Component Interactions in Jet Fuels. Fuel System Icing Inhibitor Additive[†]

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ABSTRACT

In view of its widespread application in aviation turbine fuel, diethyleneglycol monomethylether (DiEGME), and its interactions with water and *n*-heptane have been characterized using turbidity, interfacial tension, water activity and water absorption measurements. This additive has been implicated in a number of problems in recent years, which have arguably arisen from its various physico-chemical interactions with fuel and fuel system components, for which few data were hitherto available. The present study has therefore addressed the more fundamental aspects underlying such interactions using *n*-heptane as the hydrocarbon. Turbidity results indicate an increased level of water solubilization owing

to the formation of DiEGME-water clusters ($\sim 1:8$ ratio) as the DiEGME concentration exceeds its specification maximum value of 0.15% (w/v) in fuel. Interestingly, this same composition is found in separated water resulting from additive partitioning from fuel leading to $\sim 50\%$ DiEGME/water mixtures. The combined use of interfacial tension, water activity and absorption measurements, and solubility parameters is able to explain this tendency as being due to a reduction in water activity in the presence of DiEGME, this latter property being reduced significantly above 50% DiEGME, which therefore appears to be the most thermodynamically-stable composition. Water activity considerations also provide the basis for understanding the action of DiEGME as a *thermodynamic* icing inhibitor, consistent with the role that hydrogen bonding plays in reducing water activity, and in line with water activity-based ice nucleation theory (Koop, T.; Luo, B.; Tsias, A.; Peter, T. *Nature* **2000**, *406*, 611-614). Correspondingly, the thermodynamic activity of DiEGME, derived herein using a Gibbs-Duhem treatment of water activity data, is shown to be reduced considerably in the presence of low levels of water (< 0.1 mole fraction), which would be sufficient to restrict the fuel solubility of this material as observed in practice.

KEYWORDS: absorption, diethyleneglycol monomethylether, DiEGME, filter-water monitors, FSII, icing inhibitor, interfacial tension, jet fuels, partitioning, turbidity, water activity

Introduction

Jet fuel is a complex mixture of hydrocarbons to which industry-approved additives are regularly introduced to improve lubricity, prevent corrosion, reduce the build up of static electricity, and reduce oxidative fuel degradation. In addition, jet fuel for use in military aircraft includes a fuel system icing inhibitor (FSII) added to a permitted maximum level of 0.15% (w/v) to prevent operational problems arising from the presence of water as well as acting in an antimicrobial capacity.

Water is invariably associated with jet fuels during the various stages of their production and

subsequent handling and has to be removed to avoid potential problems in aircraft fuel systems. The presence of undissolved (or “free” water), in particular, promotes microbiological growth and has the potential to form ice at low temperatures. Biological matter and ice particles are both capable of blocking fuel injectors and engine filters with potentially catastrophic consequences.

The introduction of water into jet fuel can potentially occur at several different stages of the distribution system, including during refinery run-down, upon contact with ships’ ballast water during transportation, or through contact with residual water following washing of road tankers. Upon storage, water may also be incorporated in the fuel by contact with humid air, or as a result of rain or snow ingress into poorly sealed tanks. Even during flight, fuel may be exposed to humid air resulting from fuel tank venting used for pressure compensation.

The aviation industry takes considerable measures to minimize the presence of water through the use of methods that are dependent on how intimately the water is associated with the fuel. Thus, “free” water may be either extremely finely dispersed (as a result of nucleation by cooling of previously water-saturated fuel) or present as undispersed “slugs.” In general, dispersed free water droplets produced by mechanical agitation during fuel handling would typically range between ten microns and several mm; together with the slugs, these are effectively separated from the fuel by a combination of coalescence and gravity settling.

The smallest dispersed droplets are conveniently enlarged using fibrous filtration/coalescence. Coalescer cartridges used for this purpose comprise perforated metal support tubes covered with an initial wrapping of filtration media to remove solid contaminants. Loose-structured resin-bonded glass fiber layers then surround the filter, the whole assembly being covered by a tightly fitting hydrophobic cotton fabric “sock” which facilitates release of enlarged droplets.

Mechanistically, the water droplets carried along by the fuel flow are preferentially held up by a wetting attachment to the fibers, whereupon coalescence occurs with neighboring attached droplets or by impaction with incoming water droplets.¹ Coalescence continues until the enlarged water drops are

eventually swept out from the coalescer under the flow hydrodynamics and are subsequently allowed to separate under gravity.²

A further measure to guard against the co-introduction of water with fuel involves the use of filter/monitors as a “last line of defense” immediately upstream of the aircraft tanks. These devices typically contain filtration media sandwiching layers of superabsorbent polymer; the latter swells considerably to form a gel when contacted by sufficient water, which restricts the passage of fuel through the filter/monitor vessel, thereby increasing the differential pressure across the vessel and rapidly shutting off the fuel flow to the aircraft.

Even under ideal conditions, these physical separation methods will always leave a saturation water concentration of ca. 50-100 ppm dissolved in the fuel. Providing that this level of residual water remains soluble through to the combustion zone of the engine, it is unlikely to present a problem during flight. However, since water solubility in hydrocarbons is temperature sensitive, governed in part by the breakage of hydrogen bonds,³ any reduction in fuel temperature as the aircraft gains altitude will lead to phase separation and freezing; ice particles so formed will either settle out and collect in the fuel tanks or, more critically, carried along with the fuel toward the engine where they have the potential to clog in-line filters. As a safety measure, commercial aircraft have heaters fitted to the fuel filters. However, military aircraft are not usually equipped with such heaters and, instead, rely on the addition of FSII to the fuel. The only FSII additive currently approved for jet fuel use is diethyleneglycol monomethylether (DiEGME). Glycols are well known for their antifreeze properties, and DiEGME was originally selected on the basis of its jet fuel solubility and comparatively acceptable toxicity properties.

