Physical Structure of Asphaltenes[†]

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While colloidal models of asphaltenes were extremely beneficial in the early stages of understanding asphaltene behavior, these analogies are often overused. The evidence often cited showing asphaltenes to be particles several nanometers in size is small-angle neutron and X-ray scattering (SANS and SAXS) results. Data from other techniques are often interpreted with the assumption that the asphaltenes form colloids or micelles. Asphaltenes are molecules which can undergo a thermodynamic liquid−liquid phase separation from solution. The asphaltene-rich phase is often below its glass transition and therefore appears solid, exhibiting a fractal-like morphology only because of the kinetic inability for the "droplets" to coalesce. Its colloidal appearance at micrometer to millimeter lengths should not be confused with or be used to imply such colloidal structure for solvated asphaltenes at nanometer length scales. From SAXS and SANS we show that the scattering often attributed to asphaltene colloidal aggregates is the result of ephemeral dynamically fluctuating compositional inhomogenieties similar to those observed in any one-phase liquid mixture of unlike molecules. By freeing ourselves from taking the colloidal analogies too seriously, we can potentially make substantial progress toward understanding the role of asphaltenes in effecting phase behavior, morphology, and viscosity.

Introduction

The colloidal and micellar models for asphaltenes, employing the idea of "primary aggregates" undergoing flocculation, have been extremely beneficial in the early stages of understanding their behavior.[1,2] They provide simple pictures for explaining particular observations. The picture of an ordered structure with an asphaltene colloid at its core surrounded by a shell of surfactant-like resins, shielded by the aromatics from the saturates, is appealing. The problem arises when they are taken too seriously and the simplified explanatory pictures are used as though they were microscopically correct, as a basis for more detailed understanding and developing a consistent model for asphaltene behavior. For the majority of situations, where asphaltenes are not phase separated, the colloidal analogies are over used and not justified. The most supposedly "direct" evidence showing the picture of the asphaltene as existing in a well-defined aggregate several nanometers in size comes from neutron and X-ray scattering results.[2−19] There is a difference, however, between (a) knowing that one has micelles or colloids (as in the cases of SDS surfactants or latex spheres) and using a technique such as X-ray scattering to determine their size, polydispersity, etc., and (b) assuming that the liquid contains colloids and computing the size of the supposed colloids from scattering data.

Asphaltenes, as well as the other components of petroleum, are molecules. They have a range of solubility parameters (i.e., polarity and aromaticity) and molecular weights. The molecular weights even for the asphaltene molecules are not more than a few thousand amu.[20−23] With the exception of *n*-alkanes, which might be present and crystallize as waxes, the molecules are of such complicated isomeric structures that specific association to form well-ordered crystalline structures

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(1) Pfeiffer, J. P.; Saal, R. N. J. *J. Phys. Colloid Chem.* **1940**, *44*, 139.
(2) Dickie, J. P.; Yen, T. F. *Anal. Chem.* **1967**, *39*, 1847.
(3) Dwiggins, C. W. *J. Appl. Crystallogr.* **1978**, *11*, 615.
(4) Storm, D. A.; Sheu, E. Y.; DeTar, M. M. *Fuel* **1993**, *72*, 977.
(5) Savvidis, T. G.; Fenistein, D.; Barre, L.; Behar, E. *AIChE J.* **2001**, *47*, 206.
(6) Thiyagarajan, P.; Hunt, J. E.; Winans, R. E.; Anderson, K. B.; Miller, J. T. *Energy Fuels* **1995**, *9*, 829.
(7) Fenistein, D.; Barre, L.; Broseta, D.; Espinat, D.; Livet, A.; Roux, J. N.; Scarsella, M. *Langmuir* **1998**, *14*, 1013.
(8) Barre, L.; Espinat, D.; Rosenberg, E.; Scarsella, M. *Rev. Inst. Fr. Pet.* **1997**, *52*, 161.
(9) Carnahan, N. F.; Quintero, L.; Pfund, D. M.; Fulton, J. L.; Smith, R. D.; Capel, M.; Leontaritis, K. *Langmuir* **1993**, *9*, 2035.
(10) Overfield, R. E.; Sheu, E. Y.; Liang, K. S.; Sinha, S. K. *Fuel Sci. Technol.* **1989**, *7*, 611.
(11) Tanaka, R.; Hunt, J. E.; Winans, R. E.; Thiyagarajan, P.; Sato, S.; Takanohashi, T. *Energy Fuels* **2003**, *17*, 127.
(12) Roux, J. N.; Broseta, D.; Deme, R. *Langmuir* **2001**, *17*, 5085.
(13) Lin, M. Y.; Sirota, E. B.; Gang, H. *Proc. 7th UNITAR Intl. Conf. Heavy Crude Tar Sands* **1998**, *42*, 161.
(14) Pollack, S. S.; Yen, T. F. *Anal. Chem.* **1970**, *42*, 623.
(15) Xu, Y.; Koga, Y.; Strausz, O. P. *AOSTRA* **1993**, *883*.
(16) Sheu, E. Y.; Liang, K. S.; Sinha, S. K.; Overfield, R. E. *J. Colloid Interface Sci.* **1992**, *153*, 399.
(17) Wiehe, I. A.; Liang, K. S. *Fluid Phase Equilib.* **1996**, *117*, 201.
(18) Sirota, E. B. *Petrol. Sci. Technol.* **1998**, *16*, 415.
(19) Gawrys, K. L.; Spieker, P. M.; Kilpatrick, P. K. *Pet. Sci. Technol.* **2003**, *21*, 461.
(20) Yarranton, H. W.; Alboudwarej, H.; Jakher, R. *Ind. Eng. Chem. Res.* **2000**, *39*, 2916.
(21) Groenzin, H.; Mullins, O. C. *J. Phys. Chem. A* **1999**, *103*, 11237.
(22) Speight, J. G.; Wernick, D. L.; Gould, K. A.; Overfield, R. E.; Rao, B. M. L.; Savage, D. W. *Rev. Inst. Fr. Pet.* **1985**, *40*, 51.
(23) Strausz, O. P.; Peng, P.; Murgich, J. *Energy Fuels* **2002**, *16*, 800.

