

Precipitation of asphaltenes from solvent-diluted heavy oil and thermodynamic properties of solvent-diluted heavy oil solutions

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Abstract

Ratios of *n*-heptane (hep) to toluene (tol) affect the solubility of the asphaltenes in heavy oil extraction processes. Consequently phase changes and time after mixing *n*-heptane and heavy oil in toluene are important for understanding produced emulsions. The kinetics of phase change when *n*-heptane is added to toluene-diluted heavy oils, and the thermodynamic properties of partially deasphalted heavy oils were studied. The methods used were monitoring precipitation in time using light microscopy, quantitative asphaltenes analysis by near infrared spectroscopy, refractive index and densities measurements, and calculated solubility parameters of mixtures. At critical mass ratios of hep/tol from 1.37 to 2.0 in diluted heavy oil the precipitated asphaltene particles were observed under the microscope after lag times from 2 h to instantly. Lag times were longer at low initial oil concentration. The floc growth time decreased as heavy oil concentration in toluene increased. The growth patterns in time appeared as dots to beads (strings) to clusters (fractal-like flocs). Final wt% precipitated asphaltenes vs. mass fraction (hep+tol)/heavy oil followed sigmoidal relationships. Curves showing wt% soluble asphaltenes vs. mass fraction hep/tol after 24 h initially followed the same shape as time zero curves and diverged at the onset ratios of hep/tol. Slope for precipitated asphaltenes vs. solubility parameters curve showed a break at 16.4 MPa^{1/2}. Linear correlations were established for concentrations of soluble asphaltenes in residual oils and density, for refractive index and density and for refractive index and solubility parameter. The latter correlation was in accordance with Lorenz–Lorentz theory. These equations provided a means by which oil density, refractive index and solubility parameter can be predicted when these measurements are difficult to measure practically.

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1. Introduction

The solubilities and physical properties of heavy oil-in-solvent toluene (tol) with added nonsolvent *n*-heptane (hep) (mixtures known as *heptol*) are useful for understanding heavy oil extraction processes [1,2], upgrading, and emulsion treatments. Model oils used to study crude oil emulsion stability [3–5] are often mixtures of *n*-heptane and toluene into which asphaltenes or crude oils are added as the stabilizers. Volume ratios of 50:50 or 70:30 hep:tol have been used in forming water-in-oil emulsions with crude oils or asphaltenes as the stabilizers [6,7]. However, the phase changes in the heptol–asphaltene solutions as time progressed were not

considered as factors impacting on the emulsions. The preparations of the oil phases in these fundamental studies are important when asphaltenes are considered the stabilizers.

There are two routes in oil phase preparations for study. For the first, the extracted asphaltene solids [8] are redissolved in a solvent [9], but in this case the solubility/dissolution curves show hysteresis [10,11]. The configuration of the asphaltene might change on redissolution. For the second, the asphaltenes are removed incrementally from the toluene diluted heavy oil by adding a nonsolvent such as *n*-heptane, and soluble asphaltenes remain in the heptol. In the second case, it is necessary to know the concentration of the heavy oil in toluene, the ratio of toluene to *n*-heptane, and when the system reaches equilibrium or when asphaltene precipitation begins and ceases. The physical properties and the soluble asphaltenes concentrations in residual diluted

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heavy oils after partial removal of asphaltenes are still lacking. Only recently sensitive accurate techniques became available for measuring low soluble asphaltenes concentrations. The results reported herein have filled this gap for Canadian heavy oils and provide new data to add to the extensive published works on the science of asphaltenes [7, 12–33]. The semi-empirical and theoretical relationships developed between oil physical properties and compositions would allow predictions of the physical properties of diluted heavy oils. The results presented herein thus fulfil this need.

In this study, firstly, the kinetics of asphaltene precipitation is investigated by microscopic observations as a function of time. Secondly, the solubility parameters of oil solutions with varied asphaltene/resin content are calculated, mass balances of the contents of the oils after 24 h equilibration in toluene, and in heptol (various ratios of *n*-heptane and toluene) are determined. The physical properties such as densities, and refractive index are measured and correlated with the calculated Hildebrand solubility parameters of the mixtures.

2. Experimental and theory

2.1. Materials

Primrose heavy oil represents typical heavy oils in Alberta and was selected from representative Canadian heavy oils and bitumens for detailed study. The heavy oil is named by location in Alberta, Canada. The properties of Primrose are compared with Cold Lake heavy oil, and Athabasca bitumen (Syncrude coker feed) in Table 1. There are only small variations in the concentrations of SARA (saturates, aromatics, resins, and asphaltenes) hydrocarbon class compositions [34].

All solvents (toluene, *n*-heptane, chloroform, and acetone) were of spectroscopic grade (Optima) and were obtained from Fisher Scientific.

Table 1
Sources of heavy oils and their properties

Source heavy oil/API	Primrose ^a 10–11	Cold Lake ^b 11	Athabasca ^b 8.2–9.1
Saturates, % w/w	23	21	16.9
Aromatics, % w/w	21.1	19	18.3
Resins (polars), % w/w	38.8	44	44.8
Asphaltenes, % w/w	17.1	16	17.2
MWt, g/mol	534 ^c	585 ^c	532 ^c
Density at 22 °C, g/mL	1.003	1.0035	1.019 ^b
Viscosity at 24 °C, mPa s	> 10,000	17,600–20,000	> 300,000

^a Data from this work.

^b From Ref. [8].

^c By gel permeation chromatography [9].

2.2. Method of *n*-heptane addition to toluene-diluted heavy oil

Primrose heavy oil was first weighed into four glass jars containing preweighed masses of toluene (90, 83, 75, 65 g) to make stock heavy oil concentrations of 10, 17, 25 and 35 wt%. Each stock toluene-diluted heavy oil sample was mixed for 2 h by a horizontal shaker until dissolved. Dissolution was deemed complete after a sub-sample of stock was examined under the light microscope and oil particles were absent. Duplicate sets of nine subsamples of each starting concentration of 10, 17, 25, and 35 wt% heavy oil in toluene were treated with *n*-heptane (in nine separate additions per set) to a total of 72 titrations. Following this, a third test set involved a series of combinations of heavy oil and toluene (total of 34) for which a prescribed solubility δ was achieved when an aliquot of *n*-heptane was added. The solubility parameter δ ranging from 15.2 to 18.2 MPa^{1/2} was used for characterizing the miscibility of the crude oil fluids in the solvents.

Each of the four concentrations of toluene-diluted heavy oils 10, 17, 25, and 35 wt% were titrated as follows. Nine 5-g aliquots of the stock diluted heavy oil were weighed into nine separate 100-mL glass jars and capped immediately. For each experimental trial a known mass of *n*-heptane was added to one 5-g aliquot of the diluted oil in the 100-mL jar (e.g. for 10 wt% heavy oil, nine separate *n*-heptane aliquots ranging from 5.01 to 35 g or the volumes equivalents 7.34 to 51.28 mL were added to nine jars of oil). Each jar was capped and gently hand mixed in 20 end-to-end inversions for total time of 20 s. Immediately after mixing, a sample of the oil-in-heptol mixture was removed for microscopic observations. A portion of the sample was placed in the 100- μ m (or 250- μ m) deep Helma cell, sealed with a 18-mm glass coverslip, and viewed continuously over time using the objectives (40 $\times$, 60 $\times$) of the microscope. Photomicrographs of the undisturbed sample were recorded immediately and thereafter at selected time intervals (every minute for the first 10 min, every 15 min for the first hour, every hour for 4 h, and after 24 or 48 h) as particles began to appear. The sizes and shapes of precipitates and flocs formed were captured in the photomicrographs. This procedure was repeated for the next *n*-heptane addition. For 17 or 25 wt% heavy oil, the added *n*-heptane ranged from 3.51 to 35.0 g or (5.14–51.28 mL), and for 35 wt% the added *n*-heptane ranged from 3.51 to 45.0 g or (5.14–65.92 mL). The first aliquots of *n*-heptane were added as controls to show no precipitate for 24 h in the heptol.

Only two trials could be studied per day. After 24 h of monitoring, the reacted mixture was centrifuged at 1500 $\times$ g force for 30 min at 22 °C. The supernatant was aspirated with a disposable pipette, and collected in another glass jar. It was also examined under the microscope to ensure that no precipitated solids were present. Next, the concentration of residual soluble asphaltene in particle-free supernatant was directly analysed using the CANMET asphaltene analyzer

described below. Refractive index and density of these solutions were measured as well.

Correlations of the calculated Hildebrand solubility parameters of the solution mixtures and their measured refractive indices, and between density and refractive index were determined for all partially deasphalted oils. Comparisons were made with data of the other heavy oils and bitumen dissolved in toluene only. The mass ratios of heptane/toluene (hep/tol) responsible for initiating phase separations in the diluted oils were noted for each oil concentration tested.

