Manuscript Number: JFUE-D-10-01208R1

Title: Thermal Destabilisation of Bitumen-in-Water Emulsions - A Spinning Drop Tensiometry Study

Article Type: Original Research Paper

Keywords: Bitumen
Emulsion resolution
Heavy crude oil
Interfacial tension
Nonionic surfactants
Oil-in-water emulsions
Phase separation
Spinning drop tensiometry

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Abstract: Nonionic surfactant-stabilised oil-in-water emulsions offer a potentially useful vehicle for transporting heavy crude oils from oilfields to refineries or distribution terminals. Prior to refining, separation of the oil from the emulsion is necessary. Previous studies have suggested that heating the emulsion is sufficient for destabilisation and recovery of the oil. The present work examines this process on a batch laboratory scale and monitors the effect of thermal treatment on the heavy oil/water interfacial tension using spinning drop tensiometry. The present research has confirmed that heating Wolf Lake (Canada) bitumen-in-water emulsions to a temperature close to the cloud point of the surfactant results in efficient bitumen/water resolution, together with separation of a dense surfactant-rich coacervate phase that could be recycled in a commercial heavy oil transportation process. The corresponding temperature dependence of the bitumen/water interfacial tension provides further insight into the emulsion resolution process.

Editor, *Fuel*

8th September 2010

Dear Sir,

I would be grateful if you would consider the manuscript entitled “Thermal Destabilisation of Bitumen-in-Water Emulsions - A Spinning Drop Tensiometry Study” for publication in *Fuel*.

There is resurgence in interest in emulsions for transporting the vast reserves of heavy oil from production locations, but the final stage of the scheme, that of resolving the emulsion and recovering the heavy oil for refining, has hitherto received very little attention. I believe the paper to be timely, therefore, in that it attempts to address this issue for nonionic surfactants that have been considered as suitable emulsifiers for such oils. I notice that *Fuel* has published relevant papers recently dealing with heavy oil emulsion transportation and rheology, and so I think it is an ideal vehicle for the present submission.

The paper contains various applied and fundamental aspects of the emulsion resolution process, and so I have suggested reviewers whose individual interests and expertise are relevant to these different topics.

I would like Figure 6 to be published in colour for the online version. I have included a black & white version (Fig6_blackand white.pdf) for the print version, should the paper be accepted

Yours faithfully,

Spencer Taylor

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Editor, Fuel

24th May 2011

Dear Professor Patrick,

I have submitted my revised manuscript, having made the changes recommended by the reviewers. In particular, I have removed all of the references to 'we'. I admit that there was overuse, even though I believe that it is acceptable to use the royal 'we' in scientific publications. However, I do think that the changed version is an improvement. Specifically, the changes requested by Reviewer 2 have all been made:

p.3, para.3: Three 'we's removed and rephrased appropriately.
p.5, para.2: Slightly rearranged to allow for reviewer's correct identification of incorrect placement of 'but'.
p.13, line 21: 'we' replaced by 'it is'.
p.13, line 42: ditto
p.14, line 1: 'we' removed and sentence changed.
p.14, line 6: 'we' removed, replaced by 'as' and sentence changed appropriately.
p.14, line 15: 'we' removed and rephrased.
p.15, lines 36-37: ditto.

As I said, I think the paper is better for these small changes. Thank you for your patience and assistance.

Yours faithfully,

Spencer Taylor

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Highlights

> Oil/water emulsions are potentially useful for bitumen transportation from field to refinery. > We studied thermal destabilisation of nonionic emulsions. > Surfactant phase behaviour important – potential for recycling? > Oil/water interfacial tensions determined.

Figure captions

Figure 1. Simplified emulsion transportation scheme as applicable to heavy oil/bitumen, highlighting the three main stages, production, transportation and resolution. M represents a mixing stage.

Figure 2. Surface tension-NP(EO)₂₀ concentration plot used for determining residual aqueous surfactant concentrations. The surface tension was determined at 20 °C using the Wilhelmy plate method after an equilibration time of 2 minutes.

Figure 3. Density-temperature plots for WL1 (filled circles), WL2 (filled squares), aqueous 0.5% NP(EO)₂₀ solution (open squares) and 0.5% NP(EO)₂₀ + 1% NaCl solution (open circles). The dashed curve is drawn from literature data for pure water under equilibrium saturation conditions [42].

Figure 4. Schematic summarising the effects of temperature and time on the phase separation in 2.5 and 5% NP(EO)₂₀ solutions. The observed behaviour was independent of salinity (in the range 0 to 1% NaCl).

Figure 5. Schematic summarising the effects of temperature, time and salinity (NaCl) on the resolution/phase separation in 50% WL1 bitumen-in-water emulsions stabilised with (a) 2.5 % and (b) 5% NP(EO)₂₀.

Figure 6. Photographs illustrating the effects of salinity and temperature on the resolution and coacervate phase separation in a 50% WL1 bitumen-in-water emulsion at different NP(EO)₂₀ and NaCl concentrations at 105 and 125 °C.

Figure 7. Effect of temperature on the aspect ratio of spinning drops of WL1 bitumen in aqueous 0.5 % NP(EO)₁₀ solutions. Circles: no NaCl present; squares: 1% NaCl. The curves are Gaussian fits to the data. The arrows indicate the respective cloud points.

Figure 8. Effect of temperature on the aspect ratio of spinning drops of WL1 bitumen in aqueous 0.5 % NP(EO)₁₅ solutions. Circles: no NaCl present; squares: 1% NaCl. The curves are Gaussian fits to the data. The arrows indicate the respective cloud points.