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is not possible. There is, therefore, no reason such a system will not exhibit solution behavior. However, many approximations often employed in simple solution theories are not valid for these systems.

First, we must consider that the solution is a mixture near the point of phase separation. The enthalpic interaction between molecules causing similar molecules to prefer each other is not much less than the entropy of mixing. The mixture cannot be simply considered a binary mixture, but a very wide and continuous distribution of solubility parameters and molecular weights is indeed present. Just because the mixture is a single thermodynamic phase does not mean that the molecules will be distributed randomly.

The micellar picture of asphaltene aggregation, while descriptive of associating systems and helpful as an analogy, is problematic if one takes it too seriously. Micelles are well defined in surfactant systems.[24] One of the distinguishing features of micellar aggregation is the formation of a specific structure based on the geometry of the molecules. Thus, there is a well-defined aggregation number. While each micelle, especially in a polydisperse system, will exhibit variation of the number of molecules in an aggregate, the distribution of aggregate sizes will peak about a finite mean value, typically >20. More molecules or fewer molecules could not complete a structure necessary to shield the internal functionalities from the outside medium with which they are incompatible. Besides being in micelles, the surfactants would exist as monomers (or possibly dimers if the specific interaction favors it). Therefore, the distribution of aggregate sizes will be highly bimodal. There is no proof that asphaltenes in solution exhibit such an aggregation behavior and no reason such molecules would do so. Asphaltene solution data is often analyzed in terms of a critical micelle concentration.[25−27] In micelle forming systems a change in the surface tension versus concentration profile occurs at the cmc; however, such behavior does not necessarily imply the formation of micelles. It could, for example, signify the saturation of the surface, limiting further reduction of the surface tension.

When asphaltenes phase separate from solution due to addition of a poor solvent, the solid phase can indeed be considered colloidal in many respects. However, for the majority of situations, where asphaltenes are not yet phase separated, the colloidal analogies are not justified. Unfortunately, data on asphaltenes are often analyzed as though an asphaltene solution was in fact a suspension of colloids.

Below we will show how typical scattering data in such systems is consistent with a behavior of asphaltenes similar to that of other miscible liquids in the vicinity of phase separation. Morphological data on the shape of the asphaltene precipitates will then be presented and explained in terms of the high glass-transition temperature of the asphaltenes. Finally, the picture is completed by explaining the high and strongly temperature-dependent viscosity of asphaltenic liquids by their proximity to the glass transition.

Experimental Section

Small-angle neutron scattering (SANS) data were taken on the NG7 30 M diffractometer at the NIST Cold Neutron Research Facility, configured at a wavelength $\lambda = 6.0$ Å and collected using a two-dimensional area detector. The sample to detector distance was 2 m for low resolution and 15 m for high resolution. Thus, the overall range of scattering wave vectors studied was $0.002\ \text{Å}^{-1} < q < 0.15\ \text{Å}^{-1}$. $q = (4\pi/\lambda)\sin\theta$, where 2θ is the scattering angle.