DiEGME is a relatively hydrophilic molecule with the potential for strong hydrogen bonding to water. Considering the relatively small size of the molecule and its polarity (we have calculated the (gas phase) dipole moment of DiEGME to be 1.16 D using Gaussian 98)⁴ the terminal methyl group confers sufficient, but limited, fuel solubility. The less polar ethyleneglycol monomethylether (EGME, with a much smaller dipole moment (0.15 D) than DiEGME, calculated in the same way⁴) was previously the

approved FSII, but its high toxicity necessitated a replacement being found. Although DiEGME is an improvement on EGME, it is still somewhat toxic, and attempts are occasionally made to find more acceptable alternatives.⁵

However, the presence of hydrophilic inhibitors such as DiEGME in jet fuel is double-edged. On one hand, an additive possessing sufficient affinity for water is required to prevent ice crystal formation in aircraft fuel tanks,⁶ but on the other, a number of problems have been identified by the aviation industry in recent years that are considered to be related to the presence of DiEGME and its interaction with water. The following are some examples:

- The hygroscopic nature of DiEGME leads to the uptake of atmospheric water and adversely affects its dissolution in the fuel during blending operations. Water will therefore inevitably be absorbed by DiEGME being stored in drums, often exposed to a range of humidity and temperature conditions. Additionally, it is possible that small quantities of water can also be produced as a result of oxidative instability of DiEGME during storage.⁷ In order to demonstrate the dissolution behavior of DiEGME containing water in the laboratory, Rickard and Wills at Qinetiq (formerly DERA) in the UK,⁸ and separately, Chang and Krizovensky at the Naval Research Laboratory⁷ added controlled quantities of water to DiEGME and assessed the subsequent dissolution of these mixtures in different fuels. Using DiEGME concentrations in the fuel around the specification maximum of 0.15 vol%, both groups observed that <1 wt% water in DiEGME had no significant effect on its fuel solubility, but higher concentrations were found to retard dissolution. This result takes on added significance, since water levels in excess of 1 wt% were typically found in DiEGME sampled from operational sites; as this is several times the respective US and UK military maximum specification water concentrations of 0.1 or 0.15 wt% for aviation fuel use, it suggests that current test requirements may not be stringent enough to prevent this situation from occurring.
- During transportation and storage, partitioning of DiEGME from the fuel can often lead to

“water bottoms” containing up to 40-50 wt% DiEGME separating under gravity.⁹ Unless replenished by further addition, this would leave the fuel unprotected in terms of anti-icing properties. Moreover, the concentrated DiEGME/water mixtures so formed can be aggressive toward tank linings and the above-mentioned superabsorbent polymers used in filter/monitors. In the latter case, highly viscous gels have been reported at numerous fuel handling sites, which have been identified as consisting of compositionally variable mixtures of water, DiEGME and acrylate polymer (from filter/monitor cartridges).⁹

- Following on from the previous point, the presence of DiEGME in the water associated with the fuel can impair the performance of filter/monitors. Industry specification organizations, such as the UK’s Energy Institute (EI), have issued warnings against the fail-safe condition of these systems when used for fuels containing DiEGME.¹⁰ Filter manufacturers, such as Velcon, advise in their operation manuals against allowing excessive accumulation of separate water.¹¹
- Under normal operating conditions, filter/coalescers are extremely efficient at removing “free” water. However, partitioning of amphiphiles such as DiEGME from the fuel into aqueous phases alters the bulk and interfacial properties of the dispersed water droplets such that the separation efficiency of these systems can also be compromised.¹²

Thus, the motivation behind the present study was to examine the phase and interfacial behavior of the DiEGME/water/hydrocarbon system in order to gain a better understanding of the various operational issues outlined above. The study has therefore been principally concerned with various aspects of the physical chemistry of this ternary liquid system, and focuses on interfacial tension, turbidity, water activity and absorption behavior. Little information on the physical and interfacial properties of this particular glycol system has hitherto been formally reported.¹³

Experimental

Materials. Deionized water from a Milli-Q system was used throughout. DiEGME (99% Purity) from Aldrich and HPLC quality *n*-heptane from JT Baker were both used as-received. Samples of hydrophilic water-absorbing media were removed from an unused commercial Velcon filter/monitor cartridge (CDF-230K) in current usage in aviation fuel applications.

Methods. Interfacial tension determinations.¹⁴ Two methods have been used to determine interfacial tensions of DiEGME/water mixtures against *n*-heptane at $25 \pm 1^\circ\text{C}$. The first uses ring tensiometry with a Krüss K10 tensiometer with a clean platinum ring (cleaned before each measurement by flaming, dipping in concentrated sulfuric acid, thoroughly rinsing with deionized water, and re-flaming). Aqueous DiEGME solutions were made up on a weight basis (n.b. water and DiEGME have almost identical densities at 25°C), and 20 mL samples were introduced into clean 60 mm diameter glass Petri dishes. After positioning the ring just under the aqueous DiEGME surface and correcting the instrument for buoyancy effects, heptane was carefully added to the surface. Lifting the ring slightly into the interface initiated the measurement process.

