered in the present work, the effect of water vapour concentration on thermal conductivity is only of the order of 0.5%, i.e. within the uncertainty of [4.14], and so its effect could be neglected.

4.2 Experimental results

A total of 20 experiments was performed with pure water drops, covering a 16-fold range of evaporation rates. Experiments were performed with relative humidities ranging from 3 to 92% and temperatures ranging from 13 to 29°C. Full details of all the experiments performed are given in Appendix D.

The majority of the experiments were performed with drops suspended from glass fibre supports, but three experiments were performed with drops suspended on thermocouple supports to check that the model was correctly predicting drop temperatures. The sequence of photographs shown in Figure 4.2 portrays the evaporation of a pure water drop suspended on a thermocouple. As can clearly be seen, the thermocouple was positioned well inside the drop throughout the drop's lifetime, so ensuring that the thermocouple was measuring the true drop temperature. Figure 4.3 shows the results of three typical experiments; as can be seen, graphs of the square of diameter against time are good straight lines as would be expected from the Maxwell equation. To compare theory and experiment more quantitatively, it is necessary to calculate values of dD^2/dt from the experimentally observed, and theoretically predicted, variation of diameter with time and compare them. This is done in Figure 4.4 which shows that if convection is assumed absent ($Sh=Nu=2$) the model under-predicts the evaporation rate. Ranz and Marshall (1952) obtained correlations for heat and mass transfer to spheres by natural convection

$$\left. \begin{aligned} Sh &= 2 + 0.6 Sc^{1/3} Gr^{1/4} \\ Nu &= 2 + 0.6 Pr^{1/3} Gr^{1/4} \end{aligned} \right\} \quad [4.15]$$

but it can be seen from Figure 4.4 that the evaporation rates predicted on the basis of these correlations are serious over-estimates. This is

Figure 4.2 The evaporation of a pure water drop

The sequence of photographs (a) - (e) shows the evaporation of a pure water drop suspended from a thermocouple support into air at 25°C and 12% relative humidity. The photographs have been magnified 25x and the whole sequence took place over a period of 15 minutes.

Photograph (f) is an enlarged copy of (e) at a magnification of 75x.

Figure 4.3. The evaporation of pure water drops.

Figure 4.4

because the correlations really only apply to drops evaporating into an infinite medium. For a drop evaporating in a cell of finite size, the presence of the cell walls inhibits the formation of convection currents. Confirmation of this has been provided by Fuchs (1959, p46). He noted that for a 1 mm drop with a 10°C temperature difference between it and the surrounding air, $Gr \approx 1$ and according to [4.15] convection should increase the quantity of heat transferred to the drop by approximately 30%, but that no such effect had been observed experimentally. Since most experimenters who have investigated the evaporation of pure water drops have placed their drops in relatively small environmental cells (typically 2-3 cm in diameter), it seems likely that convection was indeed absent in their work. By comparison the author's cell was relatively large, and it seems probable that at least some convection was present.

The obvious way to account for the presence of some convection was to use [4.15] with a reduced coefficient in front of the convective term. As can be seen from Figure 4.4, the best agreement was obtained between theory and experiment when the following correlations were used

$$\left. \begin{aligned} Sh &= 2 + 0.1 Sc^{1/3} Gr^{1/4} \\ Nu &= 2 + 0.1 Pr^{1/3} Gr^{1/4} \end{aligned} \right\} \quad [4.16]$$

This suggests that, for the size of cell used, convection currents were just beginning to become significant. Considering that the model uses the values of a large number of physical constants, few of which are known with better than 1% accuracy, and also includes a number of approximations, the agreement is excellent.

Figure E1 in Appendix E shows the agreement between the temperature of a pure water drop as predicted by integrating [4.12] and that measured experimentally by suspending the drop on a thermocouple. As can be seen, the error between the two is well within the calibration error of the thermocouple. The significance of the other graphs plotted on Figure E1 and the method used to calculate the predicted temperature are explained in Section 5.1.

5 SURFACTANT SOLUTION DROPS: EXPERIMENTAL RESULTS

5.1 Introduction

Experiments were performed with a series of surfactants over a wide range of concentrations and evaporation rates. For the bulk of the work the sodium salts of the C_{12} - to C_{18} - carboxylic acids were used. This series was chosen to illustrate the effect of carbon chain length on evaporation rates.

The sequences of photographs shown in Figures 5.1 and 5.2 portray the evaporation of two surfactant solution drops. There are three noticeable differences between these sequences and the corresponding sequence for a pure water drop shown in Figure 4.2. Firstly a film of surfactant forms at the drop surface and, if the evaporation is allowed to proceed for long enough, the film becomes thick enough to make the drop surface opaque. Secondly the surfactant contaminated drops evaporated very slowly, as the surface film greatly hindered the loss of water from the drops. The effect of the different surfactants studied on drop evaporation rates is discussed in detail in Sections 5.2 to 5.6. The third difference between the sequences is that because the surface film compresses unevenly as the surface area of the drop shrinks, the drops cease to be perfectly spherical as the evaporation advances. This is unfortunate since it introduces an uncontrollable factor into the experiments, and hence leads to some loss of reproducibility in the results.

In order to separate as far as possible the effects of the surfactant and environmental conditions on drop evaporation rates, it was decided to present the results in terms of the variation of the dimensionless Sherwood number (Sh) which can be regarded as a dimensionless evaporation rate as it can easily be shown to be twice the ratio of the actual evaporation rate to that predicted by the Maxwell equation for a pure water drop (Fuchs, 1959).

The pure water rate can easily be calculated (Section 4.1), but in order to calculate the experimental evaporation rate it is necessary to determine the variation of D^2 with time and then differentiate it.

Figure 5.1 The evaporation of a drop of surfactant solution

The sequence of photographs (a) - (f) shows the evaporation of a drop of 70 ppm sodium stearate solution into air at 25°C and 12% relative humidity. The photographs have been magnified 25x and the whole sequence took place over a period of 7 hours.

Figure 5.2 The evaporation of a drop of surfactant solution

The sequence of photographs (a) - (e) shows the evaporation of a drop of 100 ppm sodium stearate solution into air at 25°C and 12% relative humidity. The photographs have been magnified 25x and the whole sequence took place over a period of 4 hours.

Photograph (f) (magnified 75x) shows the residual volume of surfactant at infinite time i.e. when all the water in the drop has evaporated.

Unfortunately the process of differentiation is an inherently unstable one and in differentiating data subject to experimental error the process tends to amplify errors unless special precautions are taken e.g. smoothing the data. A glance through the results presented in Appendix E will show that the variation of diameter with time frequently showed large, almost discontinuous, changes in gradient. This made it impractical to represent the variation of diameter squared with time by a simple polynomial because any single polynomial capable of representing these large changes in gradient would represent the experimental data so exactly as to provide almost no smoothing, and so give seriously erroneous evaporation rates when differentiated.

Accordingly it was decided to use a least squares cubic spline. The basic idea behind a spline is to split the range of the original data into a number of subregions and represent the data by a different cubic polynomial in each subregion. The boundaries of the subregions are known as knots and must be chosen by the user based on his knowledge of the form of the original data. By forcing the individual polynomials to agree with each other in value and gradient at the knots, it is possible to obtain a smooth curve. If the polynomials are chosen to fit the data in a "least squares" sense, then we have a curve with the desired properties i.e. it smooths out experimental error but is still capable of representing large changes in gradient.

A listing of the program used to process the experimental data is given in Appendix F. The program fits a least squares spline to the squares of the experimentally measured diameters and differentiates it to calculate the variation of Sherwood number with time. Simultaneously it also predicts the variation of drop temperature with time by integrating the heat balance [4.12]. The coefficients of the spline polynomials could have been calculated using a standard constrained minimisation technique such as Lagrange multipliers (Klaus and Van Ness, 1967) but the NAG library subroutines used by the program (E02BAF and E02BCF) are actually based on a rather more sophisticated technique (NAG, 1977). Detailed description of the method is beyond the scope of this thesis.

A serious problem with splines of this sort was in selecting the position and number of knots to be used. Inevitably, this choice is subjective to some degree, and ultimately a decision about the acceptability or otherwise of a fit can only be made by careful examination of the distribution of experimental points about the fitted line. Accordingly the calculated variation of Sherwood number with time is subject to a certain amount of uncertainty. Fortunately, for those experiments performed with drops suspended from thermocouples, the agreement between measured and calculated drop temperatures provided an independent check of the correctness or otherwise of the knots chosen.

Throughout this chapter, all surfactant concentrations are given in ppm (parts per million on a weight basis). The molarities corresponding to 100 ppm for the different surfactants are: NAST - 3.27×10^{-4} mol/l; NAPA - 3.60×10^{-4} mol/l; NAMY - 4.00×10^{-4} mol/l and NALA - 4.50×10^{-4} mol/l.

5.2 Sodium stearate (C_{18})

The evaporation behaviour of water drops contaminated by sodium stearate is strongly dependent on concentration. The Sherwood number always decreased with increasing concentration, but the variation was complex as Figure 5.3 shows.

At concentrations below 50 ppm (Figures E2-E7), the drops initially evaporated at the same rate as pure water drops ($Sh=2$). After a period dependent on the initial concentration, there was a rapid fall in the Sherwood number to a value approximately one twentieth of the pure water value. The evaporation rate then continued to decline, though more slowly, until the drop had evaporated. The duration of the initial "constant rate" period, when the drops evaporated at the pure water rate, fell steadily as the surfactant concentration rose until at 50 ppm it was too short to observe. The results of experiments during which drop temperatures were measured (Figures E4, E5 and E9), show that the drops' temperatures were almost exactly constant in this initial period, as would be expected for a drop evaporating at a constant rate. At the end of one experiment (Figure E5) the evaporation rate appeared to rise again for

Figure 5.3 Summary of Figures E2-E47

a short while; however this was probably a false effect caused by a badly positioned thermocouple distorting the drop and hence its evaporation rate.

At concentrations above 50 ppm (Figures E8-E15) the Sherwood number decreased steadily during the course of an experiment, though at high concentrations, the rate of change became very slow towards the end leading to a long period of evaporation at nearly constant Sherwood number. The final Sherwood numbers reached fell with increasing concentration and could become very low indeed (see e.g. Figure E12 where $Sh \approx 0.001$). This was despite the fact that the drops were still composed almost entirely of water (at the end of the experiment shown in Figure E12, the mean surfactant concentration was still only 0.2%). Furthermore the final volume reached by a drop was never significantly different from the initial volume of surfactant dissolved in the drop showing that evaporation of the surfactant was negligible. This is an important point as it has been suggested (Garrett, 1971) that very low drop evaporation rates are measurements of the rate of evaporation of surfactant rather than water.

In general the difference between measured drop temperatures and those calculated from [4.12] was within the calibration error of the thermocouples, indicating that the surfactant's heat transfer resistance was negligible in sharp contrast to its large mass transfer resistance.

To sum up, the evaporation behaviour of drops contaminated with sodium stearate can be described by a combination of constant and falling rate periods. The duration of the constant rate period and the evaporation rate in the falling rate period both fell with increasing stearate concentration.

5.3 Sodium palmitate (C_{16})

While the evaporation behaviour of drops contaminated by sodium palmitate bore similarities to that of drops contaminated by sodium stearate, there were many differences in detail. As in the case of sodium stearate the evaporation rate was strongly dependent on

surfactant concentration (see Figure 5.3).

At concentrations of 25 ppm and below (Figures E16-E18), drops initially evaporated at the pure water rate ($Sh=2$). There was then a sharp fall in the Sherwood number as the surfactant began to exert an influence on the evaporation rate. However in some experiments (see particularly Figure E32 but also E16-E17), the Sherwood number did not fall continuously, but a second constant rate period was observed at a Sherwood number of about 1. As with sodium stearate, the duration of the initial constant rate period fell with increasing concentration.

At higher concentrations (40-50 ppm) the first constant rate period vanished and the variation of Sherwood number with time began to develop a maximum i.e. the Sherwood number initially rose with time. This was in sharp contrast to the results for sodium stearate which showed a sharp fall in Sherwood number as the evaporation proceeded. The minima observed in measured drop temperatures (Figures E20 and E33) confirmed that this maximum was a real effect and not just an artifact caused by the splines. There is at present no wholly satisfactory explanation for these observations.

At concentrations above 50 ppm (Figures E21-E24) the initial Sherwood number was substantially below two and continued to fall with increasing surfactant concentration as would be expected. As at lower concentrations, the Sherwood number passed through a maximum, but the peak was much shallower. After the initial peak, the Sherwood number fell monotonically to a minimum value.

Qualitatively, the behaviour of sodium palmitate differed from that of sodium stearate in two main ways: firstly the presence of an additional constant rate period at $Sh=1$, and secondly the presence of a maximum Sherwood number after the start of evaporation. Like sodium stearate, sodium palmitate showed a strong mass transfer resistance which rose with palmitate concentration, but no heat transfer resistance. The mass transfer resistance was weaker than that of stearate but appeared earlier in a drop's lifetime.

5.3.1 The effect of relative humidity

The majority of the experiments with contaminated drops were performed at a relative humidity of 12%. However some experiments were performed at different relative humidities for sodium palmitate and sodium stearate.

The evaporation of drops contaminated by 50 ppm sodium palmitate was studied over the range 3% to 75.8% (Figures E33-E36 and E26). The main changes were that the initial Sherwood number rose slightly as the humidity increased and the maximum in the graph of Sherwood number against time became less prominent. The former effect is easily understood as relative humidity has a very strong effect on the evaporation rate of pure water drops so the experiments at higher humidities took place over a much longer timescale. This made it easier for the surfactant to diffuse away from the drop's surface, and hence lead to higher Sherwood numbers. To investigate this effect, a contaminated drop was allowed to evaporate for 25 minutes, then placed in a 100% humidity environment for the same period of time to permit the concentration gradients within the drop to relax, and then finally allowed to evaporate again (Figure E22). As expected the Sherwood number rose slightly.

Experiments performed with sodium stearate and sodium palmitate at 3% relative humidity (Figures E13-E15 and E28-E32) gave results which were very similar to those for the same concentration at 12%. Similarly experiments at 53.8% with sodium palmitate (Figures E25-E27) showed the same decrease in evaporation rate with increasing surfactant concentration which was seen at 12% relative humidity.

In general the effect of relative humidity was remarkably small. Its effect could be explained almost entirely by the variation of the pure water evaporation rate with relative humidity.

5.3.2 The effect of air temperature

This was only investigated for sodium palmitate. Three experiments were performed with drops made from 40 ppm solutions at air temperat-

ures of 15.6, 25.0, and 33.8°C (Figures E37-E39). It was impractical to use temperatures outside this relatively narrow range because condensation tended to occur in the system at lower temperatures, and at higher temperatures the drops evaporated too fast for accurate measurements with the existing equipment.

It is clear from the results that the effect of temperature was weak and the variation of Sherwood number with time followed very similar patterns at all three temperatures; in fact the shapes of the curves at 15.6 and 33.8°C are almost identical. The timescale was of course different for each drop because the evaporation rate of pure water drops is a strong function of temperature. The only other apparent difference between the three experiments was that the initial relative evaporation rate appeared to be higher at 25°C than at the other two temperatures.

5.4 Sodium myristate (C₁₄)

The results for sodium myristate (Figures E40-E44) are more confused than for the two surfactants discussed above, though similar general trends are still apparent. Part of the reason for this confusion is that sodium myristate (and also sodium laurate) retarded water evaporation relatively poorly, so drops contaminated with these materials tended to evaporate almost as fast as pure water drops. This made it difficult to measure the drop diameter enough times in a single experiment to determine the evaporation rate with accuracy.

At low myristate concentrations, drops initially evaporated at a rate near that of pure water, but the evaporation rate decreased steadily as the drop evaporated. At higher concentrations, the initial Sherwood number was below 2 and decreased with increasing surfactant concentration. At concentrations of 75 and 150 ppm the Sherwood number approached an asymptote of ≈ 0.4 as the drop evaporated.

Overall, sodium myristate showed a lower mass transfer resistance than either sodium stearate or palmitate and no detectable heat transfer resistance.

5.5 Sodium laurate (C₁₂)

In general sodium laurate behaved similarly to sodium stearate, though very much higher concentrations were necessary to produce the same degree of evaporation retardation (Figures E45-E47). Drops contaminated with sodium laurate initially evaporated at the "pure water" rate ($Sh=2$), but as evaporation proceeded the Sherwood number fell to a value of approximately 1.2. At higher concentrations this fall was more abrupt and started sooner in the drop's lifetime. This pattern is very similar to that observed for sodium stearate at low concentrations. Unfortunately it was not possible to perform experiments with concentrations above 250 ppm as the drop surface tension became so low that the drops invariably climbed up the supporting fibres used.

5.6 Other surfactants

A total of four other surfactants were investigated: Sodium lauryl sulphate (NALS, Figure E51); Cetyl trimethylammonium bromide (CTAB, Figures E48-E49); Triton X-100 (TRTN, Figures E52-E53); and Glycerol monostearate (GMST, Figure E50). Of these only the last produced evaporation rates significantly different from those of pure water. As might be expected, its evaporation resistance was broadly comparable to that of sodium stearate, but the formation of the evaporation resistance was delayed (cf. Figures E50 and E7). This may be because the more bulky end group of GMST relative to sodium stearate causes more steric hindrance, making formation of a close-packed surface layer a slower process.

The lack of resistance of CTAB to evaporation is surprising in view of the strong effect produced by sodium palmitate, which has a carbon chain of the same length. This suggests that this compound's hydrophilic group, a relatively bulky tetra-substituted ammonium group, prevents it from forming a densely packed surface layer which can retard water evaporation. This factor seems to be less important for the longer chain tetra-substituted ammonium compounds used by previous workers for which significant evaporation resistances have been reported (see Section 2.3).

The result for NALS is unsurprising in view of the low resistance of sodium laurate and is in agreement with results reported in the literature (see Section 2.3). The difference between NALS and sodium laurate must be due to the greater hydrophobicity of a carboxylate compared to a sulphate group. This would give NALS both a higher solubility and diffusivity in water, so it would have a smaller tendency to accumulate at the surface of an evaporating drop and present less of an evaporation resistance when it did accumulate there.

As can be seen from its formula, triton X-100 does not have a straight hydrocarbon chain anywhere in its structure, and the large number of oxygen atoms in its molecule make it quite hydrophilic, so it is not very surprising that it does not retard water evaporation.

5.7 Conclusions

The main conclusion is that while surfactants can display very high mass transfer resistances, they show no detectable resistance to heat transfer.

The evaporation resistance is determined exclusively by the type and quantity of the surfactant present. While the air temperature and relative humidity have a strong effect on the evaporation rate of pure water drops, they have only a weak effect on the Sherwood number.

While NAST, NAPA, NAMY and NALA all show a measurable ability to retard water drop evaporation, the evaporation resistance falls off rapidly as the length of the carbon chain decreases. NAST has a carbon chain only two atoms longer than that of NAPA, but drops contaminated with it take over twice as long to evaporate as drops containing the same quantity of NAPA. Similar differences are observed between the other surfactants. By contrast, the time lag before the first evaporation resistance appears rises with increasing chain length, so while NAST shows the highest overall resistance, it also takes longest to appear (cf. E2 and E16, E3 and E17 etc.). This is consistent with the idea that larger molecules have greater difficulty in arranging themselves at the air-water interface to form an evaporation barrier.

The effect of surfactant concentration is quite complex and varies to some extent between surfactants. However the following trends are clear:

- 1) The evaporation resistance rises with surfactant concentration;
- 2) At low surfactant concentrations, the initial evaporation rate is constant at the pure water rate. The duration of this initial "constant rate" period falls with increasing surfactant concentration;
- 3) At high surfactant concentrations, the Sherwood number tends to a low asymptotic value as the drop evaporation nears completion.

6 SURFACTANT SOLUTION DROPS: THEORY

6.1 Single drop model

The behaviour of a drop of surfactant solution as it evaporates is clearly far more complex than that of a pure water drop. In addition to the heat transfer from, and mass transfer to, the air around the drop there is movement of surfactant within the drop itself. This will be strongly dependent on the type and concentration of surfactant present. As heat and mass transfer to drops through air has already been discussed in Chapter 4, the problem of modelling the evaporation of surfactant solution drops can be broken down into two main subproblems: predicting the change in the surface concentration of surfactant as the drop evaporates, and calculating the effect of this change on the evaporation rate.

6.1.1 The concentration distribution in an evaporating drop

In a freshly formed drop, any surfactant present will be uniformly distributed throughout the drop. As the drop evaporates, the drop surface will recede, surfactant will start to accumulate at the surface and a concentration profile will build up as the accumulation is compensated for by surfactant molecules diffusing back into the drop bulk. So the concentration distribution in an evaporating drop is determined by the solution of the diffusion equation in spherical coordinates with a moving boundary at the drop surface. This problem is easy to formulate mathematically, but rather more difficult to solve. The concentration of surfactant at any point in the drop is determined by Fick's second law of diffusion

$$\frac{\partial C}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[D r^2 \frac{\partial C}{\partial r} \right] \quad [6.1]$$

It was reasonable to use this form of Fick's law, which is strictly only valid for diffusion in dilute liquid solutions, as the surfactant solutions used in this study were all extremely dilute. The initial and boundary conditions associated with this equation are

$$C(r,0) = C_0 ; \quad 0 \leq r \leq R ; \quad [6.2]$$

$$\left. \frac{\partial C}{\partial r} \right|_{r=0} = 0 ; \quad t > 0 ; \quad [6.3]$$

and

$$-D \left. \frac{\partial C}{\partial r} \right|_{r=R} = C(R,t) \frac{\partial R}{\partial t} ; \quad t > 0 . \quad [6.4]$$

Where: $C(r,t)$ is the surfactant concentration at radius r and time t ;
 D is the diffusion coefficient in the solution; and
 R is the drop radius.

Conditions [6.2] and [6.3] arise from the assumptions that the concentration distribution in the drop is initially uniform, and is always symmetrical about the drop centre. The derivation of [6.4] is given in Appendix G.

The moving boundary at the drop surface makes exact analytical solution of this partial differential equation (P.D.E.) very difficult, though analytical solutions have been found for the corresponding case of evaporation from a plane surface (Jackson and Krause, 1963, Meadley, 1971). Several workers (Charlesworth and Marshall, 1960, Schluender, 1964, Buikov, 1966) have obtained approximate analytical solutions to the P.D.E. when special conditions apply e.g. for short times or at low evaporation rates. However these are of little use for the current problem. Fortunately a useful approximate analytical solution does exist. The basis of the method used is to assume that the solution is of the form

$$C = C_0 + (C_\zeta(t) - C_0) \left[\left(\frac{R+r}{2R} \right)^{n(t)} + \left(\frac{R-r}{2R} \right)^{n(t)} \right]$$

and force $n(t)$ and $C_\zeta(t)$ to satisfy an integrated form of [6.1]. The details of the method are given in Appendix H and the solutions obtained are

$$\left. \begin{aligned} C_\zeta(t) &= C_0 \left[1 + (Pe+\beta) \frac{\theta}{\alpha} + \sqrt{\left[(Pe+\beta) \frac{\theta}{\alpha} \right]^2 + 2Pe \frac{\theta}{\alpha}} \right] \\ \text{and} \\ n(t) &= Pe-\beta + \sqrt{(Pe+\beta)^2 + 2Pe \frac{\alpha}{\theta}} \end{aligned} \right\} \quad [6.5]$$

where $\theta = \left[\frac{R_0^3}{R^3} - 1 \right]$, $Pe = - \frac{R}{D} \frac{dR}{dt}$ (the Peclet number), $\alpha = 6.1043$ and $\beta = 2.8385$.

As a check on the accuracy of the above solution, the P.D.E. was also solved numerically. The numerical solution of P.D.E.'s using

finite difference methods is a well known technique, and many textbooks on the subject are available (e.g. Gerald, 1978, Smith, 1978). The method consists of replacing the derivatives at a point by finite difference approximations based on a grid of function values. However, to solve the equation using finite difference methods, it is first necessary to fix the moving boundary by transforming to a coordinate system based on equal quantities of solute rather than equal distances. The boundaries are fixed in such a coordinate system because the total mass of solute in the drop is constant irrespective of its distribution inside the drop. The transformation required is

$$dM = 3 U \rho^2 d\rho \quad \text{or, in integrated form,} \quad \rho = \left[\int_0^M \frac{1}{U} dM \right]^{1/3} \quad [6.6]$$

where $U=C/C_0$, $\rho=r/R_0$ and M is the new coordinate (which will always be unity at the drop surface and zero at the drop centre). It can be shown (see Appendix I) that the transformed equation to be solved is

$$\frac{1}{9 U \rho^4} \frac{\partial U}{\partial Fo} \Big|_M = \frac{\partial}{\partial M} \left[f(U) U \frac{\partial U}{\partial M} \Big|_{Fo} \right]_{Fo} + f(U) \frac{\partial U}{\partial M} \Big|_{Fo} \left[\frac{4}{3\rho^3} - \frac{\partial U}{\partial M} \Big|_{Fo} \right]$$

with boundary conditions

$$U = 1 \quad \text{at} \quad Fo=0 \quad ; \quad \frac{\partial U}{\partial M} = 0 \quad \text{at} \quad M=0 \quad ;$$

and

$$\frac{dU}{dM} = \frac{Pe}{3 f(U) (1-2PeFo)^{3/2}} \quad \text{at} \quad M = 1 \quad ;$$

where $Fo=D_0t/R_0^2$ and $f(U)=D/D_0$.

Unfortunately the new P.D.E. has nonlinear coefficients so a special finite difference scheme had to be used. The method chosen was a three time-level method due to Lees (1966) who considered the non-linear P.D.E.

$$\Phi \left[X, t, U, \frac{\partial U}{\partial X} \right] \frac{\partial U}{\partial t} = \frac{\partial}{\partial X} \left[\Omega \left[X, t, U \right] \frac{\partial U}{\partial X} \right] + \Psi \left[X, t, U, \frac{\partial U}{\partial X} \right] \quad [6.7]$$

He showed that it was possible to obtain a finite difference representation of [6.7] which was linear in the unknowns by evaluating the non-linear coefficients Φ, Ω and Ψ at a time level of known solution values. The finite difference approximation used was

$$\Phi \left[\frac{U_{i,j+1} - U_{i,j-1}}{2 \Delta t} \right] = \omega^+ \left[\frac{\hat{U}_{i+1,j} - \hat{U}_{i,j}}{\Delta X^2} \right] - \omega^- \left[\frac{\hat{U}_{i,j} - \hat{U}_{i-1,j}}{\Delta X^2} \right] + \Psi$$

where: $U_{i j}$ is the value of U at time t_j and position x_i ;

Δt and ΔX are the time and distance grid spacings respectively;

$$\hat{U}_{i j} = (U_{i j+1} + U_{i j} + U_{i j-1}) / 3;$$

$$\phi = \phi \left[x_i, t_j, U_{i j}, (U_{i+1 j} - U_{i-1 j}) / 2\Delta X \right];$$

$$\omega^+ = \omega \left[(x_{i+1} + x_i) / 2, t_j, (U_{i+1 j} + U_{i j}) / 2 \right];$$

$$\omega^- = \omega \left[(x_i + x_{i-1}) / 2, t_j, (U_{i j} + U_{i-1 j}) / 2 \right];$$

and $\psi = \psi \left[x_i, t_j, U_{i j}, (U_{i+1 j} - U_{i-1 j}) / 2\Delta X \right].$

Such a scheme would normally be unstable (Smith, 1978, p54), but Lees overcame this problem by the averaging of $U_{i j}$ over three time levels. He maintained accuracy by using central-difference approximations and showed that, for sufficiently small values of Δt and ΔX , the maximum error in the calculated solution $\leq A (\Delta t^2 + \Delta X^2)$ where A is a constant. The method was implemented in the FORTRAN subroutine NLPDE and tested out using the non-linear example given by Smith (1978, p55). The test problem was solved using both Dirichlet and derivative boundary conditions and, when run with the same step sizes, reproduced the solution given by Smith to seven decimal places. The full program used is listed in Appendix J.

One of the major advantages of this method of solution is that it is easy to check the accuracy of the solution obtained because of the nature of the transformation used to fix the moving boundary. For a constant Peclet number, the drop radius can be calculated at any time from

$$R(t) = R_0 \sqrt{(1 - 2PeFo)}$$

But, if the solution to the P.D.E. is known, the drop radius can also be calculated from equation [6.6]. Obviously any difference between these two radii will be a measure of the error in the P.D.E. solution. In the program this difference is calculated by the subroutine RCHECK which evaluates the integral in [6.6] numerically using Simpson's rule. The extra error introduced by this step is minimal since the error in Simpson's rule is proportional to ΔX^4 , while the error in the P.D.E. solution is proportional to $(\Delta t^2 + \Delta X^2)$. For the step sizes given in

the program listing, the maximum difference between the two radii was 0.026% and the program took 4400 seconds of CPU time to run. In addition the program was run for a series of values of Δt and ΔX to check that its results converged as $\Delta t \rightarrow 0$ and $\Delta X \rightarrow 0$.

Van der Lijn (1976) also solved this problem numerically using a similarly transformed P.D.E. but a different finite difference method. His results are shown in Figure 6.1 along with the author's two solutions. As can be seen the agreement is good and the approximate analytical solution agrees with the author's numerical solution to within 10% over a wide range of Peclet and Fourier numbers. The curves representing Van der Lijn's solution were traced from an enlarged copy of Figure 2 in Van der Lijn (1976) and this probably accounts for the apparent difference between the two numerical solutions.

6.1.2 The effect of surfactant on evaporation rate

As a drop evaporates, its surface recedes and the concentration of surfactant at the surface will rise. When it passes a critical concentration, a separate film of surfactant will form at the surface and the properties of the drop surface will change dramatically. This change is much greater for surfactants than for other solutes because of the special orientational behaviour of surfactants at interfaces. The film will become steadily thicker as the drop continues to evaporate. Figure 6.2 shows a schematic diagram of the concentration profiles in this system. A surface film of surfactant could modify the drop's evaporation rate in two ways. Firstly, since water molecules would be evaporating from a surface which was primarily surfactant rather than water, the vapour pressure of water at the drop surface would be different. Secondly, since water molecules would have to diffuse through the layer of surfactant to get to the surface there would also be a diffusional resistance to the passage of water molecules. The model presented here assumes that both mechanisms have an effect.

Equations [6.5] can be used up to the point when the surface concentration of surfactant reaches its critical value. After this point, however, it is necessary to predict: a) the development of the

Figure 6.1

Figure 6.2. Concentration profiles in an evaporating solution drop

surfactant's concentration profile within the drop bulk; b) the increase in film thickness; and c) the rate of water transfer through the surface film (and hence the decrease in drop size).

Once the critical concentration has been reached, the surfactant concentration cannot rise any further as any excess surfactant will pass over into the surface film. The derivation of equations [6.5] can be extended to take this restriction into account (see Appendix K(a)) and hence the surfactant's concentration profile within the drop will be described by $C_L(t)$ and $n(t)$ as before but with $C_L(t)$ constant and $n(t)$ given by the solution of

$$\frac{dn}{dt} = \left[n D_1 + 2 R \frac{dR}{dt} (1-3 F) \right] / 2 R^2 \frac{dF}{dn} \quad [6.8]$$

where $F(n) = \frac{2(n^2 + n + 2)}{(n+1)(n+2)(n+3)}$.

The rate of accumulation of surfactant in the surface film can be calculated from the difference between that swept into the film by the receding drop surface and that diffusing back into the body of the drop. The result (derived in Appendix K(b)) is

$$\frac{d\Gamma}{dt} = 2\pi R \left[n D_1 (C_0 - C_R^-) - 2 R \frac{dR}{dt} C_R^- \right] \quad [6.9]$$

where Γ , the total mass of surfactant in the film is related to the film thickness δ by

$$\delta = \Gamma / 4\pi R^2 \rho_f \quad [6.10]$$

Because the surface film is very thin, its relaxation time will be small compared to the drop's lifetime and so it can be regarded as being in a quasi-steady state. A simple flux balance (Appendix K(c)) then gives

$$\rho_1 R \frac{dR}{dt} = \frac{Sh}{2} D_g (\rho_0 - \rho_\infty) \quad [6.11]$$

where

$$Sh = \frac{2}{1 + \left[\frac{D_g A \delta}{D_2 R} \right]} \quad [6.12]$$

and A is a Henry's law type constant (see below).

Equations [6.8] to [6.12] form a system of coupled ordinary differential equations. They are too complex for analytical solution,

but are readily integrated numerically using e.g. the Runge-Kutta method (see Section 4.1). Subroutine DERIV3 in Appendix L specifies these differential equations in a form suitable for numerical integration. It only remains to specify the five surfactant-specific physical constants needed by the system: these are the critical surface concentration at which a surface film forms, the two diffusivities D_1 and D_2 , the Henry's law constant A , and the density of the surface film ρ_f .

The behaviour of surfactants in aqueous solution is unusual in that above a certain critical concentration (the critical micelle concentration or CMC), molecular agglomerates (or micelles) form in solution. They may take a number of shapes depending on the surfactant and its concentration, but in each case the hydrophilic parts of the surfactant molecules are on the outside surface of the micelle and the hydrophobic parts are inside. Similarly surfactant molecules absorbed at an air-water interface will orientate themselves so that the hydrophobic parts of the molecules are as far away from the water surface as possible. The orientation process needed in each case is very similar so it seems reasonable to take the CMC as the critical surface concentration above which a separate surface layer will form. The CMC's of all four surfactants have been measured (Lin and Somasundaran, 1971) and are tabulated in Table 6.1.

Table 6.1

Surfactant	Molecular weight	CMC ppm	$D_1 \times 10^{+10}$ m ² /s	δ nm	R s/m	$D_2 \times 10^{+14}$ m ² /s	Sh*
NALA	222	4830	3.25	1.60	11.8	13.5	1.32
NAMY	250	1100	3.06	1.87	32.2	5.8	0.83
NAPA	278	250	2.90	2.13	87	2.44	0.418
NAST	306	55	2.76	2.40	238	1.01	0.177

* Calculated from [6.12] for a monolayer on a 0.6 mm radius drop.

The diffusion of surfactants in dilute aqueous solutions has been studied in some detail because of its complexity (Cussler, 1984). However, there are no diffusivity data in the literature for the fatty

acid salts studied here, and so it was necessary to estimate D_1 . Liquid diffusivities can be predicted from e.g. the Stokes-Einstein equation (Cussler, 1984)

$$D = \frac{k_B T}{6\pi \mu R_0} \quad [6.13]$$

where k_B is Boltzmann's constant, μ is the solvent viscosity and R_0 is the solute radius, but since [6.13] strictly only applies for large spherical solute molecules its predictions are not guaranteed to be reliable. So instead it was decided to pick a surfactant for which experimental diffusivity data were available, and use [6.13] to adjust the data as necessary. Of the surfactants for which diffusivity data were available, sodium dodecyl sulphate was the most similar to the fatty acid salts used here. While a number of workers have measured its diffusivity at relatively high concentrations (Okuyama, 1957, Weinheimer et al., 1981, Evans et al., 1983) only Fainerman and Zhidkov (1976) have made measurements at surfactant concentrations comparable to the very low values used here. Fortunately their diffusivities were only weakly concentration dependent and it was possible to take a mean value of $2.85 \times 10^{-10} \text{ m}^2/\text{s}$. The diffusivities of the fatty acid salts were then scaled from this value by using [6.13] and assuming that their solute radii were proportional to the square root of their molecular weight. The results obtained are shown in Table 6.1.

