Design and Technical Evaluation of a Conceptual Process for Transferring Solvent Precipitated Asphaltenes into Water Utilising Surfactant Phase Behaviour

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Keywords: asphaltenes, phase transfer, refinery residues, solvent deasphalting, surfactant phase behaviour, water dispersions

ABSTRACT

Experiments are described which demonstrate that asphaltenes precipitated from a refinery tar using an excess of *n*-heptane spontaneously partition into a contacting water phase in the presence of an ethoxylated nonionic surfactant by effecting a temperature change. The process appears to be related to the temperature-dependent phase behaviour of the particular surfactant. Hot (ca. 80-90°C) aqueous octa(ethyleneoxy) nonylphenylether (NPE8) and the heptane-diluted tar, were thoroughly and vigorously mixed for a short time and then allowed to stand and cool under quiescent conditions. A distinct oil/water interface rapidly appeared after the mixing had stopped and, at a specific temperature, asphaltene particles were observed to begin to “rain” into the lower aqueous phase, producing an

aqueous asphaltene suspension. The temperature at which asphaltene transfer occurred was close to the phase inversion temperature of the NPE8/heptane system. Subsequent to different laboratory batch experiments, a larger-scale semi-continuous operation was carried out allowing other aspects of the process to be investigated. Rigorous economic analyses of the process have not been included in this study, although it is apparent that surfactant recycling would need to be ensured in order to approach commercial viability, even if the technical concepts translate well to large-scale operation.

1. Introduction

The present paper describes an experimental investigation of a conceptual approach to the separation of precipitated asphaltenes from a solvent-diluted refinery residue into water, assisted by a surfactant exhibiting temperature-dependent oil/water phase partitioning behaviour.

Asphaltenes constitute the heaviest, most polar and currently the least valuable components of crude oil. Structurally, they comprise lightly functionalised polycondensed aromatic molecules, including heteroatomic sulphur, nitrogen and oxygen centres which are able to co-ordinate heavy metals such as nickel and vanadium. Various physicochemical parameters indicate the intermediate polarity of asphaltenes. For example, intermediate solubility parameters of $\approx 20\text{--}30 \text{ MPa}^{1/2}$ have been quoted (Rogel, 1998; Angle et al. 2006), the specific values depending on the crude oil source and the extent of any thermal treatment. Likewise, asphaltenes possess relatively high dipole moments, e.g. 11.7 D for Dagang crude atmospheric residue (Zhang et al., 2007) and are traditionally thought to exist in a relatively homogeneous state in many crude oils and thermally treated residual oils only through associations with other components, such as the resin fractions, which possess characteristics intermediate between the asphaltenes and the remainder of the oil (the maltenes). The nature of the interactions between asphaltenes and resins has been the subject of much conjecture over the years, involving acid-base, hydrogen bonding and/or electrostatic interactions (León et al., 2002). Asphaltene molecular weight has also been debated at length, but is now generally regarded to be in the range 500-1000 daltons, with the higher values quoted being due to aggregation (Mullins, 2007).

Largely as a result of their contrasting nature compared with the majority hydrocarbon components of crude oils, asphaltenes are implicated in a number of problems affecting production and refining operations, e.g. stabilization of water-in-oil emulsions (Mohammed et al., 1993; Spiecker, 2003) and deposition in pipelines and heat exchangers (Matsushita et al. 2004).

Removal of the lighter hydrocarbon fractions of crude oils in refineries by distillation at atmospheric

pressure and under vacuum results in the formation of residues which contain high concentrations of asphaltenic and other high molecular weight material (e.g. resins and waxes). Subsequently, thermal and catalytic cracking processes operating at different degrees of severity (temperature and hydrogen pressure) are then used to ‘crack’ susceptible paraffinic chains on the high molecular components to increase the yield of lower boiling, more valuable distillate fractions. Processing of this type leads to an increase in the polarity of the resultant polycondensed aromatic components derived from the original asphaltenes and resins. These products are variously called asphalts, pitches or tars. Excessive thermal treatment leads initially to precipitation of cracked asphaltenes and ultimately to the formation of coke (Rahmani et al., 2003).

Different residue upgrading schemes have been developed to maximize the production of distillates, while at the same time managing the production of the heavy residues as effectively as possible (Rana et al, 2007). Schemes in popular use at the present time are based on delayed coking or selective solvent deasphalting (SSDA). In the former process, the controlled thermal treatment of atmospheric or vacuum residues results in the production of distillates and to extensive residue cracking, with the deliberate formation of various types of petroleum coke. In SSDA, precipitated asphaltene (PA) is produced in the residue feed using low carbon number *n*-alkanes, such as propane, butane and pentane, with solubility parameters in the range 14 to 15.4 MPa^{1/2} (Barton, 1991). Operating the process under supercritical conditions (for the *n*-alkanes) is more energy and process efficient, and the ROSE™ process developed by Kerr-McGee, and UOP/Foster-Wheeler’s Solvent Deasphalting (SDA) process are such examples. The precipitating solvent is recovered by distillation and recycled, and the resulting DAO is refined conventionally. The question then remains as to how to dispose of the PA. Heavy asphalts are used for road surfacing and as the base components for marine bunker fuels. However, being largely devoid of stabilizing components, the production of marine bunker fuels will require relatively large quantities of valuable aromatic diluents to ensure complete asphaltene solubilisation. In order to avoid using hydrocarbon diluents, asphaltene dispersions in water have also been considered for use as boiler fuels

(Logaraj et al., 2000; Shirodkar and McKeon, 2000). In consideration of the recent volatility of the price of a barrel of crude oil, it is clearly advantageous to consider using residual oils in the most efficient manner possible, and the present conceptual approach could add to potential options. At the present time, production of asphaltene dispersions currently requires high temperature emulsification (Logaraj et al., 2000) or the dispersion of pulverized solidified PA in a residual oil emulsion (Shirodkar and McKeon, 2000).