Figure 9. Effect of temperature on the aspect ratio of spinning drops of WL1 bitumen in aqueous 0.5 % NP(EO)₂₀ solutions. Circles: no NaCl present; squares: 1% NaCl. The curves are Gaussian fits to the data. The arrows indicate the respective cloud points.

Figure 10. Effect of temperature on the aspect ratio of spinning drops of WL2 bitumen in aqueous 0.5 % NP(EO)₂₀ solutions in the presence and absence of NaCl. Circles: no NaCl present; squares: 0.5% NaCl; triangles: 1% NaCl.

Figure 11. Effect of temperature on the interfacial tension between WL1 and aqueous 0.5% NP(EO)₁₀ solutions in the absence (circles) and presence (squares) of 1% NaCl.

Figure 12. Effect of temperature on the interfacial tension between WL1 and aqueous 0.5% NP(EO)₁₅ solutions in the absence (circles) and presence (squares) of 1% NaCl.

Figure 13. Effect of temperature on the interfacial tension between WL1 and aqueous 0.5% NP(EO)₂₀ solutions in the absence (circles) and presence (squares) of 1% NaCl.

Figure 14. Effect of temperature on the interfacial tension between aqueous 0.5% NP(EO)₂₀ + 1% NaCl solution and WL1 (circles) or WL2 (squares).

Figure 15. Schematic sequence of the suggested effect of increasing the temperature of aqueous surfactant solution in the presence of bitumen: (a) micellar surfactant solution and adsorption at bitumen surfaces; (b) commencement of surfactant aggregation in bulk solution and on surfaces; (c) further aggregation upon reaching the cloud point and separation of coacervate phase.

Submitted to Fuel/Sept 2010 – Revised version May 2011

Thermal Destabilisation of Bitumen-in-Water Emulsions - A Spinning Drop Tensiometry Study

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Abstract

Nonionic surfactant-stabilised oil-in-water emulsions offer a potentially useful vehicle for transporting heavy crude oils from oilfields to refineries or distribution terminals. Prior to refining, separation of the oil from the emulsion is necessary. Previous studies have suggested that heating the emulsion is sufficient for destabilisation and recovery of the oil. The present work examines this process on a batch laboratory scale and monitors the effect of thermal treatment on the heavy oil/water interfacial tension using spinning drop tensiometry. The present research has confirmed that heating Wolf Lake (Canada) bitumen-in-water emulsions to a temperature close to the cloud point of the surfactant results in efficient bitumen/water resolution, together with separation of a dense surfactant-rich coacervate phase that could be recycled in a commercial heavy oil transportation process. The corresponding temperature dependence of the bitumen/water interfacial tension provides further insight into the emulsion resolution process.

Keywords

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Phase separation

Spinning drop tensiometry

1. Introduction

With the continuing re-evaluation of the world's petroleum resources, production of heavy crude oil (herein also referred to as natural bitumen) is becoming increasingly important, most notably in Canada and Venezuela. However, production and handling these materials, which have viscosities (at 25°C) ranging typically from 1000 to 100,000 mPa.s, introduces completely different challenges compared with lighter oils. Recovery methods necessarily involve reducing the viscosity of the oil in the reservoir, either by using steam to heat the production zone, as in cyclic steam stimulation or steam-assisted gravity drainage (SAGD) processes [1], or through controlled combustion of part of the bitumen deposit (e.g. in-situ combustion) [2].

The produced and dehydrated bitumen is then diluted with available condensate to meet pipeline viscosity requirements for transportation to a refinery or export terminal. However, suitable diluents are often in limited supply and more innovative technical schemes for transporting viscous oils through pipelines have been proposed and investigated, most notably core-annular flow [3] and oil-in-water emulsions [4].

The present paper focuses on aspects of oil-in-water emulsion technology, as there has been a resurgence of activity in the development of emulsions for transportation in various heavy oil-producing regions, including Egypt [5,6], India [7], Iran[8] and Oman [9]. In particular, it is concerned with the final stage of an emulsion transportation scheme, i.e. resolving the emulsion into its constituent bitumen and water phases. Of specific consideration is temperature-induced emulsion resolution and the corresponding effects on bitumen/water interfacial tension.

1.1 Heavy oil emulsion transportation.

Fig. 1 shows a simple schematic of the emulsion transportation process [10]. Dehydrated, hot bitumen is emulsified with the required ratio of an aqueous surfactant solution in the mixing section, M, to produce a bitumen-in-water emulsion containing $\approx 70\%$ by volume bitumen, which typically has a viscosity of <500 mPa.s at a shear rate of $\approx 100 \text{ s}^{-1}$. The emulsion is allowed to cool and is stored until required for pipeline (or other means of) transportation. Upon reaching its destination, it is then necessary to resolve the emulsion.

[Fig. 1]

The potential use of oil-in-water emulsions has been considered for the transportation of crude oils for approximately 40 years, and was initially applied to mobilising waxy crudes [11]. More recently, attention turned to the technical feasibility of producing heavy oil emulsions possessing the required stability and rheology for pipeline transportation. In fact, the feasibility has been thoroughly realised on a commercial scale.

The largest demonstrated production and export of bitumen-in-water emulsions was, until recently, that of Orimulsion. In this example, Venezuelan Cerro Negro bitumen (≈ 9 °API) was emulsified in water, originally using an ethoxylated nonylphenol surfactant, although this was subsequently changed on environmental and economic grounds [12]. Since 1990, some 27 million tonnes of Orimulsion has been produced and exported around the world [13]. This product was developed for use directly as a fuel in power stations, with no requirement to recover the bitumen for refining, unlike in transportation/refining schemes.