2.3. Instruments, procedures and theory

Microscopic observations were made using a Nikon Eclipse E600 microscope equipped with a Nikon Coolpix AE950 digital camera. This microscope was fitted with polarizers, analysers and an Abbé condenser. The objectives used were Plan Fluor ELWD 10×, 40×, and 60×, DICM. The fluids were sealed under the glass cover slip and thus the growth of particles was uninfluenced by any capillary forces in the slide. Observations were performed in the transmittance mode using sodium halogen lamps, and sometimes in fluorescence mode (using mercury lamps) when needed.

Concentrations of asphaltenes in solution before and after *n*-heptane treatment were measured using a near infrared spectroscopic technique developed at CANMET [36]. This CANMET asphaltenes analyzer measures a wide concentration range of up to 20 wt% and as low as 0.01 wt% of soluble asphaltenes in toluene and in heptol. Spectroscopic information on the sample is acquired through a transmittance probe via a fibre optic bundle transmitting light from a tungsten halogen source coupled to a spectrophotometer. Absorption spectra in the near infrared 900–1700 nm region were acquired and treated statistically using principal component analysis. The asphaltenes concentrations in solution were calculated based on the spectroscopic fingerprints and the calibration model. Several calibration curves were made for C-5 asphaltenes in toluene, and for bitumen and heavy oils of known asphaltene content in toluene. After verification with the known standard, the test fluids were measured by directly inserting the probe into the sample. Details on this instrumental technique are published elsewhere [36].

Densities were measured with an Anton Paar DMA 4500 density meter with a precision of ± 0.00001 as certified to NIST (National Institute of Standard and Technology) standards. The sample was injected directly into the cell held at 22.00 ± 0.01 °C, allowed to equilibrate then measured.

Refractive indices of the samples were measured at 22 ± 0.02 °C using an Abbé refractometer by Leica, accurate to ± 0.000015 . The ASTM standard procedures used required exact adherence to all precautionary measures and calibrations for acquiring accurate and precise data to the

fifth decimal place [37]. The solutions must be free of particles that would disperse light. Such samples must therefore be centrifuged before measuring.

The molecular refraction $[R]$ as reported by James and Prichard [38] was defined as follows:

$$[R]_A = \frac{n_D^2 - 1}{n_D^2 + 2} \frac{M_A}{\rho} \quad (1.1)$$

$[R]_A$ is the molecular refraction and has units of molecular volume cubic meter. They defined the molar refraction of the mixture $[R]_{A,B}$ as the sum of the contributions of the components. The definition used for the molecular refractions of the two components in the mixture of A and B, $[R]_{A,B}$ is thus

$$[R]_{A,B} = x_A[R]_A + x_B[R]_B$$

$$= \frac{n_{A,B}^2 - 1}{n_{A,B}^2 + 2} \left(\frac{x_A M_A + x_B M_B}{\rho_{A,B}} \right) \quad (1.2)$$

Here M_A , M_B are the molar masses of substances A and B, x_A and x_B are the mole fractions of A and B.

The Hildebrand solubility parameter δ describes the miscibility of solvents [39], where δ in $\text{MPa}^{1/2}$ is defined as

$$\delta = \left(\frac{\Delta E^{\text{V}_m}}{V_m} \right)^{1/2} = \left(\frac{\Delta H^{\text{V}_m} - RT}{V_m} \right)^{1/2} \quad (1.3)$$

and ΔE is the internal energy of vaporization, V_m is the molar volume of the liquid, ΔH is the enthalpy of vaporization, R is the universal gas constant, and T is absolute temperature. SI units are used throughout.

The solubility parameter (also related to the cohesion energy density c , where $c = \delta^2$) of a mixture is useful for indicating when immiscibility occurs [40]. This is useful for gauging conditions for emulsion stability in mixed diluents. The solubility parameter for mixtures (δ_{mix}) can be used to determine phase separation in the diluted heavy oil systems, under the framework of regular solution theory and may be calculated by

$$\delta_{\text{mix}} = \sum_i^n \delta_i \Phi_i \quad (1.4)$$

where δ_i is the solubility parameter (in $\text{MPa}^{1/2}$) of component i and Φ_i is the volume fraction of i .

Two correlations were developed for the present study, relating solubility parameters with the measured refractive indices δ_{mix} vs. n_D , and n_D vs. densities for the mixtures. These correlations are useful for determining either density or refractive index of heavy oil in relatively nonpolar solvents when either property is known and instruments are unavailable to measure the other.

The London dispersion interactions are related to solubility parameter through dispersive interactive forces between molecules [23,39]. Energy of vaporization and ultimately the solubility parameter depends on dispersive

forces [40]. The molar refraction R_A is

$$R_A = \frac{n_D^2 - 1}{n_D^2 + 2} \frac{\text{MWt}}{\rho} = \frac{N_A \alpha}{3\epsilon_0} \quad (1.5)$$

and the fractional refractive index F_{RI} is

$$F_{RI} = \frac{n_D^2 - 1}{n_D^2 + 2} = \frac{\rho N_A \alpha}{3\epsilon_0 \text{MWt}} \quad (1.6)$$

where refractive index $RI = n_D$, ρ is the density, ϵ_0 is the permittivity of a vacuum, N_A is Avogadro's number, and MWt is molecular weight, α is polarizability [38,41,42].

We adopt the arguments of Buckley et al. [23] used for their study on the onset of asphaltenes precipitation in crude oils. They used the Lorenz–Lorentz equation [43] and correlated refractive index and the solubility parameter.

They also used the established relationship between the van der Waals equation of state cohesion parameter a and solubility parameter δ ($\text{MPa}^{1/2}$):

$$\delta \approx \frac{a^{1/2}}{V_m} = \frac{\left(\frac{2\pi N_A^2 C}{3r^3}\right)^{1/2}}{V_m} = \frac{\left(\frac{2\pi N_A^2 C}{3r^3}\right)^{1/2}}{\frac{\text{MWt}}{\rho}} \quad (1.7)$$

Substituting C where

$$-\frac{C}{r^6} = -\frac{\sqrt{3}h\nu_e(n_D^2 - 1)^2(r/2)^6}{4(n_D^2 + 2)^{3/2}r^6} \quad (1.8)$$

$$\delta \approx \left[\frac{3\pi h\nu_e}{384r^3}\right]^{1/2} \frac{r^3}{V_m/N_A} \left(\frac{n_D^2 - 1}{(n_D^2 + 2)^{3/4}}\right) \quad (1.9)$$