In the present paper, however, we explore the possibility of transferring PAs directly from the precipitation medium into water.

1.1 Transfer of particles between bulk phases

In recent years there has been interest directed towards the *interfacial* partitioning of particles contained in a mixture which have a certain affinity for droplet interfaces, as created in an emulsion for example (Jauregi et al., 2001). Inherent in this approach is the requirement for the particles to have an appropriate wettability. In another relatively new development, the use of surfactant phases into which aqueous-based solutes are able to partition has also been used as a separation method. Termed *cloud point extraction* (CPE), this latter approach relies on the formation of a separate surfactant phase in the mixture that is triggered by a temperature, pH or salinity change (Bai et al., 2001). CPE is therefore proving to be particularly useful in pre-concentrating analytes for quantitative analysis and has also been considered for the remediation of oil-contaminated soils (Komaromyhiller and von Wandruszka, 1995). Additionally, in one particular development of this, the use of CPE for the separation of the clay mineral saponite from aqueous dispersions has been demonstrated (Ito et al., 2003).

Although none of the above examples specifically considers partitioning of a solid phase *between* contacting bulk liquid phases, there are some precedents involving this general principle. For example, phase partitioning has been used as a means of separating biological cells and polymers for some 30 years. In this application, aqueous-based immiscible polymer systems (e.g. poly(ethylene glycol) and

dextran) are used to create the biphasic system (Albertsson, 1978). To introduce specificity for the cells, one of the polymer phases is usually tagged with a biospecific ligand, assisting its preferential phase transfer.

However, in contrast to this, the present system is one which involves an assumed “non-critical” solid phase, with partitioning occurring as a consequence of achieving a critical condition in a ternary oil/water/surfactant system. Somewhat related, perhaps, is the work of Gallagher and Maher (1992) who investigated the behaviour of colloidal polystyrene spheres, including phase partitioning, in the binary 2,6-lutidine (2,6-dimethylpyridine)/water system which possesses a lower critical temperature of ca. 33.8°C (Loven and Rice, 1963). In their system, two stages were identified upon approaching the critical temperature, i.e. partitioning to a preferred phase/interface, followed by flocculation of the particles near the two-phase boundary. The driving force behind the observed behaviour of the colloidal particles was suggested by the authors as being the formation of wetting layers of the preferred phase on the particle surfaces as phase separation is approached, resulting in the inclusion of all particles within the more-wetted phase.

1.2 Surfactant phase characteristics and critical phenomena

With the ongoing development of new surfactants for diverse technological applications, solution phase behaviour is an extremely important characteristic. The existence and coexistence of different phases of a given surfactant is influenced considerably by solution composition (e.g. ionic strength, pH, the presence of organic species) and temperature (Buzier and Ravey, 1983). Moreover, “scanning” these variables with respect to the solution behaviour reveals critical conditions for the appearance and disappearance of phase boundaries as single-phase systems become two-phase, and *vice versa*, and this is also reflected in the corresponding interfacial tension (Aveyard et al., 1985) and wetting properties (Kolev et al., 2003). However, considering that critical point phenomena have been described theoretically and their existence confirmed in model experiments (Boucher, 1989), direct practical

applications have received comparatively little attention. In one study, in which non-critical colloidal particles were exposed to a critical condition, flocculation occurred (Netz, 1996), suggesting that particle interaction forces were being modified as a consequence of the phase behaviour.

Depending on aqueous phase composition, in particular salinity, it is found that heating aqueous solutions of nonionic ethoxylated surfactants can result in the separation of small droplets of surfactant-rich phase at a specific temperature, producing a hazy appearance in the solution. The temperature at which the onset of haziness occurs is known as the cloud-point, T_{CP} . Coalescence of these droplets can occur on surfaces, leading to the formation of larger drops. This has been observed by the present author when carrying out variable temperature spinning drop tensiometry experiments on heavy crude oil (unpublished observations). Phase separation of this type, occurring as the temperature is increased towards T_{CP} , is believed to be a consequence of the aggregation of surfactant micelles, as the ethylene oxide headgroup dehydrates rendering the surfactant more hydrophobic and less water soluble. Consequently, T_{CP} depends on the structure of the surfactant, as well as factors that influence inter-micellar forces, such as pH and ionic strength (Huibers et al., 1997). Above T_{CP} , aqueous surfactant solubility gives way to preferential oil solubility. When used to stabilize emulsions, such changes in surfactant characteristics are reflected in “phase inversion” (or complete phase separation), e.g. oil-in-water becoming water-in-oil, at the phase inversion temperature (T_{PI}) (Shinoda and Kunieda, 1985). It will become apparent that some of the above features are relevant to the present process.

2. Materials and methods

Water was deionised from a Milli-Q unit (Millipore). The residue was a sample of tar from a combicracker unit at Vohburg Refinery, Germany that had been “fluxed” with 15% gas oil. An exhaustive determination of heptane-insoluble asphaltenes using Soxhlet extraction yielded a value of $16.1 \pm 0.3\%$ w/w. Selected analytical data for the as-received tar are given in Table 1.

Table 1. Analytical data for the combicracker tar sample used in the present study.