1.2 Heavy oil-in water emulsion resolution.

To date, there has been relatively little work published on the resolution stage of the heavy oil emulsion transportation process. In 2004, Saniere et al. considered that the (emulsion) resolution stage presented a problem, since “such a process is not available” [14]. However, a Canadian trial conducted in 1982 outlined how a Wolf Lake bitumen emulsion, also stabilised with an ethoxylated nonylphenol surfactant, was effectively destabilised upon heating to 120-140 °C [1]. In another study [15], Zaki required a commercial demulsifier to resolve Geisum crude oil emulsions at 50°C stabilised with an anionic surfactant. Grosmont crude oil emulsions stabilised by NaOH activation of latent crude oil surfactants were breakable upon re-acidification, but no further details were given [16].

Salager and co-workers [17,18] outlined the general requirements for an emulsion transportation process, including requirements for a thermal resolution stage. The proposed approach stresses the importance of formulation variables, in particular the surfactant hydrocarbon group and (for ethoxylated surfactants) the number of ethylene oxide units per molecule (EON); the alkane carbon number (ACN) of the oil phase; and the aqueous phase salinity. The “hydrophile-lipophile deviation” reflecting the solubility tendencies of the surfactant is expressed by the generalised equation [17]:

$$\text{HLD} = \alpha - (\text{EON}) - k (\text{ACN}) + bS + C_T (T - 25) \quad (1)$$

where α quantifies the surfactant lipophilic group, k , b and C_T are system-dependent constants, S is the salinity and T the temperature (in °C). When $\text{HLD} = 0$, the surfactant possesses equal affinity for each phase, leading to an “optimum condition” of minimum interfacial tension. This is achieved by varying (“scanning”) any of the formulation variables shown in eq. 1 which, as the authors indicate, can be used to control emulsion properties such as stability and droplet size. This treatment is based on the assumption that the surfactant will reside in either or both of the major phases within the range of conditions used during scanning the variables.

Clearly, the use of heat alone offers the most straightforward option for the resolution stage of any emulsion transportation process. Several emulsion transportation schemes have reported the use of ethoxylated nonionic surfactants as stabilisers, owing to their

tolerance to the variable salinity of formation waters likely to be employed as emulsification media. The temperature-dependent phase behaviour of surfactants of this type is well known, such that low temperatures favour aqueous solubility, and consequent stabilisation of oil-in-water (o/w) emulsions. At a certain temperature, known as the cloud point (T_{cp}) of the surfactant, a surfactant-rich (coacervate) phase separates as a haze from aqueous solutions. For ethoxylated nonionic surfactants, T_{cp} increases with the EON and is also influenced (both positively and negatively) by the presence of hydrocarbons and other solubilisates, as demonstrated in the classic work of Shinoda and Arai [19]. Oil-in-water emulsions stabilised with the same type of surfactant are destabilised at the phase inversion temperature (PIT), which is also influenced by the structure of the surfactant and the nature of the oil and can differ from the corresponding T_{cp} by up to 20 °C for *n*-alkanes [19]. T_{cp} and PIT are both dependent on the ionic composition of the aqueous phase as they are influenced by water structure-making and breaking tendencies and colloidal electric double layer interactions [20]. NaCl, used in the present study, would be expected to lower both T_{cp} and PIT [20].

Whether inversion (to a water-in-oil emulsion) or clean separation of the two phases occurs during the resolution process is not fully understood in the literature. Conceivably it involves both kinetic and thermodynamic factors related to the nature of the oil phase and the ability of the surfactant to stabilise the inverse water-in-oil (w/o) emulsions at high temperature. In this latter regard, demulsification of the w/o emulsions by phase-separated coacervate droplets may occur, as has been invoked for their action as antifoam agents [21].

1.3 Bitumen/water interfacial tension studies

By analogy with results from studies involving pure oils and surfactants [22,23], oil/water interfacial tension is a key indicator of the state of the system in terms of stability and the preferred location of the surfactant, consistent with thermodynamic considerations [23]. For compositionally complex bitumens, however, predicting specific effects will be more challenging, a situation made even more difficult using polydisperse surfactants [24], making a more empirical approach necessary.

A few interfacial tension determinations involving natural bitumens and surfactants have been reported in the literature. The main difficulties involving making such measurements are the high viscosity and density of these materials. The results generally indicate that minimum interfacial tensions in the region of 0.1 – 3 mN m⁻¹ are produced in nonionic surfactant-stabilised bitumen emulsions. This range contrasts to the ultra-low values of 10⁻³ – 10⁻² mN m⁻¹ required for enhanced oil recovery, which can also be generated by using alkaline activation of indigenous surfactants [25]. Ahmed et al.[6] determined the interfacial tension of the Egyptian Geisum heavy oil (18 °API) against 2.5% NP(EO)₁₁ solution to be ≈ 0.4 mN m⁻¹ at 30 °C. Moran et al. [26] used a micro-tensiometric method to determine the interfacial tension of a Canadian bitumen (Syn crude Canada) as a function of pH. In neutral water, an interfacial tension of 15 – 20

mN m^{-1} was measured which is lower than values for pure oil systems, a consequence of indigenous surface-active material in heavy oils [25].