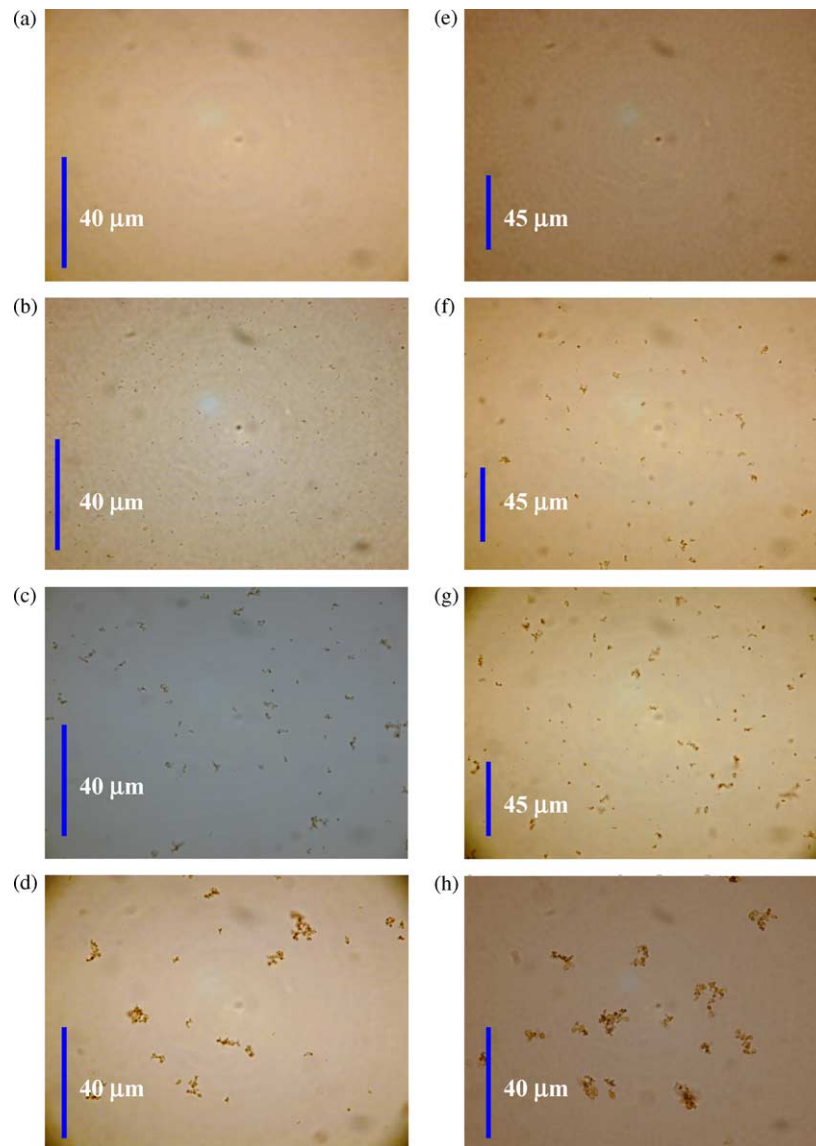


Fig. 1. (a)–(h) Micrographs of asphaltenes particles precipitated in time after ((a)–(d)) 6.14 g *n*-heptane (mass ratio hep/tol = 1.37), and ((e)–(h)) 6.83 g *n*-heptane (mass ratio hep/tol = 1.52) were added to two separate 5 g aliquots of a 10-wt% heavy oil in toluene. Time of observation, (a)–(d) 0, 2, 2.5, 24 h; (e)–(h) 0, 1, 2, 4 h. Scale is on micrograph.

$$\delta \propto \frac{n_D^2 - 1}{n_D^2 + 2} \quad (1.10)$$

where a is the van der Waals cohesion parameter $a = (2\pi N_A C)/3r^3$; C is the coefficient of the distance dependence of species; r is the hard sphere diameter. Buckley et al. assumes $r/2$ is the equivalent radius of the asphaltene molecule [23]; V_m is the molar volume, which equals MW/ρ ; h is Planck's constant; and ν_e is the absorption frequency of light [23]. Buckley et al. [23] indicated the right side Eq. (1.8) is the energy of interaction between asphaltene molecules in a solvent medium at the same absorption frequency (London dispersion interaction is defined in the text by Israelachvili, 1991 [44]). London's energy of interaction $-C/r^6$ between individual molecules at distance r defined in terms of frequency of light and polarizability is

also described in classical physical chemistry textbooks[41, 45,46]. Although the Lorenz–Lorentz treatment has not been extended to mixtures, the above linear relationship could be paralleled with the correlations found between measured F_{RI} and a calculated *effective* $\bar{\delta} = \delta_{mix}$ in this work. Provided the material is relatively nonpolar, δ can be related to the fractional refractive index. Therefore, the effective $\bar{\delta}$ for these relatively nonpolar materials should be related to the refractive index by Eq. (1.9) as summarized by previous authors.

3. Results and discussion

The de-asphalting of Primrose heavy oil as a function of time is shown in micrographs of Figs. 1–5 for each starting

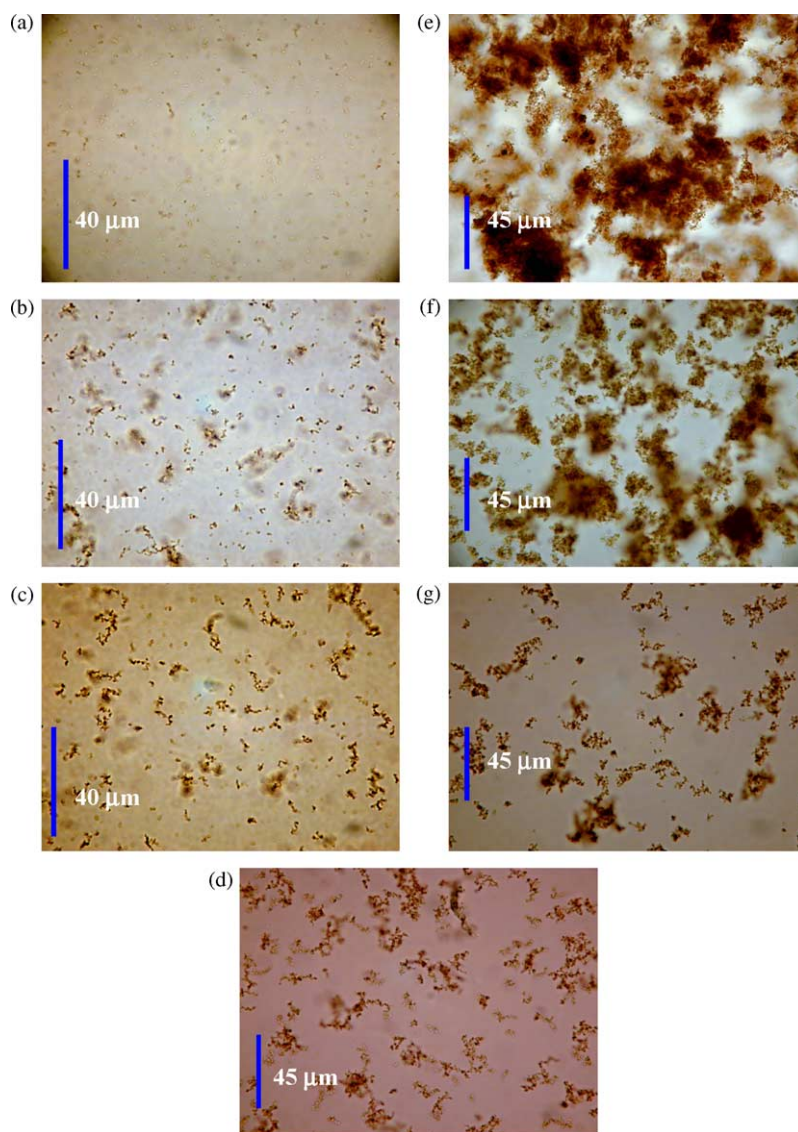


Fig. 2. (a)–(g) Micrographs of asphaltene particles precipitated in time after 7.51 g of *n*-heptane was added to 5 g of a 10-wt% heavy oil in toluene (mass ratio hep/tol 1.67). Time of observation (a)–(g) 0, 5, 6, 35 min, 1, 2, 24 h. Scale is on micrograph.

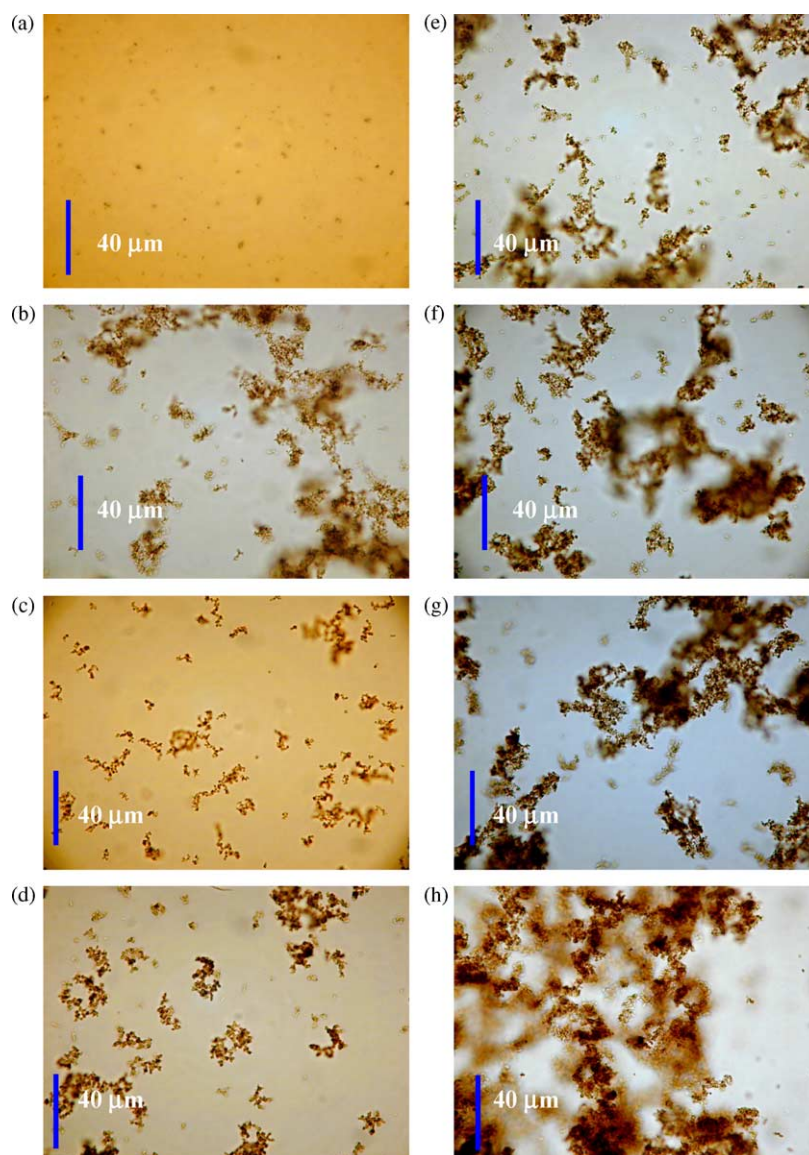


Fig. 3. (a)–(h) Micrographs of asphaltenes particles precipitated in time after ((a)–(d)) 7.51 g *n*-heptane (mass ratio hep/tol 1.81) and ((e)–(h)) 10.03 g *n*-heptane (mass ratio hep/tol 2.4) were added to 5 g aliquots of 17 wt% heavy oil in toluene. Time of observation (a)–(d) 0, 1, 2, 24 h; (e)–(h) 0, 1, 2, 24 h. Scale is on micrograph.