In the absence of any direct measurements of the diffusivity of water through surfactants, or even any reliable methods of predicting D_2 , it was necessary to use an indirect estimate. Comparing [6.11] and [6.12] with previous models (see e.g. equations [2.3] and [2.5]) it is clear that the term $\delta A/D_2$ is equivalent to the monolayer resistance R . So provided δ and A are known, D_2 can be estimated from experimental measurements of R made using monolayers on Langmuir troughs. This procedure probably underestimates the diffusivity as a multimolecular surfactant layer is likely to present less of a resistance to the passage of water than a highly ordered monolayer. While R and δ have not been measured for the sodium fatty acid salts used here, they are known for the corresponding pure acids which can be used instead as a reasonable approximation. The thickness of a stearic acid monolayer is 2.4 nm (Langmuir and Schaefer, 1943) and the thickness of the other monolayers can easily be determined by scaling down in proportion to

the length of the surfactant's carbon chain. The evaporation resistances of the C₁₇ to C₂₃ fatty acids monolayers have been thoroughly investigated (see Table 2.2) and have been shown to follow the relationship (Archer and La Mer, 1955)

$$\log_{10}(R) = 0.21734 \left[\text{number of carbon atoms} \right] - 1.5355$$

from which it was a simple matter to calculate the corresponding values of D₂ (Table 6.1). The estimated values all fall within the expected range of 10⁻¹⁰ to 10⁻¹⁹ m²/s for solid diffusivities (Cussler, 1984).

There is very little information in the literature on the vapour pressure of water above concentrated surfactant solutions at ambient temperature, though a limited amount of work has been performed on the phase equilibria of commercial soaps at moderate to high temperatures. McBain and Lee (1943) presented vapour pressure data for five pure soaps and a commercial soap. Unfortunately, their pure soap data were obtained for the temperature range 65–130°C, and even for the commercial soap the lowest temperature used was 40°C. As a result only an estimate of the vapour pressure at 25°C can be made. In view of this uncertainty, and the low concentrations of water present in the surfactant films, the relationship between water concentrations in the air (ρ) and surfactant film (W) was assumed to follow the linear form ρ = A W. The value of A was calculated from McBain and Lee's data as 1.0 × 10⁻³.

The density of the surface film was difficult to estimate as it was formed under quite different conditions to those of the original powdered surfactant. However, as the surfactants appeared to have nearly neutral buoyancy in their original solid form (during solution), ρ_f was assumed to be 1000 kg/m³.

The mathematical model and associated physical constants needed to predict the evaporation behaviour of single drops of surfactant solution has now been completely specified. The next Section compares the model's predictions with the experimental data presented in Chapter 5.

6.1.3 Comparison with experiment

The model was used to predict the evaporation behaviour of drops contaminated with 10, 20, 50, 75 and 150 ppm of sodium stearate, palmitate, myristate and laurate at 25°C and 12% relative humidity. Figure 6.3 shows a comparison of these predictions with typical experimental results. No predictions are shown for low concentrations of sodium myristate and sodium laurate because there were no experimental data to compare with, and it is clear from the figure that the model would predict negligible evaporation resistances for these cases.

In the case of sodium stearate agreement was quite good, particularly when it is borne in mind that the model has no fitted parameters. The model predicted the concentration dependence of the end of the constant rate period well, but was less good at predicting the fall in the Sherwood number during the falling rate period. There were two differences between theory and experiment during this period. The first was that, in cases where the onset of the falling rate period was later than predicted, the measured Sherwood number fell rapidly so that it had soon rejoined or even overtaken the predicted curve rather than following a completely different path. This suggests that the formation of a surface film is analogous to the supercooling of e.g. a saturated salt solution where a supersaturated solution can persist for a significant period of time in the absence of seeds for crystallization. To predict the presence and effects of seeds in such a solution quantitatively would be extremely difficult, but it gives a possible qualitative explanation of the observed fact that the evaporation resistance was formed slightly later and more rapidly than predicted by theory. The second difference was that the asymptotic Sherwood number approached towards the end of evaporation was higher than predicted. There are two possible explanations for this. One is that, as discussed in the previous Section, the value of D_2 used might be an underestimate of the diffusivity of water through a multi-molecular surfactant film. The other is that the model, by under-estimating the quantity of surfactant diffusing back into the drop bulk, is overestimating the thickness of the surface film. It is not possible to test either of these explanations without extensive further experimental work.

Figure 6.3 Comparison of theory and experiment

Notwithstanding these differences, the model is clearly far superior to those which have appeared in the literature (see Sections 2.2 and 2.4), none of which is capable of predicting even the qualitative behaviour of sodium stearate, still less its quantitative behaviour.

The experimental results for sodium palmitate, however, are not readily explicable in terms of the model presented above. In particular the model is incapable of explaining either the very early formation of the evaporation resistance or the maxima in Sherwood number. The speed with which the evaporation resistance formed must be related to the absorption of surfactant molecules at the air-water interface, and some observations made by Kudritskii et al. (1981) may be of relevance here. As part of an investigation to find the time needed for a saturated monolayer to form on the surface of a drop, they measured the surface tension of sessile drops placed in an environmental cell at 100 % relative humidity over time. The drops were made from potassium stearate solutions with a range of concentrations. They found that if the initial surfactant concentration was below the CMC, the drop surface tension slowly declined to an equilibrium value over one to two hours as expected. However, if the initial concentration was above the CMC, the surface tension fell through a minimum before rising again to its equilibrium value. The time to reach the minimum rose with concentration up to a maximum of approximately twenty minutes. They were unable to provide a convincing explanation of these minima, but suggested that they might be due to the surfactant hydrolysing in solution.

Unfortunately Kudritskii et al.'s parallel measurements of drop evaporation rates were not sensitive enough to show whether potassium stearate contaminated drops showed a corresponding maximum in their evaporation rates. But clearly, if a drop's surface tension can pass through a minimum, it is possible for surfactant molecules to both adsorb to and desorb from the drop surface, and hence a maximum in the drop evaporation rate is also possible. Unfortunately modelling such phenomena requires a detailed knowledge of the absorption behaviour of surfactants at air-water interfaces. That knowledge is lacking for the surfactants used in the present study, though a comparison of the initial Sherwood number for a sodium palmitate contaminated drop ($Sh=1$)

with that for a monolayer covered drop (0.42, see Table 6.1) suggests that sodium palmitate forms a partial monolayer very quickly except at very low concentrations.

As might be expected, given their shorter carbon chains, sodium myristate and laurate show behaviour which is even more difficult to predict. Overall then, while it is possible to use the theory presented above to predict the evaporation of relatively long chain fatty acid salts such as sodium stearate, short chain fatty acid salts show more complex behaviour and would need a correspondingly more complex model.

6.2 Aerosol model

It is now possible to attempt the objective given in Chapter 1, namely to construct a model to describe the the evaporation of a contaminated aerosol, and compare its predictions with the experimental measurements of Raper et al. (1982) of the changes in size distribution of aqueous aerosols passing down the length of a wind tunnel. This required a number of extensions to the single drop model described in Section 6.1.

Firstly as the drops in an aerosol are not supported, it was necessary to take the loss of droplets by settling under gravity into account. For the small drop sizes present in an aerosol it was reasonable to assume that the drops would rapidly attain their terminal velocities and then continue to settle at that rate. The terminal velocities of the drops were calculated from the terminal Reynolds numbers, which in turn were calculated from the Best number N_D (Clift et al., 1978)

$$N_D = 4 D^3 \rho_g (\rho_l - \rho_g) g / 3 \mu^2$$

where μ is the gas viscosity and ρ_g and ρ_l are the densities of the gas and drop respectively. The correlations used for Re were:

(a) $N_D \leq 73$

$$Re = N_D (1/24 + N_D (-1.7569 \times 10^{-4} + N_D (6.9252 \times 10^{-7} - N_D 2.3027 \times 10^{-10}))),$$

(b) $73 < N_D \leq 580$

$$\log_{10}(Re) = -1.7095 + \log_{10}(N_D) \left[1.33438 - \log_{10}(N_D) 0.11591 \right],$$

or (c) $580 < N_D$

$$\log_{10}(\text{Re}) = -1.8139 + \log_{10}(N_D) \left[1.34671 + \log_{10}(N_D) \left[-0.12427 + \log_{10}(N_D) 0.006344 \right] \right] .$$

Integrating the terminal velocity with respect to time gives the height fallen and hence whether or not a given drop is still within measurement range.

Secondly, because the terminal velocities of water drops in air are quite large, it was necessary to allow for the effect of relative movement between the drop and air on the Sherwood and Nusselt numbers by including a wind factor (Fuchs, 1959) hence

$$\text{Sh} = 2 \left(1 + 0.276 \text{Re}^{1/2} \text{Sc}^{1/3} \right)$$

and

$$\text{Nu} = 2 \left(1 + 0.276 \text{Re}^{1/2} \text{Pr}^{1/3} \right).$$

This effect reduces the lifetime of a 100 μm diameter droplet by approximately 30%.

Finally, the third difference was that, instead of just predicting the behaviour of a single drop having a given initial size, it was necessary to predict the behaviour of a number of drops each having a different initial drop size. The original drop size distribution of the aerosol was divided into a number of size fractions and the behaviour of each fraction represented by the evaporation and settling of a single drop. By integrating the differential equations describing the behaviour of single drops (see Section 6.1.2) for a number of different initial drop sizes and then combining the predicted drop sizes with the number of drops of each size, the overall size distribution could be predicted. Providing the number of size fractions is not too few, this will give a good approximation to the real distribution. As in the case of previous models, the computer program produced was run for a series of values of Δt and number of size fractions to confirm that the results converged as $\Delta t \rightarrow 0$ and the number of size fractions $\rightarrow \infty$. The program as listed in Appendix L took 1900 seconds of CPU time to run for the step sizes shown.

6.2.1 Comparison with experiment

It was first necessary to confirm that the model was capable of accurately predicting the behaviour of pure water aerosols. Most experimental work on the evaporation and settling of pure water drops has been performed with either very large or very small drops, since drops in the 10-100 μm size range are difficult to suspend physically and too large to suspend using electrostatic forces. However, Lambert and Quince (1969) studied drops in this intermediate range by determining 'cut-off radii' (the drop size in an aerosol which just evaporated on falling through a fixed height) from the drop size distributions at the top and bottom of a vertical tube. Their results for a tube 3.57 m high kept at a constant temperature of 28.3°C are shown in Figure 6.4 for comparison with theoretical predictions.

Agreement is excellent over the whole relative humidity range. The only noticeable difference occurs between the two theoretical curves at 90% where Lambert and Quince predicted a slightly smaller cut-off radius, and hence a slightly slower evaporation rate. It is difficult to know how much weight to give this point as Lambert and Quince used graphical integration to predict cut-off radius and gave no indication of the number of calculations undertaken, only a graph. In any event the author's predictions are in better agreement with the experiment results, and so can be taken as correctly predicting both drop settling and evaporation.

The aerosol experiments of Raper et al. (1982) used a wet wind tunnel with four observation ports each spaced 1 m apart. A Malvern laser droplet detector was used to measure the drop size distribution of the aerosol as it passed each port and hence follow the changes in the size distribution over time. Figure 6.5 shows three sets of their results, and the experimental conditions used are summarised in Table 6.2.

Figure 6.4

Figure 6.5

Key to Figures 6.5-6.9

Observation port	Symbol
1	— $\triangle$ —
2	- - - ∇ - - -
3	... $+$...
4	- · - $\times$ - · -
5	- - - $\square$ - - -
6	- - - $\diamond$ - - -
7	- - - $\bigcirc$ - - -

Table 6.2

Experiment number	Temperature (°C)	% Relative humidity	Velocity (m/s)
1	32	32	2
2	26	55	3
3	30	97	3

In the period immediately after generation, the drop size distribution of a pure water aerosol would be expected to narrow as large drops settled out and small drops evaporated to extinction. As can be seen, however, the results for experiments 2 and 3 show the proportion of small drops increasing over time, and even in the case of experiment 1 the decrease is only short lived. As discussed in Section 1.1, Raper et al. hypothesised that surfactant contaminants in their system were retarding the evaporation of small drops and hence producing the observed rise in their number.

To test this theory, the aerosol model was used to try to predict the evaporation behaviour of these contaminated aerosols. Unfortunately it soon became clear that while surfactants could produce qualitatively similar results to those shown in Figure 6.5, their effect was too weak to reproduce quantitatively the large effects observed experimentally. To understand this, it is necessary to consider Table 6.3 which compares various theoretical predictions of the proportion of small drops at the last observation port.

Table 6.3 Weight % under 10 μm at observation port 4

Experiment number	Raper et al. (experiment)	Pure water (predicted)	Evaporation stopped at	
			10 μm	8 μm
1	9.6	0.9	14.1	9.0
2	10.6	0.4	17.3	12.9
3	21.5	4.9	10.3	7.0

The second and third columns of the table confirm that Raper et al.'s results cannot be explained in terms of pure water evaporation as the observed weight % of small drops are all an order of magnitude larger than the predicted values. This was expected, however, the observed weight % are also larger than any value which could plausibly be produced by the effect of surfactants. The fourth column in the table shows the predicted weight % of small drops on the assumption that drops larger than 10 μm evaporate at the pure water rate, but drops below 10 μm do not evaporate at all. This gives the maximum number of small drops possible, as no drop will ever stop evaporating completely in the presence of a surfactant and some drops will start to evaporate more slowly well before they reach 10 μm . Even given this extremely optimistic assumption, it is impossible to account for the results of experiment 3. Furthermore, if the diameter at which evaporation stops is lowered to 8 μm to give a slightly less optimistic prediction (the fifth column in the table), it also becomes impossible to account for the results of experiment 1. This strongly suggests that the presence of surfactants cannot explain Raper et al.'s results, and a large number of numerical experiments with the mathematical model confirmed that even surfactants with very large evaporation resistances were only capable of increasing the weight % under 10 μm to 2.3 % for experiment 1.

The basic problem here is that while a highly retarding surfactant can bring the evaporation of existing small drops virtually to a halt, the number of small drops will only rise significantly if the evaporation of larger drops is still rapid enough for drop shrinkage to keep supplying new small drops. In practice, real surfactants cannot discriminate by size in this way and tend to slow the evaporation of all drops to some extent.

To confirm this conclusion, the model was used to predict the development of a contaminated aerosol's size distribution over time for each of the three experimental conditions given in Table 6.2. Various concentrations of sodium stearate were used to represent the contaminant, and the results are shown in Figures 6.6-6.8. To facilitate comparison with Raper et al.'s experimental results, the drop size distributions measured at their first observation port were

Figure 6.6

Figure 6.7

Figure 6.8

used as the starting point for the model in each case. This introduces a slight error into the predictions as the drops actually started to evaporate as soon as they left the aerosol generator, and so some redistribution of surfactant might have taken place within the drops before they reached the first observation port. Since the drop size distribution produced by the aerosol generator is unknown, it is impossible to correct this error, but it is probably small for the short time interval involved.

As the model predicted relatively small changes in the drop size distributions along a wind tunnel of the length used by Raper et al., the model was also used to predict the larger changes that would occur along a tunnel twice as long. As before the observation ports were spaced 1 m apart, but there were now seven of them, the first four of which corresponded to those used experimentally.

The predictions for experiment 1 (Figure 6.6) show a steady decline in mean droplet diameter as the aerosol passes along the wind tunnel irrespective of surfactant concentration. However, the decline became smaller as the surfactant concentration rose. This is because drop evaporation becomes very slow for surfactant concentrations above 40 ppm, and so for the short timescales of interest here the primary factor influencing the drop size distribution was settling of the larger drops. This is in contrast to the case of a pure water aerosol where drop evaporation is the primary factor.

The proportion of small drops in a pure water aerosol initially falls as they evaporate faster than larger drops can shrink to replace them. This effect is later reversed as the mean drop size gets smaller and small drops become proportionately more important. However, when a surfactant is added to the aerosol it slows the evaporation of the smaller, more rapidly evaporating, drops first, so the initial decline in the proportion of small drops is diminished or even eliminated entirely if the surfactant concentration is high enough. The number of small drops rises very little in the presence of high surfactant concentrations because larger drops evaporate too slowly to increase it.

Comparing the predictions and experimental results, it is clear that while similar qualitative features are present in each, there is no quantitative agreement between the two at any surfactant concentration. There is a superficial resemblance between the measured size distribution at the fourth observation port and that predicted for the seventh for 10 ppm sodium stearate, however, it seems extremely unlikely that Raper et al.'s velocity measurements were in error by a factor of two, and this must be coincidence.

The predictions for experiment 2 (Figure 6.7) are very similar to those for experiment 1 except in one respect. As the drop size distribution measured at the first observation port had a relatively large number of drops under 10 μm in size, the initial decline in their number was much more noticeable. As before the number of small drops increased over time as small slowly evaporating drops accumulated. In complete contrast, Raper et al.'s measurements showed no decline at all in the number of drops below 10 μm , but a steady increase over time. As before, the decline and later rise in the proportion of small drops became progressively smaller as the concentration of surfactant rose, and the drops' evaporation was retarded sooner.

At very high relative humidities (as in experiment 3, Figure 6.8) the model predicted very small changes in the drop size distribution even over twice the timescale studied experimentally. In the absence of surfactant there was a slight narrowing of the drop size distribution due to small drops evaporating to extinction and large drops settling out, though neither effect was large. This was because the high relative humidity greatly slowed droplet evaporation anyway and the relatively small maximum drop size meant that drop settling was also slow. Even using 150 ppm sodium stearate to stop drop evaporation entirely merely eliminated changes at the lower end of the size distribution. These predictions are in sharp contrast to Raper et al.'s observations of large changes in the drop size distribution.

To examine how sensitive these predictions were to the assumption of sodium stearate as the contaminant, the sensitivity of the model's predictions to changes in the five surfactant specific parameters (D_1, D_2, ρ_f, A and CMC) was examined (Figure 6.9). The base case was

Figure 6.9

taken to be experiment 1 with 10 ppm sodium stearate as the contaminant. Each of the parameters was varied over a range of two orders of magnitude about the value for sodium stearate. Table 6.4 shows the exact values used. For clarity, predictions are only shown for observation ports four and seven (differentiated by line type as in previous figures) along with the initial size distribution at the first port for comparison.

Table 6.4. Key to Figure 6.9

Symbol	Value	$D_1 \times 10^{10}$ m ² /s	$D_2 \times 10^{14}$ m ² /s	ρ_f kg/m ³	CMC ppm	A -
A	NAST*10	27.60	10.10	10000	550.0	0.0001
B	NAST*2	5.52	2.02	2000	110.0	0.0005
C	NAST	2.76	1.01	1000	55.0	0.001
D	NAST/2	1.38	0.50	500	27.5	0.002
E	NAST/10	0.28	0.10	100	5.5	0.01

The parameters D_2 , ρ_f and A each only occur in one position in equations [6.10] and [6.12], and if [6.10] is substituted into [6.12] they all occur in a single position as the ratio $A/D_2\rho_f$. Hence the sensitivity of the model to proportional changes in D_2 and ρ_f will be identical, that to changes in A will be directly inverse, and so the sensitivity of all three parameters can be shown on the same graph as in Figure 6.9.

It is clear from the predicted size distributions that the model is remarkably insensitive to even quite large changes in the surfactant's physical properties. This is particularly marked in the case of the fourth observation port. While the mean drop size at this point does vary slightly (particularly with variations in CMC) the weight % of drops smaller than 10 μm varies by very little. Clearly changing the surfactant's physical properties will not move the predictions any closer to the experimental results. By the time the seventh port is reached the predictions are much more sensitive (again particularly to variations in CMC). The proportion of small drops now varies

significantly because the mean drop size is varying so much. As would be expected, increases in D_2 , ρ_f and the CMC and decreases in A all lead to lower evaporation resistances and hence lower mean drop sizes. By contrast the base value of D_1 produces a lower evaporation resistance than either higher or lower values of D_1 . Overall, the results seem to be more sensitive to changes in the parameters which govern when the surfactant starts to exert a retarding effect (C_0 and CMC) than to those which determine the evaporation resistance itself (D_2 , ρ_f and A).

The final conclusion must be that while surfactants can influence aerosol evaporation dramatically, they cannot be responsible for the specific effects observed by Raper et al., though they are capable of producing many qualitatively similar features. Clearly there must be another explanation for their experimental results, and the most likely is experimental error. The distance between the aerosol generator and first observation port was only 1 m, so it is possible that the aerosol was not evenly distributed across the height and width of the wet wind tunnel by the time it reached the observation ports. In these circumstances the drop size size distributions measured by the Malvern laser droplet detector would not be representative of the true size distributions, and the expected effects due to droplet evaporation and settling would be confounded with effects due to the movement of different size fractions across the height and width of the tunnel.

The results presented here have been restricted to the behaviour of aerosols being transported along a horizontal duct, but the model could easily be extended to predict the behaviour of contaminated aerosols in other similar situations e.g. in transport up or down vertical ducts, in fogs etc.

7 CONCLUSIONS

While the experimental work presented here confirms the literature consensus that surfactants are capable of displaying very high mass transfer resistances, it also showed that their behaviour is more complex than has hitherto been acknowledged.

No evidence was observed of surfactants giving rise to heat transfer resistances or causing evaporation rates above those of pure water, though drops contaminated with sodium palmitate could show maxima in their evaporation rates.

The mass transfer resistance varied strongly with the type and quantity of surfactant present, but only weakly with the air temperature and relative humidity. The resistance increased rapidly with the length of the surfactant's carbon chain, though the time lag before it first appeared also increased with chain length. The resistance always rose with increasing surfactant concentration, but not in a simple manner. At low surfactant concentrations, there was an initial "constant rate" period when the drop evaporated at the pure water rate. The duration of this period fell with increasing surfactant concentration, eventually disappearing altogether. At high surfactant concentrations the Sherwood number tended to a low asymptotic value as the drop's evaporation neared completion.

A mathematical model of the effect of surfactants on the evaporation of single water drops was formulated, solved and shown to give good agreement with the experimental data for sodium stearate. It was unable to predict the behaviour of the other surfactants because its model of molecular behaviour at the water-surfactant film interface was too simplistic. To correct this deficiency, it would be necessary to make measurements of the adsorption kinetics of surfactant at the air-water interface and incorporate these in the model. In the case of sodium palmitate, the chemical kinetics of any hydrolysis reactions might also be needed. It would be desirable to make direct measurements of the diffusivity of surfactants in surfactant-water systems over the full concentration range. It would then be worth replacing the approximate analytical solution used here to describe diffusion

within the drop by a more accurate numerical solution.

A model was also constructed to predict the evaporation behaviour of surfactant contaminated aerosols. Numerical experiments with the model showed that even very low concentrations of surfactants were capable of substantially altering the evolution of an aerosol's drop size distribution over time and slowing the reduction in mean size. The predictions of the model were reasonably sensitive to changes in the parameters which governed when the surfactant started to exert a retarding effect (C_0 and CMC), but relatively insensitive to those which determined the evaporation resistance itself (D_2 , ρ_f and A).

The model was used to show that the results of Raper et al. cannot be explained quantitatively by a surface active contaminant, though surfactants can produce qualitatively similar results, and it must be concluded that their results were probably caused by experimental error.

Appendix A. The evaporation rate of two adjacent drops

The partial differential equation describing the evaporation of a single drop is Fick's second law

$$\frac{\partial \rho}{\partial t} = D_g \nabla^2 \rho$$

The associated boundary conditions are unit concentration on the drop's surface and zero concentration an infinite distance from the drop. In the case of two drops, the same equation applies but it is necessary to satisfy an additional boundary condition that the concentration on the surface of the second drop must also be unity.

If the evaporating drops are assumed to be in a quasi-steady state, derivatives with respect to time can be ignored and the problem reduces to solving Laplace's equation

$$\nabla^2 \rho = 0$$

for the boundary conditions shown in Figure A1. This system can be solved by using the method of images to solve the analogous electrical problem. Ferrari (1975) discusses the method of images in some detail, so only an outline of the method is presented here.

Figure A1

In the analogous electrical system, the evaporating drops are replaced by conducting spheres each of which has its surface at unit potential. The distribution of potential (V) around the spheres is governed by Laplace's equation

$$\nabla^2 V = 0$$

with the boundary conditions that $V=1$ at the surfaces of the spheres and $V=0$

an infinite distance from them. Clearly concentration and potential are analogues. Since mass flux is proportional to concentration gradient and electrical flux is proportional to potential gradient, mass and electrical flux are also analogous, and the evaporation rate of the two water drops can be determined from the total electrical flux from the analogue spheres.

The potential distribution around a single isolated sphere can be described by a single unit charge at the drop centre; however, when a second conducting sphere is brought into the vicinity of the first, its charge will induce a small additional charge in the second sphere (the first order image). At the same time, the unit charge on the second sphere will induce a corresponding charge in the first sphere. Each of these first order images will in turn induce a smaller second order image, and the process can be continued ad infinitum or until the images are too small to have any practicable effect. By summing up the contributions due to each of the images, the potential (and by analogy the concentration) at any point can be found. The magnitude and positions of the first few images are given by

$$\begin{array}{lll} \text{Zeroth order images} & q_0 = 1 & \text{at} \quad \pm \epsilon_0 = \epsilon \\ \text{(isolated spheres)} & & \end{array}$$

$$\text{First order images} \quad q_1 = \frac{-q_0}{(\epsilon + \epsilon_0)} \quad \text{at} \quad \pm \epsilon_1 = \epsilon - \frac{1}{(\epsilon + \epsilon_0)}.$$

In general the ' $i+1$ 'th order images are related to the ' i 'th order images by

$$q_{i+1} = \frac{-q_i}{(\epsilon + \epsilon_i)} \quad \text{at} \quad \pm \epsilon_{i+1} = \epsilon - \frac{1}{(\epsilon + \epsilon_i)}$$

Summing the contributions of all the images, we obtain

$$\rho = \sum_{i=0}^{\infty} q_i \left[\frac{1}{\sqrt{(X + \epsilon_i)^2 + Y^2}} + \frac{1}{\sqrt{(X - \epsilon_i)^2 + Y^2}} \right]$$

for the concentration distribution around the two evaporating drops. This solution can easily be shown to satisfy the required boundary conditions by summing the infinite series.

In the electrical analogue the drop evaporation rate is equivalent to the total electrical flux crossing the drop's surface. However, Gauss's law (Ferrari, 1975, p15) states that the integral of the electrical flux over any surface is simply the total quantity of charge enclosed by that surface. Since electrical flux and evaporation rate are analogues, the drop evaporation rate can be written down immediately as

$$F = \sum_{i=0}^{\infty} q_i$$

In the case of a single isolated drop the only charge present is $q_0=1$ and so $F=1$ as would be expected.

Figure A2 shows the calculated dependence of F on 2ϵ for a pair of drops. As can be seen, the evaporation rate declines rapidly as the two drops approach each other. When the drop centres are three radii apart the evaporation rate is reduced to approximately 75% of the unhindered rate.

Figure A2. The evaporation rate of adjacent drops

Appendix B. The flow of heat to an evaporating drop along a fibre

In order to decide if suspending a drop on a fibre will significantly alter its evaporation rate, it is necessary to estimate the extra flow of heat to the drop due to the fibre having a higher thermal conductivity than air.

By Fourier's law the heat flow by conduction through the air to the drop is

$$-k_g 4\pi R^2 \frac{\partial T}{\partial r} \Big|_{r=R}$$

while the quantity of heat conducted down the (cylindrical) fibre is

$$-k_f \pi r_f^2 \frac{\partial T_f}{\partial r} \Big|_{r=R}$$

so Q_r , the ratio of these two quantities, is

$$Q_r = \frac{1}{4} \frac{k_f}{k_g} \frac{r_f^2}{R^2} \frac{\partial T_f}{\partial r} \Big|_R / \frac{\partial T}{\partial r} \Big|_R$$

If, as in Section 4.1, the quasi-steady state assumption is made, all temperatures can be assumed independent of time. Substituting for $\partial T / \partial r$ by differentiating [4.11], the equation simplifies to

$$Q_r = - \frac{1}{4} \frac{k_f}{k_g} \frac{r_f^2}{R^2} \frac{dT_f}{dr} \Big|_R \cdot \frac{R}{(T_O - T_\infty)}$$

It is helpful at this stage to introduce the dimensionless variables $X = x/R$, $X_f = r_f/R$, $\tau = (T_f - T_\infty)/(T_O - T_\infty)$ and $K_f = k_f/k_g$, hence

$$Q_r = - \frac{1}{4} K_f X_f^2 \frac{d\tau}{dX} \Big|_{X=1} \quad (B1)$$

The problem of finding Q_r has now been reduced to that of solving Laplace's equation to find the temperature distribution along the fibre and hence $d\tau/dX$. The boundary conditions and geometry of the problem are shown in Figure B1 below.

Figure B1

Obtaining an exact analytical solution to this problem is very difficult because the drop boundary is spherical while the fibre boundary is cylindrical. These incompatible coordinate systems also make numerical solution using finite differences inconvenient, so instead an approximate analytical solution was developed.

The simplest possible assumption which can be made is to assume that the fibre is a cone having its apex at the drop centre. For such a fibre, the temperature distribution would be the same as for an unsupported drop, as the spherical temperature contours would be orthogonal to the air-fibre boundary. As a result $\partial\tau/\partial X = -1$ and

$$Q_r = 0.25 K_f X_f^2 \quad (B2)$$

This equation overestimates Q_r because the fibres used to support drops were much closer to cylinders than cones in shape, and the effective area for heat flow of a cylinder is much less than that of a cone when both have the same diameter at the drop surface. Nevertheless (B2) provides a useful bound for the maximum possible value of Q_r .

If the fibre is regarded as being surrounded by a cylinder of air through which heat is conducted, it can be treated as a simple fin governed by the following ordinary differential equation (Fuchs, 1959, p15)

$$\pi r_f^2 k_f \frac{d^2 T_f}{dx^2} = (T_f - T_y) \frac{2\pi k_a}{\ln(Y/r_f)} \quad (B3)$$

If the effect of the drop on the temperature distribution in the air surrounding the fibre is ignored, T_y can be assumed constant and equal to T_∞ . Defining $Y = y/R$ and simplifying reduces (B3) to

$$\frac{1}{2} X_f^2 K_f \ln(Y/X_f) \frac{d^2 \tau}{dX^2} = \tau$$

with the boundary conditions $\tau=1$ at $X=1$ and $\tau=0$ at $X=\infty$. This equation can be integrated analytically to give the well known Fuchs formula:

$$Q_r = X_f \sqrt{\frac{K_f}{8 \ln(Y/X_f)}} \quad (B4)$$

In practice, the drop's effect on the temperature distribution cannot be ignored and Fuchs' formula over-estimates the temperature difference between the fibre and surrounding air and hence Q_r (see

Table B1). When using (B4), y was taken as the internal diameter of the air cell in which the drop was suspended.

The assumption that $T_y = T_\infty$ can be relaxed by assuming that the fibre is surrounded by an air cylinder Y drop radii in diameter, and that heat leaves the fibre by conduction through this cylinder, but that the temperature on the outside of the cylinder is what it would be in the presence of an unsupported drop i.e.

$$T_y = T_\infty + (T_0 - T_\infty) / \sqrt{(X^2 + Y^2)}.$$

Substituting into (B3) and simplifying as before gives

$$\frac{1}{2} X_F^2 K_F \ln(Y/X_F) \frac{d^2\tau}{dX^2} = \tau - \frac{1}{\sqrt{(X^2 + Y^2)}} \quad (B5)$$

As would be expected, this equation tends to (B3) as Y tends to ∞ . While this differential equation cannot be integrated analytically in terms of elementary functions, it can be solved numerically. The procedure used was to divide the length of the fibre into N intervals and replace the second order derivative in each interval by the finite difference formula

$$\frac{d^2\tau}{dX^2} = \frac{(\tau_{i+1} - 2\tau_i + \tau_{i-1}))}{\Delta X^2}$$

substituting this and $\omega = X_F^2 K_F \ln(Y/X_F) / 2 \Delta X^2$ into (B5) gives

$$-\omega \tau_{i+1} + (1+2\omega)\tau_i - \omega \tau_{i-1} = \frac{1}{\sqrt{X_i^2 + Y^2}}$$

By applying this difference equation in each interval, and using the boundary conditions to specify τ_0 and τ_N , the problem of finding the temperature distribution in the fibre is reduced to that of solving a tridiagonal system of algebraic equations. This is easily performed by Gaussian elimination. The boundary condition at $X=1$ is trivial ($\tau_0=1$); however the condition at $X=\infty$ implies the need for an infinite number of equations which is impractical. To deal with this problem, it was assumed that the temperature of the fibre reached that of the air at $X=B$, a large (but finite) distance from the drop. For a fibre divided into N intervals, $\Delta X=B/N$ and $\tau_N=1/B$.

Once the values of τ are known, the value of Q_x can be found by calculating $d\tau/dX$ from the finite difference formula

$$\left. \frac{d\tau}{dX} \right|_{X=1} = \frac{(-3\tau_0 + 4\tau_1 - \tau_2)}{2\Delta X}$$

and substituting into (B1).

A computer program was used to calculate Q_r for a series of values of B, Y, K_f and X_f with the aim of fitting an empirical equation to the results. In practice B and Y were found to have little effect on Q_r , and so the equation fitted was

$$Q_r = 0.178 K_f^{0.798} X_f^{1.74} \quad (B6)$$

From Table B1 it can be seen that the value of $Q_r(B6)$ is always lower than $Q_r(B2)$, as would be expected, but that $Q_r(B4)$ is not. Equation (B6) is therefore preferable to (B4) which can overestimate Q_r by as much as a factor of three. (B6) was obtained by a least squares fit to 110 values of Q_r covering the range of values of X_f and K_f shown in the table. B and Y were taken as 20 and 0.2 respectively. Over the range of values represented by (B6), the average error introduced by the least squares fit was 5% which was considered acceptable as (B5) is itself only an approximation to the underlying differential equations.

Table B1 Comparison of (B2), (B4) and (B6)

X_f ^a	K_f ^b	$Q_r(B2)$	$Q_r(B4)$	$Q_r(B6)$
0.01	10	<0.001	<0.001	<0.001
0.10	10	0.025	0.049	0.020
0.01	900	0.023	0.038	0.013
0.10	900	2.250	0.461	0.738

^a $X_f=0.01$ is representative of conditions at the start of an experiment and $X_f=0.1$ of conditions at the end.