Total asphaltenes (%)	%C	%H	%S	ppm N	ppm Na	ppm V	ppm Ni
16.1	86.8	10.9	2.3	5580	56	135	50

n-Heptane was a sample of ASTM standard reference fuel. The surfactants used were all oligooxyethylene nonylphenylethers (nonylphenol ethoxylates, NPE_x), each of which has a distribution of ethylene oxide chain lengths and average degrees of ethoxylation (*x*) of 4, 6, 8, 10 and 15, and were obtained from ICI (Synperonic NP series) or Dow Surfactants (Tergitol NP series). The ecotoxicity of these surfactants and especially their (bio)degradation products nonylphenol and low ethoxylates (i.e. NPE1 or NPE2) has been well documented, e.g. see Staples (2004). Further developments of the present work would arguably necessitate selection of an environmentally acceptable equivalent surfactant (see later).

2.1 Determination of NPE8 concentration

Surfactant concentrations in the water and oil phases were determined using the respective dependence of surface and interfacial tension on NPE8 concentration. Some discussion on the errors associated with this approach is given by Ravera et al. (2000). (Whilst the simpler method of UV-visible spectroscopy would normally be the method of choice for a surfactant containing an aromatic chromophore, the dark DAO/heptane phase and possible presence of tar-derived aromatic moieties in the aqueous phase precluded its use.) The plots of surface and interfacial tension (γ) against log(NPE8 concentration, *c*) shown in Fig.1 were used to provide estimates of surfactant concentrations in the respective water and oil phases. In analysing the aqueous phase, a known weight (ca. 1 g) of filtered sample (0.45 μ m Millipore membrane to remove asphaltene particles) was diluted (as appropriate, but typically by at least 100-fold) with deionized water, and the surface tension of the resultant solution was determined (Krüss K10 tensiometer) at $20.0 \pm 0.5^\circ\text{C}$. It was the aim to achieve a suitable dilution such

that the surface tension fell within the sub-micellar concentration region in which $d\gamma/d\log c$ was non-zero and therefore provides a sensitive measure of concentration. It is appreciated that this method relies on the composition of the surfactant in the sample matching that used for the calibration. However, as discussed below, it is considered possible that there could be a change in the oligomer distribution as a result of phase partitioning (Graciaa et al., 2006), but no detailed distribution analyses have been performed in the present work. It has to be assumed, therefore, that some additional errors could be associated with these measurements as a result of changes in oligomer distribution, which may also explain the scatter in data obtained (see later). The corresponding oil phase NPE8 concentration was determined from the interfacial tension calibration plot (Fig.1). In this case, samples (ca. 1 g) were again filtered (0.45 μm Millipore) and diluted appropriately with *n*-heptane prior to interfacial tension determination. Based on measurement repeatability, errors in each of these determinations are estimated to be of the order of $\pm 10\%$ of the quoted values for aqueous surfactant concentrations and $\pm 15\%$ for the corresponding oil surfactant concentrations.

2.2 Other analyses

Optical microscopy and a Galai CIS-1 instrument using time-of-transition analysis were used to determine the size of precipitated and transferred asphaltene particles. For the relatively dilute aqueous dispersions, direct observation and measurement were possible. On the other hand, the dark colour of the heptane-diluted residue precluded this direct course of action, and these samples were therefore filtered through a 0.45 μm Millipore membrane filter in order to collect precipitated asphaltenes, which were then re-suspended in heptane to provide a sufficiently dilute sample for the analysis. Quantification of asphaltene concentrations in water was performed gravimetrically by filtering a known weight of separated aqueous phase through a 0.45 μm Millipore membrane filter and drying at 90°C to constant weight. Water content of the oil samples was determined by Karl Fischer titration.

2.3 Laboratory partitioning experiments

Samples of the tar were typically diluted in a (w/w) ratio of 1 part tar to 4 parts *n*-heptane, the result of which was precipitation of asphaltene particles. (The relatively unstable nature of this tar ensured that a significant proportion of the total asphaltenes present were precipitated using this ratio of solvent to tar.)

2.3.1 *Small-scale experiments*

In initial scoping experiments, small samples (ca. 25 mL) of the diluted tar and typically an equal volume of aqueous surfactant solutions were mixed thoroughly at 85°C, following which the samples were cooled and qualitatively assessed by visual inspection for phase separation and any evidence of asphaltene partitioning. Slightly larger scale (100 mL) experiments were used to quantify the efficiency of surfactant and asphaltene partitioning for a range of conditions using the most promising candidate surfactant, NPE8. Again, the diluted tar and the appropriate aqueous surfactant solutions were mixed thoroughly at the required water:oil ratio (WOR) at 85°C and were maintained at this temperature for typically 20 minutes. The mixtures were then cooled to 70°C slowly over a period of approximately 30 minutes. Following this period, samples of the upper and lower phases were removed for surfactant concentration determination.

2.3.2 *Intermediate-scale experiments*

A larger, litre-scale batch system was set up in order to provide better temperature control to determine the best conditions to use for subsequent pilot-plant tests and to provide visualization of asphaltene partitioning. The system comprised a 1-L flanged jacketed glass vessel fitted with overhead stirrer and thermocouple, as shown in Fig.2. Temperature control was via circulating water supplied from a thermostat bath initially set to a temperature of 85°C, with temperature reduction being provided by a cooling coil from a chiller unit.