concentration of heavy oil in toluene as the asphaltenes precipitated during equilibration. Indicated are the mass ratios of hep/tol and the time after *n*-heptane addition. Fig. 6(a) and (b) shows the relationships between concentrations of asphaltenes in solution before and 24 h after *n*-heptane addition for each starting oil concentration. Fig. 7 describes the relationships between the mass ratios of precipitated/added asphaltenes vs. the mass ratios hep/tol/heavy oil. Fig. 8 describes a phase diagram in terms of volume fractions of toluene, oil and *n*-heptane indicating the conditions where asphaltenes precipitated for each starting oil concentration. The measured refractive indices as a function of densities of solutions are presented in Fig. 9. Included in the data set of Fig. 9 are data for the supernatant of mixtures after 24 h of

observation, for other nonpolar pure solvents, for asphaltenes solutions in toluene, and for maltenes in heptol. The supernatants of the partially deasphalted heavy oils (PDHO) consist of mixtures of *n*-heptane, toluene, maltenes and residual asphaltenes. Fig. 10 shows plots of solubility parameter of mixture δ_{mix} vs. fractional refractive index F_{RI} for heavy oils and asphaltenes in toluene only. Fig. 11 shows the linear correlation of solubility parameter δ_{mix} ($\text{MPa}^{1/2}$) vs. fractional refractive index F_{RI} measured for all supernatants of *n*-heptane-treated heavy oil after 24 h equilibration. Fig. 12 shows $\Delta\delta_{\text{mix}}$, ($\text{MPa}^{1/2}$) (calculated from δ_{mix} of mixtures minus predicted (1.16)) vs. F_{RI} . Fig. 13 shows wt% asphaltenes precipitate vs. solubility parameter δ_{mix} of residual supernatant 24 h after *n*-heptane addition.

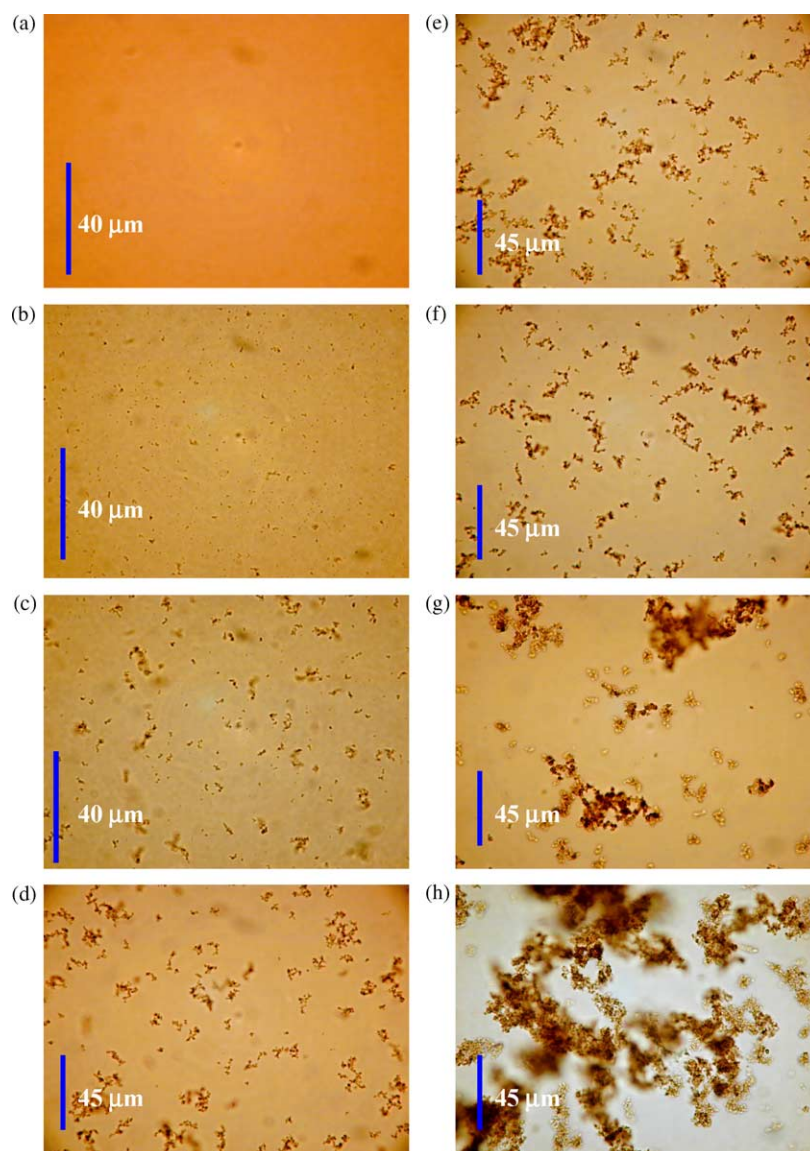


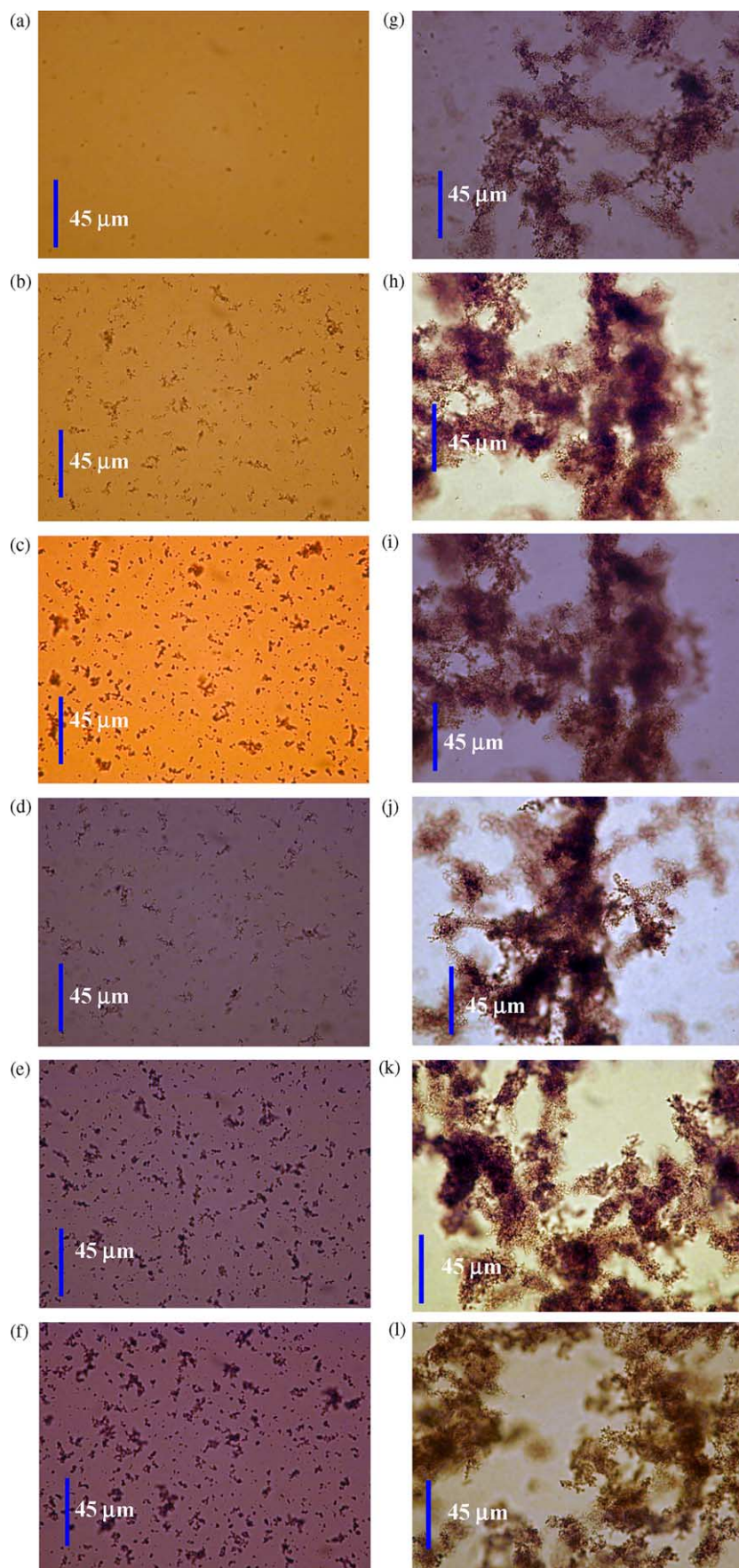
Fig. 4. (a)–(h) Micrographs of asphaltene particles precipitated in time after ((a)–(g)) 7.51 g *n*-heptane (mass ratio hep/tol 2.0) and (h) 35 g *n*-heptane (mass ratio hep/tol 9.0) were added to 5 g aliquots of 25 wt% heavy oil in toluene. Time of observation (a)–(g) 0, 2, 18, 45 min, 1, 2, 24 h; (h) 0. Scale is on micrograph.