^b $K_f=10$ is representative of a glass fibre support and $K_f=900$ of a thermocouple support.

Appendix C. Listing of FORTRAN program PUREWATER

This, and the programs listed in later appendices, have been written in standard FORTRAN IV as far as is possible, and so should run under most FORTRAN compilers without modification. All program variables have been explicitly typed, and the programs are largely self-documented.

The structure of program PUREWATER is shown in Figure C1, from which it can be seen that the main program uses three subprograms INPUT1, EQTMP1 and RK4. In turn these subprograms use others e.g. EQTMP1 uses DQ1, RK4 uses DERIV1 and so on.

Figure C1. Program structure.

```

C *****
C *
C * PUREWATER: This program predicts the evaporation behaviour of *
C * a pure water drop evaporating into still air. Given a series *
C * of experimentally measured drop diameters at various times, it *
C * calculates the predicted drop diameter and temperature for *
C * comparison with the experimental values. *
C *
C * The program integrates the differential equations describing *
C * the drop's behaviour (the Maxwell equation and the drop heat *
C * balance) numerically using the fourth order Runge-Kutta *
C * method. A general integration subroutine (RK4) was used to *
C * perform the integration, so a separate subroutine (DERIV1) had *
C * to be supplied to define the differential equations to be *
C * solved. *
C *
C *****
C
C     INTEGER I, NPTS
C     REAL T, D, Y, DELTAT, TIME, TC, TINF, RELHUM, PRESS
C
C The arrays D and T hold the experimentally measured drop diameters
C and their corresponding times.
C
C     DIMENSION T(100),D(100),Y(20)
C     COMMON /CONDS/ TINF, RELHUM, PRESS
C     EXTERNAL DERIV1
C
C DELTAT is the time step used in the numerical integration.
C
C     DATA DELTAT/0.5/
C
C Read in the experimental data from a datafile.
C
C     CALL INPUT1(T,D,NPTS)
C
C The integration is started at the first experimental point.
C
C     TIME=T(1)
C
C The initial drop diameter is taken as the first experimentally
C measured value...
C
C     Y(1)=D(1)
C
C ...and the initial drop temperature is calculated by EQTMP1 on the
C assumption that the drop is in thermal equilibrium with the sur-
C rounding air by the time the first measurement of diameter is taken.
C
C     Y(2)=TINF
C     CALL EQTMP1(Y(2),Y(1))
C
C TC is the drop temperature in Centigrade.
C

```

```

      TC=Y(2)-273.1
C
C *** MAIN INTEGRATION LOOP ***
C
      WRITE(6,20)T(1),D(1),TIME,Y(1),TC
      DO 30 I=2,NPTS
C
C Advance the integration of the 2 differential equations specified
C in the subroutine DERIV1 by one time step.
C
10      CALL RK4(DERIV1,TIME,Y,DELTAT,2)
      IF(TIME.LT.T(I))GOTO 10
C
C At each experimental point the program writes out the measured
C and predicted drop diameters and the predicted drop temperature.
C
      TC=Y(2)-273.1
      WRITE(6,20)T(I),D(I),TIME,Y(1),TC
20      FORMAT( 2(OPF9.1, 1PE12.4), OPF9.3)
C
C Stop the integration if the predicted drop diameter gets too small.
C
      IF(Y(1).LT.300E-6)STOP 7
30      CONTINUE
      STOP
      END
C *****
C *
C * INPUT 1: This subroutine reads in all the experimental data *
C * required by the program and converts it into a form suitable *
C * for further processing. This is the only part of the program *
C * where non-S.I. units are used. *
C *
C * The variables describing the environmental conditions around *
C * the drop are passed to the rest of the program via COMMON *
C * block /CONDS/. These are atmospheric temperature (TINF), % *
C * relative humidity (RELHUM) and pressure (PRESS). *
C *
C * COMMON block /SUPPRT/ passes details of the drop support used *
C * to the rest of the program. SPDIAM(1) holds the diameter of a *
C * thermocouple wire, SPDIAM(2) holds the diameter of a glass *
C * fibre, and ITYPE indicates which type of support has been *
C * used. Possible values of ITYPE are: 1 - no support; 2 - glass *
C * fibre; 3 - thermocouple; 4 - glass fibre and thermocouple. *
C *
C * Arguments passed back to the main program are - *
C *
C * T      A vector of size 100 containing the times corresponding *
C *         to the diameters stored in D. *
C *
C * D      A vector of size 100 containing the experimentally *
C *         measured drop diameters. *
C *
C * NPTS   The number of experimental points read into T and D. *

```

```

C  *
C  *****
C
SUBROUTINE INPUT1(T,D,NPTS)
  INTEGER EXPNO, SUPNAM, SUPDIA, I, NPTS, ITYPE
  REAL TINF, PRESS, RELHUM, T, D, SPDIAM
  DIMENSION T(100), D(100), SUPNAM(12)
  COMMON /CONDS/ TINF, RELHUM, PRESS
  COMMON /SUPPRT/ SPDIAM(2), ITYPE
C
C  Read in experimental data from specially formatted data file
C
  READ(5,10,END=20)EXPNO, TINF, PRESS, RELHUM, SUPNAM, SUPDIA,
1    (T(I),D(I),I=1,100)
10  FORMAT(18X,I8/ 12X,F7.1/ 9X,F7.1/ 14X,F6.1/ 14X,12A1/
1    15X,I6/ // (F9.0,F11.3))
20  NPTS=I-1
C
C  Convert to S.I. units
C
  TINF=TINF+273.1
  PRESS=PRESS*101325./760.0
  DO 30 I=1,NPTS
    D(I)=D(I)*1.0E-3
30  CONTINUE
C
C  Define type and size of drop support.
C
  ITYPE=2
  IF(SUPNAM(1).EQ.'T')ITYPE=4
  SPDIAM(1)=12.0E-6
  SPDIAM(2)=FLOAT(SUPDIA)/1.0E6
  RETURN
  END
C  *****
C  *
C  *  DQ1: This function calculates the net heat flow between an *
C  *  evaporating water drop and the surrounding air. This is *
C  *  simply the difference between the heat flow to the drop (as *
C  *  calculated by QIN) and the product of the latent heat of *
C  *  evaporation and the rate of change of drop mass with time. *
C  *  DSQDOT is used to calculate the evaporation rate of a pure *
C  *  water drop. *
C  *
C  *  Arguments are - *
C  *
C  *  TDROP The drop temperature. *
C  *
C  *  DPDIAM The drop diameter. *
C  *
C  *****
C
REAL FUNCTION DQ1(TDROP,DPDIAM)
  REAL TDROP, DPDIAM, QLATNT, HLATNT, DSQDOT, QIN, PI

```

```

DATA PI/3.14159/
QLATNT=DSQDOT(DPDIAM,TDROP)*PI/4.0*DPDIAM*1000.0 *HLATNT(TDROP)
DQ1=QLATNT + QIN(TDROP,DPDIAM)
RETURN
END

```

```

C *****
C *
C * EQTMP1: This subroutine calculates the temperature at which *
C * the rate of heat transfer to a pure water drop just balances *
C * the heat loss due to the latent heat of evaporation - i.e. *
C * the equilibrium temperature of a drop with negligible thermal *
C * mass. *
C *
C * The routine uses Newton's method to find the temperature at *
C * which the net heat flow to the drop (as calculated by DQ1) is *
C * zero. It iterates until the net heat flow is less than a *
C * tolerance TOL. For ease of computation the derivative of DQ1 *
C * needed by Newton's method is estimated numerically using a *
C * first order finite difference formula. *
C *
C * Arguments are - *
C *
C * TDROP The drop temperature. On entry TDROP should contain an *
C * estimate of the equilibrium drop temperature. On exit *
C * it will contain the calculated value. *
C *
C * DPDIAM The drop diameter. *
C *
C *****
C

```

```

SUBROUTINE EQTMP1(TDROP,DPDIAM)
REAL TDROP, DPDIAM, DELTA, TOL, DQ1, F1, F2
DATA DELTA/0.01/, TOL/1.0E-7/
10 F1=DQ1(TDROP-DELTA,DPDIAM)
F2=DQ1(TDROP,DPDIAM)
TDROP=TDROP - F1 / ((F2-F1)/DELTA)
IF(ABS(F1).GT.TOL)GOTO 10
RETURN
END

```

```

C *****
C *
C * RK4: This subroutine solves a system of NEQN first order *
C * ordinary differential equations using the fourth order *
C * Runge-Kutta method. If more than 20 equations are to be *
C * solved, the dimensions of Y,YDOT,YNEW and K must be altered *
C * accordingly. *
C *
C * Arguments are - *
C *
C * DERIVS A subroutine that computes the values of the NEQN *
C * derivatives. It must be declared external by the *
C * caller, and is invoked by *
C * CALL DERIVS(X,Y,YDOT). *
C *
C

```

```

C  * X      The independant variable.
C  *
C  * Y      An array of size 20 holding the values of the dependant
C  *          variables corresponding to X.
C  *
C  * YDOT    An array calculated by DERIVS, holding the derivatives
C  *          of the dependant variables with respect to X.
C  *
C  * DELTAX  The step size by which the integration is to be
C  *          advanced on each call to RK4.
C  *
C  * NEQN    The number of differential equations to be solved.
C  *
C  *****
C
SUBROUTINE RK4(DERIVS,X,Y,DELTAX,NEQN)
  INTEGER I, J, NEQN
  REAL X, Y, DELTAX, YDOT, YNEW, XNEW, K, COEFF
  DIMENSION Y(20), YDOT(20), YNEW(20), K(20,3)
  EXTERNAL DERIVS
  COEFF=0.5
  CALL DERIVS(X,Y,YDOT)
  DO 20 J=1,3
    IF(J.EQ.3)COEFF=1.0
    XNEW=X+DELTAX*COEFF
    DO 10 I=1,NEQN
      K(I,J)=YDOT(I)*DELTAX
      YNEW(I)=Y(I)+K(I,J)*COEFF
10    CONTINUE
    CALL DERIVS(XNEW,YNEW,YDOT)
20  CONTINUE
    X=XNEW
    DO 30 I=1,NEQN
      Y(I)=Y(I) + (K(I,1)+ 2.0*(K(I,2)+K(I,3)) +YDOT(I)*DELTAX) /6.0
30  CONTINUE
    RETURN
  END
C  *****
C  *
C  * DERIV1: This subroutine specifies the differential equations
C  *          which RK4 is to integrate. It calculates the derivatives with
C  *          respect to time of drop diameter and temperature as functions
C  *          of drop diameter and temperature.
C  *
C  * Arguments are -
C  *
C  * TIME    The independant variable - time.
C  *
C  * Y       A vector of size 20 of which only the first two
C  *          elements are used. On entry it holds the values of the
C  *          dependant variables at TIME. Y(1) holds the drop
C  *          diameter; Y(2) holds the drop temperature.
C  *
C  * YDOT    A vector of size 20 of which only the first two

```



```

C *      elements are used. On exit it contains the derivatives *
C *      calculated from the differential equations. YDOT(1) *
C *      holds dD/dt; YDOT(2) holds dT/dt. *
C * *
C *****
C
C      SUBROUTINE DERIV1(X,Y,YDOT)
C      REAL X,Y,YDOT,CP,PI,DQ1,DSQDOT
C      DIMENSION Y(20),YDOT(20)
C
C      CP is the specific heat of liquid water.
C
C      DATA CP/4200.0/, PI/3.14159/
C
C      MASS BALANCE
C
C      YDOT(1)=(DSQDOT(Y(1),Y(2)))/Y(1)/2.0
C
C      HEAT BALANCE
C
C      YDOT(2)=DQ1(Y(2),Y(1)) / (CP*1000.0*PI*(Y(1)**3)/6.0)
C      RETURN
C      END
C *****
C *
C *      AIRVIS: This function calculates the viscosity of air as a *
C *      function of absolute temperature. The empirical equation used *
C *      is due to Watson (1972) who estimated that the maximum error *
C *      over the range 270-600 K was 0.25%. *
C * *
C *      Argument - *
C * *
C *      TEMP The absolute temperature. *
C * *
C *****
C
C      REAL FUNCTION AIRVIS(TEMP)
C      INTEGER I
C      REAL TEMP, S, A, P, SUM
C      DIMENSION A(5)
C      DATA A/0.55279544, 2.8108916, -13.50834, 39.353086, -41.419387/
C      S=100.0/TEMP
C      SUM=A(1)
C      P=1.0
C      DO 10 I=2,5
C          P=P*S
C          SUM=SUM+A(I)*P
10  CONTINUE
C      AIRVIS=SQRT(TEMP)/SUM*1.E-6
C      RETURN
C      END
C *****
C *
C *      DIFFC: This function calculates the diffusion coefficient of *

```

```

C  * water vapour in air using an empirical equation to determine *
C  * the effects of temperature and pressure.                      *
C  *                                                                *
C  * Arguments are -                                              *
C  *                                                                *
C  * TEMP    The air temperature.                                *
C  *                                                                *
C  * PRESS   The air pressure.                                    *
C  *                                                                *
C  * *****
C
      REAL FUNCTION DIFFC(TEMP,PRESS)
      REAL TEMP, PRESS
      DIFFC=0.225E-4 * (101325./PRESS) * (TEMP/273.1)**1.82
      RETURN
      END
C  * *****
C  *
C  * DSQDOT: This function calculates the evaporation rate (rate *
C  * of change of diameter squared with respect to time) of a pure *
C  * water drop using Maxwell's equation.                          *
C  *                                                                *
C  * Arguments are -                                              *
C  *                                                                *
C  * DPDIAM  The drop diameter.                                    *
C  *                                                                *
C  * TDROP   The drop temperature.                                *
C  *                                                                *
C  * *****
C
      REAL FUNCTION DSQDOT(DPDIAM,TDROP)
      REAL TDROP, TINF, RELHUM, PRESS, CDROP, CINF, VPDROP, VPINF,
      1 TEFF, DIFFC, SHBY2, DPDIAM
      COMMON /CONDS/ TINF, RELHUM, PRESS
C
C  Calculate the water vapour concentration at the drop surface
C  (saturated air).
C
      CALL WVC ONC(TDROP,100.0,PRESS,CDROP,VPDROP)
C
C  Calculate the water vapour concentration an infinite distance from
C  the drop.
C
      CALL WVC ONC(TINF,RELHUM,PRESS,CINF,VPINF)
C
C  Because of its temperature dependance, the diffusion coefficient
C  must be evaluated at the geometric mean air temperature.
C
      TEFF=SQRT(TDROP*TINF)
C
C  Maxwell's equation: The first continuation line is a correction for
C  Stefan flow (Fuchs, 1959, p4); the second for the effect of
C  convection.
C

```

```

DSQDOT=-8.0*DIFFC(TEFF,PRESS)*(CDROP-CINF)/1000.0
1      * (1.0 + (VPDROP+VFINF*RELHUM/100.0)/2.0/PRESS)
2      * SHBY2(DPDIAM,TDROP)

```

```

RETURN
END

```

```

C *****
C *
C * GR: This function calculates the Grashof number for mass *
C * transfer from, or heat transfer to, a drop evaporating into *
C * still air. *
C * *
C * Arguments are - *
C * *
C * DPDIAM The drop diameter. *
C * *
C * TDROP The drop temperature. *
C * *
C *****

```

```

REAL FUNCTION GR(DPDIAM,TDROP)
REAL DPDIAM, TDROP, TINF, RELHUM, PRESS, VP, VPH2O, R, G,
1 RHODRP, RHOINF, AIRVIS, MWAIR, MWH2O
COMMON /CONDS/ TINF, RELHUM, PRESS

```

```

C Define the gas constant (R), the acceleration due to gravity (G),
C and the molecular weights of air and water.

```

```

DATA R/8.314/, G/9.81/, MWAIR/0.029/, MWH2O/0.018/

```

```

C Calculate the density of the humid air above the drop surface.

```

```

VP=VPH2O(TDROP)
RHODRP=( MWAIR*(PRESS-VP)+MWH2O*(VP) )/R/TDROP

```

```

C Calculate the density of the humid air an infinite distance from
C the drop.

```

```

VP=VPH2O(TINF)*RELHUM/100.0
RHOINF=( MWAIR*(PRESS-VP)+MWH2O*(VP) )/R/TINF

```

```

C The absolute value of the density driving force must be used as
C otherwise when the temperature difference between drop and air is
C small, bouyancy forces will dominate the convection, give a negative
C driving force, and so a negative Grashof number.

```

```

GR=(RHOINF+RHODRP)/2.0 * G * ABS(RHODRP-RHOINF) * DPDIAM**3
1      / AIRVIS((TINF+TDROP)/2.0)**2
RETURN
END

```

```

C *****
C *
C * HLAINT: This function calculates the latent heat of *
C * evaporation of water using an empirical equation to determine *
C * the effect of temperature. *

```

```

C  *
C  * The empirical equation used was obtained by a least squares *
C  * fit to the data given by Mayhew and Rogers (1978) for the *
C  * range 0-100 C. It reproduces the original data to within an *
C  * accuracy of 0.05%. *
C  *
C  * Argument - *
C  *
C  * TEMP The water temperature. *
C  *
C  * *****
C
C  REAL FUNCTION HLATNT(TEMP)
C  REAL TEMP
C  HLATNT=134.5E3*(783.0-TEMP)**0.4688
C  RETURN
C  END
C  * *****
C  *
C  * KAIR: This function calculates the thermal conductivity of *
C  * air using an empirical equation to determine the effect of *
C  * temperature. *
C  *
C  * Argument - *
C  *
C  * TEMP The air temperature. *
C  *
C  * *****
C
C  REAL FUNCTION KAIR(TEMP)
C  REAL TEMP
C  KAIR=0.0241*(TEMP/273.1)**0.84
C  RETURN
C  END
C  * *****
C  *
C  * NUBY2: This function calculates one half of the Nusselt *
C  * number for a drop evaporating into still air. It uses a *
C  * correlation derived by Ranz and Marshall (1952) for heat *
C  * transfer by natural convection from spheres. *
C  *
C  * Arguments are - *
C  *
C  * DPDIAM The drop diameter. *
C  *
C  * TDROP The drop temperature. *
C  *
C  * *****
C
C  REAL FUNCTION NUBY2(DPDIAM,TDROP)
C  REAL DPDIAM, TDROP, PR, GR
C
C  The Prandtl number for air (taken from Ranz and Marshall, 1952)
C  is almost independant of temperature and so can be treated as a

```

```

C  constant.
C
C    DATA PR/0.72/
C
C  Function GR calculates the Grashof number.
C
C    NUBY2=1.0 + 0.05 *PR**0.333 *GR(DPDIAM,TDROP)**0.25
C    RETURN
C    END
C  *****
C  *
C  *  QIN: This function calculates the total rate of heat flow to *
C  *  an evaporating drop. It sums the contributions due to (a) *
C  *  conduction through the surrounding air, (b) radiation, and (c) *
C  *  conduction along the drop support (if present). *
C  *
C  *  Arguments are - *
C  *
C  *  TDROP The drop temperature. *
C  *
C  *  DPDIAM The drop diameter. *
C  *
C  *****
C
C    REAL FUNCTION QIN(TDROP,DPDIAM)
C    REAL TDROP, TINF, DPDIAM, QCOND, QRAD, QSUP, PI, SIGMA, EMISS,
C    1 TEFF, KAIR, RELHUM, PRESS, K, NUBY2
C    COMMON /CONDS/ TINF, RELHUM, PRESS
C
C    EMISS is the emissivity of liquid water (from McAdams, 1954, p478)
C
C    DATA PI/3.14159/, SIGMA/5.67E-8/, EMISS/0.95/
C    TEFF=SQRT(TINF*TDROP)
C    K=KAIR(TEFF)
C
C    Conduction through the surrounding air
C
C    QCOND=2.0*PI*DPDIAM*K*(TINF-TDROP)
C
C    Natural convection
C
C    QCOND=QCOND*NUBY2(DPDIAM,TDROP)
C
C    Radiation
C
C    QRAD=PI*DPDIAM*DPDIAM*EMISS*SIGMA*(TINF**4-TDROP**4)
C
C    Calculate total heat flow
C
C    QIN=QCOND+QRAD+QSUP(QCOND,DPDIAM,K)
C    RETURN
C    END
C  *****
C  *

```

```

C  *  QSUP: This function calculates the rate of heat flow to an  *
C  *  evaporating drop along the thermocouple or glass fibre on  *
C  *  which the drop is suspended. It uses an empirical equation  *
C  *  which is an approximation to the solution of the underlying  *
C  *  differential equation.  *
C  *  *  *
C  *  Arguments are -  *
C  *  *  *
C  *  QCOND The rate of heat flow to the drop via conduction.  *
C  *  *  *
C  *  DPDIAM The drop diameter.  *
C  *  *  *
C  *  K      The thermal conductivity of the air in which the drop  *
C  *          is immersed.  *
C  *  *  *
C  *  *****  *
C
C      REAL FUNCTION QSUP(QCOND,DPDIAM,K)
C      INTEGER ITYPE
C      REAL QCOND, DPDIAM, K, SPCOND, SPDIAM, QFIBRE, KRATIO, DRATIO
C      DIMENSION SPCOND(2)
C      COMMON /SUPPRT/ SPDIAM(2), ITYPE
C
C  Define support thermal conductivities: SPCOND(1) is an average of
C  the conductivities of chromel and constantan (Benedict, 1969,
C  p151); SPCOND(2) is a typical conductivity for soda glass (Weast,
C  1982).
C
C      DATA SPCOND/ 21.5, 1.1/
C
C  The empirical equation used is expressed in terms of dimensionless
C  ratios (support:air thermal conductivity and support:drop diameter)
C
C      QFIBRE(KRATIO,DRATIO)=0.178 *KRATIO**0.798 *DRATIO**1.74
C      GOTO(10,20,30,40),ITYPE
C
C  No support
C
C 10      QSUP=0.0
C          RETURN
C
C  Glass fibre
C
C 20      QSUP=QFIBRE((SPCOND(2)/K),(SPDIAM(2)/DPDIAM))
C          GOTO 50
C
C  Thermocouple
C
C 30      QSUP=QFIBRE((SPCOND(1)/K),(SPDIAM(1)/DPDIAM)) *2.0
C          GOTO 50
C
C  Thermocouple + glass fibre
C
C 40      QSUP=QFIBRE((SPCOND(1)/K),(SPDIAM(1)/DPDIAM)) *2.0 +

```



```

1      QFIBRE((SPCOND(2)/K),(SPDIAM(2)/DPDIAM))
50     QSUP=QSUP*QCOND
      RETURN
      END
C     *****
C     *
C     * SHBY2: This function calculates one half of the Sherwood *
C     * number for a drop evaporating into still air. It uses a *
C     * correlation derived by Ranz and Marshall (1952) for mass *
C     * transfer by natural convection from spheres. *
C     *
C     * Arguments are - *
C     *
C     * DPDIAM The drop diameter. *
C     *
C     * TDROP The drop temperature. *
C     *
C     *****
C
      REAL FUNCTION SHBY2(DPDIAM,TDROP)
      REAL DPDIAM, TDROP, SC, GR
C
C The Schmidt number for air (taken from Ranz and Marshall, 1952) is
C almost independant of temperature and so can be treated as a
C constant.
C
      DATA SC/0.68/
C
C Function GR calculates the Grashof number.
C
      SHBY2=1.0 + 0.05 *SC**0.333 *GR(DPDIAM,TDROP)**0.25
      RETURN
      END
C     *****
C     *
C     * VPH2O: This function calculates the vapour pressure of liquid *
C     * water using an empirical equation to determine the effect of *
C     * temperature. Since the equation is too complex to permit *
C     * reliable extrapolation, the function outputs a warning message *
C     * if an attempt is made to use the equation outside its valid *
C     * range. *
C     *
C     * The empirical equation used was obtained by a least squares *
C     * fit to the data given by Weast (1982) for the range 0-100 C. *
C     * It reproduces the original data to within an accuracy of 0.1%. *
C     *
C     * Argument - *
C     *
C     * TEMP The water temperature. *
C     *
C     *****
C
      REAL FUNCTION VPH2O(TEMP)
      REAL TEMP, A, B, C, D

```

```

DATA A/25.94927/, B/-4684.69043/, C/-23.85172/, D/-2.70608E-3/
IF(TEMP.LT.273.1 .OR. TEMP.GT.373.1)WRITE(1,10)TEMP
10  FORMAT('WARNING: VAPOUR PRESSURE DATA DOES NOT EXTEND TO',F6.1,
1    ' K')
    VPH2O=EXP(A + B/(TEMP+C) + D*TEMP)
    RETURN
    END
C *****
C *
C * WVCONC: This subroutine calculates the concentration of water *
C * vapour in air for any given temperature, pressure, and *
C * relative humidity. *
C *
C * It also returns the vapour pressure of water at the specified *
C * temperature. *
C *
C * Arguments are - *
C *
C * TEMP The air temperature. *
C *
C * RELHUM The % relative humidity. *
C *
C * PRESS Atmospheric pressure. *
C *
C * CONC The calculated water vapour concentration. *
C *
C * VPPRES The vapour pressure of water. *
C *
C *****
C
C SUBROUTINE WVCONC(TEMP,RELHUM,PRESS,CONC,VPPRES)
C REAL TEMP, RELHUM, PRESS, CONC, VPPRES, ABSHUM, HUMVOL, VPH2O
C
C Calculate vapour pressure.
C
C VPPRES=VPH2O(TEMP)
C
C Calculate absolute humidity (Kg H2O / Kg DRY AIR).
C
C ABSHUM=(18.0/29.0)*VPPRES*RELHUM/100.0/(PRESS-VPPRES*RELHUM/100.0)
C
C Calculate humid volume (m3 (air + H2O) / Kg dry air). The equation
C used is taken from Treybal (1980, p234).
C
C HUMVOL=TEMP*(0.00283+0.00456*ABSHUM)
C
C Calculate water vapour concentration.
C
C CONC=ABSHUM/HUMVOL
C RETURN
C END

```

Appendix D. Experimental results for pure water drops

Experiment number: 14
 Temperature: 25.1 ± 0.1 °C
 Pressure: 763.6 ± 0.2 mm Hg
 Rel. Humidity: 53.8 ± 0.5 %
 Support type: Glass fibre
 Fibre diameter: 24 ± 4 μ m

Time Drop diameter

sec ± 0.004 mm

350 1.458

440 1.438

564 1.407

650 1.385

744 1.361

857 1.332

992 1.298

1088 1.275

1201 1.239

1280 1.220

1416 1.183

1525 1.150

1661 1.110

1791 1.066

1892 1.031

1988 1.001

2108 0.961

2186 0.934

2355 0.872

2426 0.845

2492 0.819

2596 0.773

2671 0.741

2781 0.696

2862 0.655

2921 0.627

2975 0.597

3040 0.561

3088 0.533

3153 0.493

3206 0.455

3244 0.427

3290 0.393

3337 0.346

3380 0.308

3414 0.268

Experiment number: 15
 Temperature: 25.1 ± 0.1 °C
 Pressure: 763.5 ± 0.2 mm Hg
 Rel. Humidity: 53.8 ± 0.5 %
 Support type: Glass fibre
 Fibre diameter: 22 ± 4 μ m

Time Drop diameter

sec ± 0.004 mm

203 1.285

307 1.258

449 1.220

617 1.170

696 1.149

844 1.103

948 1.070

1097 1.022

1355 0.936

1469 0.896

1536 0.870

1648 0.827

1753 0.786

1855 0.741

1928 0.708

2005 0.671

2090 0.630

2161 0.591

2221 0.558

2274 0.528

2343 0.482

2409 0.436

2455 0.402

2519 0.346

2566 0.298

2607 0.250

Experiment number: 16
 Temperature: 25.1 ± 0.1 °C
 Pressure: 756.0 ± 0.2 mm Hg
 Rel. Humidity: 53.8 ± 0.5 %
 Support type: Glass fibre
 Fibre diameter: 49 ± 4 μ m

Time	Drop diameter
sec	± 0.004 mm
130	1.407
199	1.393
320	1.364
459	1.328
608	1.292
744	1.256
876	1.219
986	1.189
1234	1.113
1338	1.084
1463	1.044
1627	0.991
1750	0.949
1846	0.912
1936	0.882
2035	0.843
2116	0.812
2191	0.783
2259	0.751
2346	0.714
2423	0.678
2493	0.642
2567	0.605
2640	0.566
2698	0.532
2768	0.486
2824	0.446
2883	0.402
2925	0.367
2971	0.324
3014	0.278

Experiment number: 17
 Temperature: 25.1 ± 0.1 °C
 Pressure: 756.6 ± 0.2 mm Hg
 Rel. Humidity: 53.8 ± 0.5 %
 Support type: Glass fibre
 Fibre diameter: 40 ± 4 μ m

Time	Drop diameter
sec	± 0.004 mm
173	1.266
225	1.253
323	1.229
437	1.197
560	1.162
701	1.117
784	1.096
875	1.064
950	1.043
1058	1.007
1140	0.981
1242	0.945
1347	0.911
1434	0.876
1520	0.845
1578	0.820
1672	0.782
1725	0.760
1821	0.717
1922	0.671
2016	0.622
2128	0.562
2199	0.521
2259	0.480
2324	0.435
2361	0.406
2432	0.344
2467	0.310
2502	0.271

Experiment number: 18
 Temperature: 25.0 ± 0.1 °C
 Pressure: 756.5 ± 0.2 mm Hg
 Rel. Humidity: 75.8 ± 0.5 %
 Support type: Glass fibre
 Fibre diameter: 23 ± 4 μ m

Time Drop diameter

sec ± 0.004 mm

154	1.335
265	1.322
457	1.296
593	1.281
755	1.256
959	1.232
1144	1.206
1335	1.177
1525	1.152
1707	1.124
1880	1.097
2057	1.070
2237	1.041
2420	1.011
2610	0.978
2968	0.916
3134	0.885
3317	0.849
3527	0.809
3705	0.769
3872	0.731
4046	0.690
4239	0.642
4412	0.594
4581	0.546
4699	0.509
4820	0.470
4937	0.426
5066	0.377
5175	0.324
5298	0.258

Experiment number: 19
 Temperature: 24.7 ± 0.1 °C
 Pressure: 759.8 ± 0.2 mm Hg
 Rel. Humidity: 75.8 ± 0.5 %
 Support type: Glass fibre
 Fibre diameter: 33 ± 4 μ m

Time Drop diameter

sec ± 0.004 mm

121	1.418
191	1.408
383	1.387
617	1.359
867	1.324
1039	1.306
1218	1.281
1411	1.256
1632	1.225
1840	1.200
2084	1.162
2274	1.137
2465	1.107
2659	1.075
2852	1.047
3017	1.021
3232	0.984
3409	0.954
3579	0.922
3766	0.891
3947	0.855
4109	0.823
4269	0.789
4401	0.764
4554	0.728
4669	0.703
4819	0.667
4950	0.635
5053	0.608
5168	0.575
5276	0.545
5403	0.506
5513	0.470
5590	0.443
5667	0.414
5732	0.386
5813	0.350
5901	0.310
5959	0.275
6005	0.248

Experiment number: 21
 Temperature: 24.6 ± 0.1 °C
 Pressure: 763.3 ± 0.2 mm Hg
 Rel. Humidity: 33.2 ± 0.5 %
 Support type: Glass fibre
 Fibre diameter: 30 ± 4 μ m

Time	Drop diameter
------	---------------

sec	± 0.004 mm
-----	----------------

146	1.291
214	1.263
308	1.225
383	1.192
456	1.163
548	1.120
618	1.088
714	1.043
780	1.011
862	0.968
936	0.931
1022	0.883
1082	0.846
1149	0.807
1236	0.751
1291	0.716
1373	0.657
1431	0.612
1510	0.545
1574	0.486
1632	0.423
1700	0.338
1739	0.278

Experiment number: 22
 Temperature: 24.7 ± 0.1 °C
 Pressure: 763.2 ± 0.2 mm Hg
 Rel. Humidity: 33.2 ± 0.5 %
 Support type: Glass fibre
 Fibre diameter: 30 ± 4 μ m

Time	Drop diameter
------	---------------

sec	± 0.004 mm
-----	----------------

183	1.391
285	1.351
437	1.289
525	1.253
607	1.219
680	1.187
749	1.159
855	1.114
942	1.068
1061	1.012
1130	0.977
1210	0.934
1260	0.906
1336	0.863
1397	0.830
1467	0.784
1534	0.741
1590	0.704
1666	0.648
1715	0.611
1791	0.548
1857	0.485
1927	0.412
1970	0.354
2013	0.294
2046	0.235

Experiment number: 23
 Temperature: 24.7 ± 0.1 °C
 Pressure: 759.5 ± 0.2 mm Hg
 Rel. Humidity: 92.0 ± 0.5 %
 Support type: Glass fibre
 Fibre diameter: 27 ± 4 μ m

Time	Drop diameter
sec	± 0.004 mm
192	1.239
498	1.226
915	1.210
1631	1.182
2327	1.152
3012	1.123
3755	1.093
4369	1.064
5084	1.034
5752	1.004
6672	0.958
7363	0.924
7828	0.901
8508	0.863
9058	0.835
10629	0.737
11190	0.698
11767	0.661
12129	0.635
12528	0.605
12825	0.579
13147	0.561
13448	0.529
13733	0.502
14030	0.473
14334	0.442
14611	0.413
14889	0.379

Experiment number: 24
 Temperature: 15.6 ± 0.1 °C
 Pressure: 745.1 ± 0.2 mm Hg
 Rel. Humidity: 12.8 ± 0.5 %
 Support type: Glass fibre
 Fibre diameter: 28 ± 4 μ m

Time	Drop diameter
sec	± 0.004 mm
195	1.246
285	1.207
364	1.173
441	1.136
504	1.110
555	1.085
630	1.049
713	1.007
821	0.951
876	0.920
951	0.872
1033	0.829
1089	0.792
1153	0.753
1275	0.666
1324	0.629
1384	0.579
1432	0.537
1519	0.450
1577	0.382
1624	0.317
1677	0.266

Experiment number: 25
 Temperature: 29.4 ± 0.1 °C
 Pressure: 757.5 ± 0.2 mm Hg
 Rel. Humidity: 75.6 ± 0.5 %
 Support type: Glass fibre
 Fibre diameter: 28 ± 4 μ m

Time	Drop diameter
sec	± 0.004 mm
99	1.261
235	1.244
467	1.210
715	1.171
972	1.129
1241	1.084
1448	1.050
1698	1.005
1933	0.965
2181	0.916
2454	0.858
2669	0.813
2894	0.761
3081	0.718
3262	0.671
3477	0.611
3617	0.570
3809	0.506
3975	0.445
4163	0.364
4320	0.280

Experiment number: 30
 Temperature: 25.5 ± 0.1 °C
 Pressure: 748.4 ± 0.2 mm Hg
 Rel. Humidity: 12.0 ± 0.5 %
 Support type: Thermocouple
 Fibre diameter: 25 ± 4 μ m

Time	Drop diameter
sec	± 0.004 mm
255	1.181
546	0.989
667	0.889
795	0.778
906	0.671
959	0.616
1033	0.521
1092	0.434
1160	0.301

Experiment number: 35
 Temperature: 25.0 ± 0.1 °C
 Pressure: 772.0 ± 0.2 mm Hg
 Rel. Humidity: 12.0 ± 0.5 %
 Support type: Thermocouple
 Fibre diameter: 38 ± 4 μ m

Time	Drop diameter
sec	± 0.004 mm
144	0.923
211	0.868
324	0.771
403	0.694
491	0.602
529	0.552
623	0.409
682	0.292

Experiment number: 42
 Temperature: 24.9 ± 0.1 °C
 Pressure: 776.2 ± 0.2 mm Hg
 Rel. Humidity: 3.0 ± 0.5 %
 Support type: Glass fibre
 Fibre diameter: 22 ± 4 μ m

Time	Drop diameter
sec	± 0.004 mm
160	1.169
220	1.128
274	1.089
341	1.036
558	0.851
597	0.815
655	0.754
735	0.674
795	0.595
841	0.534
888	0.464
932	0.385
971	0.298

Experiment number: 47
 Temperature: 25.1 ± 0.1 °C
 Pressure: 734.5 ± 0.2 mm Hg
 Rel. Humidity: 3.0 ± 0.5 %
 Support type: Glass fibre
 Fibre diameter: 25 ± 4 μ m

Time	Drop diameter
sec	± 0.004 mm
155	1.101
210	1.059
286	0.996
445	0.857
482	0.819
532	0.770
599	0.696
657	0.627
709	0.558
788	0.428
831	0.351
863	0.260

Experiment number: 48
 Temperature: 24.9 ± 0.1 °C
 Pressure: 754.9 ± 0.2 mm Hg
 Rel. Humidity: 3.0 ± 0.5 %
 Support type: Glass fibre
 Fibre diameter: 21 ± 4 μ m

Time	Drop diameter
sec	± 0.004 mm
229	1.152
288	1.109
456	0.973
670	0.780
708	0.740
758	0.686
810	0.625
857	0.563
900	0.501
950	0.415
1000	0.312

Experiment number: 52
 Temperature: 13.0 ± 0.1 °C
 Pressure: 759.3 ± 0.2 mm Hg
 Rel. Humidity: 3.0 ± 0.5 %
 Support type: Glass fibre
 Fibre diameter: 23 ± 4 μ m

Time	Drop diameter
sec	± 0.004 mm
119	1.137
201	1.100
299	1.054
393	1.008
492	0.956
605	0.897
717	0.832
816	0.770
887	0.723
968	0.665
1031	0.619
1099	0.560
1151	0.513
1211	0.456
1258	0.400
1314	0.325
1354	0.262

Experiment number: 59
 Temperature: 25.0 ± 0.1 °C
 Pressure: 754.4 ± 0.2 mm Hg
 Rel. Humidity: 12.0 ± 0.5 %
 Support type: Glass fibre
 Fibre diameter: 26 ± 4 μ m

Time	Drop diameter
sec	± 0.004 mm
148	1.185
221	1.137
296	1.090
443	0.983
494	0.944
562	0.890
629	0.834
729	0.745
791	0.682
871	0.594
950	0.495
1012	0.398
1056	0.316

Experiment number: 58
 Temperature: 25.0 ± 0.1 °C
 Pressure: 754.9 ± 0.2 mm Hg
 Rel. Humidity: 3.0 ± 0.5 %
 Support type: Glass fibre
 Fibre diameter: 25 ± 4 μ m

Time	Drop diameter
sec	± 0.004 mm
188	0.961
257	0.898
341	0.820
402	0.758
479	0.675
543	0.594
592	0.527
630	0.470
681	0.379
715	0.302

Experiment number: 61
 Temperature: 25.1 ± 0.1 °C
 Pressure: 766.6 ± 0.2 mm Hg
 Rel. Humidity: 12.0 ± 0.5 %
 Support type: Thermocouple
 Fibre diameter: 16 ± 4 μ m

Time	Drop diameter
sec	± 0.004 mm
204	0.870
316	0.774
394	0.700
426	0.666
540	0.536
591	0.462
644	0.369
689	0.269

Appendix E. Experimental results for contaminated dropsKey for Figures E1-E53

- o Drop diameter squared (measured).
- xxxxxx Drop temperature (measured).
- — Drop diameter squared (calculated from spline).
- — Drop temperature (calculated from [4.12]).
- Sherwood number (calculated from (K7)).
- Δ Time coordinate of a spline knot.