2.4 Pilot-scale tests

The test rig was configured as depicted schematically in Fig.3. A 4:1 (w/w) mixture of *n*-heptane and the tar sample was prepared in 50-L batches sufficient to fill a 200-L drum which was constantly stirred during storage at ambient temperature ($22 \pm 1^\circ\text{C}$) to prevent sedimentation of the precipitated asphaltene particles. This heptane/tar feed mixture was pumped into the test rig using a previously-calibrated positive displacement pump through $\frac{1}{2}$ -inch (nominal bore) heated stainless steel lines where it was contacted with aqueous surfactant solution, introduced via a calibrated dosing pump into the oil feed through fine capillaries, immediately upstream of a differential pressure mix-valve, V. Temperatures in the oil and water lines were controlled in order to ensure the temperature at V was ca. 85°C . The resultant oil/water/surfactant mixture then flowed through heated lines (also set at 85°C) to the separator vessel, which was fitted with a cooling coil, enabling it to be controlled at the lower temperature of 70°C . Care was necessary to ensure even fluid distribution and plug-flow conditions in order to maintain interface stability when introducing the mixture into the separator. In initial tests it was found that introducing the mixture via a ring distributor proved to be problematic, most probably as a result of asphaltene particles blocking the distribution holes. Removing this distributor improved the stability of the system.

Prior to introducing the oil and aqueous surfactant mixture into the separator, an aqueous/oil interface was created by filling the separator with 2.5% w/w NPE8 aqueous surfactant solution to the required level (at, or just below, the entry point for the oil and aqueous surfactant), followed by the oil feed (see Fig.3). This ensured that the oil/surfactant solution mixture subsequently introduced initially contacts the oil phase. The process of cooling the incoming mixture from ca. 85° to 70°C promoted the expected oil/water separation as seen in the laboratory experiments, with the aqueous phase settling under gravity to the oil/water interface. As mentioned earlier, the interface level was controlled by a capacitance probe linked to an automatic water dump valve, although manual override was also used. Oil and water phases were sampled from points A to C (Fig.3) for analysis of asphaltene and surfactant (in water) and

surfactant and water (in oil).

3. Results and Analyses

3.1 Initial laboratory experiments

Scoping experiments were conducted by thoroughly mixing the appropriate quantities of residue, *n*-heptane and typically 2.5% w/w aqueous surfactant solution, initially held at 90°C (i.e. ca. 10°C below the boiling points of both liquid phases). At this initial temperature the surfactants chosen are expected to partition almost exclusively into the oil phase (comprising *n*-heptane + residue) with the expectation (and finding) that a water-in-oil macroemulsion would be formed upon agitating the two phases. Cooling the different mixtures (at a rate of ca. 1 K min⁻¹) to a temperature just below the respective T_{PI} values generally resulted in bulk phase separation, with asphaltene particles being seen to be present in the lower aqueous phase. On the basis of the initial tests octaoxyethylene nonylphenylether, NPE8, was found to produce the cleanest separation in terms of oil/water interface quality, together with qualitatively low observed levels of oil entrainment and highest levels of asphaltenes in the aqueous phase; this therefore prompted further testing with this surfactant to examine the effects of water:oil ratio (WOR, expressed as v/v) and surfactant concentration, prior to scaling up to pilot plant conditions.

3.1.1 Effect of WOR on surfactant partitioning.

Fig. 4 shows the effect of WOR on residual surfactant concentrations in oil and water phases following an asphaltene partitioning thermal cycle and using an initial surfactant concentration of 2.5% w/w in the aqueous phase. Even allowing for errors associated with the determination of surfactant concentrations (particularly in the oil phase), it is apparent that the trends in the aqueous phase composition are more regular; analysis of oil phase samples produces somewhat more erratic results, ranging between 0.2 and 0.6% w/w. This behaviour is considered to be most likely associated with inconsistencies in sampling the oil phase, which is likely to contain dispersed, rather than dissolved,

surfactant. Fig.5 shows the corresponding effect of WOR on the aqueous phase asphaltene concentration. With increasing WOR, the aqueous phase asphaltene concentration is seen to increase in a regular manner. Since the maximum theoretical aqueous phase concentration can be calculated from:

$$\text{Asphaltene concentration in water (\%w/v)} = \frac{2.4}{\text{WOR}} \quad (1)$$

where 2.4% (w/v) is the asphaltene concentration in the feed tar/heptane mixture, the concentration data from Fig.5 can be converted into transfer efficiency data, as shown in Fig.6. These data indicate a linear relationship between asphaltene transfer and system composition, such that 100% transfer efficiency is achieved at a WOR of ≥ 1.7 , whereas below $\text{WOR} \leq 0.4$ transfer becomes negligible.

3.1.2 Effect of initial surfactant concentration on surfactant partitioning

In Fig.7, the surfactant concentrations in oil and water phases subsequent to asphaltene partitioning are plotted as a function of initial surfactant concentration. Even at the lowest initial NPE8 concentrations, it can be seen that the residual concentrations in the oil phase remain relatively high compared with the corresponding aqueous phase concentrations. The range covered by the measured oil phase concentrations can be explained essentially as discussed in the previous section. Additionally, it should be pointed out that for the two lowest NPE8 concentrations studied, 1.0 and 1.5% w/w, no significant asphaltene partitioning was observed, suggesting that a minimum surfactant concentration is necessary to facilitate transfer of the particles between the two phases.

In Fig.8 are shown excess surfactant concentrations following temperature cycling (and asphaltene partitioning) as a function of the initial NPE8 concentration in the mixed system. This plot represents the surfactant that is unaccounted for in the bulk oil and water phases and therefore is assumed to be present as a surfactant-rich Winsor type III phase. Fig.8 includes data where WOR is varied at constant aqueous surfactant concentration (2.5 % w/v) and aqueous surfactant concentration is varied at

constant WOR (= 1). These data confirm the necessity for a minimum surfactant concentration before a surfactant-rich phase is produced; the linear plot of unit slope shown in Fig.8 yields an intercept on the x -axis corresponding to a “critical NPE8 concentration” of ca.0.3% w/v. The reduced asphaltene partitioning efficiency observed at low NPE8 concentrations suggests an association between the formation of a surfactant-rich phase and asphaltene partitioning.