X-ray scattering measurements were performed using a high-flux Rigaku 18 kW rotating anode X-ray generator with a copper anode. Cu Kα radiation was selected using a vertically bent graphite monochromator, which also focused the beam. The beam size at the sample was determined by slits to be 1 mm horizontal and 2 mm vertical. The sample was located in the center of a Huber two-circle diffractometer. The scattered X-rays were detected using a Bicron single-channel detector behind a horizontal slit, 1 mm in width. This gave an arm-zero full-width half-max of ~0.12°. The samples were contained in 1.5 mm diameter quartz capillary tubes. The entire experiment was automated using Spec software from Certified Scientific running on a LINUX operating system and interfaced using CAMAC hardware.

Microscopy was performed using an Olympus BH2 microscope in transmission mode. The micrographs were collected with a CCD camera and downloaded to a Macintosh computer.

Viscosity measurements were performed on a Rheometrics DSR-200 stress-controlled rheometer.

Results and Discussion

Small-Angle Scattering. Small-angle X-ray and neutron scattering are structural probes often used in asphaltenic systems.[3−16,18,19] The small-angle scattering signal which is typically observed for asphaltenes solvated in their oil or in model solvents is monotonically decaying with increasing scattering angle. If you know that you have particles, then the interpretation of this scattering using the Guinier formalism can give information on their size or size distribution. If you are uncertain about both the polydispersity and the aspect ratio, then it is difficult to determine both with accuracy. Because of this ambiguity the literature contains many discussions of whether the supposed "asphaltene colloids" are spherical, prolate, or oblate ellipsoids.[6,11,15,16] Such questions already *assume* that they are particles. We argue here that interpretation of scattering data as particles is incorrect.

Asphaltenes are molecules with high solubility parameters and moderately high molecular weights.[17,28−31] Having a high aromatic content, they form true solutions in acceptably aromatic solvents. However, since their molecular weight is moderately high, the entropy of mixing is not sufficient to keep them in solution if the interaction with the remainder of the solution becomes unfavorable, such as upon addition of an aliphatic fluid. The phase separation which ensues is thermodynamically a liquid−liquid phase separation which can be understood in the context of solution theory of molecules. The solidlike character of the

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(24) Safran, S. A. *Statistical thermodynamics of surfaces, interfaces, and membranes*; Addison-Wesley: Reading, MA, 1994.

(25) Sheu, E. Y.; DeTar, M. M.; Storm, D. A.; DeCanio, S. J. *Fuel* **1992**, *71*, 299.

(26) Rogel, E.; Leon, O.; Torres, G.; Espidel, J. *Fuel* **2000**, *79*, 1389.

(27) Rogacheva, O. V.; Rimaev, R. N.; Gubaidullin, V. Z.; Khakimov, D. K. *Kolloid. Z.* **1980**, *42*, 586.

(28) Mitchell, D. L.; Speight, J. G. *Fuel* **1973**, *52*, 149.

(29) Redelius, P. G. *Fuel* **2000**, *79*, 27.

(30) Wiehe, I. A. *Fuel Sci. Technol. Int.* **1996**, *14*, 289.

(31) Schabron, J. F.; Pauli, A. T.; Rovani, J. F. *Fuel* **2001**, *80*, 529.

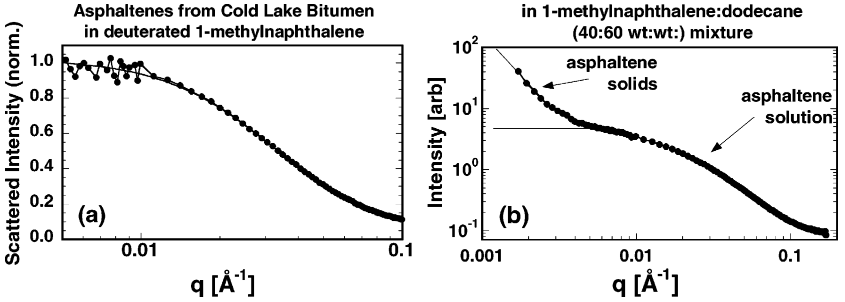

Figure 1. (a) Small-angle neutron scattering from a 1% solution of asphaltenes derived from Cold Lake Bitumen dissolved in perdeutero-1-methylnaphthalene, measured at room temperature. The fit is to the Lorentzian line shape discussed in the text. (b) Same asphaltenes but in a deuterated 1-methylnaphthalene:dodecane (40:60 w/w) mixture. Only part of the asphaltenes is soluble, and thus, scattering from the asphaltene solution coexists with scattering from the fractal asphaltene solids. The fit is to a Lorentzian plus a power law, as discussed in the text.

asphaltene-rich phase which is thus formed is only due to the fact that the material in the heavier phase is below its glass-transition temperature. The solid precipitate has a fractal-like structure since its extremely high viscosity typically does not let it condense into a low-surface-area morphology.