Figure E1

Experiment number: 61
 Surfactant: 0±2 ppm ----
 Temperature: 25.1±0.1 °C
 Pressure: 766.6±0.2 mm Hg
 Rel. Humidity: 12.0±0.5 %
 Support type: Thermocouple
 Fibre diameter: 16±4 µm
 Time Drop diameter
 sec ±0.004 mm
 204 0.870
 316 0.774
 394 0.700
 426 0.666
 540 0.536
 591 0.462
 644 0.369
 689 0.269

Drop temperature °C

Figure E2

Experiment number: 64
 Surfactant: 10 $\pm$ 2 ppm NAST
 Temperature: 25.1 $\pm$ 0.1 $^{\circ}$ C
 Pressure: 756.0 $\pm$ 0.2 mm Hg
 Rel. Humidity: 12.0 $\pm$ 0.5 %
 Support type: Glass fibre
 Fibre diameter: 32 $\pm$ 4 μ m
 Time Drop diameter
 sec $\pm$ 0.004 mm

180	1.204
247	1.161
320	1.114
482	1.001
565	0.938
620	0.893
709	0.818
816	0.717
866	0.666
933	0.590
1011	0.493
1063	0.423
1117	0.385
1172	0.365
1209	0.353
1278	0.326
1347	0.308
1412	0.288

Drop temperature $^{\circ}$ C

Figure E3

Experiment number: 63
 Surfactant: 20 ± 2 ppm NAST
 Temperature: 25.0 ± 0.1 °C
 Pressure: 759.7 ± 0.2 mm Hg
 Rel. Humidity: 12.0 ± 0.5 %
 Support type: Glass fibre
 Fibre diameter: 37 ± 4 μ m

Time sec	Drop diameter ± 0.004 mm
140	1.212
221	1.158
294	1.113
356	1.068
468	0.990
532	0.941
630	0.854
712	0.793
806	0.705
908	0.615
967	0.584
1039	0.550
1109	0.519
1194	0.488
1259	0.467
1313	0.452
1387	0.431
1461	0.412
1611	0.376
1681	0.359
1760	0.340
1859	0.320
1940	0.300
1987	0.288
2059	0.272

Figure E4

Experiment number: 88
 Surfactant: 20±2 ppm NAST
 Temperature: 25.1±0.1 °C
 Pressure: 761.2±0.2 mm Hg
 Rel. Humidity: 12.0±0.5 %
 Support type: Thermocouple
 Fibre diameter: 28±4 µm
 Time Drop diameter
 sec ±0.004 mm

144	1.199
192	1.168
253	1.131
389	1.035
452	0.993
497	0.956
555	0.913
612	0.868
683	0.809
767	0.756
809	0.734
880	0.700
935	0.677
1010	0.646
1080	0.621
1162	0.593
1229	0.572
1383	0.531
1488	0.506
1673	0.461
1829	0.424
2027	0.386

Figure E5

Experiment number: 31
 Surfactant: 26±2 ppm NAST
 Temperature: 25.1±0.1 °C
 Pressure: 742.3±0.2 mm Hg
 Rel. Humidity: 12.0±0.5 %
 Support type: Thermocouple
 Fibre diameter: 25±4 µm

Time sec	Drop diameter ±0.004 mm
249	1.178
306	1.146
389	1.090
463	1.042
533	1.014
594	0.997
676	0.975
778	0.950
898	0.925
1101	0.875
1211	0.851
1436	0.805
1626	0.763
1860	0.716
2092	0.672
2355	0.626
2564	0.589
2845	0.542
2986	0.519
3102	0.505
3236	0.482
3411	0.457
3546	0.429
3635	0.406
3771	0.373
3946	0.320
4048	0.290

Figure E6

Experiment number: 67
 Surfactant: 30±2 ppm NAST
 Temperature: 25.0±0.1 °C
 Pressure: 757.6±0.2 mm Hg
 Rel. Humidity: 12.0±0.5 %
 Support type: Glass Fibre
 Fibre diameter: 36±4 µm

Time sec	Drop diameter ±0.004 mm
118	1.330
175	1.299
261	1.249
340	1.201
502	1.109
583	1.076
670	1.048
755	1.022
883	0.984
1007	0.950
1118	0.922
1316	0.871
1473	0.840
1705	0.790
2077	0.719
2267	0.681
2399	0.665
2701	0.618
3050	0.569
3470	0.513
3768	0.473

Drop temperature °C

Figure E7

Experiment number: 65
 Surfactant: 40 ± 2 ppm NAST
 Temperature: 25.1 ± 0.1 °C
 Pressure: 753.9 ± 0.2 mm Hg
 Rel. Humidity: 12.0 ± 0.5 %
 Support type: Glass Fibre
 Fibre diameter: 22 ± 4 μ m

Time sec	Drop diameter ± 0.004 mm
125	1.156
172	1.126
256	1.076
352	1.041
451	1.013
542	0.988
609	0.971
701	0.948
811	0.919
948	0.888
1223	0.824
1413	0.785
1565	0.757
1875	0.699
2082	0.664
2531	0.597
2855	0.556
3101	0.526
3403	0.496
3749	0.460
4202	0.403
4292	0.391

Figure E8

Experiment number: 66
 Surfactant: 50±2 ppm NAST
 Temperature: 25.1±0.1 °C
 Pressure: 753.3±0.2 mm Hg
 Rel. Humidity: 12.0±0.5 %
 Support type: Glass Fibre
 Fibre diameter: 28±4 µm

Time sec	Drop diameter ±0.004 mm
129	1.206
169	1.182
324	1.117
391	1.103
522	1.072
638	1.043
745	1.021
915	0.984
1123	0.940
1300	0.904
1474	0.868
1651	0.835
1907	0.787
2154	0.741
2408	0.698
2768	0.643
3089	0.599
3461	0.550
3758	0.517
4119	0.475
4454	0.449
4814	0.415
5179	0.389
5546	0.379
6058	0.362
6511	0.354
6933	0.337
7396	0.323

Figure E9

Experiment number: 87
 Surfactant: 50±2 ppm NAST
 Temperature: 25.1±0.1 °C
 Pressure: 760.2±0.2 mm Hg
 Rel. Humidity: 12.0±0.5 %
 Support type: Thermocouple
 Fibre diameter: 37±4 µm

Time sec	Drop diameter ±0.004 mm
175	1.158
217	1.148
286	1.134
389	1.112
458	1.098
579	1.071
827	1.018
892	1.004
997	0.981
1102	0.961
1297	0.923
1402	0.902
1654	0.855
1909	0.810
2137	0.771
2388	0.734
2655	0.695
2906	0.663
3188	0.628
3487	0.604
4864	0.523
5460	0.502
8771	0.391

Figure E10

Figure EII

Experiment number: 69
 Surfactant: 100±2 ppm NAST
 Temperature: 25.0±0.1 °C
 Pressure: 757.0±0.2 mm Hg
 Rel. Humidity: 12.0±0.5 %
 Support type: Glass fibre
 Fibre diameter: 36±4 µm

Time	Drop diameter
sec	±0.004 mm
114	1.121
182	1.103
279	1.082
397	1.057
576	1.020
766	0.982
1061	0.928
1297	0.885
1578	0.839
1899	0.790
2161	0.752
2547	0.707
2830	0.675
3132	0.649
3424	0.624
3710	0.600
3983	0.583
4251	0.568
4559	0.555

Drop temperature °C

Figure E12

Experiment number: 68
 Surfactant: 150±2 ppm NAST
 Temperature: 25.0±0.1 °C
 Pressure: 757.5±0.2 mm Hg
 Rel. Humidity: 12.0±0.5 %
 Support type: Glass Fibre
 Fibre diameter: 35±4 µm

Time sec	Drop diameter ±0.004 mm
196	1.030
253	1.014
310	1.005
605	0.956
1082	0.880
1427	0.833
1793	0.784
2253	0.729
2634	0.694
3040	0.659
3584	0.620
4096	0.589
4613	0.566
5157	0.546
5840	0.523
6593	0.513
7705	0.502
8777	0.493
10166	0.488
11320	0.482
12326	0.477
14162	0.477
18831	0.453
19447	0.456

Drop temperature °C

Figure E13

Experiment number: 55
 Surfactant: 45 $\pm$ 2 ppm NAST
 Temperature: 25.0 $\pm$ 0.1 $^{\circ}$ C
 Pressure: 764.4 $\pm$ 0.2 mm Hg
 Rel. Humidity: 3.0 $\pm$ 0.5 %
 Support type: Glass fibre
 Fibre diameter: 29 $\pm$ 4 μ m

Time sec	Drop diameter $\pm$ 0.004 mm
113	1.041
181	1.007
285	0.966
425	0.911
542	0.865
623	0.834
747	0.792
896	0.748
1038	0.708
1312	0.645
1423	0.624
1604	0.591
1810	0.557
1976	0.535
2225	0.505
2503	0.479
2799	0.459
3105	0.440
3528	0.423
4114	0.404
4830	0.359
5151	0.331
5488	0.315
6027	0.286

Drop temperature $^{\circ}$ C

Figure E14

Experiment number: 54
 Surfactant: 50±2 ppm NAST
 Temperature: 25.0±0.1 °C
 Pressure: 762.0±0.2 mm Hg
 Rel. Humidity: 3.0±0.5 %
 Support type: Glass Fibre
 Fibre diameter: 29±4 µm

Time sec	Drop diameter ±0.004 mm
130	1.062
184	1.035
298	1.001
399	0.973
448	0.955
589	0.915
770	0.865
958	0.819
1532	0.684
1583	0.672
1968	0.588
2033	0.573
2772	0.470
2841	0.467
2935	0.457
3546	0.396
3872	0.359
4298	0.315
4694	0.271
4752	0.269

Drop temperature °C

Figure E15

Experiment number: 56
 Surfactant: 50±2 ppm NAST
 Temperature: 25.0±0.1 °C
 Pressure: 761.8±0.2 mm Hg
 Rel. Humidity: 3.0±0.5 %
 Support type: Glass Fibre
 Fibre diameter: 24±4 µm
 Time Drop diameter
 ±0.004 mm

sec	153	0.989
	233	0.951
	301	0.920
	396	0.879
	483	0.846
	619	0.800
	750	0.755
	957	0.691
	1245	0.616
	1584	0.534
	1665	0.520
	1896	0.478
	2347	0.416
	2713	0.382
	3151	0.348
	3735	0.319
	3949	0.305
	4183	0.285
	4274	0.275

Drop temperature °C

Figure E16

Experiment number: 79
 Surfactant: 10 $\pm$ 2 ppm NAPA
 Temperature: 25.1 $\pm$ 0.1 $^{\circ}$ C
 Pressure: 758.2 $\pm$ 0.2 mm Hg
 Rel. Humidity: 12.0 $\pm$ 0.5 %
 Support type: Glass Fibre
 Fibre diameter: 23 $\pm$ 4 μ m

Time sec	Drop diameter $\pm$ 0.004 mm
119	1.027
177	0.985
231	0.947
410	0.801
444	0.768
495	0.721
546	0.669
587	0.629
634	0.587
691	0.533
730	0.496
786	0.440
847	0.370
882	0.329
916	0.289
951	0.250

Figure E17

Experiment number: 74
 Surfactant: 20 $\pm$ 2 ppm NAPA
 Temperature: 25.0 $\pm$ 0.1 $^{\circ}$ C
 Pressure: 747.5 $\pm$ 0.2 mm Hg
 Rel. Humidity: 12.0 $\pm$ 0.5 %
 Support type: Glass Fibre
 Fibre diameter: 19 $\pm$ 4 μ m

Time sec	Drop diameter ± 0.004 mm
112	1.074
173	1.034
269	0.962
331	0.917
405	0.864
477	0.816
544	0.768
607	0.725
683	0.667
769	0.593
836	0.541
906	0.475
947	0.436
994	0.392
1032	0.359
1083	0.317

Drop temperature $^{\circ}$ C

Figure E18

Experiment number: 37
 Surfactant: 25±2 ppm NAPA
 Temperature: 25.1±0.1 °C
 Pressure: 765.0±0.2 mm Hg
 Rel. Humidity: 12.0±0.5 %
 Support type: Glass fibre
 Fibre diameter: 30±4 µm

Time sec	Drop diameter ±0.004 mm
125	1.156
196	1.109
291	1.055
369	1.008
489	0.934
577	0.881
636	0.845
709	0.800
789	0.755
856	0.715
940	0.668
994	0.639
1075	0.596
1143	0.560
1206	0.524
1322	0.468
1391	0.441
1486	0.406
1577	0.383
1665	0.346
1753	0.319
1851	0.291
1962	0.262
2037	0.242

Figure E19

Experiment number: 38
 Surfactant: 50 $\pm$ 2 ppm NAPA
 Temperature: 24.9 $\pm$ 0.1 $^{\circ}\text{C}$
 Pressure: 762.3 $\pm$ 0.2 mm Hg
 Rel. Humidity: 12.0 $\pm$ 0.5 %
 Support type: Glass fibre
 Fibre diameter: 22 $\pm$ 4 μm

Time	Drop diameter
sec	± 0.004 mm
266	1.089
335	1.061
421	1.018
608	0.928
767	0.850
915	0.773
999	0.736
1075	0.699
1180	0.655
1268	0.620
1395	0.571
1526	0.523
1674	0.475
1800	0.440
1973	0.393
2203	0.355
2382	0.321
2819	0.253

Figure E20

Experiment number: 86
 Surfactant: 50±2 ppm NAPA
 Temperature: 25.1±0.1 °C
 Pressure: 762.3±0.2 mm Hg
 Rel. Humidity: 12.0±0.5 %
 Support type: Thermocouple
 Fibre diameter: 33±4 µm

Time sec	Drop diameter ±0.004 mm
155	1.048
232	1.029
297	1.009
374	0.979
444	0.951
560	0.899
627	0.869
723	0.823
798	0.786
887	0.740
960	0.703
1074	0.645
1159	0.602
1217	0.576
1299	0.539
1396	0.500
1473	0.468
1574	0.431
1705	0.382
1769	0.367
1838	0.347
1902	0.331
1984	0.309
2050	0.291
2116	0.274

Figure E2I

Experiment number: 72
 Surfactant: 74±2 ppm NAPA
 Temperature: 25.0±0.1 °C
 Pressure: 753.3±0.2 mm Hg
 Rel. Humidity: 12.0±0.5 %
 Support type: Glass Fibre
 Fibre diameter: 31±4 µm

Time sec	Drop diameter ±0.004 mm
91	1.035
160	1.021
267	1.000
426	0.963
606	0.917
739	0.882
884	0.838
1099	0.776
1236	0.736
1355	0.705
1531	0.659
1697	0.619
1891	0.570
2038	0.541
2226	0.504
2441	0.464
2615	0.435
2848	0.399
3091	0.359
3336	0.321
3582	0.281

Drop temperature °C

Figure E22

Experiment number: 92
 Surfactant: 73 $\pm$ 2 ppm NAPA
 Temperature: 24.9 $\pm$ 0.1 $^{\circ}$ C
 Pressure: 751.8 $\pm$ 0.2 mm Hg
 Rel. Humidity: 12.0 $\pm$ 0.5 %
 Support type: Glass Fibre
 Fibre diameter: 27 $\pm$ 4 μ m
 Time Drop diameter
 sec $\pm$ 0.004 mm

134	1.111
206	1.099
361	1.071
530	1.037
715	0.995
867	0.957
1035	0.918
1193	0.878
1392	0.829
1590	0.778
3362	0.733
3428	0.716
3539	0.687
3730	0.640
3905	0.597
4040	0.566
4199	0.533
4353	0.498
4688	0.431
4932	0.385
5137	0.352
5373	0.318
5580	0.286
5743	0.263

Drop temperature $^{\circ}$ C

Figure E23

Experiment number: 34
 Surfactant: 130±2 ppm NAPA
 Temperature: 24.9±0.1 °C
 Pressure: 752.0±0.2 mm Hg
 Rel. Humidity: 12.0±0.5 %
 Support type: Glass fibre
 Fibre diameter: 23±4 µm

Time	Drop diameter
sec	±0.004 mm
111	1.103
177	1.092
268	1.077
390	1.051
491	1.029
595	1.009
700	0.982
821	0.957
956	0.927
1117	0.891
1226	0.866
1381	0.830
1511	0.802
1654	0.770
1763	0.748
1942	0.710
2119	0.676
2303	0.641
2457	0.610
2606	0.584
2771	0.553
2931	0.524
3164	0.486
3345	0.456
3476	0.434
3623	0.409
3854	0.367
4023	0.333
4198	0.290

Figure E24

Experiment number: 71
 Surfactant: 150±2 ppm NAPA
 Temperature: 25.0±0.1 °C
 Pressure: 757.6±0.2 mm Hg
 Rel. Humidity: 12.0±0.5 %
 Support type: Glass Fibre
 Fibre diameter: 32±4 µm
 Time Drop diameter
 sec ±0.004 mm

116	1.115
191	1.103
463	1.051
711	0.995
1001	0.924
1209	0.873
1417	0.827
1628	0.774
1847	0.722
2087	0.667
2274	0.625
2436	0.586
2880	0.486
3048	0.450
3253	0.404
3415	0.367
3927	0.242
3968	0.234

Drop temperature °C

Experiment number: 39
 Surfactant: 25±2 ppm NAPA
 Temperature: 25.0±0.1 °C
 Pressure: 764.3±0.2 mm Hg
 Rel. Humidity: 53.8±0.5 %
 Support type: Glass fibre
 Fibre diameter: 21±4 µm

Time sec	Drop diameter ±0.004 mm
140	1.096
233	1.067
290	1.049
445	0.997
543	0.968
700	0.912
822	0.866
946	0.822
1051	0.781
1228	0.710
1385	0.643
1556	0.569
1624	0.543
1725	0.498
1852	0.445
1986	0.379
2076	0.329
2126	0.297
2215	0.247

Figure E25

Figure E26

Figure E27

Experiment number: 41
 Surfactant: 99 $\pm$ 2 ppm NAPA
 Temperature: 24.9 $\pm$ 0.1 $^{\circ}$ C
 Pressure: 768.0 $\pm$ 0.2 mm Hg
 Rel. Humidity: 53.8 $\pm$ 0.5 %
 Support type: Glass Fibre
 Fibre diameter: 24 $\pm$ 4 μ m

Time sec	Drop diameter ± 0.004 mm
95	1.014
153	1.005
252	0.994
523	0.951
680	0.927
886	0.892
1039	0.866
1259	0.827
1456	0.792
1661	0.755
1858	0.722
2090	0.683
2325	0.643
2526	0.609
2772	0.572
3119	0.521
3395	0.482
3624	0.454
3945	0.414
4251	0.379
4552	0.349
4828	0.318
5126	0.287
5423	0.263

Drop temperature $^{\circ}$ C

Figure E28

Experiment number: 50
 Surfactant: 40±2 ppm NAPA
 Temperature: 25.1±0.1 °C
 Pressure: 770.1±0.2 mm Hg
 Rel. Humidity: 3.0±0.5 %
 Support type: Glass fibre
 Fibre diameter: 29±4 µm

Time sec	Drop diameter ±0.004 mm
116	1.098
178	1.084
249	1.063
358	1.031
550	0.973
632	0.946
744	0.910
1222	0.746
1334	0.709
1484	0.659
1603	0.622
1750	0.580
1969	0.522
2174	0.477
2377	0.436
2560	0.409
2778	0.383
3082	0.346
3310	0.326
3616	0.297

Drop temperature °C

Figure E29

Experiment number: 51
 Surfactant: 40±2 ppm NAPA
 Temperature: 25.1±0.1 °C
 Pressure: 768.1±0.2 mm Hg
 Rel. Humidity: 3.0±0.5 %
 Support type: Glass Fibre
 Fibre diameter: 27±4 µm
 Time Drop diameter
 sec ±0.004 mm
 155 1.112
 218 1.081
 314 1.026
 512 0.903
 609 0.831
 740 0.732
 909 0.583
 964 0.534
 1066 0.454
 1180 0.392
 1308 0.345
 1546 0.283
 1642 0.257

Drop temperature °C

Figure E30

Experiment number: 45
 Surfactant: 45 $\pm$ 2 ppm NAPA
 Temperature: 25.2 $\pm$ 0.1 $^{\circ}$ C
 Pressure: 759.8 $\pm$ 0.2 mm Hg
 Rel. Humidity: 3.0 $\pm$ 0.5 %
 Support type: Glass Fibre
 Fibre diameter: 24 $\pm$ 4 μ m

Time sec	Drop diameter $\pm$ 0.004 mm
167	1.131
231	1.095
328	1.035
430	0.965
542	0.887
615	0.830
723	0.738
808	0.655
888	0.565
957	0.481
1017	0.421
1073	0.373
1135	0.340
1201	0.314
1283	0.292
1379	0.264
1521	0.227

Figure E3I

Experiment number: 46
 Surfactant: 45±2 ppm NAPA
 Temperature: 25.1±0.1 °C
 Pressure: 754.0±0.2 mm Hg
 Rel. Humidity: 3.0±0.5 %
 Support type: Glass Fibre
 Fibre diameter: 25±4 µm

Time	Drop diameter
sec	±0.004 mm
151	1.178
215	1.150
293	1.114
371	1.076
458	1.031
533	0.993
622	0.945
704	0.900
800	0.849
886	0.798
963	0.757
1049	0.710
1128	0.670
1223	0.624
1314	0.581
1394	0.543
1488	0.502
1554	0.476
1639	0.455
1742	0.408
1835	0.381
1933	0.358
2044	0.331
2161	0.306
2284	0.282
2400	0.261

Figure E32

Figure E33

Figure E34

Experiment number: 36
 Surfactant: 50 $\pm$ 2 ppm NAPA
 Temperature: 25.1 $\pm$ 0.1 $^{\circ}\text{C}$
 Pressure: 772.0 $\pm$ 0.2 mm Hg
 Rel. Humidity: 12.0 $\pm$ 0.5 %
 Support type: Glass Fibre
 Fibre diameter: 26 $\pm$ 4 μm
 Time Drop diameter
 ± 0.004 mm

Figure E35

Experiment number: 77
 Surfactant: 47±2 ppm NAPA
 Temperature: 25.0±0.1 °C
 Pressure: 759.5±0.2 mm Hg
 Rel. Humidity: 33.2±0.5 %
 Support type: Glass Fibre
 Fibre diameter: 27±4 µm

Time	Drop diameter
sec	±0.004 mm
291	1.089
349	1.072
441	1.043
560	1.002
689	0.959
853	0.901
964	0.861
1079	0.815
1213	0.764
1302	0.730
1401	0.691
1504	0.650
1590	0.621
1695	0.582
1770	0.556
1875	0.523
1984	0.489
2105	0.453
2219	0.427
2341	0.399
2444	0.379

Drop temperature °C

Figure E36

Experiment number: 78
 Surfactant: 50±2 ppm NAPA
 Temperature: 25.1±0.1 °C
 Pressure: 761.3±0.2 mm Hg
 Rel. Humidity: 75.8±0.5 %
 Support type: Glass Fibre
 Fibre diameter: 35±4 µm

Drop diameter
 ±0.004 mm

Drop temperature °C

Figure E37

Experiment number: 75
 Surfactant: 40±2 ppm NAPA
 Temperature: 15.6±0.1 °C
 Pressure: 756.0±0.2 mm Hg
 Rel. Humidity: 12.8±0.5 %
 Support type: Glass Fibre
 Fibre diameter: 24±4 µm

Time sec	Drop diameter ±0.004 mm
88	0.998
147	0.991
288	0.956
423	0.919
553	0.879
670	0.841
786	0.800
894	0.759
1041	0.704
1130	0.665
1229	0.623
1336	0.573
1425	0.532
1508	0.492
1621	0.433
1702	0.389
1762	0.365
1824	0.348
1874	0.330
1929	0.320
1991	0.313
2080	0.305
2140	0.301
2236	0.293
2325	0.287
2417	0.282
2497	0.278

Drop temperature °C

Figure E38

Experiment number: 73
 Surfactant: 40±2 ppm NAPA
 Temperature: 25.0±0.1 °C
 Pressure: 756.4±0.2 mm Hg
 Rel. Humidity: 12.0±0.5 %
 Support type: Glass Fibre
 Fibre diameter: 30±4 µm

Time sec	Drop diameter ±0.004 mm
94	1.081
154	1.054
235	1.014
326	0.961
411	0.912
501	0.856
573	0.809
636	0.765
723	0.706
776	0.667
829	0.625
884	0.584
941	0.540
993	0.501
1059	0.453
1119	0.417
1180	0.381
1226	0.363
1264	0.349
1312	0.333
1361	0.320
1406	0.310
1474	0.296
1529	0.288
1576	0.277
1612	0.268

Drop temperature °C

Figure E39

Experiment number: 76
 Surfactant: 40±2 ppm NAPA
 Temperature: 33.8±0.1 °C
 Pressure: 759.7±0.2 mm Hg
 Rel. Humidity: 11.7±0.5 %
 Support type: Glass Fibre
 Fibre diameter: 29±4 µm
 Time Drop diameter
 sec ±0.004 mm
 124 0.991
 189 0.950
 236 0.920
 296 0.878
 337 0.850
 388 0.813
 452 0.762
 509 0.715
 590 0.646
 633 0.604
 706 0.536
 775 0.468
 813 0.431
 867 0.386
 928 0.357
 973 0.342
 1042 0.318
 1078 0.305
 1132 0.285
 1192 0.262
 1255 0.241

Drop temperature °C

Figure E40

Experiment number: 84
 Surfactant: 20±2 ppm NAPHY
 Temperature: 25.2±0.1 °C
 Pressure: 759.2±0.2 mm Hg
 Rel. Humidity: 12.0±0.5 %
 Support type: Glass fibre
 Fibre diameter: 30±4 µm

Time sec	Drop diameter ±0.004 mm
225	0.973
263	0.941
311	0.905
370	0.856
422	0.818
495	0.758
544	0.718
606	0.662
666	0.605
736	0.528
790	0.464
831	0.412
892	0.319
919	0.275

Drop temperature °C

Figure E4I

Drop temperature °C

26 24 22 20 18 16 14 12 10 8 6 4 2 0

X10²

Time (Sec)

X10⁻¹

Diameter squared (sq.mm) or Sherwood No

Figure E42

Experiment number: 85
 Surfactant: 50 $\pm$ 2 ppm NAMY
 Temperature: 25.1 $\pm$ 0.1 $^{\circ}$ C
 Pressure: 763.0 $\pm$ 0.2 mm Hg
 Rel. Humidity: 12.0 $\pm$ 0.5 %
 Support type: Thermocouple
 Fibre diameter: 27 $\pm$ 4 μ m

Time	Drop diameter
sec	± 0.004 mm
154	1.029
226	0.986
287	0.947
396	0.877
452	0.839
510	0.798
591	0.745
666	0.692
736	0.623
787	0.584
893	0.498
923	0.472
980	0.432
1050	0.377
1137	0.311
1168	0.289

Drop temperature $^{\circ}$ C

Figure E43

Experiment number: 80
 Surfactant: 75±2 ppm NAMY
 Temperature: 25.2±0.1 °C
 Pressure: 760.7±0.2 mm Hg
 Rel. Humidity: 12.0±0.5 %
 Support type: Glass Fibre
 Fibre diameter: 34±4 µm

Time sec	Drop diameter ±0.004 mm
153	1.124
217	1.096
307	1.048
392	1.006
478	0.964
568	0.918
674	0.865
763	0.819
857	0.771
975	0.710
1068	0.665
1175	0.608
1218	0.584
1306	0.540
1363	0.507
1444	0.460
1503	0.420
1578	0.366
1625	0.328
1666	0.293
1710	0.247

Drop temperature °C

Figure E44

Experiment number: 81
 Surfactant: 150 $\pm$ 2 ppm NAMY
 Temperature: 25.3 $\pm$ 0.1 $^{\circ}$ C
 Pressure: 762.9 $\pm$ 0.2 mm Hg
 Rel. Humidity: 12.0 $\pm$ 0.5 %
 Support type: Glass Fibre
 Fibre diameter: 28 $\pm$ 4 μ m

Time sec	Drop diameter $\pm$ 0.004 mm
109	1.055
186	1.020
256	0.990
333	0.955
393	0.918
496	0.884
615	0.830
731	0.774
832	0.731
1022	0.644
1090	0.609
1154	0.571
1225	0.527
1297	0.473
1356	0.428
1412	0.379
1469	0.330
1505	0.293
1550	0.242

Drop temperature $^{\circ}$ C

Figure E45

Experiment number: 90
 Surfactant: 75±2 ppm NALA
 Temperature: 25.0±0.1 °C
 Pressure: 759.2±0.2 mm Hg
 Rel. Humidity: 12.0±0.5 %
 Support type: Glass Fibre
 Fibre diameter: 31±4 µm

Time sec	Drop diameter ±0.004 mm
137	1.273
235	1.215
316	1.167
399	1.115
459	1.073
521	1.027
602	0.970
673	0.915
731	0.866
799	0.810
842	0.770
914	0.706
987	0.634
1051	0.580
1106	0.519

Drop temperature °C

Figure E46

Experiment number: 89
 Surfactant: 149±2 ppm NALA
 Temperature: 25.1±0.1 °C
 Pressure: 754.8±0.2 mm Hg
 Rel. Humidity: 12.0±0.5 %
 Support type: Glass fibre
 Fibre diameter: 33±4 µm

Time	Drop diameter
sec	±0.004 mm
125	1.072
191	1.029
235	0.995
290	0.955
350	0.911
409	0.860
480	0.802
540	0.748
578	0.719
643	0.662
684	0.624
726	0.584
762	0.551

Drop temperature °C

Figure E47

Experiment number: 91
 Surfactant: 247±2 ppm NALA
 Temperature: 25.1±0.1 °C
 Pressure: 756.1±0.2 mm Hg
 Rel. Humidity: 12.0±0.5 %
 Support type: Glass Fibre
 Fibre diameter: 31±4 µm
 Time Drop diameter
 sec ±0.004 mm
 136 0.996
 187 0.958
 249 0.909
 311 0.859
 394 0.789
 444 0.746
 490 0.709
 565 0.640
 607 0.603
 741 0.458
 784 0.400
 823 0.344

Drop temperature °C

Figure E48

Experiment number: 27
 Surfactant: 49±2 ppm CTAB
 Temperature: 24.9±0.1 °C
 Pressure: 744.8±0.2 mm Hg
 Rel. Humidity: 12.0±0.5 %
 Support type: Glass fibre
 Fibre diameter: 17±4 µm
 Time Drop diameter
 sec ±0.004 mm
 92 1.121
 180 1.066
 306 0.973
 464 0.848
 644 0.678
 754 0.558

Drop temperature °C

Figure E49

Experiment number: 26
 Surfactant: 448 $\pm$ 2 ppm CTAB
 Temperature: 25.0 $\pm$ 0.1 $^{\circ}$ C
 Pressure: 753.2 $\pm$ 0.2 mm Hg
 Rel. Humidity: 12.0 $\pm$ 0.5 %
 Support type: Glass Fibre
 Fibre diameter: 31 $\pm$ 4 μ m
 Time Drop diameter
 sec $\pm$ 0.004 mm
 220 1.032
 291 0.984
 329 0.956
 403 0.898
 460 0.852
 521 0.799
 573 0.752
 651 0.673

Drop temperature $^{\circ}$ C

Figure E50

Experiment number: 60
 Surfactant: 46±2 ppm GMST
 Temperature: 25.0±0.1 °C
 Pressure: 750.8±0.2 mm Hg
 Rel. Humidity: 12.0±0.5 %
 Support type: Glass Fibre
 Fibre diameter: 28±4 µm

Time sec	Drop diameter ±0.004 mm
135	1.176
208	1.130
401	0.994
463	0.945
575	0.853
703	0.742
766	0.679
933	0.506
1023	0.485
1121	0.463
1301	0.427
1489	0.392
1673	0.359
1880	0.321
2126	0.281

Drop temperature °C

Figure E5I

Experiment number: 20
 Surfactant: 878±2 ppm NALS
 Temperature: 24.8±0.1 °C
 Pressure: 760.0±0.2 mm Hg
 Rel. Humidity: 75.8±0.5 %
 Support type: Glass fibre
 Fibre diameter: 33±4 µm
 Time Drop diameter
 sec ±0.004 mm
 66 1.362
 232 1.341
 507 1.306
 1992 1.097
 2185 1.067
 3030 0.928
 3168 0.903
 3300 0.880
 4494 0.608
 4626 0.569
 4792 0.521
 5039 0.440
 5258 0.353
 5370 0.298
 5411 0.274

Figure E52

Experiment number: 83
 Surfactant: 553 $\pm$ 2 ppm TRIN
 Temperature: 25.2 $\pm$ 0.1 $^{\circ}$ C
 Pressure: 757.8 $\pm$ 0.2 mm Hg
 Rel. Humidity: 12.0 $\pm$ 0.5 %
 Support type: Glass Fibre
 Fibre diameter: 25 $\pm$ 4 μ m

Time	Drop diameter
sec	± 0.004 mm
136	0.936
185	0.900
240	0.855
307	0.801
378	0.735
429	0.686
487	0.626
541	0.565
592	0.502
642	0.427

Drop temperature $^{\circ}$ C

Figure E53

Experiment number: 28
 Surfactant: 640±2 ppm TRTN
 Temperature: 25.0±0.1 °C
 Pressure: 745.9±0.2 mm Hg
 Rel. Humidity: 12.0±0.5 %
 Support type: Glass Fibre
 Fibre diameter: 25±4 µm
 Time Drop diameter
 sec ±0.004 mm
 132 0.921
 241 0.830
 434 0.649
 522 0.541
 623 0.393
 682 0.273

Drop temperature °C

Appendix F. Listing of FORTRAN program CONTDROP

The routines DIFFC, DSQDOT, HLATNT, QIN and RK4 are required by CONTDROP, but have already been listed in Appendix C, and so are not reproduced here.