3.1.3 Intermediate scale testing and visualization of asphaltene partitioning

As a prelude to the pilot-scale tests, it was helpful to scale up and visualize the asphaltene phase transfer process. Since the stainless steel vessels comprising the pilot plant provided no capability to observe the separation process, the glass system shown in Fig.2 was used to identify an optimum asphaltene partitioning temperature, which was the key parameter for the subsequent pilot plant tests. A system based on WOR = 1, 2.5% w/w NPE8 solution and a 4:1 dilution of tar, as described in the Experimental section, was examined. It is recognised that the WOR is not optimum, based on the small-scale laboratory tests, but a 1:1 ratio was more convenient for visual observation.

Initially, the temperature of a thoroughly mixed system was held at 85°C for typically 20-30 minutes. Other than the phase separation of the bulk oil and water phases, no asphaltene partitioning was evident at this high temperature, the appearance of the phases being identical to that depicted in Fig.2. It was not until the temperature had fallen to 77°C that asphaltene particles began to be seen to disengage from the interface into the lower water phase; the sequence of images shown in Fig.9 show the course of partitioning. During this sequence, the system was quiescent, with the stirrer (in the aqueous phase) switched off, allowing for better visualization of the asphaltene transfer. With the stirrer turned on, the lower aqueous phase darkens more rapidly, as a result of more efficient disengagement of the asphaltene particles from the interface. Thermal equilibration throughout the biphasic system would also have been improved with stirring. However, as it was evident that partitioning occurs more effectively below 77°C, temperatures at or close to this were chosen for use during the pilot-scale tests. Consideration was also

given to the consequences of using too low a temperature for partitioning, for which stabilization of oil-in-water emulsions might be expected to occur.

3.2 Pilot-scale tests

3.2.1 Operational aspects

Limitations with the volume of feed during the larger-scale pilot plant tests prevented a full and complete evaluation of all experimental variations. However, the results serve to exemplify and extend the concepts involved, and demonstrate the feasibility of operation in a batch or semi-continuous mode.

3.2.2 Time course for surfactant-mediated asphaltene transfer

Following the initial evaluation of the process parameters described above, and having determined the operational requirements for stability of the separator vessel under dynamic conditions for short periods of time, longer duration tests in excess of six hours were carried out. Typically, following the procedures given in the Experimental section as well as the results of the intermediate batch tests, the operational conditions selected were as summarized in Table 2.

Table 2. Operating conditions used in the pilot-scale tests.

T_1 (°C)	79 ± 1
T_2 (at the interface) (°C)	68 ± 1
Total fluids flow rate (L h ⁻¹)	10
Ratio of heptane to residue (w/w)	4:1
Aqueous NPE8 surfactant concentration (% w/w)	2.5
Aqueous surfactant solution flow rate (L h ⁻¹)	5
Residence time in separator vessel (min)	Oil: ≈ 30 Water: ≈ 30
Mix-valve ΔP (kPa)	Zero

After setting up the separator vessel with the heptane/residue mixture and aqueous surfactant solution interface, the feed surfactant solution and diluted residue mixture was introduced. Interface level control involved a combination of the automatic water off-take system and manual control, as it was suspected that operation of the automatic system may have been impaired by the presence of asphaltene particles. Samples of the feed heptane/residue mixture and outlet oil and water phases were taken at suitable times during the course of the tests.

Figs. 10 and 11 show the analytical data obtained run 12, which was one of two tests (the other being run 16 which is considered below) which ran for over 6 hours, allowing a reasonable degree of stability to be achieved, and it is for this reason that we will focus on the results of these two particular tests, which demonstrate that the batchwise laboratory process can also operate successfully under dynamic conditions over this timescale. In Fig.10 it can be seen that the oil phase surfactant and water concentrations reach reasonably steady levels after ca. 1.5 hours on stream. The surfactant concentration data show slightly improved consistency compared with the laboratory results described earlier, reaching a reasonably steady value of ca. 0.5% w/w. Water concentrations in the outlet oil were also reasonably constant, also being in the region of 0.5% v/v. If steady-state conditions are assumed for the water and surfactant in the latter stages of run 12, this corresponds to a molar ratio of water to NPE8 of ca. 50:1 which is suggestive of the presence of microemulsified water, or swollen surfactant micelles (Rosen, 1989).

The corresponding aqueous surfactant concentration profile shown in Fig.11 indicates a rapid loss of surfactant during the course of the first hour on stream, decreasing from the starting concentration of ca. 2.5 - 3% (the slightly higher value possibly arises through phase separation upon being left to stand prior to starting the test) to a steady value of $0.07 \pm 0.01\%$ w/w (i.e. 1.2 mM), approximately 20-fold greater than the critical micelle concentration of 0.0036% w/w (6.2×10^{-2} mM) based on Fig.1, cf. the literature value of 6.8×10^{-2} mM (Dai and Tam, 2003). From the concentration profile shown in Fig.12 it is

evident that asphaltene transfer steadily increases the aqueous asphaltene concentration over the course of the first ca. 3 hours, reaching a concentration that is similar to that in the heptane/tar feed (i.e. $\approx 2 - 2.5\%$ w/w).

It is reasonable to assume that the difference between the amount of surfactant entering the separator vessel and that leaving it most likely is a result of the accumulation of a surfactant-rich phase, as found in the laboratory tests. Sampling the appropriate region of the separator (the interfacial region) to confirm this assumption was not possible with the present separator vessel configuration, thereby precluding a full surfactant mass balance analysis. However, under the present test conditions, it appears that the majority of the surfactant leaving the separator was via the oil phase, which could be present as discrete droplets of surfactant-rich phase.