The second method involved determining the force acting upon a small diameter glass fiber (taken from glass wool, ex BDH, Poole, UK) suspended from the “fiber position” of a Dynamic Contact Angle Analyzer (DCA, Cahn Instruments) when advancing or retracting through heptane/air and heptane/aqueous DiEGME interfaces simultaneously. This has been termed the dual-liquid approach¹⁴ and from the force-distance profiles produced upon retraction of the fiber (assumed as representing a zero contact angle condition) with either a knowledge of the fiber diameter ($= 13.0 \mu\text{m}$ determined by optical microscopy), or assuming the value for the surface tension of heptane, the heptane/aqueous DiEGME interfacial tension can be readily determined.¹⁴

Turbidity measurements. Turbidity was measured as a function of water and DiEGME concentration at $25 \pm 1^\circ\text{C}$. Required volumes of deionized water were successively added to *n*-heptane/DiEGME solutions (50 mL) via a microliter syringe and dispersed for one minute using a water-filled Camlab Transsonic T570 ultrasonic bath. The dispersion created in this way was then left to stand for a further

four minutes, before a sub-sample was removed using a disposable polyethylene pipette and transferred to a 1-cm path length silica cuvette and its UV-visible spectrum recorded, exactly five minutes after starting the ultrasonic treatment. A Cary 50 UV-visible spectrophotometer operated at a medium scan rate (taking approximately 20s) was used to determine dispersion turbidity (absorbance) in the range 300-1000 nm, after correcting for the baseline absorption from the cuvette and the original *n*-heptane/DiEGME mixtures.

The light transmission (turbidity) of a dispersion comprising spherical, monodisperse and independently scattering particles or droplets has been known for many years to be related to their size and concentration. Depending on the size of the scattering material relative to the wavelength (λ) of the incident light, different theories have been developed in order to quantify the effects of ideal scatterers. In reality, disperse systems rarely conform to ideal requirements since they often comprise aggregates possessing variable size, shape, and internal structure, such that the optical properties of the aggregates cannot be assigned unambiguously. However, by making certain assumptions, it is possible to derive some useful information from these simple measurements.

The turbidity (τ) of a dispersion resulting from light *scattering* (analogous to optical density in light-*absorption*) is given by

$$I = I_0 \exp(-\tau l) \quad (1)$$

where I_0 and I are the respective intensities of the incident and transmitted light and l is the path length.

Considering a path length of 1-cm and a system of monodispersed particles of radius a and concentration N (particles per cm^3), then

$$\tau = K\pi a^2 N \quad (2)$$

where K is the total scattering coefficient (ratio of the optical to the geometric cross-sections of the spheres). The value of K can be obtained from Mie theory for the case of optically homogeneous spheres with $a \geq \lambda$. Although this is strictly no longer possible where the particles deviate from the ideal case, i.e. are non-spherical or aggregated as has been considered previously,¹⁵ it may be reasonably

assumed that K will still be a function of the radius of the scattering unit, the wavelength of the incident light, and the complex refractive index (n and absorption coefficient, k) of the scattering unit. Since K is dimensionless, it has also been argued that it must involve the ratio a/λ . Thus, it has been considered that K can be expressed as the function:^{15,16}

$$K = K_0 (a/\lambda)^m \quad (3)$$

where K_0 is the size-independent component of the scattering coefficient which will be dependent on the optical properties of the disperse phase, and m is the wavelength exponent, which is independent of disperse phase concentration.

For a monodisperse system, m can be determined by measuring the turbidity as a function of wavelength, the value of m being determined from the slope of the $\log \tau$ vs. $\log \lambda$ plot based on eq. 4.

$$\tau = \text{constant } (\lambda)^{-m}. \quad (4)$$

The value of m is expected to range between 4 (the Rayleigh limit, for $a \ll \lambda$) and -2.2 as calculated from Mie theory and later extensions.¹⁷ In the present work, however, it has been found that a residual turbidity, or absorption, has to be taken into account when analyzing the wavelength dependence data, such that throughout the subsequent discussions, data have been fitted to the equation:

$$A = A_0 + B\lambda^{-m} \quad (5)$$

where turbidity has been replaced by absorbance for practical purposes. Eq. 5 generally provides fits to the experimental data with R^2 better than 0.990 over the wavelength range 300-1000 nm; the empirical constant B is expected to have some identity with K . The residual absorbance derives from the presence of droplets with $a \gg \lambda$ which do not exhibit wavelength-dependent turbidity.

Determination of Water Activity of DiEGME Mixtures. The success of DiEGME as an anti-icing inhibitor, as well as some of the consequential operational problems mentioned above, result from specific interactions with water. In such multi-component aqueous systems in which various complex interactions may be occurring, it has been argued that concentration is rarely the most suitable parameter for assessing the behavior of water.¹⁸ Instead, the impact of such interactions involving water can be

better considered in terms of its thermodynamic activity.¹⁹ In an aqueous system, the chemical potential (μ_1) of water (component subscript 1) is given by:

$$\mu_1 = \mu_1^0 + RT \ln a_1 \quad (6)$$

where μ_1^0 is the chemical potential of pure water in its standard state and a_1 the water activity. By definition, the activity of water in its standard state is unity, and will be reduced by the presence of solutes.