Two studies have been published which were pertinent to the characterisation of the interfacial tension of bitumen/water interfaces in Orimulsion. Mohammed et al. considered the competition between natural surfactants in bitumen and the added emulsifier (Intan-100; NP(EO)_{17.5}) [27]. Using a pendant drop approach, these workers determined the adsorption characteristics of this surfactant at the Cerro Negro bitumen/water interface at 30, 45 and 60 °C. Minimum interfacial tensions of $\approx 3 \text{ mN m}^{-1}$ were obtained for surfactant concentrations above the CMC. A subsequent spinning drop tensiometry study using the same surfactant investigated the diluted Cerro Negro bitumen/water interface and the undiluted bitumen/heavy water interface [28]. The authors concluded that the use of heavy water is to be preferred to diluting the bitumen, and interfacial tension values of 3.7, 2.1 and 1.4 mN m^{-1} were obtained at 30, 60 and 75 °C, respectively. Results from maximum bubble pressure measurements indicate that the Cerro Negro bitumen/water interfacial tension is ≈ 10.5 and $\approx 8.0 \text{ mN m}^{-1}$ at 75 and 90 °C, respectively [29].

2. Experimental

2.1 Materials

Two samples of Wolf Lake bitumen were obtained from production sites within the marine sandstones of the Clearwater Formation near Cold Lake in north-eastern Alberta. The first, WL1, was produced using steam stimulation, and WL2 was produced using a pilot *in situ* combustion process.

Some physical and compositional properties of Wolf Lake bitumen are shown in Table 1 [30].

[Table 1]

Water was deionised, sodium chloride was AnalaR grade from Sigma-Aldrich and the nonylphenol ethoxylate surfactants, designated NP(EO)_x, where *x* is the number of ethyleneoxy units per molecule (i.e. the EON), were from the ICI (Synperonics) or Dow Surfactants (Tergitol) respective NP series and were used as received. Throughout this paper, all concentrations are expressed as % by wt.

2.2 Methods

2.2.1 Batch emulsion resolution experiments

Stock 90% WL1-in-water emulsions were prepared with a mean droplet diameter of 10 ± 2 μm using the high internal phase ratio (HIPR) method [31,32] and 2.5 and 5% solutions of NP(EO)₂₀; droplet size distributions are consistent with those shown elsewhere [31,32]. For the resolution experiments, the stock emulsions were blended with the appropriate quantity of the respective surfactant solutions to produce bitumen concentrations of 50%. Sodium chloride was pre-dissolved in the additional surfactant solutions to yield the required aqueous phase concentrations.

Samples of the bitumen-in-water emulsions and surfactant/NaCl solutions for comparison were sealed into graduated glass tubes (created from 10 mL disposable pipettes that had previously been flame-sealed at the lower tip and necks created towards the upper end to facilitate flame sealing after sample addition). The sealed tubes were then equilibrated in ovens at 90, 105 and 125 °C. Resolution progress was typically monitored over a period of 24 h.

For the phase separation tests conducted at 125 °C using aqueous NP(EO)₂₀ solutions alone, residual surfactant concentrations in separated aqueous phases were determined by surface tensiometry, after appropriate dilution, using the Wilhelmy plate technique (Krüss model K10 tensiometer at 20 °C; measurement made after an equilibration time of two minutes). After equilibration, the phase tubes were quenched by freezing in liquid nitrogen and carefully opened to remove the separated frozen aqueous phase. The surface tensions of the thawed aqueous solutions were then compared with a calibration plot of surface tension *versus* log[NP(EO)₂₀ concentration] (Fig. 2). This method assumes that the chain length distribution of the surfactant remains constant and that there is no surfactant decomposition. However, in reality, the aqueous phase surfactant distribution might be expected to become enriched with the most hydrophilic components; hydrophobic, less water soluble components would become enriched in the coacervate [33].

[Fig. 2]

2.2.2 *Spinning drop tensiometry*

Determination of low interfacial tensions by spinning drop tensiometry is a standard technique that has previously been well described in the literature [34,35].

A University of Texas Model 500 spinning drop tensiometer was used in the present study. The principle of the method is to spin a horizontally mounted glass capillary tube (i.d. 1.9 mm) filled with the denser (aqueous) phase containing a small bitumen drop (volume ≈ 0.02 -10 μL depending on the interfacial tension) about its longitudinal axis, and measuring the dimensions of the drop. Temperature and the speed of revolution were the physical variables employed in this work. The main difficulty encountered when applying this technique to the analysis of the viscous bitumen samples was the introduction of a suitable drop into the tube. However, by trial-and-error it was found that

pre-heating the bitumen to ≈ 60 °C allowed a suitable volume to be successfully introduced using a microsyringe into the tube containing the relevant aqueous phase at the same temperature. Once the bitumen drop is introduced into the tube, a typical experiment involves allowing the tube and its contents to cool to ambient temperature before commencing a heating/cooling procedure in the tensiometer.

By sealing the tube with a tight-fitting silicone rubber septum, it was possible to attain a maximum tube temperature of ≈ 140 °C during the heating cycle. The tensiometer was then set at its maximum rotation speed, equivalent to a period of rotation (p) of 7 ms/rev (≈ 8500 rpm). After allowing sufficient time for equilibration at each temperature (estimated by determining the speed of response to changes in rotation speed), the diameter (d) and length (l) of the distorted drop were recorded from which interfacial tension data could be calculated using the Vonnegut equation together with bitumen/water density differences and droplet shape correction factors, $f(l/d)$, calculated by Princen et al. [36] and Manning [37]:

$$\gamma = 1.234 \times 10^6 \frac{d^3 \Delta \rho}{p^2 n^3} f(l/d) \quad (2)$$

The largest uncertainties in the calculated interfacial tension arise from the density differences and measurements of the drop dimensions. Owing to the relatively small differences in density for bitumen/water systems, the absolute error in the density difference, $\Delta \rho$, will be ± 0.001 gcm $^{-3}$ (see below), which corresponds to an error of $\approx 10\%$ in the density differences which are of the order of 0.01 gcm $^{-3}$. n is the refractive index of the external liquid phase and is applied as a correction for the magnifying effect of the glass tube [38,39]. A value for n of 1.33 was used in the calculations over the entire temperature range, since the refractive index of water is virtually invariant with temperature and this will introduce minimal errors to the calculation [40]. The small corrections for surfactant and salt content were ignored. Errors in measuring the drop dimensions, together with the associated effects on $f(l/d)$ are generally estimated to contribute a further 2% error to the final interfacial tension result. For a more detailed discussion of errors in this technique, see Scriven et al. [41].

Following measurements at the highest temperature for each solution, the tube was allowed to cool slowly to allow further measurements to be made on the downward part of the temperature cycle. However, depending on the maximum temperature reached, these measurements were limited due to the ingress of air into the tube as it contracted during cooling.

As the temperature was increased, the first appearance of cloudiness in the surfactant solutions was noted as being the cloud point, T_{cp} (± 0.5 °C).

2.2.3 Density measurements

Densities of all the phases were measured as a function of temperature using 10 mL pycnometers within their calibrated temperature ranges. Estimated uncertainties in the

density measurements are $\pm 0.0005 \text{ g cm}^{-3}$. Fig. 3 shows the results of density measurements for the different liquids. Below the (extrapolated) temperature of $\approx 140 \text{ }^{\circ}\text{C}$, the WL1 bitumen sample used in the majority of the spinning drop experiments is seen to be less dense than water, allowing the use of the spinning drop method. The presence of NaCl, and to a lesser extent surfactant, increases the water density. For the present purposes, the effect of temperature on the solution densities was assumed to follow the same behaviour over the temperature range studied as pure water reported in the literature [42], allowing the densities at temperatures $> 60 \text{ }^{\circ}\text{C}$ to be estimated from the measured lower temperature values.

[Fig. 3]

3. Results

3.1 Coacervate phase formation in 2.5 and 5% aqueous NP(EO)₂₀ solutions

Equilibrating aqueous NP(EO)₂₀ surfactant solutions at $125 \text{ }^{\circ}\text{C}$ resulted in the separation of a dense, almost colourless, surfactant-rich coacervate phase within 30 minutes. The effect appeared to be independent of salinity (0, 0.1, 0.5 and 1.0 % NaCl tested). On the other hand, no evidence of separation of a coacervate phase was observed at 90 and $105 \text{ }^{\circ}\text{C}$, even after 24 hours. The effects are summarised schematically in Fig. 4.

[Fig. 4]

3.2 Destabilisation of WL1 bitumen-in-water emulsions

The corresponding behaviour of 50% WL1 bitumen-in-water emulsions, shown schematically for 2.5 and 5.0% NP(EO)₂₀ in Fig. 5 (a and b, respectively), is substantially similar as the surfactant solutions alone. Separation of coacervate phase is seen to occur within 1 h at $125 \text{ }^{\circ}\text{C}$ for the two surfactant concentrations. However, the complete resolution of the emulsion into its components within this timescale requires the presence of NaCl. In the presence of NaCl, it can be seen in Fig. 6 that separation of the 50% emulsion appears quantitative (however, residual water concentrations in the oil were not determined), and in the absence of NaCl, formation of the coacervate phase is difficult to see clearly, owing to the incomplete bitumen/water separation, although the presence of a dense phase is discernible upon close inspection.

[Fig. 5]

At the two lowest temperatures studied, emulsion resolution is incomplete within the experimental timescale. The phase tube images at 105 °C in Fig. 6 reveal the initial stages of emulsion resolution and coacervate phase formation in the presence of NaCl.

[Fig. 6]

3.3 Bitumen/water interfacial tension

In order to exemplify the effect of temperature on the distortion of the bitumen drops, the aspect ratio ($= l/d$) is shown in Figs. 7 to 9 for WL1 in 0.5% NP(EO)₁₀, NP(EO)₁₅ and NP(EO)₂₀ solutions in the presence and absence of 1.0 % NaCl. In some cases, it can be seen that $l/d < 1$; this is particularly noticeable for some of the lower temperature data shown in Figs. 8 and 9 in the absence of salt. This is due to the drops remaining slightly deformed following their introduction into the tensiometer tube under the experimental conditions described earlier, clearly making these results unsuitable for calculating the interfacial tension, but indicating that higher interfacial tensions prevail under these conditions.

[Figs. 7-9]

However, apart from its use in calculating the interfacial tension, the behaviour of the aspect ratio with temperature is worthy of further comment. Generally, high interfacial tension and viscous forces predominate at low temperatures, such that $l/d \approx 1$, and the highest rotation speed employed is insufficient to impart significant drop deformation. As the temperature is increased, both interfacial tension and viscosity decrease, and a temperature exists for each surfactant above which l/d begins to increase.

The general behaviour observed with increasing the temperature from ambient is that l/d increases from unity and reaches a maximum value (of between 2 and 8 in these systems) before decreasing at higher temperatures. The maximum value corresponds approximately to the temperature at which the aqueous phase becomes turbid (i.e. the cloud point). As can be seen in Figs. 7 to 9, the aspect ratios are generally larger in the presence of NaCl. The curves drawn through the experimental data are Gaussian fits, which, apart from guiding the eye, have no theoretical significance at this stage. The proximity of the maximum aspect ratios to the observed cloud points is evident from the data shown in Figs. 7 to 9. Table 2 summarises the cloud point temperatures for the surfactant solutions in the presence of WL1 bitumen in the spinning drop experiments.