As in Appendix C, the program structure is shown in Figure F1. GINO is a library of subroutines for producing graphical output. The subroutines E02BAF and E02BCF are part of the NAG library (NAG, 1977).

Figure F1. Program structure.

```

C *****
C *
C * CONTDROP: This program analyses experimental measurements of
C * the evaporation behaviour of contaminated water drops. Given
C * a series of measured drop diameters at various times, it
C * calculates the Sherwood number, drop temperature and
C * evaporation resistance at NFIT uniformly spaced times. The
C * output produced by the program also includes a graph of actual
C * and interpolated diameter squared, Sherwood number and drop
C * temperature against time.
C *
C * The method used was to interpolate between the experimental
C * values of diameter squared against time by using a least
C * squares cubic spline, differentiate the spline to obtain an
C * estimate of the experimentally observed evaporation rate, and
C * use this to calculate the Sherwood number and evaporation
C * resistance. As with the program PUREWATER, the drop
C * temperature was calculated by integrating the drop heat
C * balance numerically using the fourth order Runge-Kutta method.
C *
C *****
C
C   INTEGER I, NPTS, OK, NFIT
C   REAL TINF, RELHUM, PRESS, DELTAT, TINT, TIME, DPDIAM, DDSQ, AVDEV,
C   1 RFILM
C
C   The arrays are:
C   T - experimental time; DSQ - diameter squared (measured at T);
C   T2 - interpolated time; DSQ2 - diameter squared (interpolated);
C   SHERWD - Sherwood number at T2;
C   TEMP - calculated drop temperature at T2.
C
C   DIMENSION T(100), DSQ(100), T2(200), DSQ2(200), SHERWD(200),
C   1 TEMP(200), Y(20)
C   COMMON /CONDS/ TINF, RELHUM, PRESS
C   EXTERNAL DERIV2
C
C   DELTAT is the time step used in the numerical integration.
C
C   DATA DELTAT/1.0/, NFIT/100/
C
C   Read in the experimental data from a datafile.
C
C   CALL INPUT2(T,DSQ,NPTS)
C
C   TINT is the interval between interpolated points.
C
C   TINT=(T(NPTS)-T(1)-DELTAT)/FLOAT(NFIT-1)
C
C   Fit a least squares cubic spline to the experimental data.
C
C 10  CALL SPLINE(NPTS,T,DSQ,AVDEV)
C
C   The integration is started at the first experimental point...

```



```

C
  TIME=T(1)
  CALL DSQFIT(TIME,DPDIAM,DDSQ)
C
C ...by assuming that the drop is initially in thermal equilibrium
C with the surrounding air.
C
  Y(1)=TINF
  CALL EQTMP2(Y(1),DPDIAM,DDSQ)
  T2(1)=TIME
  DSQ2(1)=DSQ(1)*1.0E6
C
C Calculate and output the initial time, diameter squared, Sherwood
C number, drop temperature (C) and evaporation resistance.
C
  CALL RESIST(DPDIAM,Y(1),DDSQ,SHERWD(1),RFILM)
  TEMP(1)=Y(1)-273.1
  WRITE(6,30)T2(1),DSQ2(1),SHERWD(1),TEMP(1),RFILM
C
C *** MAIN INTEGRATION LOOP ***
C
  DO 40 I=2,NFIT
C
C Integrate the drop heat balance to calculate the new drop
C temperature at time T2(I).
C
  T2(I)=T2(1)+TINT*FLOAT(I-1)
20  CALL RK4(DERIV2,TIME,Y,DELTAT,1)
  IF(ABS(TIME-T2(I)).GT.(DELTAT/2.0))GOTO 20
C
C Interpolate using the cubic spline to find the drop diameter at
C TIME.
C
  CALL DSQFIT(TIME,DPDIAM,DDSQ)
  DSQ2(I)=DPDIAM*DPDIAM*1.0E6
C
C Output the current time, diameter squared, Sherwood number, drop
C temperature and evaporation resistance.
C
  CALL RESIST(DPDIAM,Y(1),DDSQ,SHERWD(I),RFILM)
  TEMP(I)=Y(1)-273.1
  WRITE(6,30)T2(I),DSQ2(I),SHERWD(I),TEMP(I),RFILM
30  FORMAT(F10.1,F12.4,F10.3,F10.2,F10.2)
40  CONTINUE
C
C Plot the results on a graphics screen to check them visually.
C
  CALL T4010
  CALL UNITS(0.66)
  CALL ERRMAX(999)
  CALL WINDO2(0.0,270.0,0.0,210.0)
  CALL PLOT(T,DSQ,NPTS,T2,DSQ2,SHERWD,TEMP,NFIT)
  CALL DEVENO
C

```

```

      WRITE(2,50)
50    FORMAT(// 'IS THIS FIT SATISFACTORY (Y/N) ?')
      READ(1,60)OK
60    FORMAT(A1)
      IF(OK.EQ.'N')GOTO 10
C
C    Make a paper copy of the graph if desired.
C
      WRITE(2,70)
70    FORMAT(// 'DO YOU WANT A PAPER COPY (Y/N) ?')
      READ(1,60)OK
      IF(OK.EQ.'N')STOP
C
      CALL CC906N
      CALL DEVPA(302.0,298.0,0)
      CALL PLOT(T,DSQ,NPTS,T2,DSQ2,SHERWD,TEMP,NFIT)
      CALL DEVEN
C
      STOP
      END
C *****
C *
C * INPUT2: This subroutine reads in all the experimental data *
C * required by the program and converts it into a form suitable *
C * for further processing. This is the only part of the program *
C * where non-S.I. units are used. *
C *
C * The variables describing the environmental conditions around *
C * the drop are passed to the rest of the program via COMMON *
C * block /CONDS/. These are atmospheric temperature (TINF), % *
C * relative humidity (RELHUM) and pressure (PRESS). *
C *
C * COMMON block /SUPPRT/ passes details of the drop support used *
C * to the rest of the program. SPDIAM(1) holds the diameter of a *
C * thermocouple wire, SPDIAM(2) holds the diameter of a glass *
C * fibre, and ITYPE indicates which type of support has been *
C * used. Possible values of ITYPE are: 1 - no support; 2 - glass *
C * fibre; 3 - thermocouple; 4 - glass fibre and thermocouple. *
C *
C * Arguments passed back to the main program are - *
C *
C * T      A vector of size 100 containing the times corresponding *
C *         to the values stored in DSQ. *
C *
C * DSQ    A vector of size 100 containing the squares of the *
C *         experimentally measured drop diameters. *
C *
C * NPTS   The number of experimental points read into T and DSQ. *
C *
C *****
C
      SUBROUTINE INPUT2(T,DSQ,NPTS)
      INTEGER EXNO, ICONC, SURFNM, SUPNAM, SUPDIA, I, NPTS, ITYPE
      REAL TINF, PRESS, RELHUM, T, DSQ, SPDIAM

```

```

      DIMENSION T(100), DSQ(100), SURFNM(4), SUPNAM(12)
      COMMON /CONDS/ TINF, RELHUM, PRESS
      COMMON /SUPPRT/ SPDIAM(2), ITYPE
C
C   Read in experimental data from specially formatted data file
C
      READ(5,10,END=20)EXPNO, ICONC, SURFNM, TINF, PRESS, RELHUM,
1    SUPNAM, SUPDIA, (T(I),DSQ(I),I=1,100)
10   FORMAT(18X,I8/ 11X,I4,7X,4A1/ 12X,F7.1/ 9X,F7.1/ 14X,F6.1/
1    14X,1A1/ 15X,I6/ // (F9.0,F11.3))
20   NPTS=I-1
C
C   Convert to S.I. units
C
      TINF=TINF+273.1
      PRESS=PRESS*101325./760.0
      DO 30 I=1,NPTS
        DSQ(I)=DSQ(I)*DSQ(I)*1.0E-6
30   CONTINUE
C
C   Define type and size of drop support.
C
      ITYPE=2
      IF(SUPNAM(1).EQ.'T')ITYPE=4
      SPDIAM(1)=12.0E-6
      SPDIAM(2)=FLOAT(SUPDIA)/1.0E6
      RETURN
      ~END
C *****
C *
C *   DQ2: This function calculates the net heat flow between a *
C *   drop evaporating at DDSQ sq.m/s and the surrounding air. This *
C *   is simply the difference between the heat flow to the drop (as *
C *   calculated by QIN) and the product of the latent heat of *
C *   evaporation and the rate of change of drop mass with time. *
C *
C *   Arguments are - *
C *
C *   TDROP The drop temperature. *
C *
C *   DPDIAM The drop diameter. *
C *
C *   DDSQ The drop evaporation rate (the rate of change with *
C *   respect to time of the square of the drop diameter). *
C *
C *****
C
      REAL FUNCTION DQ2(TDROP,DPDIAM,DDSQ)
      REAL TDROP, DPDIAM, QLATNT, HLATNT, DDSQ, QIN, PI
      DATA PI/3.14159/
      QLATNT=DDSQ*PI/4.0*DPDIAM*1000.0 *HLATNT(TDROP)
      DQ2=QLATNT + QIN(TDROP,DPDIAM)
      RETURN
      END

```

```

C *****
C *
C * EQTMP2: This subroutine calculates the temperature at which
C * the rate of heat transfer to a drop evaporating at DDSQ sq.m/s
C * just balances the heat loss due to the latent heat of
C * evaporation - i.e. the equilibrium temperature of a drop with
C * negligible thermal mass.
C *
C * The routine uses Newton's method to find the temperature at
C * which the net heat flow to the drop (as calculated by DQ2) is
C * zero. It iterates until the net heat flow is less than a
C * tolerance TOL. For ease of computation the derivative of DQ2
C * needed by Newton's method is estimated numerically using a
C * first order finite difference formula.
C *
C * Arguments are -
C *
C * TDROP The drop temperature. On entry TDROP should contain an
C * estimate of the equilibrium drop temperature. On exit
C * it will contain the calculated value.
C *
C * DPDIAM The drop diameter.
C *
C * DDSQ The drop evaporation rate (the rate of change with
C * respect to time of the square of the drop diameter).
C *
C *****
C
SUBROUTINE EQTMP2(TDROP,DPDIAM,DDSQ)
  REAL TDROP, DPDIAM, DELTA, TOL, DDSQ, F1, F2, DQ2
  DATA DELTA/0.01/, TOL/1.0E-7/
10  F1=DQ2(TDROP-DELTA,DPDIAM,DDSQ)
    F2=DQ2(TDROP,DPDIAM,DDSQ)
    TDROP=TDROP - F1 / ((F2-F1)/DELTA)
    IF(ABS(F1).GT.TOL)GOTO 10
    RETURN
  END
C *****
C *
C * DERIV2: This subroutine specifies the differential equation
C * which RK4 is to integrate. It calculates the derivative with
C * respect to time of drop temperature as a functions of drop
C * diameter and temperature.
C *
C * Arguments are -
C *
C * TIME The independant variable - time.
C *
C * Y A vector of size 20 of which only the first element is
C * used. On entry it holds the values of the dependant
C * variable at TIME (the drop temperature).
C *
C * YDOT A vector of size 20 of which only the first element is
C * used. On exit it contains the derivative calculated

```

```

C      *      from the differential equation (dT/dt).      *
C      *
C      * *****
C
C      SUBROUTINE DERIV2(TIME,Y,YDOT)
C      REAL TIME, Y, YDOT, CP, PI, DQ2, DDSQ, DPDIAM
C      DIMENSION Y(20),YDOT(20)
C
C      CP is the specific heat of liquid water.
C
C      DATA CP/4200.0/, PI/3.14159/
C
C      Use spline interpolation to estimate current diameter and
C      evaporation rate.
C
C      CALL DSQFIT(TIME,DPDIAM,DDSQ)
C
C      Use heat balance to calculate dT/dt.
C
C      YDOT(1)=DQ2(Y(1),DPDIAM,DDSQ) / (CP*1000.0*PI*(DPDIAM**3)/6.0)
C      RETURN
C      END
C
C      * *****
C      *
C      * RESIST: This subroutine calculates the effective Sherwood *
C      * number and the additional evaporation resistance due to the *
C      * presence of surfactant given the drop diameter, temperature *
C      * and evaporation rate. The calculation of surfactant evapora- *
C      * tion resistance is based on the assumption that the surfactant *
C      * is present as a thin film. *
C      *
C      * Arguments are - *
C      *
C      * DPDIAM The drop diameter. *
C      *
C      * TDROP The drop temperature. *
C      *
C      * DDSQ The drop evaporation rate (rate of change of diameter *
C      * squared with respect to time). *
C      *
C      * SHERWD The Sherwood number. *
C      *
C      * RFILM The evaporation resistance due to the surfactant. *
C      *
C      * *****
C
C      SUBROUTINE RESIST(DPDIAM,TDROP,DDSQ,SHERWD,RFILM)
C      REAL DPDIAM, TDROP, DDSQ, SHERWD, RFILM, RWATER, TINF, RELHUM,
C      1 PRESS, TEFF, DSQDOT, DIFFC
C      COMMON /CONDS/ TINF, RELHUM, PRESS
C
C      Calculate the Sherwood number from the actual and predicted
C      evaporation rates.
C

```

```

SHERWD=DSQ/DSQDOT(DPDAM,TDROP)*2.0
TEFF=SQRT(TDROP*TINF)

C
C Calculate the diffusional evaporation resistance presented by the
C air around the drop.
C
  RWATER=DPDIAM/DIFFC(TEFF,PRESS)/2.0

C
C Calculate the additional resistance to evaporation due to the
C presence of surfactant.
C
  RFILM=RWATER*(2.0/SHERWD-1.0)
  RETURN
  END

C *****
C *
C * PLOT: This subroutine draws a graph of the experimental and *
C * calculated results by calling subroutines in the GINO and *
C * GINOGRAPH graphics libraries. *
C *
C * It draws the spline fitted to the squares of the *
C * experimentally measured diameters, and plots the positions of *
C * the experimental points themselves. It also plots the *
C * theoretically predicted and experimentally measured drop *
C * temperatures, and the calculated Sherwood numbers. *
C *
C * A key containing all the original experimental data is drawn *
C * by the side of the graph. *
C *
C * Arguments are - *
C *
C * T      A vector of size at least NPTS holding the times *
C *        corresponding to the values in DSQ. *
C *
C * DSQ    A vector of size at least NPTS holding the squares of *
C *        the experimentally measured diameters. *
C *
C * NPTS   The number of experimental points to be plotted. *
C *
C * T2     A vector of size at least NFIT holding the times *
C *        corresponding to the values stored in DSQ2, SHERWD and *
C *        TEMP. *
C *
C * DSQ2   A vector of size at least NFIT holding the values of *
C *        diameter squared calculated from the spline. *
C *
C * SHERWD A vector of size at least NFIT holding the calculated *
C *        values of Sherwood number. *
C *
C * TEMP   A vector of size at least NFIT holding the theoretic- *
C *        ally predicted drop temperatures. *
C *
C * NFIT   The number of predicted values to be used in plotting *
C *        the curves. *

```



```

C      *
C      *****
C
C      SUBROUTINE PLOT(T,DSQ,NPTS,T2,DSQ2,SHERWD,TEMP,NFIT)
C      INTEGER NPTS, NFIT, I, NINTP7, ITEXT(26), IX, IY, NSPACE, NFIT4
C      REAL T(NPTS), DSQ(NPTS), T2(NFIT), DSQ2(NFIT), SHERWD(NFIT),
C      1 XOR, YOR, XEND, YEND, XMIN, XMAX, YMIN, YMAX, CW, HALFCW,
C      2 XAXLEN, YAXLEN, TINF, RELHUM, PRESS, Y, X, T3(100),
C      3 TEMP(NFIT), TIME(6000), EXTEMP(6000), DSQ3(100)
C      DOUBLE PRECISION XKNOT, C
C      COMMON /CONDS/ TINF, RELHUM, PRESS
C      COMMON /INTERP/ XKNOT(30), C(30), NINTP7
C      DATA IX/1/, IY/2/
C
C      Set axis limits
C
C      YMIN=0.0
C      YMAX=2.0
C      XMIN=0.0
C      XMAX=T(NPTS)
C
C      Set space limits
C
C      XOR=45.0
C      YOR=40.0
C      XAXLEN=145.0
C      YAXLEN=120.0
C      XEND=XOR+XAXLEN
C      YEND=YOR+YAXLEN
C
C      Label axes
C
C      CALL CHASIZ(3.0,4.0)
C      CALL MOVT02(103.0,23.0)
C      CALL CHAHOL('Time (Sec)*.')
```

C

```

      CALL MOVT02(100.0,172.0)
      CALL CHAHOL('Figure*.')
```

C

```

      CALL MOVBY2(-19.0,-1.0)
      CALL LINBY2(28.0,0.0)
```

C

```

      CALL CHAANG(90.0)
      CALL MOVT02(31.0,39.0)
      CALL CHAHOL('Diameter squared (sq.mm) or Sherwood No*.')
```

C

```

      CALL MOVT02(210.0,70.0)
      CALL CHAHOL('Drop temperature C*.')
```

C

```

      CALL CHASIZ(1.5,1.5)
      CALL MOVBY2(-2.2,-5.8)
      CALL CHAHOL('O*.')
```

C

```

      CALL CHAANG(0.0)
C      Mark corners of paper
C
```

```

CALL MOVT02(2.0,10.0)
CALL SYMBOL(3)
CALL MOVT02(2.0,220.0)
CALL SYMBOL(3)
CALL MOVT02(299.0,10.0)
CALL SYMBOL(3)
CALL MOVT02(299.0,220.0)
CALL SYMBOL(3)
C
C Draw X axis (Time)
C
CALL CHASIZ(2.5,3.0)
CALL AXIP0S(1,X0R,Y0R,XAXLEN,IX)
CALL AXISCA(1,10,XMIN,XMAX,IX)
CALL AXIDRA(2,1,IX)
C
C Draw Y axis (Diameter squared)
C
CALL AXIP0S(1,X0R,Y0R,YAXLEN,IY)
CALL AXISCA(1,10,YMIN,YMAX,IY)
CALL AXIDRA(-2,-1,IY)
C
C Draw background grid
C
CALL GRID(3,0,0)
C
C Mark positions of experimental points
C
CW=1.6
CALL CHASIZ(CW,CW)
DO 10 I=1,NPTS
    Y=DSQ(I)*1.0E6
    CALL GRAMOV(T(I),Y)
    CALL SYMBOL(7)
10 CONTINUE
C
C Mark positions of spline knots along the time axis
C
HALFCW=CW/2.0
IF(NINTP7.EQ.8)GOTO 30
DO 20 I=9,NINTP7
    X=XKNOT(I-4)
    CALL GRAMOV(X,0.0)
    CALL MOVBY2(0.0,HALFCW)
    CALL SYMBOL(1)
20 CONTINUE
C
C Draw the variation of Sherwood No with time
C
30 CALL GRACUR(T2,SHERWD,NFIT)
C
C Draw the fitted spline
C
NFIT4=0

```

```

DO 40 I=1,NFIT,4
  NFIT4=NFIT4+1
  DSQ3(NFIT4)=DSQ2(I)
  T3(NFIT4)=T2(I)
40  CONTINUE
  NFIT4=NFIT4+1
  DSQ3(NFIT4)=DSQ2(NFIT)
  T3(NFIT4)=T2(NFIT)
  CALL DASHED(-2,6.0,3.3,0.7)
  CALL GRACUR(T3,DSQ3,NFIT4)
  CALL DASHED(0,6.0,3.3,0.7)
C
C  Second T axis (Temperature)
C
  XOR=XOR+XAXLEN
  YMAX=TINF-273.1
  CALL CHASIZ(2.5,3.0)
  CALL AXIPOS(1,XOR,YOR,YAXLEN,IY)
  CALL AXISCA(1,10,YMIN,YMAX,IY)
  CALL AXIDRA(+2,+1,IY)
C
C  Plot predicted temperature
C
  CALL DASHED(-1,6.0,3.0,0.0)
  CALL GRACUR(T2,TEMP,NFIT)
  CALL DASHED(0,6.0,3.0,0.0)
C
C  Plot measured temperatures if required
C
  REWIND 7
  I=1
  CALL CHASIZ(CW,CW)
C33  READ(7,*,END=44)TIME(I),EXTEMP(I)
  IF(TIME(I).LT.T(1))GOTO 33
  I=I+1
  IF(TIME(I-1).LT.T(NPTS))GOTO 33
C44  NSPACE=0
  I=I-1
  IF(I.GE.200)NSPACE=I/100-1
  CALL GRASYM(TIME,EXTEMP,I,4,NSPACE)
C
C  Write key
C
  REWIND 5
  CALL CHASIZ(2.0,2.25)
  CALL MOVTO2(225.0,165.0)
50  READ(5,60,END=70)(ITEXT(I),I=1,26)
60  FORMAT(26A1)
  CALL CHAARR(ITEXT,26,1)
  CALL MOVBY2(-52.0,-3.5)
  GOTO 50
C
C  Draw special characters (plus or minus, degree symbol and mu)
C

```

```

70  CALL MOVE(16,2)
    CALL LINBY2(1.333,0.0)

```

```

C
    CALL MOVE(20,3)
    CALL LINBY2(1.333,0.0)

```

```

C
    CALL MOVE(25,3)
    CALL CHASIZ(1.0,1.1)
    CALL MOVBY2(0.0,1.0)
    CALL CHAHOL('O*')

```

```

C
    CALL MOVE(17,4)
    CALL LINBY2(1.333,0.0)

```

```

C
    CALL MOVE(21,5)
    CALL LINBY2(1.333,0.0)

```

```

C
    CALL MOVE(22,7)
    CALL LINBY2(1.333,0.0)

```

```

C
    CALL MOVE(25,7)
    CALL MOVBY2(0.0,1.0)
    CALL LINBY2(0.0,-2.0)

```

```

C
    CALL MOVE(14,9)
    CALL LINBY2(1.333,0.0)
    RETURN
    END

```

```

C *****
C *
C *  MOVE:  This subroutine moves the graphics cursor to a position *
C *  COLNO character spacings and ROWNO line spacings away from an *
C *  origin. It is used by PLOT to position the cursor before *
C *  drawing the special characters in its key. *
C *
C *  Arguments are - *
C *
C *  COLNO  The column number in the key. *
C *
C *  ROWNO  The row number in the key. *
C *
C *****

```

```

C
    SUBROUTINE MOVE(COLNO,ROWNO)
    INTEGER COLNO,ROWNO
    REAL X,Y
    X=25.0 +2.0*(COLNO-1)
    Y=165.0 -3.5*(ROWNO-1)
    CALL MOVT02(X,Y)
    RETURN
    END

```

```

C *****
C *
C *  DSQFIT: This subroutine evaluates and differentiates the *

```

```

C  * least-squares spline fitted by SPLINE to obtain estimates of
C  * the drop diameter and evaporation rate at any intermediate
C  * time between the experimentally measured values.
C  *
C  * The coefficients of the spline (which must have been
C  * calculated by a previous call to SPLINE) are stored in COMMON
C  * block /INTERP/. XKNOT holds the positions of the knots, C
C  * holds the coefficients of the splines, and NINTP7 is the
C  * number of intervals in the spline plus seven.
C  *
C  * Arguments are -
C  *
C  * TIME The time at which the values of DPDIAM and DSQDOT are
C  * required.
C  *
C  * DPDIAM The drop diameter, calculated by taking the square root
C  * of the value of the spline at TIME.
C  *
C  * DSQDOT The rate of change of diameter squared with respect to
C  * time, calculated by differentiating the spline.
C  *
C  * *****
C
C      SUBROUTINE DSQFIT(TIME,DPDIAM,DSQDOT)
C      INTEGER IFAIL, NINTP7, LEFT
C      REAL TIME, DPDIAM, DSQDOT
C      DOUBLE PRECISION XKNOT, C, FIT, DTIME
C      DIMENSION FIT(4)
C      COMMON /INTERP/ XKNOT(30), C(30), NINTP7
C      DATA LEFT/1/
C      IFAIL=0
C
C      The spline is evaluated and differentiated using NAG library
C      routine E02BCF which requires double precision arguments.
C
C      DTIME=TIME
C      CALL E02BCF(NINTP7,XKNOT,C,DTIME,LEFT,FIT,IFAIL)
C      IF(IFAIL.NE.0)WRITE(2,10)IFAIL
10  FORMAT(' FAILURE OCCURED DURING CALL TO E02BCF: IFAIL=',I3)
C      DPDIAM=DSQRT(FIT(1))
C      DSQDOT=FIT(2)
C      RETURN
C      END
C  * *****
C  *
C  * SPLINE: This subroutine computes a least-squares approxi-
C  * mation to the set of data points (T(I),DSQ(I),I=1,NPTS). The
C  * fitting function is a cubic spline with knots prescribed by
C  * the user.
C  *
C  * The spline coefficients are calculated by calling the NAG
C  * library routine E02BAF. They are passed to the interpolating
C  * subroutine DSQFIT via COMMON block /INTERP/. XKNOT holds the
C  * positions of the knots, C holds the coefficients of the

```

```

C  * splines, and NINTP7 is the number of intervals in the spline *
C  * plus seven. *
C  * *
C  * The subroutine prompts the user for a new set of knots until *
C  * the root mean square deviation of the experimental points *
C  * about the line is acceptable. *
C  * *
C  * Arguments are - *
C  * *
C  * NPTS The number of experimental data pairs. *
C  * *
C  * T A vector of size 100 holding the times corresponding to *
C  * the values in DSQ. *
C  * *
C  * DSQ A vector of size 100 holding the squares of the *
C  * experimentally measured diameters. *
C  * *
C  * AVDEV The root mean square deviation of the experimental *
C  * points about the fitted line (sq.mm). *
C  * *
C  * *****
C
C      SUBROUTINE SPLINE(NPTS,T,DSQ,AVDEV)
C      INTEGER NPTS, IFAIL, NINTP7, OK, I
C      REAL T, DSQ, AVDEV
C      DOUBLE PRECISION X, Y, W, XKNOT, WORK1, WORK2, C, SS
C      DIMENSION T(100), DSQ(100), X(100), Y(100), W(100), WORK1(100),
C      1 WORK2(4,30)
C      COMMON /INTERP/ XKNOT(30), C(30), NINTP7
C
C      Move data into double precision arrays (EOZBAF requires
C      double precision arguments).
C
C      DO 10 I=1,NPTS
C          X(I)=T(I)
C          Y(I)=DSQ(I)
C          W(I)=1.0D0
C      10 CONTINUE
C
C      Enter positions of internal knots
C
C      DO 40 I=1,20
C          WRITE(2,30)I
C      30 FORMAT('ENTER X COORDINATE OF KNOT',I3)
C          READ(1,*)XKNOT(I+4)
C          IF(XKNOT(I+4).LT.0.0D0)GOTO 50
C      40 CONTINUE
C      NINTP7=I+7
C
C      Fit spline
C
C      IFAIL=0
C      CALL EOZBAF(NPTS,NINTP7,X,Y,W,XKNOT,WORK1,WORK2,C,SS,IFAIL)
C      IF(IFAIL.NE.0)WRITE(2,60)IFAIL

```



```
60  FORMAT(' FAILURE OCCURED DURING CALL TO E02BAF: IFAIL=',I3)
C
C  Check that fit is sufficiently accurate
C
      AVDEV=SQRT((SS*1.OE12)/FLOAT(NPTS))
      WRITE(2,70)AVDEV
70  FORMAT('AVERAGE DEV=',F7.4//'IS THIS FIT SATISFACTORY (Y/N) ?')
      READ(1,80)OK
80  FORMAT(A1)
      IF(OK.NE.'Y')GOTO 20
      RETURN
      END
```

Appendix G. Derivation of equation [6.4]

The total quantity of surfactant contained in a drop at any given time must be

$$\int_0^{R(t)} C r^2 dr = C_0 R_0^3 / 3 \quad (G1)$$

Since this is a constant, its derivative with respect to time must be zero. Reversing the order of differentiation and integration gives

$$0 = \frac{d}{dt} \int_0^R C r^2 dr = \int_0^R \frac{\partial}{\partial t} [C r^2] dr + C R^2 \frac{dR}{dt}$$

hence

$$\begin{aligned} - C R^2 \frac{dR}{dt} &= \int_0^R \frac{\partial}{\partial r} \left[D r^2 \frac{\partial C}{\partial r} \right] dr \\ &= D R^2 \left. \frac{\partial C}{\partial r} \right|_{r=R} \end{aligned}$$

Which simplifies to give the desired result.

$$- C \frac{dR}{dt} = D \left. \frac{\partial C}{\partial r} \right|_{r=R} \quad (G2)$$

Appendix H. The concentration distribution in an evaporating solution drop

The concentration distribution in a drop was determined by using a heat balance integral method due to Goodman (Crank, 1984) to solve Fick's equation

$$\frac{\partial C}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[D r^2 \frac{\partial C}{\partial r} \right] \quad (\text{H1})$$

with the initial and boundary conditions

$$C(r, 0) = C_0 ; 0 \leq r \leq R_0 ; \quad (\text{H2})$$

$$C(R, t) = C_\zeta ; t > 0 ; \quad (\text{H3})$$

$$\left. \frac{\partial C}{\partial r} \right|_{r=0} = 0 ; t > 0 ; \quad (\text{H4})$$

$$- D \left. \frac{\partial C}{\partial r} \right|_{r=R} = C_\zeta \frac{\partial R}{\partial t} ; \quad (\text{H5})$$

where D is the diffusion coefficient in the solution;

$R(t)$ is the current radius; and

$C_\zeta(t)$ is the surface concentration.