Then we ask what gives rise to small-angle scattering when the molecules are in a single-phase molecular solution? It is well known that mixtures of species with unfavorable interaction will undergo liquid−liquid phase separation at low enough temperature if crystallization does not intervene. At temperatures above the phase separation temperature the species are known not to be mixed totally randomly but to have *dynamically varying compositional inhomogeneities* or concentration fluctuations. These inhomogeneities give rise to characteristic scattering.[18,32,33] The local interaction between molecules favors such molecules to find themselves in contact with like molecules with a preponderance determined by Boltzman-like weighting. Molecules in the liquid are constantly diffusing; thus, such clustering of like molecules is ephemeral. For example, in an A−B mixture if one takes a space−time average of the radial distribution function, one finds that the probability of finding an A molecule at a given position decreases exponentially to the average composition as you move further away. The distance over which that time−space average probability decays is known as the correlation length, ξ. The correlation length is known to increase as phase separation is approached and will diverge continuously if one crosses the phase boundary at a liquid−liquid critical point. One may draw aggregates of dimension ξ in schematic cartoons, but it is dangerous since these are not colloids or micelles with dimension ξ, but rather a statistical description of a liquid.

The resulting small-angle scattering arising from such an average distribution is a Lorentzian line shape, which is identical to the Guinier form in the low-angle limit.[18] X-ray and neutron scattering data are fit by this line shape well. The behavior of ξ upon changing asphaltene concentration, solvent composition, and temperature is consistent with this picture.[18] In Figure 1a we show typical scattering from solvated asphaltenes (derived from Cold Lake Bitumen with a 10:1 heptane dilution) fitted with the Lorentzian line shape: $I(q) \propto 1/[1 + (q\xi)^2]$ yielding $\xi = 31$ Å. This scattering is typical of asphaltenes in a single-phase solution. If a second phase is present where asphaltene solids are dispersed in the liquid, either because the asphaltenes are not fully dissolved or if they are partially phase separated (precipitation) but have not fallen to the bottom of the container (deposition), a power-law scattering component at very low angles will also be present. The power-law scattering originates from the fractal structure of the asphaltene solids which have phase separated from the solution. The presence of inorganic impurities will also give rise to such low-angle power-law scattering. An example of this is shown in Figure 1b. Unfortunately, in presentation, analysis, and discussion there is often confusion in distinguishing between the scattering arising from the true thermodynamic solution of asphaltenes and the scattering arising from the dispersed particles of a solid phase.

It is also useful to ask what would be the implications of this picture for a very dilute solution of asphaltenes.[34] If there were no favorable "like−like" interaction, then all molecules would be randomly distributed and the probability that asphaltenes in dilute solution would be in contact with each other would be very small indeed. Because of the energetic preference for "like" molecules to be in contact, the probability that any given asphaltene will be in contact with another asphaltene (aggregation) will be greater than its concentration.

Low-Angle Peak. It is well known that asphaltenes (when isolated from the residue using standard solvent techniques) exhibit a scattering peak at low angles corresponding to a spacing of $d = 2\pi/q_{\text{peak}} \approx 40$ Å (Figure 2a).[2,14,17,18] Such a peak is always extremely broad, which shows that this is not a peak arising from long-range order. It is not unlike a peak which would be observed from the disordered packing of colloidal spheres.[35] Thus, if you knew that you had colloidal spheres dispersed in a liquid (as polystyrene spheres in water or methanol), one could use the scattering profile to extract their size and average local packing. However, this is not the only thing that could give such scattering. Scattering is caused by inhomogeneities in the electron density (for X-rays) or hydrogen density (for neutrons). A broad peak in the scattering signifies that there is a characteristic, although not well defined,

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(32) Zimmermann, H. J.; Wendorff, J. H. *Colloid Polym. Sci.* **1986**, *264*, 292.

(33) Pusey, P. N.; Goldburg, W. I. *Phys. Rev. A: At. Mol. Opt. Phys.* **1971**, *3*, 766.

(34) Goncalves, S.; Castillo, J.; Fernandez, A.; Hung, J. *Fuel* **2004**, *83*, 1823.

(35) Sirota, E. B.; Ou-Yang, H. D.; Sinha, S. K.; Chaikin, P. M.; Axe, J. D.; Fujii, Y. *Phys. Rev. Lett.* **1989**, *62*, 1524.