For the second extended duration test (run 16), the corresponding data show a general consistency with the findings for run 12, most notably the rate of decrease in aqueous surfactant concentration and the relatively constant concentrations of surfactant, water and asphaltene. During this test, however, changes were made to the process parameters in order to determine the concomitant system response. Based on the above results, which provide an indication of the time required to achieve reasonable steady-state conditions, it is accepted that steady-state conditions were not likely to be established during run 16, although it does provide some indicative trends.

3.2.3 Effect of process parameters

(a) Oil and water phase mixing regime

Two types of mixing regime were used, viz. injection of the water into the oil feed stream through capillaries alone, and with subsequent mixing through a differential pressure mix-valve. Results indicated that the latter was unnecessary and contributed to more persistent emulsion problems (the incorporation of emulsified oil in the water phase). The preferred conditions therefore involved the simple injection of surfactant solution into the oil phase which utilizes relatively mild mixing

conditions.

(b) Water:oil ratio

It was expected that the WOR used in the process would influence partitioning through (i) the change in the total amount of surfactant in the system (for a given aqueous surfactant concentration), and (ii) the degree of contact established between oil and water phases. Laboratory experiments had originally been performed at $\text{WOR} = 1$, and consequently this was chosen as the base case for the pilot-scale studies. The original surfactant concentration was based on the initial laboratory results which indicated that a minimum level of surfactant is necessary to facilitate asphaltene transfer. This was also borne out in the pilot plant tests. From the profiles shown in Fig.13 for run 16, it is evident that for $\text{WOR} = 1$, the initial increase in asphaltene concentration in the water phase is similar to that found for run 12 (Fig.12). However, the increasing trend in asphaltene concentration was arrested upon lowering WOR (to 0.67 corresponding to a reduction in the effective available concentration of NPE8 to 80% of its original value, at constant total fluids flow rate), with the asphaltene concentration in the water phase being reduced to trace levels within approximately 30 minutes. This response was surprising and totally unexpected and in an attempt to re-establish the earlier conditions the WOR was returned to 1. This caused a rapid response during which the aqueous asphaltene concentration increasing to the expected higher level within a timescale similar to the start-up conditions (Fig.12). Increasing the WOR to 1.33 resulted in an abrupt decrease in asphaltene concentration, presumably as a reaction to the change in flow conditions, which then appeared to re-attain a more erratic, but generally lower level, as would be expected on the basis of the increased WOR, as described earlier. (Additionally, the expanded surfactant concentration data shown in the inset in Fig.13 also show evidence for response to the changes in conditions.) For low WOR, and correspondingly low surfactant levels, it is likely that asphaltene particles accumulate at the interface, but are unable to transfer into the water. Increasing the WOR would serve to increase the total surfactant concentration, thereby effecting disengagement and phase transfer of these particles from the interface, increasing the erratic nature of the asphaltene

concentration. Although the available run duration was strictly insufficient for complete steady-state conditions to be established (as found for run 12), it is nevertheless considered sufficient to establish some general trends relating to process efficiency, sensitivity and response time. In Fig.14 are shown the corresponding surfactant and water concentration profiles in the separated oil phase. It can be seen that the oil phase composition responds relatively rapidly to the change in WOR, with the water and surfactant concentrations tracking each other very well, as observed for run 12 (Fig.10). As for run 12, residual levels of water and surfactant are ca. 0.5%.

(c) Process temperature

As the process requires a change in temperature to facilitate phase transfer of asphaltene particles, maintaining adequate control over the temperature profile is essential for optimized efficiency. In the pilot-scale tests it was particularly evident that the relative values of T_1 and T_2 (Table 2 and Fig.3) influenced considerably the quality of the produced water phase, with respect to the oil and asphaltene contents. For example, if T_1 was too low ($75 - 80^\circ\text{C}$) the produced water phase contained high levels of emulsified oil, which is a consequence of the increased water solubility of NPE8 at temperatures approaching the T_{PI} for this surfactant. In the system used in this study, temperature control was not ideal, and consequently, unwanted temperature gradients were inevitably generated throughout the system, and in particular in the separator. Initially, the lower part of the separator containing the aqueous phase was slow to heat up to the working temperature T_2 , and this is reflected in the observed change in aqueous surfactant concentration at the start of the runs (in particular see Fig.11).

(d) Position of fluids injection

There are essentially three positions for injecting the fluids into the separator: (i) above the oil/water interface into the oil phase; (ii) at the precise position of the interface; and (iii) below the interface into the water phase. Injection at each of these three positions was investigated during early preliminary tests,

when it was found that the preferred position was at or just above the interface, as injection directly into the aqueous phase led to increase residual oil concentrations in the water.

3.2.4 Asphaltene mass balance

Aqueous phase asphaltene concentrations plotted in Figs.12 and 13 refer to filtered, water-washed and dried material and as such are difficult to correlate with the original asphaltene concentration in the feed oil. However, subjecting several samples of aqueous phase asphaltenes from run 12 to Soxhlet extraction (with *n*-heptane for 2 h) to remove associated oil indicates that the asphaltene particles contain 81 ± 2 % (w/w) genuine “heptane insolubles”. Repeating this with the oil phase asphaltenes allowed the calculation of a transfer efficiency of $80 \pm 10\%$ for this system. The remaining asphaltenes are presumably associated with the heptane/DAO phase, possibly being small enough to be held up during the residence time in the separator.