The method is based on assuming a particular form for the concentration distribution in the drop which automatically satisfies conditions (H2), (H3) and (H4). The form used, which was suggested by Dolinskii and Ivanitskii (1976), is

$$C = C_0 + (C_\zeta(t) - C_0) \left[\left(\frac{R+r}{2R} \right)^{n(t)} + \left(\frac{R-r}{2R} \right)^{n(t)} \right] \quad (\text{H6})$$

$n(t)$ and $C_\zeta(t)$ are then determined by forcing (H6) to satisfy an integrated form of equation (H1)

$$\int_0^R \frac{\partial C}{\partial t} r^2 dr = \int_0^R \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 D \frac{\partial C}{\partial r} \right] r^2 dr . \quad (\text{H7})$$

Simplifying the right hand side, and reversing the order of integration and differentiation on the left hand side gives

$$\frac{\partial}{\partial t} \int_0^R C r^2 dr - \frac{\partial R}{\partial t} C_\zeta R^2 = \left[r^2 D \frac{\partial C}{\partial r} \right]_0^R \quad (\text{H8})$$

From (H6)

$$\frac{\partial C}{\partial t} = \frac{n (C_\zeta(t) - C_0)}{2 R} \left[\left(\frac{R+r}{2R} \right)^{n-1} - \left(\frac{R-r}{2R} \right)^{n-1} \right] \quad (\text{H9})$$

so the right hand side of (H8) simplifies to

$$\frac{D_L (C_L(t) - C_0) n R}{2} \quad (H10)$$

Substituting (H6) into the left hand side of (H8), we obtain

$$\left(\frac{C_0 - C_L}{3} \right) \frac{\partial R^3}{\partial t} + \frac{\partial}{\partial t} \int_0^R (C_L(t) - C_0) \left[\left(\frac{R+r}{2R} \right)^{n(t)} + \left(\frac{R-r}{2R} \right)^{n(t)} \right] r^2 dr$$

Making the substitution $r=Z R$ simplifies this to

$$\left(\frac{C_0 - C_L}{3} \right) \frac{\partial R^3}{\partial t} + \frac{\partial}{\partial t} \left[\frac{R^3}{2^n} (C_L(t) - C_0) \int_0^1 Z^2 (1+Z)^n + Z^2 (1-Z)^n dZ \right] \quad (H11)$$

The integral term can be integrated by parts since

$$\int Z^2 (1+Z)^n dZ = \pm \frac{Z^2 (1+Z)^{n+1}}{(n+1)} \mp \frac{2}{(n+1)} \int Z (1+Z)^{n+1} dZ$$

and

$$\begin{aligned} \int Z (1+Z)^{n+1} dZ &= \pm \frac{Z (1+Z)^{n+2}}{(n+2)} \mp \frac{1}{(n+2)} \int (1+Z)^{n+2} dZ \\ &= \pm \frac{Z (1+Z)^{n+2}}{(n+2)} - \frac{(1+Z)^{n+3}}{(n+2)(n+3)} \end{aligned}$$

Hence

$$\int Z^2 (1+Z)^n dZ = \pm \frac{Z^2 (1+Z)^{n+1}}{(n+1)} - \frac{2 Z (1+Z)^{n+2}}{(n+1)(n+2)} \pm \frac{2 (1+Z)^{n+3}}{(n+1)(n+2)(n+3)}$$

and so

$$\begin{aligned} \int_0^1 Z^2 (1+Z)^n + Z^2 (1-Z)^n dZ &= 2^n \left[\frac{2}{(n+1)} - \frac{8}{(n+1)(n+2)} + \frac{16}{(n+1)(n+2)(n+3)} \right] \\ &\quad - 0 + 0 - \frac{2}{(n+1)(n+2)(n+3)} - 0 - 0 - 0 + 0 + 0 + \frac{2}{(n+1)(n+2)(n+3)} \\ &= \frac{2^n \cdot 2(n^2+n+2)}{(n+1)(n+2)(n+3)} \end{aligned}$$

Substituting for the integral term in (H11) and equating to (H10) gives an ordinary differential equation

$$\begin{aligned} 2 \frac{d}{dt} \left[\frac{(C_L - C_0) R^3 (n^2 + n + 2)}{(n+3)(n+2)(n+1)} \right] - \frac{(C_L - C_0)}{3} \frac{dR^3}{dt} \\ = \frac{D (C_L - C_0) n R}{2} \quad (H12) \end{aligned}$$

Dolinskii and Ivaniskii obtained

$$\frac{(n^2+n+1)}{(n+1)(n+2)(n+3)} \quad \text{instead of} \quad \frac{2(n^2+n+2)}{(n+1)(n+2)(n+3)}$$

on the left hand side here and appear to have performed the integration by parts incorrectly.

Substituting (H9) into the boundary condition (H5) produces

$$\frac{D (C_L - C_O) n}{2 R} = - C_L \frac{dR}{dt} \quad (H13)$$

After multiplying both sides of (H13) by R^2 , its left hand side turns out to be identical to the right hand side of (H12), so that

$$2 \frac{d}{dt} \left[\frac{(C_L - C_O) R^3 (n^2 + n + 2)}{(n+3)(n+2)(n+1)} \right] = - \frac{C_O}{3} \frac{dR^3}{dt} \quad (H14)$$

Integrating with respect to t from 0 to t and setting the constant of integration to 0, gives the identity

$$\frac{(C_L - C_O) R^3 (n^2 + n + 2)}{(n+3)(n+2)(n+1)} = \frac{C_O}{6} (R_O^3 - R^3) \quad (H15)$$

Equations (H13) and (H15) now give us two equations for the two unknowns $C_L(t)$ and $n(t)$. Equation (H15) is difficult to solve as it stands; however, if the approximation

$$\frac{6 (n^2 + n + 2)}{(n+3)(n+2)(n+1)} \approx \frac{\alpha}{n+2\beta} \quad (H16)$$

is made (where α and β are constants chosen to make (H16) as accurate as possible), the system can be represented in the following more tractable form:

$$\left. \begin{aligned} \frac{C_L - C_O}{n+2\beta} &= \frac{C_O}{\alpha} \left[\frac{R_O^3}{R^3} - 1 \right] \\ - D n (C_L - C_O) &= C_L 2 R \frac{dR}{dt} \end{aligned} \right\} \quad (H17)$$

Solving (H17) for $n(t)$ and $C_L(t)$ gives a pair of equations suitable for substitution in (H6) if desired.

$$C_L(t) = C_O \left[1 + (Pe+\beta) \frac{\theta}{\alpha} + \sqrt{\left[(Pe+\beta) \frac{\theta}{\alpha} \right]^2 + 2Pe \frac{\theta}{\alpha}} \right] \quad (H18)$$

and

$$n(t) = Pe - \beta + \sqrt{(Pe+\beta)^2 + 2Pe \frac{\alpha}{\theta}} \quad (H19)$$

where $\theta = \left[\frac{R_O^3}{R^3} - 1 \right]$ and $Pe = - \frac{R}{D} \frac{dR}{dt}$ (the Peclet number).

It only remains to find the values of α and β which minimise the error in the approximation (H16). This was done using the GENSTAT statistical package

which performed a non-linear least squares regression. The values found were $\alpha = 6.1043$ and $\beta = 2.8385$ and the maximum difference between the two sides of (H16) was $\leq 1.75\%$ over the range $1.7 < n < \infty$ which was considered quite acceptable.

The value of θ at which a given surface concentration is reached can be found without approximation (H16) by rearranging (H13) and substituting for n in (H15). The result is

$$\theta = \frac{6 (S-1)^2 (2Pe^2 S^2 + Pe.S(S-1) + (S-1)^2)}{(S.Pe + (S-1)) (2S.Pe + (S-1)) (2S.Pe + 3(S-1))} \quad (H20)$$

where $S = C_s/C_o$

Appendix I. The diffusion equation in solute-based coordinates

a) Partial differential equation

The basic partial differential equation to be solved is

$$\left. \frac{\partial C}{\partial t} \right|_r = \frac{1}{r^2} \frac{\partial}{\partial r} \left[D r^2 \left. \frac{\partial C}{\partial r} \right|_t \right] \quad (I1)$$

Making the substitutions $C=C_0U$, $\rho=r/R_0$, $Fo=D_0t/R_0^2$ and $D=D_0f(U)$ to make the equation dimensionless gives

$$\left. \frac{\partial U}{\partial Fo} \right|_\rho = \frac{1}{\rho^2} \frac{\partial}{\partial \rho} \left[f(U) \rho^2 \left. \frac{\partial U}{\partial \rho} \right|_{Fo} \right]_{Fo} \quad (I2)$$

In order to fix the moving boundary at the drop surface, it is necessary to convert to a coordinate system M based on equal quantities of solute rather than equal distances, so that the range 0 to M always includes a constant quantity of surfactant. The total mass balance on the solute (eqn. G1) requires:

$$\int_0^{R(t)} C r^2 dr = C_0 R_0^3 \int_0^1 dM$$

or

$$dM = 3 U \rho^2 d\rho$$

hence

$$\rho = \left[\int_0^M \frac{1}{U} dM \right]^{1/3} \quad (I3)$$

$$\text{and} \quad \left. \frac{\partial M}{\partial \rho} \right|_{Fo} = 3 U \rho^2 \quad (I4)$$

Substituting M for ρ in (I2) gives

$$\left. \frac{\partial U}{\partial Fo} \right|_\rho = 3 U \frac{\partial}{\partial M} \left[3 U f(U) \rho^4 \left. \frac{\partial U}{\partial M} \right|_{Fo} \right]_{Fo} \quad (I5)$$

But U is a function of Fo and ρ so that

$$dU = \left. \frac{\partial U}{\partial Fo} \right|_\rho dFo + \left. \frac{\partial U}{\partial \rho} \right|_{Fo} d\rho$$

and

$$\left. \frac{\partial U}{\partial Fo} \right|_M = \left. \frac{\partial U}{\partial Fo} \right|_\rho + \left. \frac{\partial U}{\partial \rho} \right|_{Fo} \frac{d\rho}{dFo} \quad (I6)$$

By the chain rule

$$\left. \frac{\partial \rho}{\partial Fo} \right|_M = - \left. \frac{\partial M}{\partial Fo} \right|_\rho / \left. \frac{\partial M}{\partial \rho} \right|_{Fo} \quad (I7)$$

From (I3)

$$M = \int_0^\rho 3 U \rho^2 d\rho \quad \therefore \quad \left. \frac{\partial M}{\partial Fo} \right|_\rho = \int_0^\rho 3 \rho^2 \left. \frac{\partial U}{\partial Fo} \right|_\rho d\rho$$

Using (I2) to substitute for $\partial U/\partial Fo$ gives

$$\frac{\partial M}{\partial Fo} \Big|_{\rho} = 3 \int_0^{\rho} \frac{\partial}{\partial \rho} \left[f(U) \rho^2 \frac{\partial U}{\partial \rho} \Big|_{Fo} \right]_{Fo} d\rho = 3 f(U) \rho^2 \frac{\partial U}{\partial \rho} \Big|_{Fo}$$

hence from (I4) and (I7)

$$\frac{\partial \rho}{\partial Fo} \Big|_M = - \frac{f(U)}{U} \frac{\partial U}{\partial \rho} \Big|_{Fo}$$

and (I6) becomes

$$\frac{\partial U}{\partial Fo} \Big|_M = \frac{\partial U}{\partial Fo} \Big|_{\rho} - \frac{f(U)}{U} \left[\frac{\partial U}{\partial \rho} \Big|_{Fo} \right]^2$$

This can now be used to eliminate $\frac{\partial U}{\partial Fo} \Big|_{\rho}$ from (I5). After rearranging, the result is

$$\frac{1}{9U} \frac{\partial U}{\partial Fo} \Big|_M = \frac{\partial}{\partial M} \left[f(U) U \rho^4 \frac{\partial U}{\partial M} \Big|_{Fo} \right]_{Fo} - f(U) \rho^4 \left[\frac{\partial U}{\partial M} \Big|_{Fo} \right]^2$$

Differentiating the first ρ^4 term with respect to M gives

$$\frac{1}{9U} \frac{\partial U}{\partial Fo} \Big|_M = \rho^4 \frac{\partial}{\partial M} \left[f(U) U \frac{\partial U}{\partial M} \Big|_{Fo} \right]_{Fo} + f(U) \left[\frac{4}{3} \rho \frac{\partial U}{\partial M} \Big|_{Fo} - \rho^4 \left[\frac{\partial U}{\partial M} \Big|_{Fo} \right]^2 \right]$$

Rearranging, we obtain the final desired result.

$$\frac{1}{9U \rho^4} \frac{\partial U}{\partial Fo} \Big|_M = \frac{\partial}{\partial M} \left[f(U) U \frac{\partial U}{\partial M} \Big|_{Fo} \right]_{Fo} + f(U) \frac{\partial U}{\partial M} \Big|_{Fo} \left[\frac{4}{3\rho^3} - \frac{\partial U}{\partial M} \Big|_{Fo} \right] \quad (I8)$$

where ρ is of course given by (I3).

b) Boundary conditions

The boundary conditions at time zero and at the drop centre can easily be converted into dimensionless variables giving

$$U = 1 \text{ at } Fo=0 \quad (I9) \quad \text{and} \quad \frac{\partial U}{\partial M} = 0 \text{ at } M=0 \quad (I10)$$

The boundary condition at the drop surface is slightly more complex. In the "constant rate period" dR^2/dt is a constant so

$$R(t)^2 = R_0^2 + \frac{dR^2}{dt} t \quad \text{and} \quad R(t) = R_0 \sqrt{1 + \frac{2R}{R_0^2} \frac{dR}{dt} t}$$

Making the substitutions $Pe = -R/D_0 dR/dt$ and $Fo = D_0 t/R_0^2$ this becomes

$$R(t) = R_0 \sqrt{1 - 2PeFo} \quad (I11)$$

Since $\frac{dR}{dt} = \frac{dR}{dFo} \frac{dFo}{dt}$ and $\frac{dFo}{dt} = \frac{D_0}{R_0^2}$, it is easy to show that

$$\frac{dR}{dt} = - \frac{D_0}{R_0} \frac{Pe}{\sqrt{1 - 2PeFo}}$$

Substituting into (G2), we obtain

$$C \frac{D_0}{R_0} \frac{Pe}{\sqrt{1-2PeFo}} = D \left. \frac{\partial C}{\partial r} \right|_R$$

Using (I4) and making the substitutions $C=C_0U$, $D=D_0f(U)$ and $\rho=R/R_0$ this equation can be simplified to give the desired boundary condition

$$\frac{dU}{dM} = \frac{Pe}{3 f(U) (1-2PeFo)^{3/2}} \quad \text{at} \quad M = 1 \quad (I12)$$

Equation (I8) with boundary conditions (I9), (I10) and (I12) now form a completely specified problem with fixed boundaries.

Appendix J. Listing of FORTRAN program CONCPROF

As in Appendix C, the program structure is shown in Figure J1. TRIDAG is largely based on a subroutine presented in Gerald (1978).

Figure J1. Program structure.

```

C *****
C *
C * CONCPROF: This program calculates the concentration profile *
C * in an evaporating drop. It uses a finite difference method *
C * to solve a transformed version of the diffusion equation in *
C * spherical coordinates. The finite difference method is *
C * implemented in subroutine NLPDE. Functions A, B and C specify *
C * the form of the P.D.E. to be solved, and BNDRY specifies the *
C * boundary conditions. Subroutine RCHECK checks the accuracy of *
C * the solution calculated by NLPDE. *
C *
C * The program outputs the variation of drop surface *
C * concentration with time for five different Peclet numbers. *
C *
C * DOUBLE PRECISION arithmetic has been used throughout. *
C *
C *****
C
C      INTEGER NPTS, NSTEP, I, K, NPRINT, J
C      DOUBLE PRECISION XMIN, XMAX, FO, DFO, U(401), A, B, C, PE, FOMAX,
C      1  PECLET(5), PEFO
C
C The COMMON block /PARAM/ passes the current value of the Peclet
C number through to RCHECK and BNDRY.
C
C      COMMON /PARAM/ PE
C      EXTERNAL A, B, C, BNDRY
C
C The finite difference grid used has 401 points in the space
C direction and 2500 in the time direction (only every fiftieth
C time step is printed out.
C
C      DATA XMIN/0.0D0/, XMAX/1.0D0/, NPTS/401/, NSTEP/50/, NPRINT/50/
C      1  ,  PECLET/ 0.5D0, 1.0D0, 2.0D0, 5.0D0, 1.0D1/
C
C The program calculates the solution to the P.D.E. for five
C different values of the Peclet number.
C
C      DO 60 J=1,5
C          PE=PECLET(J)
C          WRITE(1,10)PE
10      FORMAT(' PECLET NUMBER  =',F5.1)
C          FO=0.0D0
C
C Calculate the Fourier number at which the surface concentration
C is four times the original concentration. The formula used is
C based on an approximate analytical solution to the P.D.E.
C
C          FOMAX=(1-(1+54.D0*(32.D0*PE*PE+12.D0*PE+9.D0)/(3.D0+4.D0*PE)/
C      1  (3.D0+8.D0*PE)/(9.D0+8.D0*PE))**(-2.D0/3.D0))/PE/2.0D0
C
C Calculate the time step to be used in the integration.
C
C          DFO=FOMAX/NPRINT/NSTEP

```

```

C
C Set the dimensionless concentration to its initial value throughout
C the drop.
C
      DO 20 I=1,NPTS
        U(I)=1.0D0
20    CONTINUE
C
C Integrate the P.D.E. by calling NLPDE until the dimensionless
C surface concentration rises above 4. The surface concentration and
C PEFO (the product of the Peclet number and the square root of the
C Fourier number are written out every NSTEP time steps.
C
      WRITE(1,50) FO,U(NPTS)
      DO 30 K=1,NPRINT
        CALL NLPDE(A,B,C,BNDRY,XMIN,XMAX,NPTS,FO,DFO,NSTEP,U)
        IF(U(NPTS).GT.4.0D0)GOTO 40
        PEFO=PE*DSQRT(FO)
        WRITE(1,50) PEFO,U(NPTS)
30    CONTINUE
C
C Call RCHECK to calculate an estimate of the accuracy of the current
C solution.
C
40    CALL RCHECK(NPTS,FO,U)
50    FORMAT(F9.6,4X,F11.7)
60    CONTINUE
      STOP
      END
C *****
C *
C * NLPDE: This subroutine integrates the Non-Linear parabolic *
C * Partial Differential Equation *
C *
C *
C * 
$$B(X,T,U,--) \frac{dU}{dX} \frac{dU}{dT} = \frac{d}{dX} \left[ A(X,T,U) \frac{dU}{dX} \right] + C(X,T,U,--)$$
 *
C *
C * Subject to boundary conditions of the form *
C *
C * 
$$P(T) U + Q(T) \frac{dU}{dX} = R(T,U)$$
 *
C *
C * at XMIN and XMAX. *
C *
C * The method used is a three time level finite difference scheme *
C * due to Lees (Maths. Comp. vol. 20, p516 1966). Second order *
C * finite difference formulae are used throughout, except in *
C * approximating dU/dX at XMIN and XMAX, where more accurate 4th *
C * order formulae are used. These compensate for the higher *
C * truncation error of the assymmetric formulae which must be *
C * used at the boundary. Uniform grids are used in discretising *
C * both the time and space directions. *

```

```

C *
C * DOUBLE PRECISION arithmetic is used throughout.
C *
C * Arguments are -
C *
C * A(X,T,U)      ) Three DOUBLE PRECISION functions supplied by
C *                ) the user to calculate the values of A, B and
C * B(X,T,U,DUX)  ) C for any given values of the time and space
C *                ) co-ordinates T and X, dU/dX (DUX) and the
C * C(X,T,U,DUX)  ) dependant variable U. A, B and C must be
C *                ) declared EXTERNAL in the calling routine.
C *
C * BNDRY(T,U,IBND,P,Q,R) A subroutine supplied by the user to
C *                calculate the values of P, Q and R at XMIN (IBND=1) and
C *                XMAX (IBND=2) given the values of time T and the
C *                dependant variable U at the appropriate boundary. It
C *                must be declared EXTERNAL in the calling routine.
C *
C * XMIN          Space co-ordinate at left hand boundary.
C *
C * XMAX          Space co-ordinate at right hand boundary.
C *
C * NPTS          The number of grid points required in the interval XMIN
C *                to XMAX. XMIN and XMAX must be included as grid
C *                points. As five point finite difference formulae are
C *                used to approximate dU/dX on the boundaries, NPTS must
C *                be at least 5. Because of internally dimensioned
C *                arrays, the program as written limits NPTS to a maximum
C *                of 1001.
C *
C * TIME          The value of time corresponding to the current solution
C *                in U.
C *
C * DT            The step size to be used in the time direction.
C *
C * NSTEP         The number of time steps to be taken on each call to
C *                NLPDE. This must be at least 2 on the first call as
C *                the routine uses an explicit method to initialise
C *                itself and so takes an additional step at TIME=0.
C *
C * U             A vector of size at least NPTS. On entry it should
C *                contain the initial values of the dependant variable U.
C *                The element U(I) is the value of U at X=XMIN+(I-1)/
C *                (NPTS-1)*(XMAX-XMIN). On exit U contains the
C *                calculated values of the dependant variable at the grid
C *                points for the current value of TIME.
C *
C * *****
C
SUBROUTINE NLPDE(A,B,C,BNDRY,XMIN,XMAX,NPTS,TIME,DT,NSTEP,U)
  INTEGER NPTS,NSTEP,I,NM1,NTIMES,J,K,L,IROW,ICOL
  DOUBLE PRECISION A,B,C,XMIN,XMAX,TIME,DT,U,UA,V,X,XAV,DX,DUX,
1 APLUS,AMINUS,COEFF,UOLD,P,Q,R,BBYZDT,UEXT,FACTOR,BNDCF

```

C


```

C   If more than 1001 grid points are required, it is necessary to
C   change a) the dimensions of COEFF, X, XAV & UOLD and
C   b) the last argument in the call to TRIDAG.
C
C   DIMENSION U(NPTS),COEFF(1001,4),BND CF(5)
C
C   /SAVE/ ensures that workspace variables are not lost between calls.
C
C   COMMON /SAVE/ X(1001),XAV(1001),UOLD(1001),DX,NM1
C
C   /INDEX/ passes the subscript of the current grid point through
C   to A, B, and C.
C
C   COMMON /INDEX/ I
C   EXTERNAL A,B,C,BND RY
C   NTIMES=NSTEP
C
C   Perform initialisation if TIME = 0.
C
C   IF(TIME.GE.DT/2.0D0)GOTO 30
C
C   *** INITIALISATON ***
C
C   NM1=NPTS-1
C   DX=(XMAX-XMIN)/(NPTS-1)
C   DO 10 I=1,NPTS
C     UOLD(I)=U(I)
C     X(I)=XMIN+DX*(I-1)
10  CONTINUE
C
C   Because of the form of A, B, and C, it is necessary to calculate
C   the radius corresponding to each value of X.
C
C   CALL RADIUS(NPTS,DX,U)
C
C   Calculate U at TIME = DT using an explicit method.
C
C   XAV(1)=(X(1)+X(2))/2.0D0
C   UAV=(UOLD(1)+UOLD(2))/2.0D0
C   APLUS=A(XAV(1),TIME,UAV)
C   DO 20 I=2,NM1
C     XAV(I)=(X(I)+X(I+1))/2.0D0
C     UAV=(UOLD(I)+UOLD(I+1))/2.0D0
C     DUX=(UOLD(I+1)-UOLD(I-1))/2.0D0/DX
C     AMINUS=APLUS
C     APLUS=A(XAV(I),TIME,UAV)
C     U(I)=UOLD(I)+ DT/B(X(I),TIME,UOLD(I),DUX)
1   *( C(X(I),TIME,UOLD(I),DUX)
2     -APLUS*(UOLD(I)-UOLD(I+1))/DX/DX
3     -AMINUS*(UOLD(I)-UOLD(I-1))/DX/DX )
20  CONTINUE
C
C   Calculate U at X = XMIN.
C

```

```

TIME=DT
CALL BNDRY(TIME,UOLD(1),1,P,Q,R)
U(1)=( 12.0D0*R*DX -48.0D0*Q*U(2) +36.0D0*Q*U(3) -16.0D0*Q*U(4)
1      +3.0D0*Q*U(5) ) / (12.0D0*P*DX -25.0D0*Q)
C
C Calculate U at X = XMAX.
C
CALL BNDRY(TIME,UOLD(NPTS),2,P,Q,R)
U(NPTS)=( 12.0D0*R*DX +48.0D0*Q*U(NM1) -36.0D0*Q*U(NPTS-2)
1      +16.0D0*Q*U(NPTS-3) -3.0D0*Q*U(NPTS-4) )
2      / (12.0D0*P*DX +25.0D0*Q)
IF(NSTEP.LE.1)RETURN
NTIMES=NSTEP-1
C
C      *** MAIN INTEGRATION ROUTINE ***
C
30 DO 120 J=1,NTIMES
C
C Calculate the radii corresponding to each value of X.
C
CALL RADIUS(NPTS,DX,U)
C
C Set up finite difference equations.
C
UAV=(U(1)+U(2))/2.0D0
APLUS=A(XAV(1),TIME,UAV)
DO 40 I=2,NM1
UAV=(U(I)+U(I+1))/2.0D0
DUX=(U(I+1)-U(I-1))/2.0D0/DX
AMINUS=APLUS
APLUS=A(XAV(I),TIME,UAV)
BBY2DT=B(X(I),TIME,U(I),DUX)/2.0D0/DT
C
C Coefficient of U at X - dX.
C
COEFF(I,1)=-AMINUS/3.0D0/DX/DX
C
C Coefficient of U at X + dX.
C
COEFF(I,3)=-APLUS/3.0D0/DX/DX
C
C Coefficient of U at X.
C
COEFF(I,2)=BBY2DT -(COEFF(I,1)+COEFF(I,3))
C
C Constant term.
C
COEFF(I,4)=C(X(I),TIME,U(I),DUX) +BBY2DT*UOLD(I)
1      +COEFF(I,1)*( U(I)-U(I-1) +UOLD(I)-UOLD(I-1))
2      +COEFF(I,3)*( U(I)-U(I+1) +UOLD(I)-UOLD(I+1))
40 CONTINUE
C
C Set up the difference equation coefficients for the boundary
C condition at X = XMIN. The value of U passed to BNDRY, UEXT, is

```

C calculated by linear extrapolation from past U values.

```
C
      TIME=TIME+DT
      UEXT=2.000*U(1)-UOLD(1)
      CALL BNDRY(TIME,UEXT,1,P,Q,R)
      BNDCF(1)= -25.000*Q +12.000*DX*P
      BNDCF(2)= +48.000*Q
      BNDCF(3)= -36.000*Q
      BNDCF(4)= +16.000*Q
      BNDCF(5)= -3.000*Q
      COEFF(1,4)=          +12.000*DX*R
```

C
C Use Gaussian elimination to eliminate the off-tridiagonal terms
C introduced by the use of a five point assymetric formula for
C dU/dX on the XMIN boundary.

```
C
      DO 60 K=1,3
        IROW=5-K
        FACTOR=BNDCF(IROW+1)/COEFF(IROW,3)
        DO 50 L=1,2
          ICOL=IROW+1-L
          BNDCF(ICOL)=BNDCF(ICOL)-FACTOR*COEFF(IROW,3-L)
50      CONTINUE
        COEFF(1,4)=COEFF(1,4)-FACTOR*COEFF(IROW,4)
60      CONTINUE
```

C
C Rearrange the non-zero coefficients to obtain a pure tridiagonal
C form.

```
C
      DO 70 K=1,2
        COEFF(1,K+1)=BNDCF(K)
70      CONTINUE
```

C
C Set up the difference equation coefficients for the boundary
C condition at X = XMAX.

```
C
      UEXT=2.000*U(NPTS)-UOLD(NPTS)
      CALL BNDRY(TIME,UEXT,2,P,Q,R)
      BNDCF(1)= -25.000*Q -12.000*DX*P
      BNDCF(2)= +48.000*Q
      BNDCF(3)= -36.000*Q
      BNDCF(4)= +16.000*Q
      BNDCF(5)= -3.000*Q
      COEFF(NPTS,4)=          -12.000*DX*R
```

C
C Use Gaussian elimination to eliminate the off-tridiagonal terms
C introduced by the use of a five point assymetric formula for
C dU/dX on the XMAX boundary.

```
C
      DO 90 K=1,3
        IROW=NPTS-4+K
        FACTOR=BNDCF(6-K)/COEFF(IROW,1)
        DO 80 L=1,2
          ICOL=6-K-L
```

```

      BND CF(ICOL)=BND CF(ICOL)-FACTOR*COEFF(IROW,1+L)
80      CONTINUE
      COEFF(NPTS,4)=COEFF(NPTS,4)-FACTOR*COEFF(IROW,4)
90      CONTINUE
C
C      Rearrange the non-zero coefficients to obtain a pure tridiagonal
C      form.
C
      DO 100 K=1,2
        COEFF(NPTS,3-K)=BND CF(K)
100      CONTINUE
C
C      Use Gaussian elimination to solve the difference equations.
C
      CALL TRIDAG(COEFF,NPTS,1001)
C
C      Update the values of U and UOLD to advance the solution
C      one time step.
C
      DO 110 I=1,NPTS
        UOLD(I)=U(I)
        U(I)=COEFF(I,4)
110      CONTINUE
120      CONTINUE
      RETURN
      END
C *****
C *
C * TRIDAG : This subroutine performs gaussian elimination on a
C * tridiagonal system. The coefficients of N equations are
C * stored in the N x 4 array A. The first column of A holds the
C * elements to the left of the diagonal, the second holds the
C * diagonal elements, and the third holds the elements to the
C * right. The fourth column holds the right hand side terms.
C *
C * The solution vector is returned in the fourth column of A.
C *
C * Arguments are -
C *
C * A      Matrix of coefficients and r.h.s. as described
C *
C * N      Number of equations
C *
C * NDIM   First dimension of A in the calling program.
C *
C *****
C
      SUBROUTINE TRIDAG(A,N,NDIM)
      INTEGER N,NDIM,I,NM1,M
      DOUBLE PRECISION A
      DIMENSION A(NDIM,4)
C
C      First eliminate all below diagonal terms
C

```

```

DO 10 I=2,N
  A(I,2)=A(I,2)-A(I,1)/A(I-1,2)*A(I-1,3)
  A(I,4)=A(I,4)-A(I,1)/A(I-1,2)*A(I-1,4)
10 CONTINUE
C
C Now do the back substitution
C
  NM1=N-1
  A(N,4)=A(N,4)/A(N,2)
  DO 20 I=1,NM1
C
C The index M counts up the rows
C
    M=N-I
    A(M,4)=(A(M,4)-A(M,3)*A(M+1,4))/A(M,2)
20 CONTINUE
  RETURN
  END
C *****
C *
C * BNDRY: This subroutine is used by NLPDE (q.v.) to define the *
C * boundary conditions of the partial differential equation at *
C * the outermost values of the space coordinate (XMAX and XMIN). *
C *
C * Arguments are - *
C *
C * T The time coordinate. *
C *
C * U The value of the dependent variable on the boundary. *
C *
C * IBND This determines which boundary the values of P, Q and R *
C * are required for. Possible values are: 1 (XMIN) or *
C * 2 (XMAX). *
C *
C * P The coefficient of U in the boundary condition. *
C *
C * Q The coefficient of dU/dX in the boundary condition. *
C *
C * R The residual term in the boundary condition. *
C *
C *****
C
  SUBROUTINE BNDRY(T,U,IBND,P,Q,R)
  INTEGER IBND
  DOUBLE PRECISION T,U,P,Q,R,PE
  COMMON /PARAM/ PE
  GOTO (10,20),IBND
10 P=0.0D0
  Q=1.0D0
  R=0.0D0
  RETURN
20 P=0.0D0
  Q=1.0D0
  R=PE/3.0D0/(1.0D0-2.0D0*PE*T)**1.5D0

```

```

RETURN
END

```

```

C *****
C *
C * A: This function is one of three used by NLPDE (q.v.) to
C * define the coefficients of the partial differential equation
C * to be solved.
C *
C * Arguments are -
C *
C * X      The space coordinate.
C *
C * T      The time coordinate.
C *
C * U      The value of the dependant variable at the point (X,T).
C *
C *****

```

```

DOUBLE PRECISION FUNCTION A(X,T,U)
DOUBLE PRECISION X,T,U
A=9.0D0*U
RETURN
END

```

```

C *****
C *
C * B: This function is one of three used by NLPDE (q.v.) to
C * define the coefficients of the partial differential equation
C * to be solved.
C *
C * In addition to the arguments listed below, the function
C * requires the value of drop radius corresponding to the
C * dimensionless space coordinate X. RCUBED(I) contains the cube
C * of this value.
C *
C * The vector RCUBED must be evaluated by the separate subroutine
C * RADIUS and passed in via the COMMON block /RAD/ because
C * RCUBED(I) and X are related by an integral equation.
C *
C * The index I, passed in via COMMON block /INDEX/, is set by
C * NLPDE and simply indicates which value of RCUBED corresponds
C * to X.
C *
C * Arguments are -
C *
C * X      The space coordinate.
C *
C * T      The time coordinate.
C *
C * U      The value of the dependant variable at the point (X,T).
C *
C * DUX    The value of dU/dX at the point (X,T).
C *
C *****

```

```

DOUBLE PRECISION FUNCTION B(X,T,U,DUX)
INTEGER I
DOUBLE PRECISION X,T,U,DUX,RCUBED
COMMON /RAD/ RCUBED(401)
COMMON /INDEX/ I
B=1.0D0/U/RCUBED(I)**(4.0D0/3.0D0)
RETURN
END

```

```

C *****
C *
C * C: This function is one of three used by NLPDE (q.v.) to *
C * define the coefficients of the partial differential equation *
C * to be solved. *
C *
C * In addition to the arguments listed below, the function *
C * requires the value of drop radius corresponding to the *
C * dimensionless space coordinate X. RCUBED(I) contains the cube *
C * of this value. *
C *
C * The vector RCUBED must be evaluated by the separate subroutine *
C * RADIUS and passed in via the COMMON block /RAD/ because *
C * RCUBED(I) and X are related by an integral equation. *
C *
C * The index I, passed in via COMMON block /INDEX/, is set by *
C * NLPDE and simply indicates which value of RCUBED corresponds *
C * to X. *
C *
C * Arguments are - *
C *
C * X      The space coordinate. *
C *
C * T      The time coordinate. *
C *
C * U      The value of the dependant variable at the point (X,T). *
C *
C * DUX    The value of dU/dX at the point (X,T). *
C *
C *****

```

```

DOUBLE PRECISION FUNCTION C(X,T,U,DUX)
INTEGER I
DOUBLE PRECISION X,T,U,DUX,RCUBED
COMMON /RAD/ RCUBED(401)
COMMON /INDEX/ I
C=12.0D0/RCUBED(I)*DUX -9.0D0*DUX*DUX
RETURN
END

```

```

C *****
C *
C * RADIUS: This subroutine calculates the cube of the radius *
C * corresponding to the space coordinate of each of the grid *
C * points used in NLPDE. *
C *
C * The calculated values are stored in RCUBED and passed to the *

```



```

C * rest of the program via the COMMON block /RAD/.
C *
C * Arguments are -
C *
C * NPTS The number of grid points used by NLPDE.
C *
C * DX The space coordinate grid spacing.
C *
C * U A vector of size NPTS holding the computed solution to
C * the P.D.E.
C *
C *****
C
C SUBROUTINE RADIUS(NPTS,DX,U)
C DIMENSION U(NPTS)
C INTEGER NPTS,I
C DOUBLE PRECISION DX,U,RCUBED
C COMMON /RAD/ RCUBED(401)
C RCUBED(1)=0.000
C
C Apply Simpson's rule at X=0 assuming Symmetry ( i.e. U(0)=U(2) ),
C and then halve the area.
C
C RCUBED(2)=(2.000/U(1)+1.000/U(2))*DX/3.000
C
C Now apply standard Simpson's rule to all the other grid points in
C turn.
C
C DO 10 I=3,NPTS
C RCUBED(I)=RCUBED(I-2)+ (1.000/U(I)+4.000/U(I-1)+1.000/U(I-2))
C 1 *DX/3.000
10 CONTINUE
C RETURN
C END
C *****
C *
C * RCHECK: This subroutine checks the accuracy of the P.D.E.
C * solution computed by NLPDE. It compares two estimates of the
C * drop radius, one of which depends on the computed solution.
C *
C * In addition to the arguments listed below, the subroutine
C * requires the drop radius corresponding to XMAX. After a call
C * to RADIUS, RCUBED(NPTS) contains the cube of this value, and
C * it is passed in via the COMMON block /RAD/.
C *
C * The Peclet number PE is passed in via COMMON block /PARAM/.
C *
C * Arguments are -
C *
C * NPTS The number of grid points used by NLPDE.
C *
C * FO The Fourier number.
C *
C * U A vector of size NPTS holding the computed solution to

```

```

C      *           the P.D.E.                               *
C      *                                                    *
C      *****
C
      SUBROUTINE RCHECK(NPTS,FO,U)
      INTEGER NPTS
      DOUBLE PRECISION PE,RCUBED,DX,U,R1,R2,FO,DIFF
      DIMENSION U(NPTS)
      COMMON /PARAM/ PE
      COMMON /RAD/ RCUBED(401)
C
C      Calculate a first estimate of the drop radius from the outer
C      boundary condition.
C
      R1=(1.000-2.000*PE*FO)**0.500
      DX=1.000/(NPTS-1)
      CALL RADIUS(NPTS,DX,U)
C
C      Calculate a second estimate using the computed P.D.E. solution.
C
      R2=(RCUBED(NPTS))**0.333333333300
C
C      Calculate and write out the % difference.
C
      DIFF=100.000*(R1-R2)/R1
      WRITE(1,10)FO,R1,R2,DIFF
10    FORMAT(' FO=',F9.7,' (1-2*PE*FO)**1/2=',F9.7,
1      ' RCUBED**1/3=',F9.7,' %DIFF=',F6.3)
      RETURN
      END

```

Appendix K. The evaporation of a surfactant-contaminated drop

The method of approach adopted in this appendix is very similar to that of Appendix H. The main difference is that the drop is regarded as being composed of two regions: a thin film of surfactant at the drop surface and a spherical inner core consisting of a dilute surfactant solution (see Figure 6.2).