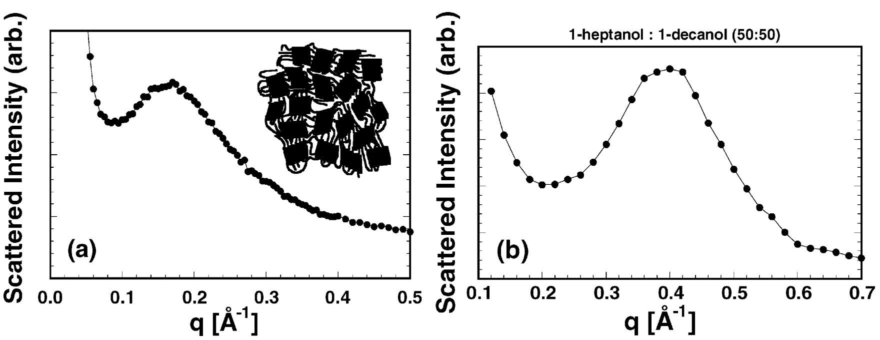

Figure 2. Low-angle X-ray scattering peaks. (a) X-ray scattering from neat asphaltenes extracted with heptane from Cold Lake Bitumen, showing a peak at small angle. (inset) Schematic depicting microphase separation in asphaltenes. (b) Scattering from a 50:50 liquid mixture of 1-heptanol and 1-decanol. (Scattering from the pure 1-alcohols is similar.)

distance between regions of high electron density. In the case of mixtures containing asphaltenes, the electron density contrast comes primarily from the difference between aliphatic and aromatic groups. Thus, for a given composition, which is *macroscopically homogeneous*, if there is a cluster rich in aromatic species, there will necessarily be a surrounding region depleted in it before the next aromatic cluster is encountered. This can be considered as a microscopic separation, as shown schematically in Figure 2a.

Such a peak, for example, is exhibited by 1-alcohols[36] in their liquid state (Figure 2b). There it arises from the −OH groups dynamically associating and the fact that the average distance between aggregates of −OH groups at any given instant will be related to the average molecular size.

Another place where scattering peaks are often observed is in spinodal decomposition.[37] This occurs during phase separation of two immiscible liquids. Phase separation begins at a short length scale, and then the length scale increases with time as the system coarsens and eventually will form macroscopically separate phases. Asphaltenes are interesting in that they contain both aliphatic and polynuclear aromatic (PNA) portions. If the aliphatic and aromatic portions of the molecules were chemically separated, then the resulting mixtures would phase separate since the PNAs would not be miscible with the aliphatics. This process may be occurring microscopically; however, the functionalities are chemically bound, and thus, the length scale cannot grow much more than the molecular size. Phase separation induced by incompatible functionalities, but limited in length scale because the functionalities are contained on the same molecule, is known as *microphase separation* and is well documented and studied in block copolymers.[38] Thus, the existence of this low-angle peak is not proof of the existence of micelles or colloids.

Precipitation at Higher Temperatures. Another phenomena which is exhibited by asphaltenic systems and often attempted to be explained with a colloidal model is the observation that asphaltene-containing systems which are stable (i.e., single phase) at low temperature become unstable with respect to asphaltene precipitation at high temperature.[39,40] The explanation often given is in terms of considering the asphaltene as a colloid and the "resins" as surfactants which sit at its surface. It is well known in colloid science that surfactants can be used to prevent colloidal flocculation. The surfactants are much smaller than the colloid. Being smaller means that they respond to temperature strongly (entropy of mixing) in terms of their solubility in the liquid phase, compared to their adsorption ability. The enhanced entropy of mixing which comes with increasing temperature, however, does little to offset the interaction between the massive colloids, and thus, the effect of temperature is mostly to drive the surfactants off the colloids and allow them to flocculate.

The problem with this analogy is that asphaltenes are not so much more massive than the resins. In fact, their molecular weight ranges strongly overlap. This behavior can be simply understood in terms of the behavior of molecules in solution. Entropy of mixing favors mixing as the temperature is elevated. However, as the temperature is increased there is a significant thermal expansion. This thermal expansion couples directly to a decrease of the solubility parameter of all the molecules. However, the solubility parameters of all species do not decrease at the same rate with temperature. Specifically, the solubility parameter of the lower molecular weight and more aliphatic molecules will decrease much faster with temperature than those of the asphaltenes. Thus, the solubility parameter difference between the asphaltenes and the rest of the fluid will increase with increasing temperature. With the interaction energy being proportional to $(\Delta\delta)^2$, this can overcome the enhanced entropy of mixing with increased T and drive the system to phase separation.