3.1. Evolution of asphaltene precipitates after *n*-heptane additions

3.1.1. *n*-Heptane additions to 10 wt% heavy oil

Photomicrographs in Figs. 1 and 2 are examples of the asphaltene precipitation observed over time for the 10-wt% diluted oils. At a *n*-heptane to toluene mass ratio (hep/tol) of 1.21 (5.01 g *n*-heptane, volume ratio of heptane/toluene = 1.54) and lower, no precipitation was observed for 24 h (no photomicrographs are shown). At hep/tol of 1.37 (6.14 g *n*-heptane, or volume ratio of heptane/toluene 1.73), a lag time of 2 h passed before the precipitates were seen under the microscope (Fig. 1(a)–(d)). Precipitation was seen first as small dots ($\sim 1\ \mu\text{m}$ —diffraction limit). The dots then grew into strings of particles and remained this way for 24 h. In Fig. 1(e)–(h) as the mass of *n*-heptane increased hep/tol =

1.52 (6.83 g *n*-heptane, and volume ratio of heptane/toluene 1.92), dots of particles started to appear after 1 h. Strings of particles appeared at 2 h, and clusters within 24 h. The 24-h and 2-h aggregates were similar. Fig. 2(a)–(g) shows hep/tol = 1.67 (7.51 g *n*-heptane, volume ratio of heptane/toluene was 2.11) where precipitation was immediate. Within 5 min, the precipitates appeared in several forms, as mixed populations of small spots, tiny dots, strings, and clusters of particles. In 35 min they grew into many larger flocs. At another higher aliquot hep/tol = 2.23 (10.03 g *n*-heptane and volume ratio of heptane/toluene 2.83), even larger flocs were formed immediately (not shown). The flocs made up of smaller strings of particles appeared like mass networks that were gel-like in appearance. These were fragile and could be broken into smaller clusters by simple wrist inversions or mixing.



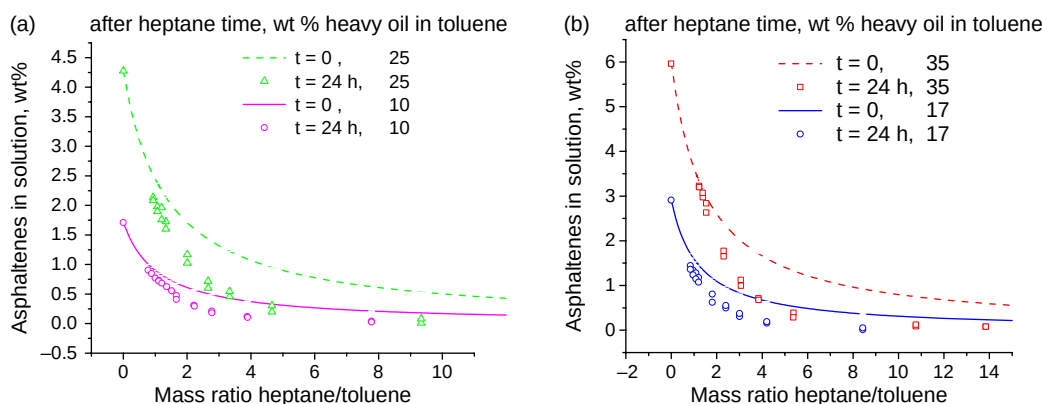


Fig. 6. (a) and (b) Soluble asphaltenes vs. mass ratio heptane/toluene at $t=0$ calculated from Eq. (1.12) (lines), analytical points are open symbols for asphaltenes measured in the supernatant after 24 h. Initial concentrations of heavy oil (a) 10, 25 wt% (b) 17, 35 wt% in toluene are shown in legend. The departure of data points from the line denotes onset of asphaltenes precipitation.

3.1.2. *n*-Heptane additions to 17 wt% heavy oil

As the concentration of the starting heavy oil increased to 17 wt%, the spots became strings sooner than for 10 wt% above. Fig. 3(a)–(d) illustrates the growth of the precipitates over time. No particles were observed at or below mass ratio hep/tol = 1.21 (5.01 g *n*-heptane, volume ratio of heptane/toluene 1.53) in 24 h. At hep/tol = 1.81 (7.51 g *n*-heptane, volume ratio of heptane/toluene 2.29), the spots appeared immediately. These grew over time into larger strings and clusters in 1, 2, and 24 h, respectively. Fig. 3(e)–(h) shows that as the *n*-heptane (10.03 g *n*-heptane, or volume ratio heptane/toluene of 3.04) increased and more asphaltenes precipitated, the interactions with other string-like flocs increased and particles clustered into larger networks of floc-like materials immediately. Large masses of gel-like flocs appeared and settled to the bottom of the vessel.

3.1.3. *n*-Heptane additions to 25 wt% heavy oil

Fig. 4(a)–(h) shows the precipitated asphaltene particles formed by *n*-heptane titration of the 25-wt% oil in toluene. At hep/tol = 1.34 (5.01 g *n*-heptane, volume ratio heptane/toluene 1.69), there were no precipitates for 24 h (no micrographs shown). A change to hep/tol = 2.00 (7.51 g *n*-heptane, volume ratio heptane/toluene 2.54) shown in Fig. 4(a)–(g), caused the appearance of small dots in 1 min, strings and more dots in 2 min, clusters in 10 min, and larger aggregates growing in 18–45 min. After 24 h the clusters appeared similar to those formed in titrating the 17-wt% heavy oil at hep/tol = 1.81 above. However, as *n*-heptane increased (e.g. hep/tol from 2.6 to 9.3), large flocs formed immediately and appeared as fractal-like masses (no micrographs shown). Fig. 4(h) shows flocs for hep/tol 9.0 (35 g *n*-heptane and volume ratio heptane/toluene 11.8). Fine-tuning of the addition of *n*-heptane at hep/tol between

1.34 and 2.00 would probably show a gradual change in the particles similar to the particle growth for the 10-wt% stock. Beyond these concentrations, as more *n*-heptane was added, the gel-like flocculated asphaltenes appeared to be networked floc particles and could not be differentiated from flocs formed at slightly lower concentrations. The mass of networked asphaltenes flocs settled out with a sharp moving interfacial boundary in time.

3.1.4. *n*-Heptane additions to 35 wt% heavy oil

At and below hep/tol = 1.39 (4.00 g *n*-heptane, volume ratio heptane/toluene 1.75), no spots or precipitates were observed during 72 h of observations (no micrographs shown). Fig. 5(a)–(c) shows for hep/tol = 1.54 (4.51 g *n*-heptane, volume ratio heptane/toluene 1.95), spots were formed immediately and, in 16 min, more aggregates appeared as strings and spots held together in groups. After 1 h and up to 24 h thereafter, all remained as small clusters. The higher dosage of hep/tol = 2.3 (5.01 g *n*-heptane and volume ratio heptane/toluene 2.9) produced clusters 2 min after addition and not immediately (Fig. 5(d)–(g)). At hep/tol = 3.07 (volume ratio heptane/toluene 3.9) the large networks were very apparent at 1 h 15 min (not shown). Fig. 5(i)–(l) shows photomicrographs of precipitates for hep/tol from 3.84 to 13.8 (9.97–45 g *n*-heptane, or volume ratio heptane/toluene 4.8–17.5, immediately after addition).