In the present investigation, a simple isopiestic vapor distillation approach (e.g. see Lin et al.²⁰) was used to determine the water activity of water/DiEGME mixtures. In the present case this involved using a series of eight saturated salt solutions (MgCl_2 , LiNO_3 , NaBr , SrCl_2 , NaNO_3 , NaCl , KCl and BaCl_2) and pure water to provide standard water activity (SWA, a_s) systems spanning the a_s range 0.33 to 1.00. Samples of each water/DiEGME mixture were equilibrated with each of the SWA systems in turn. Pairs of accurately weighed water/DiEGME and SWA solutions (each approximately 1.5 g) in uncapped cuvettes ($1\text{cm} \times 1\text{cm} \times 3\text{cm}$) as conveniently-sized containers were carefully placed in separate 50 mL glass jars, which were then hermetically sealed with air-tight screw tops. The jars were then left to equilibrate at $25.0 \pm 0.5^\circ\text{C}$ for 4 days, after which time they were opened, and the cuvettes carefully removed and rapidly reweighed.

The water activity of each water/DiEGME mixture is the x -axis intercept corresponding to zero mass loss/gain on a plot of the mean mass loss/gain for each pair of cuvettes against the corresponding a_s values.

Uptake of Water-DiEGME Mixtures by Hydrophilic Absorbents. The Cahn DCA system was also used to determine the kinetics of absorption of water-DiEGME mixtures by filter-monitor absorbent media. In these experiments, mass changes resulting from contacting accurately weighed samples of absorbent material (ca. 10 mg) suspended from the DCA “plate position” with water-DiEGME mixtures were measured as a function of time. Fig. 1 shows the typical form of an absorption profile. Upon initial contact with the liquid surface, rapid capillary wetting displaces air contained within the pore structure

of the material, with relatively little change in volume. In the case of absorbent or superabsorbent polymers, however, this is accompanied by the absorption of larger volumes of liquid, which leads to a more substantial swelling of the original structure. The majority of the mass changes shown in Fig. 1 occur as a result of this latter process. Disengagement of the sample from the water surface allows the mass change due to surface tension (the Wilhelmy effect) to be accounted for.

[Insert Fig 1 here]

Results

Turbidity of Water-in-Heptane/DiEGME Dispersions. Dispersions of water in *n*-heptane/DiEGME mixtures have been used to simulate the effects of water contamination in jet fuels. As an extreme example, Fig. 2 shows absorption spectra for 1500 ppm water in various *n*-heptane/DiEGME mixtures. As the DiEGME concentration is increased, so the absorbance (turbidity) over the entire wavelength range 300-1000 nm is seen to decrease. This is associated with increasing water solubilization as the DiEGME concentration increases; in turn, this leads to an increase in the wavelength exponent, m , in a regular manner, approaching the Rayleigh limit of 4 (Fig. 3).

[Insert Figs. 2 and 3 here]

As was suggested above, the parameter A_0 in eq. 5 represents the wavelength-independent absorption (turbidity) resulting from larger, non-Mie-scattering droplets. In Fig. 4, A_0 is plotted as a function of water concentration for different DiEGME concentrations, from which it can be seen that higher residual absorbance is associated with higher water concentrations and/or lower DiEGME concentrations, where solubilization does not significantly exceed the intrinsic water solubility.

The solubility limits for each DiEGME concentration are represented by the respective intercepts of

the extrapolated lines on the x -axis. These data have been used to construct the water solubilization isotherm, or partial phase diagram, shown in Fig. 5. The solubility of water in heptane remains constant at ca. 70 ppm for DiEGME concentrations below ca. 0.12 vol%. Thereafter, water solubility increases linearly with DiEGME concentration, which will be discussed later in this paper.

[Insert Figs. 4 and 5 here]

Fig. 6 shows the effects of DiEGME concentration and DiEGME/water ratio on the wavelength exponent. These data highlight that higher DiEGME/water ratios and higher DiEGME concentrations lead to an increase in m , which approaches the theoretical Rayleigh limiting value of 4 for $[\text{DiEGME}] \leq 0.15 \text{ wt\%}$, indicative of a general decrease in droplet size. The Rayleigh limiting wavelength exponent has been observed previously²¹ in the case of microemulsified oils, but not for dispersed water, to the author's knowledge. However, for the two highest DiEGME concentrations referred to in Fig. 6, wavelength exponents exceeding 4 are apparent. In this case, as pointed out by Kerker, when the refractive index of the disperse phase (n_1) exceeds that of the continuous phase (n_2), wavelength exponents can exceed this theoretical maximum value.²² In fact, this explanation is consistent with the respective refractive indices of DiEGME, heptane and water of 1.4264, 1.3855 and 1.3334.²³ It would therefore be expected that as the DiEGME concentration increases in the dispersed droplets, so the corresponding increase in the n_1/n_2 ratio will result in m values exceeding the Rayleigh limit.

[Insert Fig. 6 here]

Heptane-DiEGME/Water Interfacial Tension. Fig. 7 shows the interfacial tension of aqueous DiEGME mixtures against n -heptane. It is evident that the results obtained using the two experimental methods produce consistent results. Additionally, the interfacial measurements showed a rapid

establishment of interfacial equilibrium.