(a) Region 1 (the inner water core)

As before, the distribution of surfactant within the drop was derived by assuming a particular form for the concentration distribution and substituting this into an integrated form of Fick's law. The analysis closely parallels that used in Appendix H up to equation (H12):

$$2 \frac{d}{dt} \left[\frac{(C_R^- - C_0) R^3 (n^2 + n + 2)}{(n+3)(n+2)(n+1)} \right] - \frac{1}{3} \frac{dR^3}{dt} (C_R^- - C_0) = \frac{nR}{2} D_1 (C_R^- - C_0).$$

Once a surface film of surfactant has formed, C_R^- is time invariant because any excess surfactant accumulating at the surface will precipitate as a surface film, hence this differential equation can be simplified to

$$\frac{d}{dt} \left[\frac{R^3 2 (n^2 + n + 2)}{(n+1)(n+2)(n+3)} \right] = \frac{nR}{2} D_1 + R^2 \frac{dR}{dt}.$$

Making the substitution $F(n) = \frac{2(n^2 + n + 2)}{(n+1)(n+2)(n+3)}$, and performing the differentiation produces

$$3 F R^2 \frac{dR}{dt} + R^3 \frac{dF}{dn} \frac{dn}{dt} = \frac{nR}{2} D_1 + R^2 \frac{dR}{dt},$$

which can be rearranged to give the desired equation

$$\frac{dn}{dt} = \left[n D_1 + 2 R \frac{dR}{dt} (1 - 3 F) \right] / 2 R^2 \frac{dF}{dn}. \quad (K1)$$

(b) Region 2 (the surfactant film)

The thickness of the surface film (δ) can be calculated (if the presence of water is ignored) from the mass of surfactant which has accumulated at the drop surface (Γ) and its density (ρ_F)

$$\delta = \frac{\Gamma}{4\pi R^2 \rho_F}. \quad (K2)$$

In turn, the rate of increase of Γ with time can be calculated from the difference between the mass of surfactant swept into the film by the receding drop surface

$$- 4\pi R^2 C_R^- \frac{dR}{dt},$$

and the mass of surfactant diffusing back into the body of the drop, which by analogy with (H8) and (H10) is

$$2\pi R n D_1 (C_R^- - C_0^-).$$

Hence
$$\frac{dR}{dt} = 2\pi R \left[n D_1 (C_0^- - C_R^-) - 2 R \frac{dR}{dt} C_R^- \right]. \quad (K3)$$

Because the film is very thin, it can be assumed to be in a quasi-steady state, and hence (by analogy with equation [4.9]) the water concentration at radius r is given by

$$W_R + (W_{R+\delta} - W_R) \frac{(R+\delta)}{\delta} \left[1 - \frac{R}{r} \right]$$

where W_R is the concentration of water in the film at radius R . Fick's first law then gives the mass flow of water through the film as

$$- 4\pi R D_2 (W_{R+\delta} - W_R) \frac{(R+\delta)}{\delta}.$$

This can also be expressed in terms of the equivalent gas phase concentrations (by using the Henry's law type relationship $\rho = A W$ where A is a constant for a given surfactant) and the result is

$$- 4\pi R D_2 (\rho_{R+\delta} - \rho_0) \frac{(R+\delta)}{A \delta}. \quad (K4)$$

(c) Region 3 (the gas phase)

The concentration distribution in the gas phase is given by equation [4.9]

$$\rho = \rho_\infty + \frac{(R+\delta)}{r} (\rho_{R+\delta} - \rho_\infty).$$

So from Fick's first law, the rate of water loss from a drop, and hence its rate of mass change, will be

$$\frac{d}{dt} \left[\frac{4}{3} \pi R^3 \rho_1 \right] = - 4\pi (R+\delta)^2 D_g \frac{d\rho}{dr} \Big|_{R+\delta} = - 4\pi (R+\delta) D_g (\rho_{R+\delta} - \rho_\infty). \quad (K5)$$

For the very low surfactant concentrations of practical interest $\delta \ll R$ and (K5) simplifies to

$$\rho_1 R \frac{dR}{dt} = - D_g (\rho_{R+\delta} - \rho_\infty). \quad (K6)$$

$\rho_{R+\delta}$ can now be eliminated by equating (K4) and (K5) to give

$$D_2 (\rho_0 - \rho_{R+\delta}) \frac{R}{A \delta} = D_g (\rho_{R+\delta} - \rho_\infty)$$

or

$$\rho_{R+\delta} = \frac{\rho_\infty + \rho_0 \left[\frac{D_2 R}{D_g A \delta} \right]}{1 + \left[\frac{D_2 R}{D_g A \delta} \right]}.$$

Hence

$$\rho_{R+\delta} - \rho_\infty = \frac{(\rho_0 - \rho_\infty)}{1 + \left[\frac{D_g A \delta}{D_2 R} \right]}$$

and (K6) can be rewritten as

$$-\rho_1 \frac{dR}{dt} = \frac{(\rho_o - \rho_\infty)}{\frac{R}{D_g} + \left[\frac{A \delta}{D_2} \right]}.$$

This equation can be put into a slightly more convenient form by using the Sherwood number (Sh) and the general form of the Maxwell equation (Fuchs, 1959) i.e.

$$-\rho_1 R \frac{dR}{dt} = \frac{Sh}{2} D_g (\rho_o - \rho_\infty) \quad (K7)$$

where

$$Sh = \frac{2}{1 + \left[\frac{D_g A \delta}{D_2 R} \right]}. \quad (K8)$$

Equations (K1), (K2), (K3), (K7) and (K8) now form a completely specified system which is suitable for integration.

Appendix L. Listing of FORTRAN program CONTAEROSL

The routines DIFFC, DSQDOT, EQTMP1, HLATNT, KAIR, NUBY2, RK4 and WVCONC are required by CONTAEROSL, but have already been listed in Appendix C, and so are not reproduced here.

As in Appendix C, the program structure is shown in Figure L1.

Figure L1. Program structure.

```

C *****
C *
C * CONTAEROSL: This program predicts the evaporation behaviour of *
C * a surfactant contaminated aerosol as it is blown down a wind *
C * tunnel, and writes out the aerosol size distribution at *
C * intervals corresponding to the positions of observation ports *
C * in the tunnel walls. *
C *
C * The aerosol size distribution is split into a number of size *
C * fractions, and the evaporation and settling behaviour of each *
C * fraction inferred from the behaviour of the drops at the *
C * fraction boundaries. *
C *
C * The program integrates the differential equations describing *
C * the drops' behaviour numerically using the fourth order Runge- *
C * Kutta method. A general integration subroutine (RK4) was used *
C * to perform the integration, so a separate subroutine (DERIV3) *
C * is used to define the differential equations to be solved. *
C *
C *****
C
C LOGICAL NOFILM, NF
C INTEGER PORT, NDSIZE, I, WORN
C REAL CO, DELTAT, DIAM, DMIN, DUMMY, DUMMY2, ERRMAX, GASVEL,
C 1 HEIGHT, N, NUMBER, PRESS, RO, RHOO, RZERO, GAMMA, SH, T, TDROP,
C 2 TEMP, TIME, TPORT, V, XPOSN, Y
C DIMENSION XPOSN(4), Y(20)
C
C Blank common (//) is used to pass the aerosol size distribution
C (DIAM, NUMBER, NDSIZE) and the variables describing the diffusion
C of surfactant within the drops (GAMMA and N), through the program.
C The heights of the drops above the wind tunnel floor (HEIGHT),
C their temperatures (TEMP) and their radii at time zero (RZERO)
C are also stored in this common block.
C
C COMMON // HEIGHT(30), TEMP(30), DIAM(30), NUMBER(30),
C 1 GAMMA(30), N(30), RZERO(30), NDSIZE, WORN, NF(30)
C
C PRESS holds the atmospheric pressure.
C
C COMMON /CONDS/ DUMMY(2), PRESS
C
C /PARAM/ is used to pass: the initial surfactant concentration (CO);
C the initial drop radius (RO); the drop temperature (TDROP); the
C water vapour concentration at the drop surface (RHOO); and whether
C there is a surface film of surfactant or not (NOFILM) to DERIV3.
C
C COMMON /PARAM/ CO, RO, TDROP, DUMMY2, RHOO, NOFILM
C EXTERNAL DERIV3
C
C XPOSN holds the distances down the wind tunnel at which the droplet
C size distribution is to be printed out; DELTAT is the time step
C to be used in the integration; and DMIN is the minimum drop
C diameter to be included in the calculations.

```



```

C      DATA XPOSN/ 0.0, 1.0, 2.0, 3.0/, DELTAT/1.0E-3/, DMIN/1.0E-6/
C
C      Input the experimental conditions and initial size distribution.
C
C      CALL INPUT3(GASVEL)
C      TIME=0.
C      ERRMAX=DELTAT/2.
C
C      Write out the initial drop size distribution.
C
C      CALL REPORT
C
C      TPORT is the time at which the aerosol reaches each observation
C      port, and hence the time at which the next printout is due.
C
C      DO 30 PORT=2,4
C          TPORT=XPOSN(PORT)/GASVEL
C
C      The program takes each drop size fraction in turn and calculates
C      the changes taking place over time interval DELTAT by numerical
C      integration.
C
10      DO 20 I=1,NDSIZE
C          T=TIME
C
C      Drops with diameters below DMIN are assumed to have evaporated
C      completely.
C
C          IF(DIAM(I).LT.DMIN)GOTO 20
C
C      R0 is the radius of the drop at time zero.
C
C          R0=RZERO(I)
C
C      TDROP is the drop temperature.
C
C          TDROP=TEMP(I)
C
C      The drop's behaviour is described by four differential equations.
C      In order to integrate them numerically, RK4 needs to know the
C      derivatives (specified in subroutine DERIV3) and the initial values
C      of the dependent variables (held in Y).
C
C          Y(1)=DIAM(I)
C          Y(2)=GAMMA(I)
C          Y(3)=HEIGHT(I)
C          Y(4)=N(I)
C
C      It also needs to know the water vapour concentration at the drop
C      surface and whether or not there is a surface film.
C
C          CALL WVCONC(TDROP,100.0,PRESS,RH00,V)
C          NOFILM=NF(I)

```

```

C
C Perform the integration.
C
      CALL RK4(DERIV3,T,Y,DELTAT,4)
C
C Update the values of the dependent variables.
C
      DIAM(I)= Y(1)
      GAMMA(I)= Y(2)
      HEIGHT(I)=Y(3)
      N(I)=    Y(4)
      SH=      Y(6)
C
C Calculate the new drop temperature.
C
      CALL EQTMP3(TEMP(I),DIAM(I),SH)
      NF(I)=NOFILM
20  CONTINUE
C
C Update the time.
C
      TIME=T
C
C Finally, write out the aerosol size distribution as needed.
C
      IF(ABS(TPORT-TIME).GE.ERRMAX)GOTO 10
      CALL REPORT
30  CONTINUE
      STOP
      END
C *****
C *
C * DERIV3: This subroutine specifies the differential equations *
C * which RK4 is to integrate. It calculates the derivatives with *
C * respect to time of: *
C * *
C * 1 D - the drop diameter; *
C * 2 GAMMA - the mass of surfactant in the surface film; *
C * 3 HEIGHT - the drop height; and *
C * 4 N - a power law index describing the concentration *
C * distribution within the drop's water core. *
C * *
C * These derivatives are only used if a surface film of surfact- *
C * ant has formed. If it has not, the derivatives are set to *
C * zero, and the values of the variables calculated directly from *
C * analytical solutions. *
C * *
C * The subroutine also calculates the concentration of surfactant *
C * at the drop surface (CR), the Sherwood number (SH) and the *
C * thickness of the surface film (DELTA). *
C * *
C * Arguments are - *
C * *
C * T The independent variable - time. *

```

```

C      *
C      * Y      A vector of size 20 of which only the first seven
C      *          elements are used. On entry it holds the values of the
C      *          dependent variables at time T. Y(1) holds D, Y(2)
C      *          holds GAMMA, and so on. On exit Y(5), Y(6) and Y(7)
C      *          hold CR, SH and DELTA respectively.
C      *
C      * YDOT    A vector of size 20 of which only the first four
C      *          elements are used. On exit it contains the derivatives
C      *          calculated from the differential equations. YDOT(1)
C      *          holds dD/dt, YDOT(2) holds dGAMMA/dt and so on.
C      *
C      *
C      *****
C
C      SUBROUTINE DERIV3(T,Y,YDOT)
C      LOGICAL NOFILM
C      REAL A, ALPHA, BETA, CO, CR, CRM, D1, D2, DELTA, DN, DFN, DG,
C      1 DIFFC, F, F1, FN, FOURPI, N, NDBY2, PE, R, RO, RDOT, RE,
C      2 RHOO, RHOINF, RHOF, RRDOT, SC, SH, T, TDROP, TERVEL, THETA,
C      3 Y, YDOT, Z
C      DIMENSION Y(20),YDOT(20)
C
C      CO and RO are the surfactant concentration and drop radius at time
C      zero; TDROP is the temperature of the drop; RHOINF and RHOO are
C      the water vapour concentrations in the air at a large, and zero,
C      distance from the drop surface respectively.
C
C      COMMON /PARAM/ CO, RO, TDROP, RHOINF, RHOO, NOFILM
C
C      RE is the terminal Reynolds number of the drop.
C
C      COMMON /TERMRE/ RE
C
C      ALPHA and BETA are empirical constants; DN is the finite difference
C      step size used in approximating F'(N); SC is the Schmidt number.
C
C      DATA ALPHA/6.1043/, BETA/2.8385/, DN/0.005/, FOURPI/12.5664/,
C      1 SC/0.68/
C
C      D1 is the diffusivity of surfactant in water; D2 is the diffusivity
C      of water in surfactant; CRM is the concentration of surfactant on
C      the water side of the surfactant/water interface; A is a Henry's
C      law constant; and RHOF is the density of the surface film. The
C      numerical values shown here are for sodium stearate.
C
C      DATA D1/2.76E-10/, D2/1.0E-14/, CRM/0.055/, A/1E-3/, RHOF/1000.0/
C
C      F(N)=(N*N + N + 2.0) / (N + 1.0)/(N + 2.0)/(N + 3.0)
C
C      NOFILM is a flag to decide whether or not a surface film of
C      surfactant is present.
C
C      IF(T .GT.0.0)GOTO 20
C      IF(CO.LT.CRM)GOTO 10

```

```

        NOFILM=.FALSE.
        CRM=CO
        GOTO 20
10      NOFILM=.TRUE.
C
C      R is the drop radius and DELTA is the surfactant film thickness.
C
20      R=Y(1)/2.0
        DELTA=Y(2) /FOURPI/R/R/RHOF
C
C      *** EQUATION 3 (Height) ***
C
C      The rate of fall of a drop is simply its terminal velocity.
C
        YDOT(3)=-TERVEL(Y(1))
C
C      *** EQUATION 1 (Drop diameter) ***
C
        DG=DIFFC(TDROP,101325.0)
        F1=DG*( RHOO-RHOINF )
        IF(NOFILM)GOTO 50
C
        SH=2.0/( 1.0+(DG/R)*(DELTA*A/D2) )
C
C      A wind factor allows for the effect of forced convection.
C
        SH=SH*(1 +0.276 *RE**0.5 *SC**0.333)
C
C      The evaporation rate is calculated from a modified form of the
C      Maxwell equation.
C
        RRDOT=-F1/1000.0*SH/2.0
        RDOT=RRDOT / R
C
C      Finally, calculate the rate of change of drop diameter.
C
        YDOT(1)=RDOT * 2.0
C
C      *** EQUATION 2 (GAMMA) ***
C
        NDBY2=Y(4)*D1/2.0
        YDOT(2)=-FOURPI*R*R*( RDOT*CRM +NDBY2*(CRM-CO)/R)
        IF(YDOT(2).LT.0.0)YDOT(2)=0.0
C
C      *** EQUATION 4 (N) ***
C
        IF(CRM.EQ.CO)GOTO 30
        FN=F(Y(4))
C
C      F'(N) (the derivative of the function F(N)) is approximated by a
C      finite difference formula.
C
        DFN=(F(Y(4)+DN)-FN)/DN
        YDOT(4)=(R*RDOT*(1-6.0*FN) + NDBY2) / (2.0*R*R) / DFN

```

```

      GOTO 40
30    YDOT(4)=0.0
C
C    Finally save the other results.
C
40    Y(6)=SH
      Y(7)=DELTA
      RETURN
C
C    ***. NO SURFACTANT FILM ***
C
C    Analytical solutions can be used if there is no surface film
C    of surfactant.
C
50    CONTINUE
C
C    As before a wind factor allows for the effect of forced convection,
C    though the base Sherwood number is now 2:
C
      SH=2.0*(1 +0.276 *RE**0.5 *SC**0.333)
C
C    The evaporation rate is calculated from the Maxwell equation.
C
      RRDOT=-F1/1000.0*SH/2.0
      RDOT=RRDOT / R
C
      Y(6)=SH
      Y(7)=0.0
C
C    Only the first and third differential equations are needed here.
C
      YDOT(1)=RDOT * 2.0
      YDOT(2)=0.0
      YDOT(4)=0.0
C
C    For a pure water drop, the remaining equations are inapplicable.
C
      IF(CO.EQ.0.0)RETURN
      THETA=(RO/R)**3-1.0
      PE=-RRDOT/D1
      Z=(PE+BETA)*THETA/ALPHA
      CR=CO*(1+Z+SQRT(Z*Z +2*PE*THETA/ALPHA))
      Y(5)=CR
      IF(CR.GT.CRM)NOFILM=.FALSE.
C
C    Y(4) (N) is infinite at time zero.
C
      IF(R.NE.RO) Y(4)=PE-BETA+SQRT((PE+BETA)**2 +2*PE*ALPHA/THETA)
      RETURN
      END
C
C    *****
C    *
C    * DQ3: This function calculates the net heat flow between a *
C    * contaminated evaporating water drop and the surrounding air. *

```

```

C  * This is simply the difference between the heat flow to the
C  * drop (calculated by QIN3) and the product of the latent heat
C  * of evaporation, the Sherwood number, and the rate of change of
C  * drop mass with time. DSQDOT is used to calculate the evapor-
C  * ation rate of a pure water drop.
C  *
C  * Arguments are -
C  *
C  * TDROP The drop temperature.
C  *
C  * DPDIAM The drop diameter.
C  *
C  * SH The Sherwood number.
C  *
C  *****
C
C  REAL FUNCTION DQ3(TDROP,DPDIAM,SH)
C  REAL TDROP, DPDIAM, QLATNT, HLATNT, DSQDOT, QIN3, PI, SH
C  DATA PI/3.14159/
C  QLATNT=DSQDOT(DPDIAM,TDROP)*PI/4.0*DPDIAM*1000.0 *HLATNT(TDROP)
C  DQ3=QLATNT*SH/2.0 + QIN3(TDROP,DPDIAM)
C  RETURN
C  END
C  *****
C  *
C  * EQTMP3: This subroutine calculates the temperature at which
C  * the rate of heat transfer to a contaminated drop just balances
C  * the heat loss due to the latent heat of evaporation at a given
C  * Sherwood number - i.e. the equilibrium temperature of the drop
C  * neglecting its thermal mass.
C  *
C  * The routine uses Newton's method to find the temperature at
C  * which the net heat flow to the drop (as calculated by DQ3) is
C  * zero. It iterates until the net heat flow is less than a
C  * tolerance TOL. For ease of computation the derivative of DQ3
C  * needed by Newton's method is estimated numerically using a
C  * first order finite difference formula.
C  *
C  * Arguments are -
C  *
C  * TDROP The drop temperature. On entry TDROP should contain an
C  * estimate of the equilibrium drop temperature. On exit
C  * it will contain the calculated value.
C  *
C  * DPDIAM The drop diameter.
C  *
C  * SH The Sherwood number.
C  *
C  *****
C
C  SUBROUTINE EQTMP3(TDROP,DPDIAM,SH)
C  REAL TDROP, DPDIAM, DELTA, TOL, DQ3, F1, F2, SH
C  DATA DELTA/0.01/, TOL/1.0E-7/
10  F1=DQ3(TDROP-DELTA,DPDIAM,SH)

```

```

F2=DQ3(TDROP      ,DPDIAM,SH)
TDROP=TDROP - F1 / ((F2-F1)/DELTA)
IF(ABS(F1).GT.TOL)GOTO 10
RETURN
END
C *****
C *
C * INPUT3: This subroutine reads in all the experimental data *
C * required by the program and converts it into a form suitable *
C * for further processing. *
C *
C * The variables describing the environmental conditions around *
C * the drop are passed to the rest of the program via COMMON *
C * block /CONDS/. These are atmospheric temperature (TINF), % *
C * relative humidity (RELHUM) and pressure (PRESS). *
C *
C * The initial aerosol size distribution is passed back to the *
C * main program via blank common (//) along with the initial drop *
C * heights and temperatures. *
C *
C * Arguments passed back to the main program are - *
C *
C * GASVEL The velocity of the gas in which the aerosol is suspen- *
C * ded. *
C *
C *****
C
SUBROUTINE INPUT3(GASVEL)
LOGICAL LDUMMY, LD
INTEGER I, WORN, ITYPE, NDSIZE
REAL DIAM, SUM, TINF, RELHUM, PRESS, GASVEL, GAMMA, RHOINF, V,
1 N, RZERO, HEIGHT, TEMP, UFRAC, NUMBER, TUNLHT, CO, DUMMY,
2 DUMMY2, DUMMY3, DRATIO
DIMENSION UFRAC(31)
COMMON // HEIGHT(30), TEMP(30), DIAM(30), NUMBER(30),
1 GAMMA(30), N(30), RZERO(30), NDSIZE, WORN, LD(30)
COMMON /CONDS/ TINF, RELHUM, PRESS
COMMON /PARAM/ CO, DUMMY(2), RHOINF, DUMMY2, LDUMMY
COMMON /SUPPRT/ DUMMY3(2), ITYPE
C
C TUNLHT is the height of the wind tunnel, and DRATIO is the ratio
C between successive drop diameters.
C
DATA TUNLHT/0.30/, DRATIO/1.118/
ITYPE=1
C
C Read in the experimental conditions used. Converting to S.I. where
C necessary.
C
WRITE(1,10)
10 FORMAT(' Air temperature (C): ')
READ(5,*)TINF
TINF=TINF+273.1
C

```



```

WRITE(1,20)
20  FORMAT(' % Relative humidity: ')
   READ(5,*)RELHUM
C
   WRITE(1,30)
30  FORMAT(' Atmospheric pressure (mm Hg): ')
   READ(5,*)PRESS
   PRESS=PRESS*101325./760.0
   CALL WVCONC(TINF,RELHUM,PRESS,RHOINF,V)
C
   WRITE(1,40)
40  FORMAT(' Air velocity (m/s): ')
   READ(5,*)GASVEL
C
   WRITE(1,50)
50  FORMAT(' Surfactant concentration (ppm): ')
   READ(1,*)CO
   CO=CO*1.0E-3
C
C  Read in the initial drop size distribution.  The program will
C  accept either weight or number size distributions and will modify
C  its output to match.
C
   WRITE(1,60)
60  FORMAT(' Weight (W) or Number (N) %: ')
   READ(5,70)WORN
70  FORMAT(A1)
C
C  The initial drop size distribution is subdivided into NDSIZE
C  fractions.  DIAM holds the sizes of the drops bounding the fractions
C  and NUMBER holds the number of drops in each.
C
   NDSIZE=30
   SUM=0.0
   DIAM(1)=5.0E-6
   UFRACT(1)=0.0
   DO 90 I=1,NDSIZE
     IF(I.NE.1)DIAM(I)=DIAM(I-1)*DRATIO
     RZERO(I)=DIAM(I)/2.0
     WRITE(1,80)DIAM(I)
80  FORMAT(' Enter % of drops with diameter below',6PF6.1,' microme
1tres')
     READ(5,*)UFRACT(I+1)
C
C  Set up the initial height, temperature, diameter and number of the
C  drops in each size fraction.
C
   HEIGHT(I)=TUNLHT
   TEMP(I)=TINF
   CALL EQTMP1(TEMP(I),DIAM(I))
   GAMMA(I)=0.0
   N(I)=1.0E4
   NUMBER(I)=UFRACT(I+1)-UFRACT(I)
   IF(WORN.EQ.'W')NUMBER(I)=NUMBER(I)/ (DIAM(I)/SQRT(DRATIO))**3

```

```

      SUM=SUM+NUMBER(I)
90    CONTINUE
C
C    Normalise the number distribution.
C
      DO 100 I=1,NDSIZE
        NUMBER(I)=NUMBER(I)/SUM
100   CONTINUE
      RETURN
      END
C *****
C *
C *   QIN3: This function calculates the total rate of heat flow to *
C *   an evaporating drop falling at its terminal velocity. It adds *
C *   the contributions due to both convection and radiation.      *
C *
C *   Arguments are -
C *
C *   TDROP The drop temperature.
C *
C *   DPDIAM The drop diameter.
C *
C *****
C
      REAL FUNCTION QIN3(TDROP,DPDIAM)
      REAL TDROP, TINF, DPDIAM, QCONV, QRAD, PI, SIGMA, EMISS, PR, RE,
1 TEFF, KAIR, RELHUM, PRESS, K, NUBY2, QCOND
      COMMON /CONDS/ TINF, RELHUM, PRESS
      COMMON /TERMRE/ RE
C
C    EMISS is the emissivity of liquid water (from McAdams, 1954, p478)
C
      DATA PI/3.14159/, SIGMA/5.67E-8/, EMISS/0.95/, PR/0.72/
      TEFF=SQRT(TINF*TDROP)
      K=KAIR(TEFF)
C
C    Conduction through the surrounding air.
C
      QCOND=2.0*PI*DPDIAM*K*(TINF-TDROP)
C
C    Natural convection.
C
      QCONV=QCOND*NUBY2(DPDIAM,TDROP)
C
C    A wind factor allows for the effect of forced convection.
C
      QCONV=QCONV*(1 +0.276 *RE**0.5 *PR**0.333)
C
C    Radiation.
C
      QRAD=PI*DPDIAM*DPDIAM*EMISS*SIGMA*(TINF**4-TDROP**4)
C
C    Calculate total heat flow.
C

```

```

      QIN3=QCONV+QRAD
      RETURN
      END
C *****
C *
C * REPORT: This subroutine calculates and prints out the % under- *
C * size distribution of an aerosol. Because of the need to cover *
C * a wide range of diameters, a logarithmic diameter scale was *
C * used i.e. successive diameters differ by a constant ratio. *
C *
C * Information on the aerosol size distribution is passed to this *
C * subroutine via blank common (/). *
C *
C * There are no arguments. *
C *
C *****
C
      SUBROUTINE REPORT
      LOGICAL LD
      INTEGER I, NDSIZE, WORN
      REAL DIAM, DMIN, DF, F, FRACT, FTOTAL, HEIGHT, NUMBER, R, RZERO,
1 SAMPHT, TEMP, DUMMY
      DIMENSION F(30)
      COMMON // HEIGHT(30), TEMP(30), DIAM(30), NUMBER(30),
1 DUMMY(60), RZERO(30), NDSIZE, WORN, LD(30)
C
C SAMPHT is the height in the wind tunnel at which the distribution is
C desired. DMIN is the smallest drop size to be considered.
C
      DATA SAMPHT/0.15/, DMIN/1.0E-6/
      F(1)=0.0
      R=SQRT(DIAM(2)/DIAM(1))
      DO 20 I=1,NDSIZE
         IF(I.NE.1)F(I)=F(I-1)
C
C Drops smaller than DMIN are assumed to have evaporated completely.
C
         IF(DIAM(I).LT.DMIN)GOTO 20
C
C Drops which have fallen below SAMPHT will not be detected.
C
         FRACT=1.0
         IF((HEIGHT(I).GT.SAMPHT).OR.(I.EQ.1))GOTO 10
         IF(HEIGHT(I-1).LT.SAMPHT)GOTO 20
         FRACT=(HEIGHT(I-1)-SAMPHT)/(HEIGHT(I-1)-HEIGHT(I))
10      DF=NUMBER(I)*FRACT
         IF(WORN.EQ.'W')DF=DF*(DIAM(I)/R)**3
         F(I)=F(I)+DF
20      CONTINUE
C
C Finally normalise and print out the size distribution.
C N.B. the units are micrometres and % .
C
      FTOTAL=F(NDSIZE)

```

```

DO 30 I=1,NDSIZE
  F(I)=F(I)/FTOTAL
  WRITE(6,40)DIAM(I),F(I)
30  CONTINUE
40  FORMAT(6PF11.1,5X,2PF9.2)
  RETURN
  END
C *****
C *
C * TERVER: This function calculates the terminal velocity of a *
C * water drop falling through air. The correlations used are *
C * taken from Clift et al. (1978). *
C * *
C * The arguments are - *
C * *
C * DIAM The diameter of the water drop. *
C * *
C *****
C
  REAL FUNCTION TERVER(DIAM)
  REAL ND, RHOGAS, RHOLIQ, G, GASVIS, DIAM, RE, W, TINF, RELHUM,
1  PRESS
  COMMON /CONDS/ TINF, RELHUM, PRESS
  COMMON /TERMRE/ RE
C
C Define the acceleration due to gravity (G), the viscosity of air
C (GASVIS), and the density of water (RHOLIQ) and air (RHOGAS).
C
  DATA G/ 9.81/, GASVIS/ 1.85E-5/, RHOLIQ/1000.0/
  RHOGAS=1.2928*273.1/TINF
C
C ND determines which correlation is used to calculate the terminal
C Reynolds number RE.
C
  ND=4.*DIAM**3*RHOGAS*(RHOLIQ-RHOGAS)*G/3./GASVIS/GASVIS
  IF(ND.GT.73.)GOTO 10
  RE= ND*(1./24. +ND*(-1.7569E-4 +ND*(6.9252E-7 -ND*2.3027E-10)))
  GOTO 30
10  W=ALOG10(ND)
  IF(ND.GT.580.)GOTO 20
  RE=10.**(-1.7095+W*(1.33438-0.11591*W))
  GOTO 30
20  RE=10.**(-1.81391+W*(1.34671+W*(-0.12427+W*6.344E-3)))
C
C Finally calculate the terminal velocity itself.
C
30  TERVER=RE*GASVIS/RHOGAS/DIAM
  RETURN
  END

```

Appendix M. Equipment suppliers

B.D.H. CHEMICALS LTD., (All surfactants and other chemical
PARHAM DRIVE, reagents.)
BOYATT WOOD INDUSTRIAL ESTATE,
EASTLEIGH,
HANTS,
SO5 4NO.

HAMPSHIRE MICRO, (Stereomicroscope, filar micrometer
C/O THE MICROSCOPE SHOP, eyepiece, fibre optic cold light
OXFORD ROAD, source and microscope stage.)
SUTTON SCOTNEY,
HANTS,
SO21 3JG.

SINGER INSTRUMENT CO. LTD., (Micromanipulator.)
TREBOROUGH LODGE,
ROADWATER,
WATCHET,
SOMERSET,
TA23 0QL.

TEMPCON INSTRUMENTATION LTD., (Ultrafine thermocouples.)
HOLMDALE INDUSTRIAL ESTATE,
FONTWELL AVENUE,
EASTERGATE,
CHICHESTER,
W. SUSSEX.

Bibliography

The following special abbreviations have been used:

- [G] Translated from the German by Dr J.A.Lamb;
 [R] Translated from the Russian by the author;
 and [U] Translated from the Ukrainian by the author.