Morphology. Another phenomenon, which perpetuates the idea that solubilized asphaltenes are colloids, is the appearance of phase-separated asphaltenes as "fractal-like" aggregates. When colloids flocculate, they often do so in such a fractal structure. Thus, it could have been a natural conclusion that asphaltenes in solution are colloids of a submicroscopic size and that the observed structure is a result of flocculation of such colloids. We show here how the observed morphology can be explained by solution behavior.

The morphology of asphaltene precipitates can be shown to be related to the proximity to the glass transition. The single-phase solution prior to precipitation (upon adding a precipitant like heptane) is es-

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(36) Stewart, G. W.; Morrow, R. M. *Phys. Rev.* **1927**, *30*, 232.

(37) Cahn, J. W. *J. Chem. Phys.* **1965**, *42*, 93.

(38) Bates, F. S.; Fredrickson, G. H. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525.

(39) Storm, D. A.; Barresi, R. J.; Sheu, E. Y. *Fuel Sci. Technol. Int.* **1996**, *14*, 243.

(40) Storm, D. A.; Barresi, R. J.; Sheu, E. Y. *Energy Fuels* **1995**, *9*, 168.

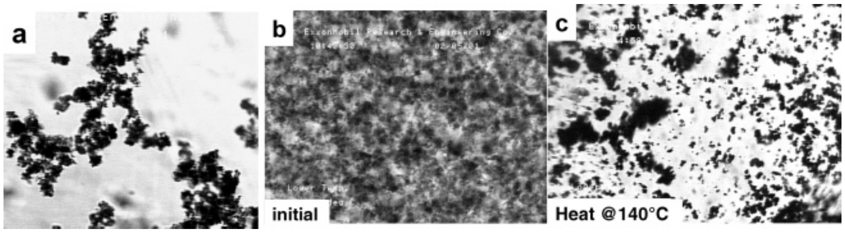

Figure 3. (a) Photomicrograph of a typical fractal-like structure obtained by precipitation of asphaltenes from Cold Lake Bitumen in a dilute solution (20:1) of heptane. (b,c) Precipitated asphaltenes in Cold Lake Bitumen diluted 4:1 with hexadecane: hexadecylnaphthalene (9:1) as prepared (b) and after heating at 140 °C for 2.5 days (c).

sentially always in the liquid state where the molecules are free to diffuse. (However, the viscosity may vary by many orders of magnitude.) When phase separation (i.e., asphaltene precipitation) occurs, the asphaltene-rich or "heavy" phase may be at such a composition and temperature that it is in either a liquid or a glassy state. (High temperature, coprecipitated resin, and swelling of the asphaltene-rich phase with light ends all favor the liquid state.) Actually, it is not simply whether the temperature is precisely above or below T_g but rather a viscosity/length-scale/time-scale-dependent effect. Assuming that the asphaltene-rich phase grows by a process of nucleation and growth of the asphaltene-rich phase followed by secondary aggregation of such asphaltene particles, it is clear that in the high-viscosity limit for the asphaltene-rich phase, a newly added asphaltene molecule, or aggregate will remain attached to the existing particle, where it initially contacted. This will result in aggregates with a "fractal-like" appearance. In the liquid limit of low viscosity, joining of two droplets or adding to an existing droplet will be followed by a smoothing out by surface tension yielding a compact spherical shape.

A high, but finite, viscosity of the asphaltene phase will then be expected to initially form a fractal shape which will evolve over time to a smooth shape. More specifically, one will expect that the shortest length scales will smooth out first. Thus, when viewed at low magnification, the time required to see it evolve from fractal to compact will be longer than when viewed at a large magnification. The driving force to smooth out the interfaces of the structure is the interfacial tension between the asphaltene-rich and asphaltene-poor phases, σ. The smoothing is impeded by the viscosity η of the more viscous asphaltene-rich phase. Using simple dimensional analysis, one can see that the time (τ) to smooth out over a length scale r is

$$\tau \propto r\eta/\sigma$$

One can see that the characteristic time is linear in the length scale. Thus, one may expect a 6 orders of magnitude difference in time to smooth out on a nanometer scale (probeable by small-angle X-ray or neutron scattering) compared to a millimeter scale visible to the naked eye. Thus, depending on the length scale and time scale of the probe, the structure may appear fractal, even significantly above T_g.

In Figure 3a we show a photomicrograph of a typical fractal-like structure obtained by precipitation of asphaltenes from Cold Lake Bitumen in a dilute solution of heptane (Cold Lake is a Canadian heavy crude). To facilitate heating, we used higher molecular weight diluents and diluted Cold Lake Bitumen 4:1 with hexadecane:hexadecylnaphthalene at a 9:1 ratio. This is shown in Figure 3b. At this composition the system has a large amount of precipitated asphaltenes and is very far from the phase boundary, so that heating will not drive the asphaltenes back into solution but rather only increase their mobility. This was heated at 140 °C for 2.5 days, and the condensation into denser clusters is apparent in Figure 3c.