[Insert Fig. 7 here]

The curve fitted to the experimental points in Fig. 7 is derived from considerations of surface thermodynamics following Adamson's classical treatise.²⁴ The surface or interfacial activity of a species i results from the difference in its activity at a surface, compared with in the bulk, i.e.,

$$\gamma_i A_i = -kT \ln \frac{a_i}{a_i^s} \quad (7)$$

where the superscript s denotes a surface property, γ_i is the surface or interfacial tension, a_i the activity of species i and A_i its molecular area, k is the Boltzmann constant and T is the absolute temperature. Statistical mechanics relates the activity of a species to its mole fraction by $a_i = x_i g_i$, where the coefficients g_i represent weighting factors of the respective energy states.

For pure liquids, eq. 7 can be rewritten as

$$\exp\left(-\frac{\gamma_i A_i}{kT}\right) = \frac{x_i g_i}{x_i^s g_i^s} = \frac{g_i}{g_i^s}. \quad (8)$$

In a binary mixture of liquids, 1 (water) and 2 (DiEGME), the following contributions are made to the interfacial tension, γ_{12} :

$$\exp\left(-\frac{\gamma_{12} A_1}{kT}\right) = \frac{x_1 g_1}{x_1^s g_1^s} \quad (9)$$

from component 1, and

$$\exp\left(-\frac{\gamma_{12} A_2}{kT}\right) = \frac{x_2 g_2}{x_2^s g_2^s} \quad (10)$$

from component 2. Since $x_1^s + x_2^s = 1$ at the surface or interface, then substitution from equations 9 and 10 leads to

$$x_1 \exp\left[\frac{A_1(\gamma_{12} - \gamma_1)}{kT}\right] + x_2 \exp\left[\frac{A_2(\gamma_{12} - \gamma_2)}{kT}\right] = 1. \quad (11)$$

A_1 and A_2 were estimated to be $(1.82 \pm 0.58) \times 10^{-19}$ and $(5.83 \pm 0.15) \times 10^{-19} \text{ m}^2$, respectively, by a

graphical analysis²⁵ and together with heptane/water and heptane/DiEGME interfacial tension data (determined from the present work to be 45.0 and 2.3 mNm⁻¹, respectively) these values have been used to compute the curve in Fig. 7.

Water Activity in Water/DiEGME Mixtures. Fig. 8 shows mass change plots allowing the determination of water activity in four different water/DiEGME mixtures. The plots are seen to be linear, and the near-identical gradients indicate very similar water vapor transport rates within each system. In this set of experiments, the kinetics of vapor transport, from high to low water activity, is largely governed by the surface area and the difference in chemical potential between the two solutions. Since the liquid/vapor surface areas remain constant (at ca. 1 cm²) by virtue of the experimental system used, the mass changes taking place will reflect differences in chemical potential, and hence water activity. The mass changes in the solutions were always less than 6% and many were less than 1%, ensuring that the concentrations (and activities) of the water/DiEGME mixtures remained largely unchanged during the course of the experiments. The presence of excess solid salt at the start and end of each test ensured that the water activity of the salt (SWA) solution also remained unchanged. Small total mass losses would be expected as a result of saturating the jar volume. The linearity of the plots shown in Fig. 8 and their constant gradients are consistent with the preceding comments and, additionally, the low DiEGME volatility.

[Insert Fig. 8 here]

Fig. 9 plots water activity as a function of water mole fraction in water/DiEGME mixtures. The data are well-described by a Flory-Huggins analysis²⁶ including a binary interaction parameter, χ_{12} ,²⁷ such that

$$\ln a_1 = \ln(1 - \phi_2) + \left(1 - \frac{1}{r_2}\right)\phi_2 + \chi_{12}\phi_2^2 \quad (12)$$

where ϕ_2 is the DiEGME weight fraction and r_2 is the DiEGME:water molar volume ratio (= 6.67). The curve shown in Fig. 9 uses this value of r_2 together with $\chi_{12} = +0.54$. The χ_{12} value contrasts both in sign and magnitude with the value of -2.3 for the ethylene glycol (EG)/water system from data based on UNIFAC calculations.²⁸ The latter value is indicative of a negative enthalpy of mixing, based on stronger water-EG interactions compared with the average of water-water and EG-EG interactions. On the other hand, the result for the DiEGME/water system indicates that mixing is endothermic, consistent with a more hydrophobic molecule. In this respect, the χ_{12} value from this study is very similar to values found for aqueous polyethylene glycol and polypropylene glycol solutions by Eliassi and Modarress (between +0.41 and +0.58).

[Insert Fig. 9 here]

Absorption of Water/DiEGME Mixtures by Hydrophilic Absorbent. Fig. 10 contains examples of the kinetic profiles for the absorption of water/DiEGME mixtures by absorbent media used in commercial filter/monitors. It is immediately apparent from these profiles that the presence of DiEGME has retarding effects on both swelling rate and the extent of swelling (termed the “swelling capacity”, expressed as the volume of liquid absorbed per unit mass of absorbent).

[Insert Fig. 10 here]

The effects of DiEGME concentration on swelling rate and swelling capacity are shown in Figs. 11 and 12, respectively. Swelling rate (k_s) data were normalized to take into account for the effect of the different viscosity (η) of each DiEGME/water mixture, using literature data.²⁹ In Fig. 11, it can be seen that the normalized swelling rate ($= k_s \times \eta$) decreases linearly with increasing DiEGME concentration.³⁰ On the other hand, the corresponding maximum swelling capacity (52 cm³g⁻¹ for this material) is

maintained up to a DiEGME concentration of 20 wt%. It can be seen that the swelling rate and swelling capacity are both reduced to negligible levels at ca. 50 wt% DiEGME (DiEGME mole fraction = 0.87). As will be discussed below, this is related to the reduction in water activity brought about by DiEGME.