From all these qualitative microscopic observations, it appears that the precipitation time for the asphaltene particles depends on the initial concentration of the heavy oil in toluene. Even at similar hep/tol values, the lag time before observing precipitation decreased with increasing starting oil concentration. The appearance of precipitates was sequenced as spots, strings, clusters, and large flocs, especially in the 10-wt% heavy oil in toluene as starting sample. This phenomenon was re-confirmed

Fig. 5. (a)–(l) Micrographs of asphaltene particles precipitated in time after ((a)–(c)) 4.51 g *n*-heptane (mass ratio hep/tol 1.54), ((d)–(g)) 5.01 g *n*-heptane (mass ratio hep/tol 2.3), and ((h)–(i)) 9.97 g *n*-heptane (mass ratio hep/tol 3.38), and ((j)–(l)) 12.49, 17.47, 45 g *n*-heptane added to 5 g aliquots of 35 wt% HvOi in toluene. Time (a)–(c) 0, 1, 21 h; (d) 13 min; (e) 20 h; (f) 21 h; (h) 0. Scale is on micrograph.

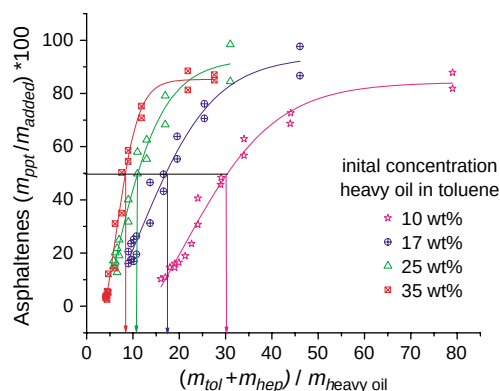


Fig. 7. Mass ratio of precipitated (ppt) to total asphaltenes vs. $(m_{\text{tol}} + m_{\text{hep}}) / m_{\text{heavyoil}}$ mass fraction of heptol in heavy oil. Arrows indicate mass heptol/mass heavy oil for which 50% of initial soluble asphaltenes are precipitated.

by observing 102 titrations for various combinations of initial concentrations of heavy oils in toluene with *n*-heptane.

The results for the measured concentrations of soluble asphaltenes after 24 h plotted against the solution physical properties appear in another section below. The onset of precipitation is in agreement with Yudin's hypothesis that onset conditions are dependent on starting concentrations of oil in the solvent [47], and supports our original hypothesis of time dependency for growth as appeared through the light microscope.

3.2. Concentration of asphaltenes in solution 24 h after *n*-heptane—at varied (*n*-heptane + toluene)/heavy oil ratio

The results are categorized by weight percentage of heavy oil in toluene (tol) starting materials before *n*-heptane addition. Volume percent asphaltenes (asph) is $100 \times \Phi_{\text{asph}}$ and volume percent precipitate (ppt) is $100 \times \Phi_{\text{ppt}}$ where m , mass; V , volume; Φ_{asph} , volume fraction asphaltenes in solution; Φ_{ppt} , volume fraction precipitated asphaltenes

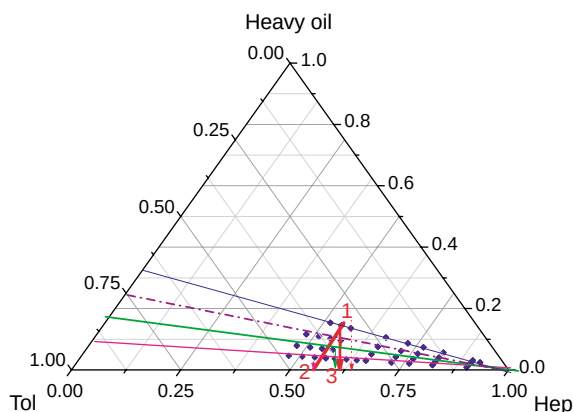


Fig. 8. The ternary diagram of volume fractions of toluene, heavy oil and heptane (clockwise). The inset triangle lines 1-2-3 show the onset-of-precipitation region at different starting concentrations of heavy oil in toluene. Beyond this region to the right, precipitation is rapid.

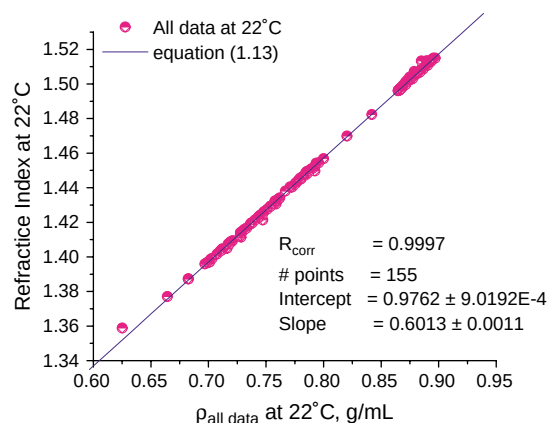


Fig. 9. Linear fit to all refractive index and density data of oils in organic solvents. See inset for slope, intercept and correlation coefficient.

(ppt), init, initial; resid, residual. The volume fraction of precipitated asphaltenes is defined as

$$\Phi_{\text{ppt}} = \frac{V_{\text{asph}}^{\text{ppt}}}{V_{\text{total}}} = \frac{m_{\text{asph}}^{\text{init}} - m_{\text{asph}}^{\text{resid}}}{\rho_{\text{asph}} V_{\text{total}}} \quad (1.11)$$

The amounts of precipitates were measured by difference from mass added and mass soluble at each concentration of toluene-diluted heavy oil after equilibrium time of 24–48 h in *n*-heptane. The density of asphaltene ρ_{asph} was measured at 1.19 g/mL by using a pycnometer and the value was confirmed using the DMA-4500 for known masses C-5 asphaltenes in toluene.

From a mass balance the analytical concentrations of asphaltenes in the heptane/toluene mixture at $t=0$ was:

$$W_{\text{asph}}^{t=0} = \frac{W_{\text{asph}}^{\text{heavyoil}}}{1 + \left(1 + \frac{m_{\text{hep}}}{m_{\text{tol}}}\right) \frac{m_{\text{tol}}}{m_{\text{heavyoil}}}} \quad (1.12)$$

where $W_{\text{asph}}^{t=0}$ is the weight percentage of asphaltenes in oil added at time $t=0$, m_{hep} is the mass of heptane in

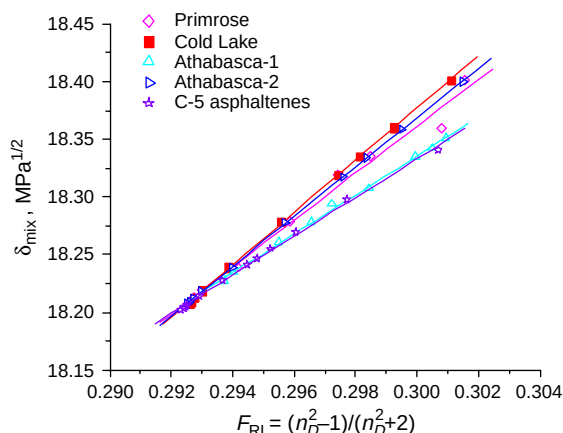


Fig. 10. Solubility parameter of mixture δ_{mix} vs. fractional refractive index F_{RI} for heavy oils and asphaltenes in toluene showing linear correlations with data. See Table 3 for constants and Eq. (1.4) for calculation of δ_{mix} in $\text{MPa}^{1/2}$.

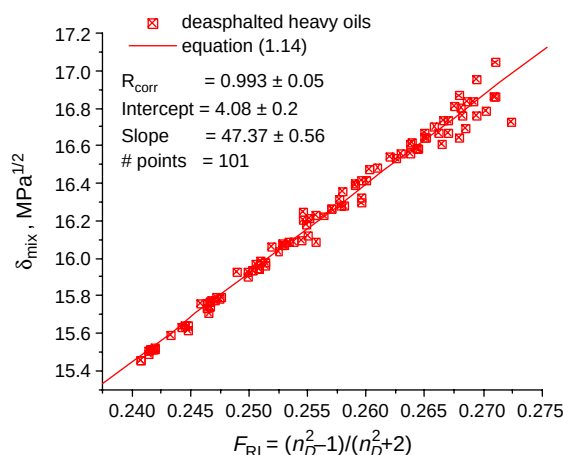


Fig. 11. Linear correlation for solubility parameter δ_{mix} ($\text{MPa}^{1/2}$) vs. fractional refractive index F_{RI} measured for all supernatants of n -heptane-treated heavy oil after 24 h equilibration.

the solution, m_{tol} is the mass of toluene in the heavy oil solution, m_{heavyoil} is the mass of heavy oil in the starting diluted sample, $W_{\text{asph}}^{\text{heavyoil}}$ is the weight percentage of asphaltenes in original heavy oil. Plots of $W_{\text{asph}}^{t=0}$ as a function of mass ratio of n -heptane to toluene for the four oils are shown in Fig. 6(a) and (b). Open symbols depict the asphaltenes content in supernatant solution after 24 h. As the hep/tol increased a reduction of soluble asphaltenes occurs.