[Table 2]

The colour of the coacervate is indicative of solubilisation of certain bitumen components; as mentioned earlier, the presence of solubilised hydrocarbons has the effect of raising the cloud points from their pure water values [19]. In the present systems it can be seen that an approximate increase of 10 °C in cloud point results from the presence of bitumen, compared with literature values in pure water.

Exceeding the cloud point temperature in the saline solutions caused the solution turbidity to decrease, and the separation of larger droplets of coacervate phase, some of which were seen to adhere to the bitumen drop. In the absence of NaCl, the solutions remained turbid.

Fig. 10 shows the effect of temperature on the aspect ratio of WL2 bitumen drops in 0.5% NP(EO)₂₀ solution in the presence of 0, 0.5 and 1.0 % NaCl. The behaviour is very similar to the corresponding results shown in Fig. 8 for WL1. Drop deformation is seen to increase in the presence of NaCl, with the largest aspect ratio being apparent for 0.5% NaCl.

[Fig. 10]

The corresponding interfacial tensions were calculated for the different systems using the Vonnegut equation, as described earlier, and are shown in Figs. 11 to 13 for NP(EO)₁₀, NP(EO)₁₅ and NP(EO)₂₀, respectively. “U-shaped” behaviour is shown by each system, the differences reflecting different cloud point temperatures of the surfactants. Thus, the interfacial tensions decrease with increasing temperature, attaining minimum values in the vicinity of the cloud point. The low interfacial tension regions extend over a range of 20-50 °C depending on the surfactant and whether NaCl is present. The results are summarized in Table 3, in which additional data [SE Taylor, unpublished] for NP(EO)₈ have also been included for comparison.

[Figs. 11-13]

[Table 3]

The presence of 1% NaCl appears to lead to higher interfacial tensions for the three lowest ethoxylate homologues and a slightly lower value for NP(EO)₂₀. This may be a consequence of the relative molar surfactant concentrations. Since the molecular weight of NP(EO)₂₀ is approximately double that of NP(EO)₈, then for a given NaCl concentration, the surfactant:NaCl molar ratio and any resultant effects will decrease as the ethoxylate chain length increases.

Similar interfacial tension behaviour can be seen for WL1 and WL2 shown in Fig. 14 for 1.0 % NaCl solutions in 0.5% NP(EO)₂₀.

[Fig. 14]

3.4 Residual surfactant concentrations

For bitumen-free systems, residual NP(EO)₂₀ concentrations in the aqueous phase were determined by surface tensiometry. The results shown in Table 4 indicate that these values are 2 to 4 times greater than the critical micelle concentration (CMC; determined in this work to be 0.016 % – see Fig. 1, and in good agreement with the value of 0.014 % reported by Misra et al. [44]).

[Table 4]

Approximate average volumes ($\pm 20\%$) of coacervate phase separating from 10 mL of 2.5 and 5% NP(EO)₂₀ solutions are respectively 0.4 and 0.75 mL, and are only slightly dependent on the NaCl concentration (corresponding masses of surfactant present = 0.25 and 0.50 g). This is consistent with $\approx 70\%$ surfactant being present in the coacervate phase, assuming a surfactant density of 1.07 g cm^{-3} [43]. The average volumes produced from 10 mL of the 50% bitumen-in-water emulsion systems (in the presence of NaCl) are 0.3 and 0.55 mL for 2.5 and 5%, respectively (corresponding masses of surfactant present = 0.125 and 0.25 g). This is consistent with $\approx 40\%$ surfactant being present in the coacervate phase. A detailed analysis of the composition of the coacervate phase has not been carried out, but it is clear that additional components are present in the phase separating from the bitumen emulsion, compared with the bitumen-free system.

4. Discussion

It has been shown that heating is an effective method for resolving WL bitumen-in-water emulsions stabilised by the nonionic surfactant NP(EO)₂₀. Temperatures in excess of 100°C are required, in accord with the phase behaviour of this surfactant. In this work it has been found that the extent of separation is improved in the presence of sodium chloride. Typically three phases are formed, viz. bitumen, dilute aqueous surfactant (and salt) and a surfactant-rich coacervate.

In the absence of bitumen, a sufficiently high temperature causes NP(EO)₂₀ solutions to separate into dilute aqueous surfactant solution and coacervate phases. This is independent of NaCl concentration (0 – 1% studied here). Separation and subsequent analysis of the dilute aqueous phase shows that the surfactant concentration is 2 to 4 times the CMC, in line with expectation based on other examples in the literature giving a value close to, or slightly above, the CMC [45]. However, it is recognised that the individual results in the present work may be distorted through re-dissolution of surfactant during the separation procedure prior to analysis.

The bitumen is likely to modify the behaviour of the system, since the coacervate phase is substantially darker than in the purely aqueous systems, indicating some extraction of coloured species from the bitumen. This is also reflected by the cloud points being raised by the presence of bitumen components [19]. It is seen from the spinning drop experiments that addition of salt increases the size of coacervate phase droplets in the NP(EO)₂₀ and lower EON systems, and it is conceivable that this phenomenon is linked to emulsion resolution, as discussed further below.