3.2.5 Characterization of the aqueous asphaltene dispersion

Fig.15 contains particle size (volume) distributions of the aqueous asphaltene dispersion samples taken from the latter stages of each of the extended runs 12 and 16 and, by way of comparison, of a feed oil sample used in run 16. The particle size distributions were found to be relative unaffected by ultrasonication, such that the differences most likely originate from the original precipitation stage. Also shown in Fig.15 are fitted log-normal distribution curves which are used to provide a guide to the major underlying distributions, attempting to eliminate effects due to aggregation. Thus, median (based on particle volume) particle sizes of 5.5, 7.8 and 9.8 μm are obtained for, respectively, the feed sample from run 16, the water-partitioned sample from the same run and a partitioned sample from run 12. The distributions are seen to be consistent with the optical photomicrographs shown in Fig. 16, from which the visual similarity between asphaltene particles in the heptane-diluted feed with the corresponding particles transferred to the water phase (for run 12) is clearly evident, and in particular the presence of

large ($> 50 \mu\text{m}$) particles (agglomerates?) in both samples.

The ca. 1.5% asphaltene-in-water dispersions produced during the pilot plant runs exhibited reasonable stability towards sedimentation, since the asphaltene density is only slightly greater than water. However, allowing the dispersions to stand for ca. 2 weeks produced compacted sediments containing ca. 20% w/w solids, which were able to be easily redispersed by stirring with a spatula.

4. Discussion

In the case of ethoxylated surfactants, the partition coefficient varies as a function of the number of ethylene oxide groups per molecule (x), and hence to the hydrophile-lipophile balance (HLB), given by

$$\text{HLB} = 20 \times \frac{44x}{(44x + 220)}. \quad (2)$$

Commercial ethoxylated nonylphenol surfactants (as used here) comprise ethylene oxide oligomers (NPE i) conforming to Poisson distributions, given by

$$X_i = \frac{x^i}{i!} \exp(-x), \quad (3)$$

where X_i is the mole fraction of oligomer with chain length i in NPE x (Schick, 1967).

Fig.17 shows a Poisson distribution for NPE8 based on eq.3, which shows that the component oligomers are distributed between NPE2 and NPE15. Each of these oligomers will be expected to partition to different extents between oil and water phases, with the most lipophilic components (lower ethoxylate chain lengths) being preferentially associated with the oil phase and the higher ethoxylated species being associated with the water phase; consequently, different mean oligomer distributions will be present in each phase, as reviewed recently by Graciaa et al. (2006). This aspect was originally investigated by Crook et al. for oligomeric octylphenyl ethoxylates, for which the partition coefficient between water and oil, $K_i = c_i^{\text{water}} / c_i^{\text{oil}}$, was found to vary with the length of the ethoxylate chain in a regular way for a given hydrophobic group; below the critical micelle concentration, K_i was found to increase by four orders of magnitude as i increased from 1 to 10 (Crook et al., 1965). Empirically, it

has been found that the relationship

$$\log K_i = \log K_0 - 0.45i, \quad (4)$$

in which K_0 is the partition coefficient for nonylphenol itself, provides an excellent correlation with experimental data at a given temperature and for a number of different hydrophobic groups. The effect of temperature was followed up more recently by Salager et al. (2000) who found that partition coefficients for oligomeric surfactant species (octylphenyl ethoxylates in their case) varied with temperature in a way that is entirely predictable with thermodynamic considerations, accordant with the free energy of transfer of the surfactant molecule from water to oil (or *vice versa*), i.e.

$$RT \ln K_i = RT \ln(c_i^{water} / c_i^{oil}) = \mu_i^{*water} - \mu_i^{*oil} = \Delta\mu_i^{*water \rightarrow oil}. \quad (5)$$

Treating $\Delta\mu_i^*$ as a thermodynamic function comprising enthalpic and entropic contributions, Δh_i^* and Δs_i^* , respectively, Salager et al. (2000) showed that the equation

$$\ln K_i = \frac{\Delta h_i^*}{RT} - \frac{\Delta s_i^*}{R} \quad (6)$$

is entirely consistent with the experimental results. Additionally, Δh_i^* and Δs_i^* were each found to show a different linear dependency on i .

As is evident from these findings, increasing the temperature or decreasing i will favour oligomer partitioning into the oil phase, with each component oligomer behaving differently, as reflected in the respective oligomer phase inversion and cloud point temperatures (Shinoda and Arai, 1964). It is not surprising, therefore, that in the present study we have observed a relatively broad temperature range over which asphaltene partitioning occurs, beginning at ca. 77°C and apparently extending down to below 60°C (e.g. Fig.9). Within this temperature range it is likely that the most hydrophilic oligomers will partition (Graciaa et al., 2006). Nor is it unreasonable that the surfactant concentration data are subject to some uncertainty.

As the critical asphaltene partitioning temperature, T_c (which may be identified with T_{PI}), is approached from a higher temperature, a surfactant-rich (coacervate) phase comprising the more

hydrophilic NPE8 components will separate, initially as discrete droplets, from the DAO/heptane phase. The high density of these droplets will facilitate their sedimentation to the interface, together with the asphaltene particles. It is also possible that these droplets could coalesce with the relatively polar asphaltene particles before reaching the interface, such that a surfactant-rich wetting layer is formed on the asphaltene surface. Whichever way the interface is formed, however, it would be expected that the presence of surfactant intimately associated with the asphaltene particles will serve to increase the affinity of the latter for the aqueous phase, facilitating phase transfer, whilst also contributing to oil phase dewetting.