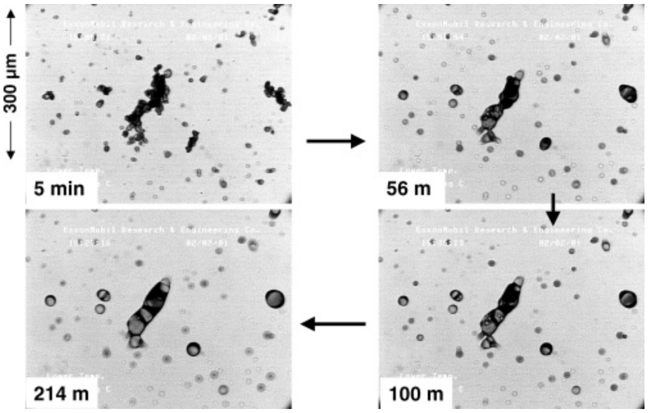

Figure 4. Evolution with time (at room temperature) of the asphaltenes precipitated from "heptane deasphalted Cold Lake Bitumen" with isooctane at 3:1 volume ratio.

In Figure 4 a more dramatic result is shown. Here, the starting material was the heptane deasphalted oil from Cold Lake Bitumen. In this case, the C7 asphaltenes were removed with a 10:1 heptane dilution, leaving a fraction of the pentane asphaltenes in the oil. Precipitation was done by diluting the C7-deasphalted oil with isooctane (iC8) at a 3:1 volume ratio. The photomicrographs were taken 5 min after dilution, until 214 min, looking at the same portion of the sample. The smoothing and condensation of the structure with time, from fractal-like to liquidlike, is clear and dramatic.

While this explanation for the morphology of these precipitates appears reasonable, investigation of glass-transition phenomena in these materials and their connection to morphology is only very recently being explored. In polymers, however, the glass transition is a well-studied phenomena. To observe this phenomena with a polymer, the system would need to be a noncrystallizing polymer with a high T_g, which could be made just barely soluble in one solvent and strongly precipitate in another. The poor solvent should be poor enough so that the glassy polymer would not be strongly swollen and plasticized. Polystyrene (PS) fulfilled this requirement, being noncrystalline and having a high T_g, toluene is a good solvent, cyclohexane is a θ solvent (dissolving polystyrene above 35 °C and not dissolving

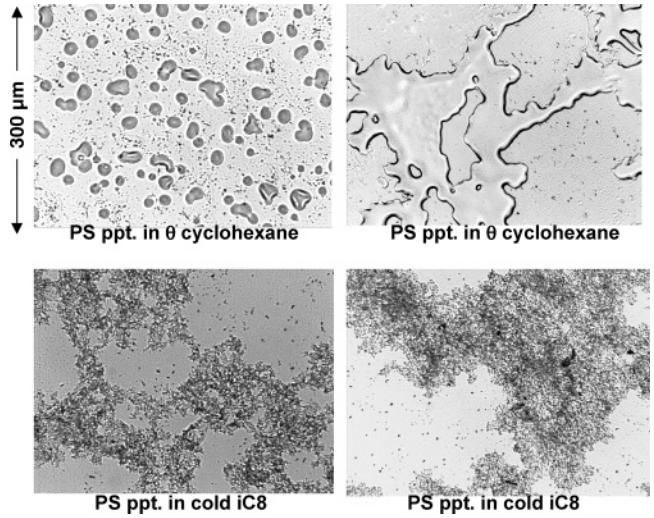

Figure 5. Photomicrographs of polystyrene after precipitation from cyclohexane by slow cooling through the θ temperature (top) or by addition to cold isooctane (bottom). Two photos are shown for each.

although swelling below), and an alkane like *n*-heptane or isooctane is a nonsolvent. Polystyrene was obtained from a Styrofoam coffee cup and dissolved in slightly warmed cyclohexane, forming a 2 wt % solution.

The polystyrene was then precipitated in two different ways: (1) by cooling in the θ solvent cyclohexane such that the polymer would be swollen and plasticized at the onset of precipitation and (2) by squirting ~0.4 mL of the warm solution into 7 mL of cold (0 °C) isooctane being rapidly stirred. (Having an even lower solubility parameter than heptane, isooctane will be an even worse solvent for, or sweller of, polystyrene.) In this case, the PS would find itself mostly in cold isooctane and precipitate in a nonswollen glassy state.