For both Wolf Lake bitumen samples, the maximum droplet distortion is seen to occur in the vicinity of T_c . On the basis of previous work on model systems [22,23], this finding is unsurprising, since at this point the system is close to an optimum condition, as mentioned in the introduction. It is found that the interfacial tensions for the ethoxylated nonylphenol surfactants begin to decrease some 20-40 K below the respective cloud points, which attain minimum values before showing signs of increasing at higher temperatures. The measured tensions are low but not ultra-low, as in the case of surfactant formulations used in EOR applications. The minimum values given in Table 3 are seen to be almost invariant of the degree of ethoxylation. However, the widths of the minimum interfacial tension range are seen from Figs. 9 to 11 to increase with the degree of ethoxylation.

At the optimum temperature condition, interfacial packing of the surfactant is normally maximised, as the hydrophilic-lipophilic characteristics of the surfactant are changed through dehydration of the ethoxylate group. This can be explained by the geometrical considerations summarised by Mitchell and Ninham [46], in which surfactant behaviour

at interfaces can be characterised by a packing ratio, $R = \frac{v}{a_0 l_c}$, where v and l_c are

respectively the volume and length of the hydrocarbon group and a_0 is the cross-sectional area of the head group, each parameter representing an effective value which includes contributions from associated water and oil molecules. When $R = 1$, planar monolayers will result, leading to a minimum interfacial tension where there is no net curvature. Temperature scans characteristically produce “V-shaped” interfacial tension behaviour reaching values as low as 10^{-3} mN m⁻¹[23].

The relevance of this in the present context will now be discussed. It is seen in Figs. 11 to 13 that the interfacial tension behaviour as a function of temperature produces U-shaped rather than V-shaped plots, and that the minimum interfacial tensions are 1-2 orders of magnitude greater than the ultra-low values that are more characteristic of the ternary

systems. This can be ascribed to low surfactant solubility in the bitumen phase. Studies on model oil systems assume that the surfactant is distributed between the two bulk phases, and that any third phase that forms does so to a relatively small extent. However, if the surfactant is not sufficiently soluble in the bitumen, on thermodynamic grounds it will form a separate phase, and will not support a planar monolayer required for ultra-low interfacial tensions. Thus, the effect may therefore be to truncate the V-shaped interfacial tension-temperature plot into U-shaped behaviour, dominated by the coacervate phase.

This proposition is given some support by three additional pieces of evidence. Firstly, as noted above, interfacial tensions measured for Cerro Negro bitumen/NP(EO)_{17.5} solution interfaces are very similar to our present values. This strongly suggests that the measurement is independent of the source of the oil, and hence its chemistry, and focuses on the dominance of the surfactant. This point is backed up by similar interfacial tensions being obtained for Geisum crude oil and NP(EO)₁₁ solutions by Ahmed et al [6]. Secondly, the interfacial tension minimum values are seen to be very similar for the different EON surfactants. It might reasonably have been expected that the range of EON studied, from 8 to 20, would have produced more variation in interfacial behaviour.

Thirdly, and perhaps most compelling, are results from the characterisation of the coacervates produced from NP(EO)₈ and NP(EO)₁₀ systems by Chaisalee et al. [21]. These workers were interested in the foam suppression effect of coacervate droplets, since, at temperatures exceeding the cloud point, foams produced from solutions of these surfactants were very unstable. They determined surface and interfacial tensions for the dilute solution and coacervate phases in fresh water and the relevant data are given in Table 5. For the same temperature range the corresponding bitumen/water interfacial tension data given in Table 3 are 0.40 and 0.14 mN m⁻¹, respectively, and it is therefore tempting to suggest that the present bitumen interfacial tensions reflect the presence of a coacervate layer at the bitumen interface. Comparing the surface tension data in Table 5 to literature data [47] also indicates that the aqueous phase NP(EO)₈ concentration after coacervate separation is at or above the CMC.

[Table 5]

From the above, a sequence to account for the observed behaviour in these systems may be postulated for the application being considered. At temperatures below the cloud point, the solution contains micelles as well as free surfactant molecules (Fig. 15a). Under these conditions, surfactant molecules are able to stabilise bitumen-in-water emulsions through adsorption, in accordance with the Gibbs equation.

[Fig. 15]

Increasing the temperature causes dehydration of the ethoxylate group and reduces the hydrophilicity of the surfactant. However, it does not necessarily follow that a reduction

in the hydrophilic character of the surfactant results in significantly increased solubility in the oil phase. The complex composition and high viscosity of bitumen may prevent effective surfactant dissolution and equilibration in this type of oil phase. Instead, the temperature increase will be accompanied by surfactant aggregation and phase separation in the aqueous phase (cloud point) and also on bitumen surfaces, as depicted in Fig. 15(b). Interfacial tension will decrease as more surfactant becomes associated, mostly in an aggregated state, with the bitumen surface. However, ultra-low tensions will not result, as planar monomolecular films are not present at the bitumen/water interface. Such aggregation processes occurring in an emulsion could potentially lead to destabilisation, through (i) disrupting the original monolayer responsible for emulsion stability and (ii) by bridging the bitumen droplets.

Further increase in temperature leads to increased bulk and surface aggregation with the eventual separation of a dense coacervate phase (Fig. 15c). The almost complete loss of surfactant as a separate phase in this temperature region results in an increase in interfacial tension.

Returning to the original application at which the present work is directed, it has been demonstrated that increasing the temperature to the cloud point of the surfactant not only leads to efficient resolution of the emulsion (separation of the phases is seen in Fig. 6 to be near-quantitative), but it is also apparent that the separation of a surfactant-rich coacervate phase suggests the possibility of recycling this component in a commercial scheme. From its appearance (Fig. 6), the emulsion-derived coacervate contains bitumen components, but a detailed analysis of the composition was beyond the scope of the present investigation and is being considered for future study.