[Insert Figs. 11 and 12 here]

Discussion

In the Introduction, several jet fuel handling problems associated with the presence of DiEGME in jet fuel were highlighted. The results of the physico-chemical investigations described above provide some insight into the reasons for the problems encountered in practice. Moreover, this knowledge enables possible means of addressing the different operational issues.

Fuel solubility of DiEGME is limited owing to its hydrophilic character. The relative affinity for water and consequential preferential partitioning is expressed as the water/oil partition coefficient K_p (eq. 13),

$$K_p = \frac{[\text{DiEGME}]_{\text{water}}}{[\text{DiEGME}]_{\text{oil}}}. \quad (13)$$

To date, few DiEGME partitioning measurements involving commercial jet fuels have been made. Based on the military JP-4 and JP-5 fuels, however, Grabel determined values in the range 500-700 at room temperature.³¹ Since the Gibbs free energy of transfer of DiEGME from fuel to water is given by $\Delta G_{\text{fuel} \rightarrow \text{water}} = -RT \ln K_p$, these partition coefficients correspond to Gibbs free energies of ca. -16 kcal mol⁻¹. In any event, such values will be specific for a given fuel, since fuel composition is a highly variable, source-dependent property.

The turbidity results from the present study have also shown that DiEGME has the capability of solubilizing relatively large concentrations of water in the hydrocarbon. The residual absorbance data from Fig. 4 convert to the solubilized water concentration data in Fig. 5, from which it can be seen that above ca. 0.15 wt% DiEGME, water solubilization in *n*-heptane increases substantially above the

intrinsic solubility levels (70-80 ppm). The straight line drawn in Fig. 5 for DiEGME concentrations greater than 0.15 wt% corresponds to a constant water:DiEGME molar ratio of 7.8, which can be interpreted in terms of the formation of $\{D_mW_n\}$ clusters ($D = \text{DiEGME}$, $W = \text{water}$; $n/m \cong 8$), rather than single hydrated DiEGME molecules as may be the case below 0.15 wt%. On an operational level, therefore, this demonstrates the need for strict adherence to the maximum specification DiEGME concentration of 0.15 wt% in order to avoid DiEGME-solubilized water being carried along with the fuel into the aircraft; subsequent dilution with fuel containing lower DiEGME concentrations would result in water separation as the solubility boundary indicated by the dotted line in Fig. 6 is crossed (left to right) from the 1-phase region into the 2-phase region.

That the $\{D_mW_n\}$ clusters are substantially smaller than dispersed droplets responsible for the residual absorbance is consistent with the higher wavelength exponent, m found at high DiEGME concentrations. It is evident from Fig. 6 that $m \rightarrow 4$ (and above) with increasing water solubilization, as Mie gives way to Rayleigh scattering, characteristic of solubilized, micellar or microemulsion systems.¹⁷ By analogy with other self-assembled structures such as surfactant micelles, it is to be expected that the cluster composition will be temperature-dependent, although its effect has not been studied here.

Trohalaki et al.³² used molecular dynamics (MD) simulations to compute oxygen atom radial distribution functions, $g(r)$, for two-component mixtures comprising water and each of twelve different FSII or potential candidate molecules. Peaks at 2.9 Å in $g(r)$ were considered to provide a measure of the average size of water clusters. These workers also assumed that anti-icing performance is proportional to the degree of hydrogen bonding occurring between the particular inhibitor and water (and hence inversely proportional to the size of the water clusters), for which agreement with measured FSII performance (assessed as a pre-freezing temperature) was found to be good. Interestingly, under these conditions, the average cluster size for DiEGME computed from this study was 8.7 water molecules, similar to the ratio found from the present turbidity experiments.

The reasonable agreement found between the previous theory³² and the present experiments adds

support to the proposed existence of DiEGME-water clusters, for which additional evidence is found in DiEGME self-diffusion coefficients measurements, determined in D₂O using NMR, which exhibit a minimum corresponding to a similar molar ratio;²⁹ restricted motion of the DiEGME molecules would be expected as a consequence of being present as clusters of the type described above. It is also interesting that the cluster stoichiometry, {D_mW_n} (n/m = 7.8), corresponds to a water mole fraction in the cluster of 0.89, or ca. 54 wt% water, which is typical of the compositions of water bottoms drained from military jet fuel storage tanks.⁹

The water activity data for water-DiEGME mixtures presented in Fig. 9 show a gradual decrease from 1 to 0.9 in a_1 is seen as x_1 is reduced from 1 (pure water) to ca. 0.2 mole fraction (ca. 40 wt% DiEGME). Thereafter, increasing the concentration of DiEGME further causes a more dramatic reduction in a_1 . In this region, the reduced water activity will impact those properties indicative of free water molecules, such as freezing and boiling point, surface and interfacial tension, viscosity, vapor pressure and solvency.