- ACKERMANN, G. (1934) "The theory of evaporative cooling." *Ingen. Archiv* 5, 124-46
- ALTSIBEEVA, A.I.; GOLUBEV, V.V.; MORACHEVSKII, V.G. (1963) "On the question of the vapour pressure above a surfactant solution." *Probl. Fiz. Atmos.* No 2, 187-91
- ALTY, T.; MACKAY, C.A. (1935) "The accommodation coefficient and the evaporation coefficient of water." *Proc. Roy. Soc. Ser. A* 149, 104-16
- ARCHER, R.J.; LA MER, V.K. (1955) "The rate of evaporation of water through fatty acid monolayers." *J. Phys. Chem.* 59, 200-8
- BAKHANOVA, R.A.; SOLYANEK, E.G.; TERZIEV, F.S. (1969) "Method for producing films of surfactants from highly dispersed aqueous suspensions of higher aliphatic alcohols for modifying the vaporization of fog." *Tr. Vses. Konf. Fiz. Oblakov. Aktiv. Vozdeistviyam*, 8th (Publ. 1970), 319-24
- BARNES, G.T. (1968) "Role of monolayers in evaporation retardation." *Nature* 220, 1025-6
- BARNES, G.T. (1978) "Insoluble monolayers and the evaporation coefficient of water." *J. Coll. I. Sci.* 65 No 3, 566-72
- BARNES, G.T.; BACON, K.J.; ASH, J.M. (1980a) "The evaporation resistances of octadecanol-cholesterol mixed monolayers." *J. Coll. I. Sci.* 76 No 1, 263-4
- BARNES, G.T.; CAMMENG, H.K. (1979) "Surface cooling during the evaporation of water." *J. Coll. I. Sci.* 72 No 1, 140-1
- BARNES, G.T.; COSTIN, I.S.; HUNTER, D.S.; SAYLOR, J.E. (1980b) "On the measurement of the evaporation resistances of monolayers." *J. Coll. I. Sci.* 78 No 1, 271-3
- BARNES, G.T.; FEHER, A.I. (1980) "The measurement of temperature gradients in water during evaporation through monolayer-free and monolayer-covered surfaces." *J. Coll. I. Sci.* 75 No 2, 584-9
- BARNES, G.T.; HUNTER, D.S. (1982) "Heat conduction during the measurement of the evaporation resistances of monolayers." *J. Coll. I. Sci.* 88 No 2, 437-43

- BARNES, G.T.; QUICKENDEN, T.I. (1971) "The theoretical evaporation resistance of an hexagonal array of monolayer molecules." J. Coll. I. Sci. 37 No 3, 581-4
- BARNES, G.T.; QUICKENDEN, T.I.; SAYLOR, J.E. (1970) "A statistical calculation of monolayer permeation by water." J. Coll. I. Sci. 33 No 2, 236-43
- BENEDICT, R.P. (1969) "Fundamentals of temperature, pressure and flow measurement." Wiley
- BEREDJICK, N. (1965) "Distilland treatment to accelerate evaporation and condensate treatment to retard evaporation." U.S. Patent No. 3,220,934
- BINGHAM, L.A. (1970) "Chemical films as evaporation suppressants." Masters Thesis, Arizona State University
- BLANK, M. (1964) "An approach to a theory of monolayer permeation by gases." J. Phys. Chem. 68 No 10, 2793-800
- BLANK, M. (1979) "Monolayer permeability." Progr. Surf. Memb. Sci. (Cadenhead, D.A.; Danielli, J.F. Eds) 13, 87-139
- BLANK, M.; MUSSELLWHITE, P.R. (1968) "The permeabilities of adsorbed monolayers to water." J. Coll. I. Sci. 27 No 2, 188-92
- BLINC, R. (1975) "Magnetic resonance in chemistry and biology." (Herak, J.N.; Adamic, K.J. Eds) Dekker, 445-53
- BORZILOV, V.A.; KLEPIKOVA, N.V.; MERKULOVICH, V.M. (1979) "Influence of surfactants on droplet growth and evaporation." Meteorologiya i Gidrologiya, No 5, 41-8
- BOSE, N.K.; CHAKRABORTY, B.N. (1955) "Diffusion coefficients of vapours into pure gases and their mixtures." Trans. Indian Inst. Chem. Eng. 8 67-72
- BRADLEY, R.S. (1955) "The rate of evaporation of micro-drops in the presence of insoluble monolayers." J. Coll. Sci. 10, 571-5
- BRADY, A.P.; HUFF, H.; MCBAIN, J.W. (1951a) "Measurement of vapour pressures by means of matched thermistors." J. Phys. Coll. Chem. 55, 304-11
- BRADY, A.P.; HUFF, H.; MCBAIN, J.W. (1951b) "The vapour pressures of aqueous solutions of some detergents." J. Phys. Coll. Chem. 55, 311-21
- BROOKFIELD, K.J.; FITZPATRICK, H.D.N.; JACKSON, J.F.; MATTHEWS, J.B.; MOELWYN-HUGHES, E.A. (1947) "The escape of molecules from a plane surface into a still atmosphere." Proc. Roy. Soc. A190, 59-67
- BROWN, H.T.; ESCOMBE, F. (1900) "VIII. Static diffusion of gases and

- liquids in relation to the assimilation of carbon and translocation in plants." Phil. Trans. Roy. Soc. B193, 223-91
- BUIKOV, M.V.; SIGAL, V.L. (1966) "Theory of the intensive evaporation of a drop of solution." Vop. Ispareniya, Gorennya Gasov. Din. Dispersnykh Sist., Mater. Vses. Nauch. Konf., 4th 5th (Fedoseev, V.A. Ed) Izd. "Naukova dumka" Kiev (Publ. 1967), 153-7 [R]
- CAMMENG, H.K. (1980) "Evaporation mechanisms of liquids." Curr. Top. Materials Sci. (Kaldis, E. Ed) 5, 335-446
- CAMMENG, H.K.; KLINGE, H.; RUDOLPH, B.E.; SCHULZE, F.W. (1975) "The influence of industrial surfactants on the transport of mass and energy in the evaporation of water. I." Tenside Deterg. 12 No 1, 19-23 [G]
- CHALENKO, V.G.; GEL'MAN, L.A.; PESTUN, T.S. (1970) "Effect of monolayers of surface active agents on the evaporation rate of water." Fiz. Aerodispersnykh Sist. No 2, 21-31
- CHANG, R.; DAVIS, E.J. (1974) "Interfacial conditions and evaporation rates of a liquid droplet." J. Coll. I. Sci. 47 No 1, 65-76
- CHARLESWORTH, D.H.; MARSHALL, W.R. (1960) "Evaporation from drops containing dissolved solids." A.I.Ch.E.J. 6 No 1, 9-23
- CLAYFIELD, E.J.; MATTHEWS, J.B. (1957) "Minima in boundary tension curves and phase changes in soluble adsorbed films." Proc. 2nd Intern. Congr. Surf. Activity, London I, 172-87
- CLIFT, R.; GRACE, J.R.; WEBER, M.E. (1978) "Bubbles, drops and particles." Academic press
- COSTIN, I.S.; BARNES, G.T. (1967) "Purification of long chain alcohols for monolayer studies." J. Coll. I. Sci. 25, 584-5
- COSTIN, I.S.; BARNES, G.T. (1975) "Two component monolayers. III. Evaporation resistances of the octadecanol-docosyl sulphate system." J. Coll. I. Sci. 51 No 1, 122-32
- CRANK, J. (1979) "The mathematics of diffusion." (2nd Ed) Clarendon Press Oxford
- CRANK, J. (1984) "Free and moving boundary problems." Clarendon Press Oxford
- CUSSLER, E.L. (1984) "Diffusion: Mass transfer in fluid systems." Cambridge University Press
- DAVIES, C.N. (1978) "Evaporation of airborne droplets." Chapter 3 of "Fundamentals of aerosol science." (Shaw, D.T. Ed) Wiley
- DAVIS, E.J. (1983) "Transport phenomena with single aerosol particles."

Aerosol Sci. & Tech. 2 121-44

- DELLICOLLI, H.T.; SHAFFER, R.E. (1973) "Artificial water fog. I. The retardation of droplet evaporation by two dimensional surface films." Edgewood Arsenal Technical Report SMUEA-TS-R
- DERYAGIN, B.V.; BAKANOV, S.P.; KURGHIN, I.S. (1960a) "The influence of a foreign film on evaporation of liquid drops." Disc. Faraday Soc. 30, 96-9
- DERYAGIN, B.V.; BAKANOV, S.P.; KURGIN, YU.S. (1960b) "The effect of monomolecular films on droplet evaporation." Dokl. Akad. Nauk SSSR 135 No 6, 1417-20
- DERYAGIN, B.V.; BAKANOV, S.P.; KURGIN, YU.S. (1961) "Kinetics of evaporation of drops covered by an insoluble film of a foreign substance." Kolloid. Zh. 23 No 3, 262-71
- DERYAGIN, B.V.; FEDOSEEV, V.A.; ROZENTSVAIG, L.A. (1966a) "Investigation of the adsorption of cetyl alcohol vapour and its influence on the evaporation of water drops." Dokl. Akad. Nauk SSSR 167 No 3, 617-20
- DERYAGIN, B.V.; FEDOSEEV, V.A.; ROSENZWEIG, L.A. (1966b) "Investigation of the adsorption of cetyl alcohol vapour and the effect of this phenomenon on the evaporation of water drops." J. Coll. I. Sci. 22, 45-50
- DERYAGIN, B.V.; KURGIN, YU.S. (1964) "Nonstationary evaporation of a droplet covered by an adsorbed layer." Dokl. Akad. Nauk SSSR 155 No 3, 644-6
- DICKINSON, E. (1978) "A hard disc fluid model of monolayer permeation and evaporation resistance." J. Coll. I. Sci. 63 No 3, 461-71
- DIJKEMA, K.M.; STOUTHART, J.C.; DE VRIES, D.A. (1972) "Measurements of the thermal conductivity of gases and gas mixtures, methods and results." Wärme und Stoffübertragung 5 47-55
- DOLINSKII, A.A.; IVANITSKII, G.K. (1976) "Distribution of concentration in a drop of solution during intensive evaporation." Fiz. Aerodispersn. Sistem. Resp. Mezhved. Nauch.-Tekhn. Sb. No 13, 19-24 [R]
- DOYLE, A.; MOFFETT, D.R.; VONNEGUT, B. (1964) "Behaviour of evaporating electrically charged droplets." J. Coll. Sci. 19, 136-43
- EISNER, H.S.; BROOKES, F.R.; QUINCE, B.W. (1958) "Stabilization of water mists." Nature 182, 1724
- EISNER, H.S.; QUINCE, B.W.; SLACK, C. (1960) "The stabilization of water mists by insoluble monolayers." Disc. Faraday Soc. 30, 86-95
- ELTON, G.A.H. (1953) "A possible method of fog dispersal." Chem. Ind.,

No 10, 219

- EVANS, D.F.; MUKHERJEE, S.; MITCHELL, D.J.; NINHAM, B.W. (1983) "Surfactant diffusion: New results and interpretations." J. Coll. I. Sci. 93 No 1, 184-204
- FAINERMAN, V.B.; ZHIDKOV, V.V. (1976) "Diffusion of surfactants in a capillary. Measurement of the diffusion coefficient at low concentrations." Kolloid. Zh. 38 No 1, 107-12
- FERGUSON, R.H.; VOLD, R.D. (1938) "The vapour pressure of commercial soaps." Oil & Soap 15, 181-3
- FERRARI, R.L. (1975) "An introduction to electromagnetic fields." Section 8.8, Van Nostrand Reinhold
- FUCHS, N.A. (1959) "Evaporation and droplet growth in gaseous media." Pergamon Oxford
- GARRETT, W.D. (1971) "Retardation of water drop evaporation with monomolecular surface films." J. Atmos. Sci. 28 No 5, 816-9
- GERALD, C.F. (1978) "Applied numerical analysis." (2nd Ed) Addison-Wesley
- GERNET, E.V.; GLIKLIKH, S.M.; KOSHITA, M.N.; FEDOSEEV, V.A. (1966) "Feasibility of fog stabilization using surfactants." Mezhevuz. Konf. Vop. Ispareniya, Goreniya Gazov. Din. Dispersnykh Sist., Mater., 6th (Fedoseev, V.A. Ed, Publ. 1968), 3-9
- GILLILAND, E.R. (1934) "Diffusion coefficients in gaseous systems." Ind. Eng. Chem. 26 No 6, 681-5
- GLAZOV, N.I. (1938) "The effect of adsorption layers on the velocity of evaporation of water." J. Phys. Chem. (U.S.S.R.) 11, 484-91
- GLAZOV, N.I. (1939a) "Effect of surface active substances on the rate of evaporation of water from solutions. II." J. Phys. Chem. (U.S.S.R.) 13, 840-5
- GLAZOV, N.I. (1939b) "Effect of surface active substances on the rate of evaporation of water from solutions. III. Effects of aliphatic acids and aromatic amines." J. Phys. Chem. (U.S.S.R.) 13, 1642-5
- GORODETSKII, E.T. (1977) "Improvement of vaporization during distillation below the boiling point." Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol. 20 No 5, 748-50 [R]
- GRUSS, H.; SCHMICK, H. (1928) "On the thermal conductivity of gas mixtures." Wiss. Veroffentl. Siemens Konzern 7 202-24, [G]
- HARROLD, S.P. (1960) "Purification of sodium dodecyl sulphate." J. Coll. Sci. 15, 280-2

- HEDESTRAND, G. (1924) "On the influence of thin surface films on the evaporation of water." J. Phys. Chem. 28, 1245-52
- HICKMAN, K.; PALMER, H.J.; BARNES, G.T. (1978) "Insoluble monolayers and the evaporation coefficient of water. Comments & reply." J. Coll. I. Sci. 65 No 3, 573-7
- HIDY, G.M.; BROCK, J.R. (1970) "The dynamics of aerocolloidal systems." Pergamon
- HOFFMAN, T.W.; GAUVIN, W.H. (1960) "Evaporation of stationary droplets in high temperature surroundings." Can. J. Chem. Eng. 38, 129-37
- HOUGHTON, H.G. (1933) "A study of the evaporation of small water drops." Physics 4 Dec, 419-24
- HUGHES, R.B.; STAMPFER, J.F. (1971) "Enhanced evaporation of small, freely falling, water drops due to surface contamination." J. Atmos. Sci. 28, 1244-51
- IVANITSKII, G.K.; SHIMANSKII, YU.I. (1967) "Evaporation of drops of surfactant solutions under quasi-stationary conditions." Kolloid. Zh. 29 No 5, 672-6
- IZMAILOVA, G.I.; PROKHOROV, P.S.; DERYAGIN, B.V. (1957) "The possibility of surface activation and passivation of nuclei in water vapour condensation." Kolloid. Zh. 19, 557-61
- JACKSON, F.L.; KRAUSE, F.P. (1963) "Diffusion controlled buildup of surface active material at the air water interface during evaporation." J. Phys. Chem. 67 No 11, 2355-60
- JARVIS, N.L. (1962) "The effect of monomolecular films on surface temperature and convective motion at the water/air interface." J. Coll. Sci. 17, 512-22
- JARVIS, N.L.; KAGARISE, R.E. (1962) "Determination of the surface temperature of water during evaporation studies. A comparison of thermistor with infrared radiometer measurements." J. Coll. Sci. 17, 501-11
- JIUSTO, J.E. (1964) "Project fog drops: Investigation of warm fog properties and fog modification concepts." NASA Contractors Report CR-72
- JOHNSON, J.C. (1950) "Measurement of the surface temperature of evaporating water drops." J. App. Phys. 21 No 1, 22-3
- KACHURIN, L.G.; MORACHEVSKII, V.G. (1965) "The kinetics of phase transitions of water in the atmosphere." Chapter 4, Leningrad Univ. Press [R]
- KIMPTON, D.D.; WALL, F.T. (1952) "Determination of diffusion coeff-

- icients from rates of evaporation." J. Phys. Chem. 56, 715-7
- KIRYUKIN, B.V.; MORACHEVSKII, V.G.; ORLOVA, M.N. (1963) "Rates of evaporation of drops of aqueous solutions of surface active substances." Probl. Fiz. Atmos. No 2, 142-50 [R]
- KLAUS, R.L.; VAN NESS, H.C. (1967) "An extension of the spline fit technique and applications to thermodynamic data." A.I.Ch.E.J. 13 No 6, 1132-6
- KOCMOND, W.C.; GARRETT, W.D.; MACK, E.J. (1972) "Modification of laboratory fog with organic surface films." J. Geophys. Res. 77 No 18, 3221-31
- KOLESNIK, I.YA. (1968) "Some aspects of the theory of drop evaporation and growth." Kolloid. Zh. 30 No 4, 527-32
- KOLESNIK, I.YA. (1969) "Asymptotic method in the theory of nonsteady state drop evaporation and growth." Kolloid. Zh. 31 No 5, 714-8
- KREMNEV, O.A.; DOLINSKII, A.A.; IVANITSKII, G.K. (1974) "The peculiarities of heat transfer through the liquid-gas boundary in the presence of a monomolecular film of surfactants." Dopov. Akad. Nauk Ukr. Rsr Ser. A 36 No 10, 932-4 [U]
- KUDRITSKII, S.B.; CHAICHUK, S.A.; DMITRIEVA, E.M. (1981) "Study of the adsorption of soluble surfactants and their effect on the evaporation of water drops." Kolloid. Zh. 43 No 4, 770-4
- KUDRITSKII, S.B.; DMITRIEVA, E.M. (1983) "Study of the effect of a monolayer of surfactants on heat transfer across the air-water interface." Fiz. Aerodispersnykh Sist. No 23, 98-100 [R]
- LA MER, K.V. (1962) "Retardation of evaporation by monolayers: Transport processes." Academic Press
- LA MER, V.K.; AYLMOORE, L.A.G.; HEALY, T.W. (1963) "The ideal surface behaviour of mixed monolayers of long-chain n-paraffinic alcohols." J. Phys. Chem. 67, 2793-5
- LA MER, V.K.; HEALY, T.W. (1965) "Evaporation of water. Its retardation by monolayers." Science 148 No 3666, 36-42
- LA MER, V.K.; HEALY, T.W.; AYLMOORE, L.A.G. (1964) "The transport of water through monolayers of long-chain n-paraffinic alcohols." J. Coll. Sci. 19, 673-84
- LANGMUIR, I.; SCHAEFER, V.J. (1943) "Rates of evaporation of water through compressed monolayers on water." J. Franklin Inst. 235, 119-62
- LE BLANC, M.; WUPPERMANN, G. (1916) "On the evaporation rate of liquid." Z. Phys. Chem. 91, 143-54 [G]

- LEE, C.Y.; WILKE, C.R. (1954) "Measurements of vapour diffusion coefficient." *Ind. Eng. Chem.* 46 No 11, 2381-7
- LEES, M. (1966) "A linear three-level difference scheme for quasilinear parabolic equations." *Maths. Comp.* 20, 516-22
- LEONOV, L.F.; PROKHOROV, P.S. (1966) "Effect of surface active agents on the evaporation of minute drops of water." *Issled. Obl. Poverkh. Sil, Sb. Dokl. Konf.*, 3rd (Deryagin, B.V. Ed, Publ. 1967), 499-505 [R]
- LEONOV, L.F.; PROKHOROV, P.S. (1967) "Effect of surface active substances on the evaporation of small water droplets." *Izv. Akad. Nauk SSSR Ser. Khim.* No 4, 735-42
- LIN, I.J.; SOMASUNDARAN, P. (1971) "Free energy changes on transfer of surface active agents between various colloidal and interfacial states." *J. Coll. I. Sci.* 37 No 4, 731-43
- LITTLEWOOD, R. (1956) "Evaporation and surface diffusion." Ph.D. Thesis, Kings Coll. London
- LYASHEV, K.F.; DUKHIN, S.S.; DERYAGIN, B.V. (1965) "Effect of adsorption layers of soluble surface-active agents on the evaporation rate of fine water droplets." *Kolloid. Zh.* 27 No 1, 64-8
- LYASHEV, K.F.; DUKHIN, S.S.; DERYAGIN, B.V. (1966) "The influence of soluble surfactants on the evaporation rate of small drops of water." *Kolloid. Zh.* 28 No 1, 155-7
- MACHE, H. (1910) "On the diffusion of water vapour in hydrogen and air." *Sber. Akad. Wiss. Wien.* 119, 1399-423 [G]
- MACRITCHIE, F. (1968) "Role of monolayers in retardation of evaporation." *Nature* 218, 669-70
- MACRITCHIE, F. (1969) "Evaporation retarded by monolayers." *Science* 163, 929-31
- MANSFIELD, W.W. (1953) "Effect of surface films on the evaporation of water." *Nature* 172 No 4389, 1101
- MANSFIELD, W.W. (1955) "Influence of monolayers on the natural rate of evaporation of water." *Nature* 175 No 4449, 247-9
- MANSFIELD, W.W.; MYSELS, K.J.; WU, J. (1972) "Evaporation retardation by monolayers." *Science* 176, 944-5
- MARCHETTI, M.J. (1972) "Laboratory experiments on warm fog dissipation." M.S. Thesis Naval Postgraduate School, Monterey, Calif.
- MAXWELL, J.C. (1890) "Collected scientific papers." II, 625 Cambridge
- MAY, K.R.; GARRETT, W.D. (1972) "Retardation of water drop evaporation

- with monomolecular surface films. Comments & reply." J. Atmos. Sci. 29 No 4, 784-7
- MAYHEW, Y.R.; ROGERS, G.F.C. (1978) "Thermodynamic and transport properties of fluids." (2nd Ed) Basil Blackwell
- McADAMS, W.H. (1954) "Heat transmission." (3rd Ed) McGRAW-HILL
- McBAIN, J.W.; LEE, W.W. (1943) "Vapour pressure data and phase diagrams and some concentrated soap-water systems above room temperature." Oil & Soap 20, 17-25
- MEADLEY, C.K. (1971) "Back-diffusion in a finite medium with a moving boundary." Quart. J. Mech. Applied Math. 24, 43-51
- MIHARA, Y. (1966) "Frost protection by fog droplets coated with monomolecular films." Nature 212 No 5062, 602-3
- MIHARA, Y. (1967) "Anti-frost dispersions for plant culture." Patent Ger. 1,246,488 (Cl. C 06d), Aug. 3
- MILES, G.D.; SHEDLOVSKY, L. (1944) "Minima in surface tension concentration curves of solutions of Na alcohol sulfates." J. Phys. Chem. 48, 57-62
- MORACHEVSKII, V.G.; SOKOLOV, YU.I. (1971) "Freezing temperature of drops of aqueous tenside solutions." Zh. Prikl. Kh. 44 No 8, 1892-4
- MORACHEVSKII, V.G.; SOKOLOV, YU.I. (1975) "Experimental study of the freezing point of drops of aqueous surfactant solutions." Fiz. Aerodispersn. Sistem. Resp. Mezhved. Nauch. Sb. , No 12, 41-7 [R]
- MORIKAWA, A.; KEII, T.; AONUMA, T. (1972) "Change in interfacial tension during mass transfer. III. Surface temperature of water during evaporation." J. Coll. I. Sci. 40 No 3, 349-59
- NARSIMHAN, G. (1955) "Measurement of vapor diffusion coefficient." Trans. Indian Inst. Chem. Eng. 8 73-5
- NAG (1977) FORTRAN library manual Mark 5 routines E02BAF and E02BCF
- NARUSAWA, U. (1971) "Measurement of the condensation and evaporation coefficients of water." Ph.D. Thesis, Michigan Univ.
- NARUSAWA, U.; SPRINGER, G.S. (1975) "Measurements of the evaporation rates of water." J. Coll. I. Sci. 50 No 2, 392-5
- NAVON, U.; FENN, J.B. (1971a) "Interfacial mass and heat transfer during evaporation: I. An experimental technique and some results with a clean water surface." A.I.Ch.E.J. 17 No 1, 131-6
- NAVON, U.; FENN, J.B. (1971b) "Interfacial mass and heat transfer during evaporation: II. Effect of monomolecular films on natural

- convection in water." A.I.Ch.E.J. 17 No 1, 137-40
- NELSON, E.T. (1956) "The measurement of vapour diffusivities in coal-gas and some common gases." J. Appl. Chem. 6, 286-92
- NUZHNYI, V.M.; SHIMANSKII, YU.I. (1965) "Experimental investigations of the rate of vaporization of water drops in a static medium." Kolloid. Zh. 27 No 3, 417-21
- NUZHNYI, V.M.; SHIMANSKII, YU.I.; IVANITSKII, G.K. (1965) "Some aspects of the diffusion theory of evaporation of drops of volatile liquids." Kolloid. Zh. 27 No 4, 583-8
- O'BRIAN, R.N.; FEHER, A.I.; LI, K.L.; TAN, W.C. (1976) "The effect of monolayers on the evaporation of H₂O and solution of O₂ in H₂O." Can. J. Chem. 54, 2739-44
- O'GRADY, V.J. (1971) "The maximum rate of vaporization of water with dissolved salts and surface contamination." Ph.D. Thesis, University Of Pennsylvania
- OKUYAMA, H. (1957) "Diffusion of surface active agents." Ann. Rept. Sci. Works, Fac. Sci., Osaka Univ. 5, 51-64
- PETIT, M.C. (1965) "A study of the diffusion of water vapour in air." C. R. Acad. Sci. Paris 260, 1368-70
- PIKKOV, L.; SIIRDE, E. (1972) "Unsteady evaporation of a pure liquid." Tr. Tallin. Politekh. Inst., Ser. A No 319, 3-8
- PILIE, R.J. (1966) "Project fog drops: Investigation of warm fog properties and fog modification concepts." NASA Contractors Report CR-368
- PILPEL, N. (1953) "Contaminated fogs." Research 6, 481-5
- PLETENEVA, N.A.; REHBINDER, P.A. (1946a) "Effect of surface active substances on evaporation of water drops in the spheroidal state." J. Phys. Chem. (U.S.S.R.) 20, 973-9
- PLETENEVA, N.A.; REHBINDER, P.A. (1946b) "Relations governing the evaporation of liquids in the spheroidal state. I." Acta Physicochim. U.R.S.S. 21 No 6, 961-77
- PLETENEVA, N.A.; REHBINDER, P.A. (1947) "Effect of surface active substances on the evaporation of water drops in the spheroidal state. II." Acta Physicochem. U.R.S.S. 22, 1-12
- PRIKHOT'KO, G.F. (1964) "The problem of the use of monomolecular films for decreasing the intensity of stream fogs." Meteorol. I Gidrol. No 11, 27-9
- QUICKENDEN, T.I.; BARNES, G.T. (1978) "Evaporation through monolayers - theoretical treatment of the effect of chain length." J. Coll. I.

Sci. 67 No 3, 415-22

- RAKHMATULINA, I.KH. (1981) "Nonsteady evaporation and growth of drops in gas(eous) medium." Int. J. Eng. Sci. 19, 1115-22
- RANDALL, M.; MCBAIN, J.W.; WHITE, A.M. (1926) "The activity coefficient of soap solutions." J. Am. Chem. Soc. 48, 2517-22
- RANZ, W.E.; MARSHALL, W.R. (1952) "Evaporation from drops." Chem. Eng. Progr. 48 No 3, 141-6, No 4, 173-80
- RAPER, J.A.; ALLEN, R.W.K.; CLIFT, R. (1982) "The evaporation of droplets in aerosols." I.Chem.E. Jubilee Symp.
- REISER, C.O.; RUHOFF, T.J. (1978) "Development and evaluation of improved films for suppressive water evaporation." Ariz. State Univ., Tempe. Dept. of Chem. Eng. Report Pb-289230/5
- REITER, E.; PIKKOV, L.; SIIRDE, E. (1972a) "Thermal relaxation of evaporating liquid drops." Tr. Tallin. Politekh. Inst., Ser. A No 319, 9-16
- REITER, E.; PIKKOV, L.; SIIRDE, E. (1972b) "Determination of the unsteady temperatures of evaporating drops." Tr. Tallin. Politekh. Inst., Ser. A No 319, 17-22
- RICHARDSON, J.F. (1959) "The evaporation of two-component liquid mixtures." Chem. Eng. Sci. 10, 234-42
- RIDEAL, E.K. (1925) "On the influence of thin surface films on the evaporation of water." J. Phys. Chem. 29, 1585-8
- RO, P.S.; FAHLEN, T.S.; BRYANT, H.C. (1968) "Precision measurements of water droplet evaporation rates." Applied Optics 7 No 5, 883-90
- ROSANO, H.L.; LA MER, V.K. (1956) "The rate of evaporation of water through monolayers of esters, acids and alcohols." J. Phys. Chem. 60, 348-53
- ROSEN, M.J. (1982) "Purification of surfactants for studies of their fundamental surface properties." J. Coll. I. Sci. 79 No 2, 587-8 (1981) & 86 No 2, 587
- SAVINOVA, O.V.; TOVBIN, M.V. (1962) "Effect of surface active substances on the kinetics of water evaporation." Visn. Kiivs'k. Univ. No 5, Ser. Fiz. to Khim. No 2, 93-5
- SCHIRMER, R. (1938) "The diffusivity of water vapour-air mixtures and the evaporation rate." Z. Verein Dt. Ingenieur Beiheft Folge 6, 170-7 [G]
- SCHLUENDER, E.U. (1964) "Temperature and mass change of evaporating drops of pure liquids and aqueous salt solutions." Intern. J. Heat Mass Transfer 7 No 1, 49-73 [G]

- SEBBA, F.; BRISCOE, H.V.A. (1940) "The evaporation of water through unimolecular films." *J. Chem. Soc.*, 106-14
- SEIMIYA, T.; SASAKI, T. (1966) "The effect of monolayers on surface concentration of solutions under evaporation." *J. Coll. I. Sci.* 21, 229-37
- SHIH, Y.; COUGHANOWR, D.R. (1968) "Evaporation of liquid droplets containing surface impurities." *A.I.Ch.E.J.* 14 No 3, 502-4
- SHINYAEV, B.M. (1967) "Effect of some substances on the coefficient of condensation for a drop of water." *Probl. Fiz. Atmos.* No 5, 253-7
- SKLYARENKO, S.I.; BARANAEV, M.K. (1938) "Effect of films of surface active substances on the rate of evaporation of solutions." *J. Phys. Chem. (U.S.S.R)* 12, 271-6
- SKLYARENKO, S.I.; BARANAEV, M.K.; MEZHUEVA, K.I. (1940) "Effect of films of surface active substances on the rate of evaporation of solutions. II." *J. Phys. Chem. (U.S.S.R)* 14, 839-43
- SKLYARENKO, S.I.; BARANAEV, M.K.; MEZHUEVA, K.I. (1944) "Effect of films of surface active substances on the rate of evaporation of solutions. III." *J. Phys. Chem. (U.S.S.R)* 18, 447-52
- SMITH, E.R.B.; ROBINSON, R.A. (1942) "The vapour pressures and osmotic coefficients of solutions of the sodium salts of a series of fatty acids at 25 C." *Trans. Faraday Soc.* 38, 70-8
- SMITH, G.D. (1978) "Numerical solution of partial differential equations: Finite difference methods." (2nd Ed) O.U.P.
- SNEAD, C.C.; ZUNG, J.T. (1968) "The effects of insoluble films upon the evaporation kinetics of liquid droplets." *J. Coll. I. Sci.* 27 No 1, 25-31
- SOKOLOV, YU.I. (1972) "Kinetics of vaporization and growth of drops of aqueous surfactant solutions at subzero temperatures." *Fiz. Aerodispersnykh Sist.* No 7, 20-5 [R]
- SOKOLOV, YU.I. (1972) "Vaporization of drops of solutions of surfactants and water at negative temperatures." *Tr. Gl. Geofiz. Observ.* No 278, 200-4 [R]
- SREZNEVSKII, B. (1882) "On the evaporation of liquids." *Zh. Russ. Fiz. Khim. Obshch.* 14 No 9, 420-69, 483-509
- SUMMERHAYS, W.E. (1930) "A determination of the coefficient of diffusion of water vapour." *Proc. Phys. Soc.* 42, 218-25
- TAYLOR, G. (1964) "Disintegration of water drops in an electric field." *Proc. Roy. Soc. Ser. A* 280, 383-97

- TODES, O.M.; FEDOSEEV, V.A.; ZUBKOV, V.I. (1966) "Calculation of the rates of evaporation or growth of a drop (sphere) with variations of its temperature taken into account." *Kolloid. Zh.* 28 No 4, 573-9
- TOULOUKIAN, Y.S.; LILEY, P.E.; SAXENA, S.C. (1970) "Thermophysical properties of matter." Volume 3 "Thermal conductivity of nonmetallic liquids and gases." IFI/Plenum
- TOVBIN, M.V.; SAVINOVA, E.V. (1957a) "Kinetics of the nonsteady state of a process at a liquid - gas interface. I. Kinetics of the nonsteady state of the evaporation of water." *Zh. Fiz. Khim.* 31, 2445-52
- TOVBIN, M.V.; SAVINOVA, E.V. (1957b) "Kinetics of the nonsteady state of a process at a liquid - gas interface. II. The effects of adsorption layers on the nonsteady-state evaporation of water." *Zh. Fiz. Khim.* 31, 2717-19 [R]
- TRAUTZ, M.; MULLER, W. (1935) "Viscosity, thermal conduction and diffusion in gas mixtures." *Ann. Phys. Ser.* 5 22, 313-352 [G]
- TREYBAL, R.E. (1980) "Mass-transfer operations." (3rd Ed) McGraw-Hill
- TURNER, S.R.; LITT, M.; LYNN, W.S. (1975) "Permeation of water vapour through lipid monolayers." *J. Coll. I. Sci.* 50 No 1, 181-93
- TVERSKAYA, N.P. (1949) "Evaporation of a falling drop." *Uch. Zap. L.G.U.* In A.A. Zhdanova No 120, Ser. Fiz. Nauk No 7, 241-66
- TVERSKAYA, N.P. (1950) "The effect of an air current on the rate of evaporation of water drops." *Izv. Akad. Nauk SSSR, Ser. Geog. Geofiz.* 14, 164-70
- TVERSKAYA, N.P. (1951) "Temperature of evaporation of droplets." *Izv. Akad. Nauk U.S.S.R., Ser. Geog. Geophys.* 15, 74-81
- VACHNADZE, I.A. (1972) "Interrelation of equilibrium vapour pressure of solvents with surface activity in dilute solutions of surface inactive and surface active substances." *Tr. Inst. Geofiz., Akad. Nauk Gruz. SSR* 28, 210-23
- VAN DER LIJN, J. (1976) "The 'constant rate period' during the drying of shrinking spheres." *Chem. Eng. Sci.* 31, 929-35
- WATSON, J.T.R. (1972) "The viscosity of gases in metric units." HMSO
- WEAST, R.C. (1982) "Handbook of chemistry and physics." (63rd Ed) CRC Press
- WEINHEIMER, R.M.; EVANS, D.F.; CUSSLER, E.L. (1981) "Diffusion in surfactant solutions." *J. Coll. I. Sci.* 80 No 2, 357-68
- WEXLER, A.; HASEGAWA, S. (1954) "Relative humidity-temperature relationships of some saturated salt solutions in the temperature range 0 to

- 50 C." J. Res. Nat. Bur. Stand. 53 No 1, 19-26
- WILHELM, E.; BATTINO, R. (1972) "Binary gaseous diffusion coefficients." J. Chem. Eng. Data 17, 187-9
- WOLF, E.; SCHULZE, F.W.; PETRICK, H.J.; CAMMENG, H.K.; BARNES, G.T. (1979) "Effect of industrial surfactants on mass and energy transport during water evaporation. II." Tenside Deterg. 16 No 2, 57-64 [G]
- WU, J. (1971) "Evaporation retardation by monolayers: Another mechanism." Science 174, 283-5
- ZAK, E.G. (1936a) "Kinetics of the evaporation of liquid drops." Zh. Geofiz. 6, 452-65
- ZAK, E.G. (1936b) "Kinetics of the evaporation of water drops in an air stream." Zh. Geofiz. 6, 466-73
- ZOLIN, A.I. (1939) "The kinetics of evaporation of solutions of surface active substances." Acta Univ. Voronegiensis (U.S.S.R) 11 No 3, 15-25
- ZOLIN, A.I. (1961) "The evaporation of solutions of some saturated monocarboxylic acids." Tr. Khar'kovsk. Sel'skokhoz. Inst. 35, 97-103
- ZUNG, J.T. (1969) "Theory of evaporation through monolayers." Amer. Chem. Soc., Div. Org. Coatings Plast. Chem., Preprints 29 No 2, 282-99