5. Conclusions

The present paper has explored aspects of the thermal resolution of Wolf Lake bitumen-in-water emulsions stabilised by an ethoxylated nonylphenol surfactant, in conjunction with interfacial tension behaviour. As the temperature approaches the cloud point of the surfactant, emulsion destabilisation occurs, together with the separation of a dense, surfactant-rich coacervate phase. The effect is enhanced by the presence of salt in the aqueous phase. During the heating process, the bitumen/water interfacial tension decreases from $\approx 12 \text{ mN m}^{-1}$ at the lowest temperatures for which a determination was possible to a minimum value of $\approx 0.5 \text{ mN m}^{-1}$ at the cloud point of $100\text{--}112^\circ\text{C}$ for NP(EO)₂₀, irrespective of the presence of salt. The interfacial tension behaviour was found to be similar for WL bitumen samples produced by two different thermal stimulation methods, suggesting that surfactant effects dominate, rather than necessarily reflecting changes in the oil. In contrast to the “V-shaped” curves characteristic of pure oil/water/surfactant systems, “U-shaped” interfacial tension-temperature curves are observed for NP(EO)₂₀ and other nonylphenol surfactants with lower degrees of ethoxylation; respective minimum values for NP(EO)₁₀ and NP(EO)₁₅ of 0.14 and 0.79 mN m^{-1} were obtained in the absence of NaCl. Where comparisons are possible, values

quoted in the literature for NP(EO)_{17.5} (Intan-100) and Cerro Negro bitumen [27,28] are intermediate between the present values for NP(EO)₁₅ and NP(EO)₂₀.

The observation that larger droplets of surfactant-rich coacervate are formed in the presence of salt, combined with the findings of Chaisalee et al. [21], suggests the possibility that the coacervate has a destabilising action on bitumen-in-water emulsions. Additionally, the same authors determined the interfacial tension for the dilute aqueous and coacervate phases to be the same as our bitumen/aqueous phase values for NP(EO)₈ and NP(EO)₁₀, which suggests that the coacervate phase dictates the bitumen interfacial tension above the surfactant cloud point. A mechanistic scheme has been proposed to account for the present findings and also to explain differences between bitumen and model oils.

Finally, it is tempting to consider that recycling the surfactant is possible by separating the coacervate phase, which could introduce an economic benefit to an emulsion-based bitumen transportation scheme.

6. Acknowledgements

The author is grateful to the initial valuable contributions of Paul Horton and Saleem Ullah Sheikh and to University of Surrey for providing facilities enabling completion of this work. BP plc are acknowledged for initial support and donation of a spinning drop tensiometer.

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Table 1. Selected chemical and physical properties of Wolf Lake bitumen [30].

API gravity	10.5°
Viscosity (mPa.s) at 20°C	24,400
Elemental composition (%wt)	C 83.8; H 10.6; N 0.25; S 4.5
SARA analysis (%wt)	Saturates 25.2
	Aromatics 37.4
	Resins 27.3
	Asphaltenes 10.1

Table 3. Interfacial tensions for WL1 bitumen and 0.5% ethoxylated nonylphenol solutions from the spinning drop experiments.

Aqueous phase composition	Minimum interfacial tension (mN m ⁻¹)	Temperature range for low interfacial tension region (°C)	
		Minimum	Maximum
NP(EO) ₈	0.40	22	42
NP(EO) ₈ + 1.0% NaCl	1.77	<35	>44
NP(EO) ₁₀	0.14	35	71
NP(EO) ₁₀ + 1.0% NaCl	0.42	35	84
NP(EO) ₁₅	0.39	≈70	110
NP(EO) ₁₅ + 1.0% NaCl	0.48	70	>130
NP(EO) ₂₀	0.71	80	130
NP(EO) ₂₀ + 1.0% NaCl	0.54	70	>130

Table 4. Residual surfactant concentrations for water/NP(EO)₂₀ systems.

Initial NP(EO) ₂₀ concentration (%)	NaCl concentration (%)	Final NP(EO) ₂₀ concentration (%)*	% loss of NP(EO) ₂₀ from aqueous phase
0.6	1.0	0.039	93.5
2.5	1.0	0.037	98.5
5.0	1.0	0.054	98.9
5.0	0.5	0.035	99.3
5.0	0.1	0.071	98.6

*estimated 10% error

Table 5. Summary of surface and interfacial tension data for coacervate systems (from Chaisalee et al.[21]).

	NP(EO) ₈			NP(EO) ₁₀
	25 °C	35 °C	45 °C	70 °C
Dilute phase surface tension (mN m ⁻¹)	30.5	30.1	30	29.9
Coacervate phase surface tension (mN m ⁻¹)	29.9	29.6	29.3	29.9
Interfacial tension between coacervate and dilute phases (mN m ⁻¹)	0.3	0.2	0.3	0.1

Table 2. Cloud point temperatures from the spinning drop experiments.

Surfactant	Cloud point (°C)*	
	Deionised water	0.5 % NaCl
NP(EO) ₁₀	78.1 (66)** (62-64)***	72.1
NP(EO) ₁₅	104.5 (93-95)***	93.7
NP(EO) ₂₀	112.6 (>100)***	103.2

*In the presence of WL bitumen.

**From Chaisalee et al. (concentration in pure water = 0.02 mol L⁻¹) [21].

***Values from Ash and Ash (for 1% solutions) [43].

Figure(s)

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