There have been a number of possible mechanisms of action of anti-icing inhibitors, depending on the application and the nature of the solute,³² including: thermodynamic (colligative) freezing-point depression; specific adsorption³³ leading to kinetic (non-colligative) suppression of heterogeneous nucleating species (e.g. dust)³⁴; inhibition of ice nucleation;³⁵ and crystal growth modification.³⁶

However, for aqueous solutions in the presence of hydrophilic solutes such as DiEGME, a particularly compelling mechanism is based on thermodynamic control of ice nucleation through water activity-based ice nucleation theory.³⁷ On this basis, Koop et al. identified a single relationship between the freezing temperature of a solution and its water activity, which is independent of the nature of the solute.³⁷ Thus, water activity-based ice nucleation theory qualifies the earlier assumption of the significance of hydrogen bonding used in modeling FSII performance.³² With reference to the mode of action of DiEGME, therefore, it is considered that preferential partitioning from the fuel into the water phase lowers the water activity by an amount governed by its aqueous concentration, which provides a

reduction in freezing temperature that should be predictable on theoretical grounds as described by Zobrist et al.³⁸

The water activity data can also be used to calculate the corresponding DiEGME activities by using the Gibbs-Duhem equation, viz.³⁹

$$d(\ln a_2) = \frac{x_1}{x_2} d(\ln a_1) \quad (14)$$

such that a plot of x_1/x_2 against $\ln a_1$ can be used to determine solute activity behavior. This treatment ideally involves an extensive set of data which includes sufficiently dilute solutions to which Henry's Law applies, therefore providing an initial limit of integration. However, in the absence of sufficiently low DiEGME concentration a_1 data, the Flory-Huggins theoretical fitted curve in Fig. 9 was used for the graphical integration of eq. 15 throughout almost the entire range of x_1 .⁴⁰

[Insert Fig. 13]

Thus the a_2 results shown in Fig. 13 are seen to mirror approximately the water activity data, as would be expected for a combination of strongly associating species, with relatively low levels of DiEGME hydration $x_1 \cong 0.1$ being sufficient to lower a_2 to < 0.2 . Interestingly, the adverse effects of low levels of water present in DiEGME on fuel solubility are reasonably consistent with these data. The “critical” water concentration of ca. 1% observed in the field and in laboratory solubility studies^{7,8} corresponds to $x_1 \cong 0.06$, which falls reasonably within the concentration range shown in Fig. 13 within which a reduction in a_2 (to ca. 0.2) would be expected to cause substantial inhibition of DiEGME dissolution in the fuel. Other examples exist whereby in the presence of a sparingly soluble component in the disperse phase of a mixture suppresses dissolution or Ostwald ripening tendencies.⁴¹

The reduced water activity in aqueous solutions containing polar solutes will also be expected to exert a negative effect on the hydrogen bonding interactions that provide the driving force for water

absorption by hydrophilic materials.⁴² Such would therefore also be the case expected during the use of superabsorbant polymers as water absorbents in filter-water monitors in the presence of DiEGME. Additionally, there are a number of other factors that will influence the polymer swelling behavior. For example, upon initial contact, water has to enter the internal structure of the fuel-wetted polymer by capillary action. Laplace pressure gradients will then be established through the generation of curved liquid-liquid interfaces. The linear rate of liquid flow (dL/dt) into an assumed cylindrical pore of radius r under a pressure gradient ΔP and making a contact angle θ with the pore surface is given by the Poiseuille equation,

$$\frac{dL}{dt} = \frac{r^2 \Delta P}{8\eta L} \quad (15)$$

which, on substitution of the Laplace pressure across the fuel-water interface, viz. $\Delta P = \frac{2\gamma \cos \theta}{r}$, leads to the simplest form of the Lucas-Washburn equation⁴³ for the initial rate of capillary absorption, which will precede polymer swelling:

$$\left(\frac{dL}{dt} \right)_{init} = \frac{r\gamma \cos \theta}{4\eta L}. \quad (16)$$

It is evident from eq.16 that the initial rate of absorption will be proportional to the ratio γ/η , which will decrease with increasing DiEGME concentration, since γ decreases (Fig. 7) and η increases.^{29,44} Overall, therefore, increasing DiEGME concentration will be expected to cause a reduction in the rate of liquid uptake by absorbent media. This is evident from the swelling profiles shown in Fig. 10.

The equilibrium extent of swelling by superabsorbent polymers is critically influenced by the solution composition, with swelling decreasing to very low levels between 0.1 and 0.2 mole fraction DiEGME. Further consideration of the equilibrium swelling of polymers by water-DiEGME mixtures can be given in terms of polymer solvent theory and expressed quantitatively through the respective solubility parameters. Chen and Shen have determined a minimum solubility parameter equivalent to ca. 35 (MPa)^{1/2} below which swelling of superabsorbent polyacrylate polymers is negligible.⁴⁵ The solubility

product of a DiEGME-water mixture, δ_{12} , based on solubility parameter additivity, is given by

$$\delta_{12} = \phi_1 \delta_1 + \phi_2 \delta_2 \quad (18)$$

where the solubility parameters δ_1 and δ_2 have the values⁴⁶ 47.8 and 22.0 (MPa)^{1/2}, respectively, and ϕ_1 and ϕ_2 are the corresponding volume fractions of water and DiEGME. The minimum solubility parameter of 35 (MPa)^{1/2} corresponds to a 50.4 wt% DiEGME-water mixture, which is in excellent agreement with the results of the present study, for polyacrylate-based filter-monitor media shown in Figs. 11 and 12.