Fig. 7 shows plots of mass fraction of asphaltenes (precipitated over added) for aliquots of n -heptane added to four starting concentrations of Primrose heavy oil in toluene after 24 h rest, plotted against the mass fraction (toluene + heptane)/heavy oil in the sample. The family of curves shows that fraction of asphaltenes precipitated depends on the starting concentration of heavy oil (see legend) and the ratio of total solvent to heavy oil.

Fig. 8 shows a phase diagram of the volume fraction soluble asphaltenes after an equilibration time of 24–48 h vs. volume fraction of heptane, toluene, and heavy oil. The

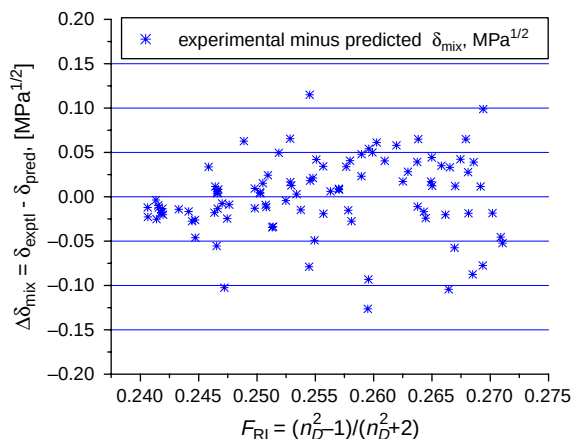


Fig. 12. $\Delta\delta_{\text{mix}}$, ($\text{MPa}^{1/2}$) (calculated from δ_{mix} of mixtures minus predicted (1.16)) vs. F_{RI} .

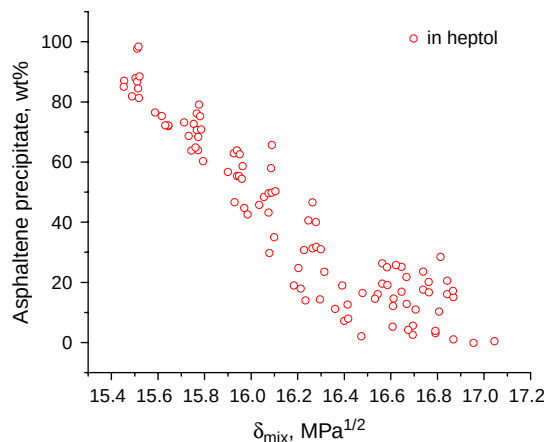


Fig. 13. Asphaltenes precipitate vs. solubility parameter δ_{mix} ($\text{MPa}^{1/2}$) of residual supernatant 24 h after n -heptane addition. Precipitate = $100 \times (\text{mass asph added} - \text{mass asph soluble}) / \text{mass asph added}$, in heptol.

small inset triangle lines show the onset-of-precipitation region, at different starting toluene and heavy oil concentrations. Right of the inset triangle region, massive precipitation occurs rapidly. Soluble asphaltenes are present in solution in finite amounts at the extreme right corner of the phase diagram.

3.3. Refractive index, density and Hildebrand solubility parameters of solutions

Fig. 9 is a plot of the refractive index (RI or n_D) vs. density ρ linearly correlated by Eq. (1.13) for data of nonpolar linear alkanes (C5–C10), toluene, bitumens, heavy oils, asphaltenes and maltenes at various concentrations. Also a linear Eq. (1.14) is derived for the fractional refractive index (F_{RI}) vs. density, which is consistent as predicted with Eq. (1.6). From this, another predictive relationship of (F_{RI}) with solubility parameters is derived using Eq. (1.9) as the theoretical basis of Eq. (1.16). One can utilize both mathematical relationships in practical situations, to determine whether one heavy oil system is more polar than another, by noting the deviation from the linearity.

Table 2 summarizes the constants for other linear equations representing refractive index and densities data for individual oils in toluene. From Eqs. (1.13) and (1.14) one can calculate the refractive indices of the difficult-to-measure materials. Buckley et al. [23] reported an extrapolated RI of 1.72 for density of 1.2 g/mL for asphaltenes. However, the temperature was not given. Asphaltene density 1.19 g/mL at 22 °C as measured in our study, gave an RI of 1.69168 from the correlations below.

$$\text{RI}^{22\text{ }^\circ\text{C}} = 0.97616 + 0.60128\rho^{22\text{ }^\circ\text{C}} \quad (1.13)$$

$$F_{\text{RI}}^{22\text{ }^\circ\text{C}} = 0.02 + 0.309\rho^{22\text{ }^\circ\text{C}} \quad (1.14)$$

The physical properties as correlated above appear to be material-independent as long as the solvents are kept

Table 2

Linear correlations between refractive index and density for various heavy oils and asphaltenes at increased concentrations and for toluene + *n*-heptane mixtures

Sample	Intercept	Slope	R_{corr}	# data points
All data	$0.9762 \pm 9.02\text{E-}4$	0.601 ± 0.001	0.9997	155
Primrose in toluene	0.970 ± 0.008	0.608 ± 0.009	0.9995	10
Cold Lake in toluene	0.9753 ± 0.003	0.6021 ± 0.003	0.9999	10
Athabasca-2 in toluene	0.990 ± 0.002	0.5851 ± 0.003	0.9999	10
C-5 Athab-2 asph in tol	0.770 ± 0.01	0.8394 ± 0.0003	0.9988	12
C-5 Athab-1 asph in tol	0.824 ± 0.05	0.777 ± 0.06	0.9914	5
Primrose residual in heptol	0.975 ± 0.001	0.603 ± 0.001	0.9998	66
Toluene + <i>n</i> -heptane	0.981 ± 0.001	0.591 ± 0.001	1.0	9

similarly nonpolar and the measuring temperatures remain at 22 °C. To date, we have found limited data in the literature correlating density and RI data in crude oils and none for diluted heavy oils. In practice as the heavy oil fraction in toluene becomes greater, measurements of refraction of light with even a sensitive refractometer is not possible. In these cases Eq. (1.13) is useful and finds an application in pilot operations for bitumen recovery. The limit for accurate measurements of refractive index was reached at about 35 wt% heavy oil in toluene. Unlike refractive index, density can be measured for much higher concentrations of heavy oils or asphaltenes in the solvent, or even without solvents.

There is a general correlation between refractive index and polarizability [39,48] and density as shown in Eq. (1.6). For the above data in Table 2 only the refractive index and density of relatively nonpolar materials are linearly related. However, if a deviation from the correlation occurs, one could postulate that perhaps contaminants or polar materials in the crude oil or sample are affecting the behaviour. This inference would be plausible provided accurate measurements were made.

The physical properties of the heavy oils, bitumens and asphaltenes in toluene and deasphalted oils in heptol follow the established basic physics described in Eqs. (1.6), (1.7) and (1.9) above for low-molecular-weight materials, even though the oils are chemically complex. The slopes and intercepts for highly correlated linear curves of δ_{mix} vs. F_{RI} (from measured RI) of the individual oils in toluene are summarized in Table 3. These differed slightly for each system.

Fig. 10 shows the graphs of δ_{mix} vs. F_{RI} for the diluted oils and asphaltenes dissolved in toluene. Initially the plots of δ_{mix} vs. F_{RI} for the various concentrations of heavy oils and asphaltenes in toluene only were not linear, as was also found for the densities. This indicates that the oils contribute to solubilities in addition to the solvents. After including the solubility parameters for heavy oils (19.1 MPa^{1/2}) and asphaltenes (20.4 MPa^{1/2}) as reported for crude oils[49] in the basic volumetric mixing rules to calculate the δ_{mix} ,

linearity occurred [50,51]. Differences in values of δ_{mix} at 22 and 25 °C were small [39,52,53].

For both heavy oils and partially deasphalted heavy oils and the solvents, the measured refractive index vs. measured density (Fig. 9 shown previously) was linear. However, δ_{mix} vs. F_{RI} data for both heavy oils and partially deasphalted Primrose do not fall on the same linear curve. Fig. 11 shows the δ_{mix} vs. F_{RI} for partially deasphalted heavy oil in heptol. Fig. 12 shows the difference, $\Delta\delta_{\text{mix}}$ (calculated parameters minus predicted) vs. F_{RI} , illustrating the spread of the data.