As indicated at the outset of this paper, the concept of asphaltene separation from alkane-diluted residues through partitioning into water may have useful applications. Results presented herein provide a demonstration of its technical feasibility, although it is conceded that surfactant losses would need to be minimised, and preferably eliminated, if an economically viable process is to be achieved. The brown, rather than black, colour of the resultant dispersed particles suggests that the particles are substantially different from asphaltene powders obtained by grinding. This may result from different surface textures or, more likely, from different composition of the partitioned material. Detailed analyses to establish this have not been carried out in the present study.

Very recently, Zhao and Wei (2008a,b) have reported a process for the simultaneous removal of asphaltene and water from water-in-bitumen emulsions at 150-180°C using a precipitating (alkane) solvent, preferably *n*-pentane. Thermal treatment of mixtures of the three main components is found to result in the production of a deasphalted oil phase (containing *n*-pentane) and an asphaltene-in-water suspension.

4.1 Practical and Economic Considerations

There are several technologies competing for asphaltene separation which will constrain the development of a surfactant-based process such as described herein. As mentioned earlier, loss of

surfactant is possibly the foremost limitation of the process. However, particular circumstances could enable the development of the present approach, providing that certain criteria are met. Firstly, there should be an application and market for an aqueous asphaltene dispersion product, most likely as a water-based boiler fuel. In this case, loss of surfactant may be sustainable, since asphaltene dispersions require stabilising surfactant. Alternatively, a surfactant recycling scheme would need to be established.

A further important consideration is that ethoxylated nonylphenol surfactants of the type used in the present demonstration are the subjects of environmental and legislative constraints, restricting the industrial use of these materials. Thus, there would be a requirement to identify suitable alternative surfactants should further development be considered.

5. Conclusions

A conceptual scheme for the temperature-induced partitioning of *n*-heptane-precipitated asphaltenes directly from an oil phase into water has been demonstrated based on the nonionic surfactant NPE8. Initial small scale laboratory testing has been scaled up in order to provide a visual demonstration of the process, which involves sedimentation of the asphaltene particles to an oil-water interface, followed by a temperature-induced disengagement of the particles from the interface into the aqueous phase in which they exhibit only modest colloidal stability. A minimum surfactant concentration has been found to be necessary before partitioning is observed. This concentration appears to correspond closely to that required for the formation of a surfactant-rich phase in the oil medium upon a temperature reduction, suggesting that the two observations are linked. The process has been further scaled up and demonstrated at a larger, semi-continuous scale for which variation in certain operational parameters has been evaluated within the constraints of material availability.

Acknowledgements

I am grateful to Mike Greenhill-Hooper, Saleem-Ullah Sheikh, Mark Aston and Hugh Bourne for their

contributions during the initial stages of the work conducted at the former BP Research Centre, Sunbury-on-Thames, Middlesex, UK, and the University of Surrey for providing a Visiting Readership enabling its completion.

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Figure 1. Concentration dependence of the surface and interfacial tension of NPE8 solutions used to determine oil phase surfactant concentrations.

Figure 2. Vessel used to demonstrate temperature-controlled asphaltene partitioning.

Figure 3. Simplified schematic flow diagram of the pilot-scale unit used in the asphaltene partitioning tests.

Figure 4. Effect of water:oil ratio on the residual NPE8 concentrations in oil and water phases following thermal cycling and asphaltene transfer. Squares - oil phase; circles - water phase. The line is drawn only to guide the eye.

Figure 5. Effect of water:oil ratio on the asphaltene concentration in the separated water phase following thermal cycling. The line is drawn only to guide the eye and has no theoretical significance.

Figure 6. Effect of water:oil ratio on the efficiency of asphaltene transfer from diluted oil to water during thermal cycling.

Figure 7. Effect of initial NPE8 concentration on the residual NPE8 concentrations in oil and water phases following thermal cycling and asphaltene transfer. Squares - oil phase; circles - water phase. The lines are drawn as guides to the eye.

Figure 8. Plot showing the excess NPE8 concentration unaccounted for in both bulk phases following asphaltene partitioning as a function of the initial total NPE8 concentration for different WORs (constant aqueous phase [NPE8] = 2.5 wt%; open symbols) and aqueous phase NPE8 concentrations (constant WOR = 1; closed symbols).

Figure 9. Still frames captured from a video sequence showing asphaltene partitioning during cooling (temperature indicated) the NPE8/water/tar/heptane system (images run sequentially down the columns, and from left to right).

Figure 10. NPE8 (squares) and water (circles) concentrations in the oil phase during the course of run 12. The lines are drawn only to guide the eye.

Figure 11. Showing the rapid decrease in NPE8 concentration in the aqueous phase during the course of run 12. The inset shows an expanded view of the steady-state NPE8 concentration.

Figure 12. Asphaltene concentrations in the water phase during the course of run 12. The line is to drawn guide the eye.

Figure 13. Water phase surfactant (squares) and asphaltene (circles) profiles showing responses to changes in water:oil ratio, from run 16.

Figure 14. Oil phase surfactant (squares) and water (circles) concentration profiles during run 16, showing the response to WOR changes.

Figure 15. Particle size (volume) distributions for (a) heptane-precipitated asphaltenes in the sample used for run 16; (b) asphaltenes partitioned into water during run 16 (sample taken after 4 h); and (c) asphaltenes partitioned into water during run 12 (sample taken after 5 h). The patterned lines are the measured distributions and the solid lines represent log-normal distributions representing the major volume of the sample, excluding larger, probably aggregated, particles.

Figure 16. (a) Photomicrographs of precipitated asphaltenes (a) in the 4:1 heptane-diluted residue from run 16, and (b) the water phase from the same run after partitioning. Each scale bar is 100 microns long.

Figure 17. Calculated Poisson distribution of the oligomers comprising a polydisperse sample of NPE8.