Finally, we turn our attention to the adverse effect of DiEGME on filter-coalescer performance, known as coalescer disarming. It has been recently reported⁴⁷ that such problems have been seen when FSII is present in the fuel. Since droplet adhesion to fiber surfaces is a principal factor in the mechanism of fibrous coalescence,^{1,14} any factors that lead to a reduction in these forces, such as the presence of increased concentrations of DiEGME which reduce interfacial tension (Fig.7), would be expected to have an adverse impact on coalescence efficiency. In the case of water-DiEGME droplets alone, any disarming effects would be expected to be reversible; however, as mentioned earlier, DiEGME-water mixtures are aggressive solvents, and can lead to extraction of surface-active materials from the fuel or contacted surfaces could lead to subsequent deposition on fiber surfaces, rendering them hydrophobic, a consequence that would lead to permanent coalescer disarming.¹⁴

Conclusions

With respect to the problems encountered during jet fuel handling described in the Introduction, the various physical measurements on the water/DiEGME/heptane system described in the present paper have highlighted the following important features:

1. Water activity is lowered by the presence of DiEGME, the most significant reductions occurring above a DiEGME mole fraction of 0.8 (ca. 50 wt% DiEGME). Significantly, perhaps, this concentration is approximately that found in water drained from water collection

points in fuel distribution systems.⁹ The water-DiEGME system is well described using Flory-Huggins theory²⁶ with a water-DiEGME interaction parameter of +0.54.

2. In the presence of DiEGME, the reduced effectiveness of hydrophilic polymers used in filter-monitors to guard against water ingress into aircraft fuel tanks is ascribed to the above reduction in water activity. *Swelling capacity* is unchanged from pure water for DiEGME concentrations below 20 wt%, but found to decrease substantially thereafter, becoming negligible above 50 wt% DiEGME, when the only mass change recorded is due to air displacement in the porous polymer. On the other hand, the *swelling rate* decreases rapidly in the presence of DiEGME, becoming negligible at ca. 50 wt%. This concentration is consistent with solubility parameter analysis given in the literature for swelling of polyacrylate-based superabsorbent polymers.⁴⁵
3. The effect of DiEGME on water activity is one possible explanation for its action as an icing inhibitor. This is consistent with the theory of homogeneous ice nucleation by Koop et al.³⁷ in that reductions in water activity as a result of the presence of solutes leads to a reduction in homogeneous nucleation rates and consequently freezing point.
4. The presence of DiEGME in water also leads to a substantial reduction in interfacial tension against heptane. As suggested previously,¹⁴ this will lead to a reduction in droplet adhesion on coalescer fibers used in dewatering jet fuels, thereby potentially reducing the effectiveness of filter-coalescers through a reduction in the ability to hold up the passage of water droplets through the coalescer fiber bed.
5. The presence of DiEGME has been found to increase the water solubilization capacity of heptane. At DiEGME concentrations above 1500 ppm, approximately 8 water molecules are solubilized by each DiEGME molecule, a value consistent with independent theoretical studies.
6. The effect of water on the solubility of DiEGME in fuel can be explained by the tendency for

the sparingly soluble water (low Ostwald coefficient) to act as an “osmotic agent”, reducing dissolution of a wet DiEGME droplet.⁴¹

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Figure legends

Figure 1. General form of the absorption profiles for the uptake of water-DiEGME mixtures on water absorbent media.

Figure 2. UV-visible absorbance *versus* wavelength (turbidity) plots for *n*-heptane containing different (indicated) DiEGME concentrations and an added water concentration of 1500 ppm.

Figure 3. Plot of the wavelength exponent as a function of DiEGME concentration for 1500 ppm water dispersions in *n*-heptane.

Figure 4. Plot of the residual (wavelength independent) absorbance as a function of added water concentration in *n*-heptane for different indicated DiEGME concentrations. The intercept on the *x*-axis denotes the solubilized water concentration for each DiEGME concentration.

Figure 5. Water solubilization curve for *n*-heptane as a function of DiEGME concentration. Above $\sim 0.15\%$, the slope of the drawn line corresponds to ~ 7.8 water molecules per DiEGME molecule. Below $\sim 0.15\%$, the water concentration is constant at ~ 70 ppm.

Figure 6. Combined plot showing the wavelength exponents as a function of water concentration for several different DiEGME concentrations in *n*-heptane. The dotted line represents the solubilization curve as defined here as the highest *m* value measured corresponding to each DiEGME concentration.

Figure 7. Plot of the interfacial tension between DiEGME/*n*-heptane and water as a function of DiEGME mole fraction.

Figure 8. Plots showing the mass change of different water-DiEGME mixtures (lines 1-4 are water mole fraction 0.3425, 0.1304, 0.0697 and 0.0363, respectively) as a function of the activity of the probe standard water activity (SWA) solutions.

Figure 9. Plot of water activity as a function of DiEGME concentration in water-DiEGME mixtures. The drawn curve is based on Flory-Huggins theory with an interaction parameter of +0.54.

Figure 10. Swelling curves for Velcon absorbent polymer in different DiEGME water mixtures (%)

DiEGME indicated). Each is of the form shown in Fig. 1 and explained in the text.

Figure 11. Plot showing the effect of aqueous DiEGME concentration on the normalized swelling rate (see text for details) of the Velcon absorbent polymer.

Figure 12. Plot of the swelling capacity of the Velcon absorbent polymer as a function of aqueous DiEGME concentration.

Figure 13. Plots comparing the measured water activity and calculated DiEGME activity as a function of water mole fraction in water-DiEGME mixtures.

Figure 1

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Figure 11

Figure 12

Figure 13