The linear equation for RI vs. δ_{mix} is Eq. (1.15) and for δ_{mix} vs. F_{RI} is, as per Eq. (1.10), is shown in Eq. (1.16) with its own constants:

$$n_D = 0.78422 + 0.03958\delta_{\text{mix}} \quad (1.15)$$

Eq. (1.15) relates RI and solubility parameter for the present data and has practical utility in the laboratory. Eq. (1.16) is the theoretically derived relationship between solubility parameter δ_{mix} (MPa^{1/2}) and fractional refractive index expected to hold for relatively nonpolar media:

$$\delta_{\text{mix}} = 4.08 + 47.37F_{\text{RI}} \quad (1.16)$$

Using data tables on the solvents published in the handbooks [39], Buckley et al. [23,43] correlated the fractional refractive index F_{RI} with the solubility parameters δ_{mix} (MPa^{1/2}) of solvents mixtures and presented the following relationship

Table 3

Linear correlations between solubility parameter of mixture δ_{mix} (MPa^{1/2}) and F_{RI} for oils in toluene

Heavy oil	Intercept	Slope	R_{corr}	# data points
Primrose	2.2 ± 0.2	20.4 ± 0.8	0.994	10
Cold Lake	11.6 ± 0.0	22.7 ± 0.1	1.0	10
Athabasca-1	13.3 ± 0.1	16.9 ± 0.3	0.999	9
Athabasca-2	11.9 ± 0.0	21.5 ± 0.1	1.0	10
Athab-1-C5-asph	13.3 ± 0.1	16.8 ± 0.0	0.999	12

$$\delta_{\text{mix}} = 2.904 + 52.042F_{\text{RI}} \quad (1.17)$$

The present linear relationships support the regular solution theory in as much as the crude oils consist of two lumped pseudocomponents, asphaltenes and deasphalted oils. For the deasphalted oils as well, only when the solubility parameter of the residual oils was proportioned into the δ_{mix} ($\text{MPa}^{1/2}$) that all the data aligned along the same straight line for δ_{mix} vs. F_{RI} .

For residual oil in heptol, the δ_{mix} vs. F_{RI} slopes and intercepts differ from the slope and intercept values of heavy oils and bitumens in toluene (cf. inset Fig. 11 and Table 3), indicating some non-polar character. Solvent properties influence the behaviour. Buckley's correlation [23] appeared to be dominated by the nonpolar dispersion properties of the solvents.

Several researchers have used the refractive index as a property for detecting the onset of precipitation. Buckley et al. [23,43,50] used the Hildebrand solubility parameters [52] along with refractive indices as indicators of the onset of asphaltene precipitation for conventional crude oils, showing that the onset occurred at $\text{RI} = 1.42$. Time was not shown to be a factor in their work.

The data plotted in Fig. 13 show the increased asphaltenes precipitation from solution as the solubility parameter δ_{mix} decreases. The particles separate out below $\delta_{\text{mix}} = 16.4$ and $F_{\text{RI}} = 0.27$ in this case. The δ_{mix} at which precipitation by *n*-heptane takes place varies with the starting concentrations of heavy oil in toluene, shown earlier. However, for δ_{mix} smaller than $16.4 \text{ MPa}^{1/2}$ the phase separation of asphaltenes from solution was observed to be very pronounced. This behaviour is in agreement with the phase separation of the particles observed by microscopy. Phase separation is gradual at decreased mass ratios of precipitant-to-solvent. Previous workers have shown correlations, in which the higher-molecular-weight asphaltenes are directly proportional to the solubility parameters of the fluids, i.e. volume ratio of precipitant to solvent and oil [35]. Resin has been ascribed as a crude oil component that complexes with asphaltenes to increase their solubility in crude oils and influence the stability of not only emulsions but those of asphaltenes in the crude oils [54–59]. These asphaltenes that remain in solution as the δ_{mix} is lowered with *n*-heptane are in a high resin to asphaltene mass ratio environment and are expected to be stable in solution.

The Hildebrand solubility parameter has been used in the thermodynamic modelling of asphaltenes phase behaviour by several authors [19,35,60]. Mitchell and Speight [12] concluded that the aromatics have greater dispersion forces and higher solution energies, making them better solvents than alkanes. Mitchell and Speight [12] related the solubility parameters of the solvent mixtures to the amount of asphaltenes precipitated. They explained the process of dissolution of asphaltenes as involving the diffusion of solvent to the micelle core. They postulated that the

components held by weaker forces in the asphaltene micelle would dissolve first. They also indicated that the system solvation energy must be suitable to overcome the cohesion forces. Cohesive energy density of the alkanes increases with their molecular weights. Pentane is therefore a better nonsolvent than *n*-heptane.

Ferworn showed in his study of heavy oils and asphaltenes, that the quantity of precipitated asphaltene can be correlated with their molecular weight and solubility parameter, as well as the number of carbon atoms in the alkane precipitant [35]. The higher molecular weights are precipitated first; hence, one can selectively remove various molecular weights by the choice of alkanes. Mitchell and Speight reported [12] that a surface tension of 25 mN/m of the solvent/precipitant was a demarcation of a solvent or a precipitant. Values larger than 25 mN/m denote a precipitant, smaller values a solvent.

The correlations shown in this present study has some practical application. With the addition of one aliquot of *n*-heptane (per sample), the remaining residual oils may contain lower molecular weight asphaltene fractions, while the precipitate contains more of the higher molecular weight asphaltenes. The measured physical properties (i.e. refractive index and density) reflect the smaller molecular weight material in heptol.

Results on the physical properties such as density, refractive index, and solubility parameters for toluene, *n*-heptane and heavy oil systems were presented. The solubility parameter is important to predict stability of heavy oil in the solution. The precipitation of asphaltene and formation of flocs in a mixed diluent may have influence on emulsion formation and stability in extraction processes. This is not surprising considering that a build-up of layers of asphaltenes in the oil/water interface occurs over time in mixed solvents. Reports are widely varied as various ratios of heptane/toluene are used with different oils [59,61–67]. For process emulsions, emulsions become unstable as flocs become larger, and the roles of the residual oil components at the interface would change as their resin and asphaltenes composition change. Thus an emulsion in mixed solvents will be more complex than a single solvent, especially in dynamic conditions [68].

4. Conclusions

The amount of asphaltenes that precipitates depends on the concentration of the starting material after equilibrium is established. Precipitation kinetics near onset point depends on the initial concentration of the heavy oil in toluene. Even at similar heptol values, lag (delay) time before precipitation decreases with increasing starting oil concentrations e.g 2 to 1 h to minutes. A lag time was confirmed by visual evidence of precipitation by microscopy.

As observed by optical microscopy, the structures of asphaltene precipitate during formation and growth depends

on time as well as both mass ratio of initial heavy oil/toluene and *n*-heptane added. The most diluted oil shows the most detailed time-dependent deposition and growth response. For the very diluted heavy oil-toluene solution, asphaltene particles precipitated in the following growth pattern: first as spots which grew into strings then strings clustered into small flocs which grew to large masses of fractal-like flocs. This sequence of growth was repeated at higher concentrations but occurred much faster.

Low asphaltene concentrations in toluene were measured for the first time with the CANMET asphaltene analyzer, making possible accurate analytical data. The concentration of soluble asphaltene left in solution at increased hep/tol after 24 h followed the same shape as the $t=0$ curve defined for starting concentrations vs. hep/tol. A phase diagram of precipitated asphaltene with solvents showed when rapid precipitation occurs. A sigmoidal relationship exists between the weight percentage of asphaltene precipitated and heptol/heavy oil ratio.

A linear relationship with correlation coefficient of 0.999 was established for refractive index and density of residual solutions of heavy oil in heptol or oil in toluene at 22 °C; $RI = 0.97616 + 0.60128 \rho$. All density/RI data for all other heavy oils and asphaltene in nonpolar solvents and mixed solvents were correlated to the same line. The equation affords some ability to calculate density from RI and vice-versa.

Solubility parameters of mixtures δ_{mix} (=effective $\bar{\delta}$) $\text{MPa}^{1/2}$ of deasphalted oils in heptol were linearly correlated with F_{RI} the fractional refractive index $\delta_{\text{mix}} = 4.08 + 47.37 F_{\text{RI}}$. Heavy oils, asphaltene, and bitumen in toluene were also linearly correlated with both refractive index and fractional refractive index, with small differences in slopes and intercepts, between oils. The correlations were close to Buckley's published correlation for crude oils. Using two equations, asphaltene density of 1.19 g/mL was found from its solubility parameter δ of $20.4 \text{ MPa}^{1/2}$. This was also confirmed by direct measurement of asphaltene density by pycnometry.

Complex heavy oils appeared to follow similar trends as low-molecular-weight nonpolar hydrocarbons. This allows us to postulate that one can detect when heavy oils are nonpolar by observing a deviation from the linearity of δ_{mix} vs. F_{RI} curve. For RI smaller than 1.45, which corresponds to a solubility parameter of $16.5 \text{ MPa}^{1/2}$, concentrations of soluble asphaltene decreased. Large amounts of asphaltene rejection start from $F_{\text{RI}} = 0.27$ and below. This corresponds to δ_{mix} of $16.4 \text{ MPa}^{1/2}$.

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