In Figure 5 we show photomicrographs of polystyrene after precipitation in the two conditions. On precipitation from the θ solvent, where the polystyrene was plasticized, compact smooth droplets formed. However, on precipitation in the cold iC8, a fractal-like structure was formed, very much like the structure formed by the precipitated asphaltene in Figure 3a. (Since PS is colorless, the optical contrast is much less than that for the asphaltene.) Polystyrene satisfies the operational definition of an asphaltene as being “toluene soluble and heptane insoluble”. When precipitated under the right conditions, polystyrene is shown here to also exhibit *the morphological characteristics of precipitated asphaltene*. The observation of this type of behavior in a polymer system where the glass transition is well established, strongly suggests that this glass-transition phenomenon is the origin of the similar morphological behavior in asphaltenic systems.

Viscosity. Another place where colloidal models for asphaltenes are often employed, is in explaining the viscosity of asphaltene-containing fluids.[7,41,42] The Einstein relation, $\eta = \eta_0(1 + 2.5\phi)$, represents the viscosity of a fluid of viscosity η_0 with dispersed spherical colloids of volume fraction ϕ. Since this obviously does not work for asphaltene-containing systems, various higher order terms and corrections (often used in colloid science) are employed for interactions and increasing the effective hydrodynamic radius. However, asphaltenes constitute a continuum of species, and the volume fraction is defined only by the solvent used to precipitate the asphaltenes. Therefore, such an approach is clearly ad hoc and requires the use of parameters without physical basis.

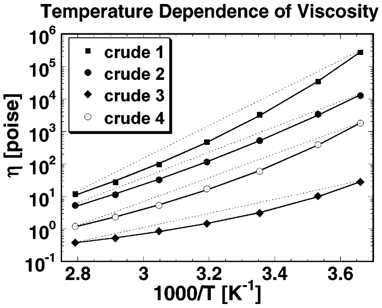

Figure 6. Temperature dependence of the viscosity of four crude oils. The solid curves are fits to the form described in the text. These oils exhibit Newtonian viscosity and are single-phase liquids at the temperatures at which viscosity is measured. The dashed curves illustrate simple Arrhenius dependence, which does not represent the data.

Before considering the concentration dependence of the viscosity, it is important to consider the temperature dependence. We found through analysis of the low-shear viscosity of a single phase (i.e., no precipitated asphaltenes or wax) a variety of asphaltene-containing fluids (resids, crudes, asphaltene solutions in model solvents, and mixtures of the above with lighter components) follows the modified Arrhenius equation over a wide temperature range, $\eta = \eta_0 \exp[c/(T - T_0)]$. Such data is shown for four different, yet typical, crude oils in Figure 6. A simple Arrhenius equation (i.e., $T_0 = 0$) cannot represent the data. The modified Arrhenius equation is known to represent the behavior of most single-phase Newtonian fluids. The parameter which is most important here is T_0, as it represents the temperature at which the viscosity would diverge. This is known as the Kauzmann temperature and is related to the glass-transition temperature, which is often defined as the temperature where the viscosity reaches 10^{13} P.[43] Understanding the rise in the viscosity as the approach to the glass transition allows one to understand the concentration dependence of the viscosity in terms of reduction of the glass transition by dilution, or “plasticization”, without assuming colloidal or micellar properties.

The glass transition in asphalt is a measurable and commonly used property. Viscosity is only easily measurable at much higher temperatures or dilutions. While in less viscous asphaltene-containing systems the glass transition is too low to be directly measured, the temperature dependence of the viscosity is its manifestation.

The very high viscosities associated with the glass transition can have implications for the apparent structures in both single-phase and phase-separated systems. The concentration fluctuations in a single phase will be slowed and frozen as the material approaches its glass transition, causing clusters to be very long lived. True phase separation would thermodynamically be favored

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(41) Storm, D. A.; Sheu, E. Y. *Fuel* **1993**, *72*, 233.

(42) Sheu, E. Y.; DeTar, M. M.; Storm, D. A. *Fuel* **1991**, *70*, 1151.

(43) Angell, C. A. *J. Non-Cryst. Solids* **1991**, *131*, 13.

at low temperatures but may be kinetically impeded, resulting in nanosized asphaltene domains. Both these possibilities should be considered when interpreting observations.

Summary and Conclusions

Asphaltenes are molecules with a high solubility parameter and moderately high molecular weight. Their phase behavior can therefore be described in terms of the solution behavior of molecular mixtures. Scattering from asphaltenes in solution is consistent with this. Ephemeral concentration fluctuations characteristic of a multicomponent single-phase solution in the vicinity of phase separation, give rise to nondivergent small-angle scattering ("Guinier"), which is observed in asphaltene solutions. Small-angle divergent scattering ("Porod") in such systems is from a second phase of insoluble asphaltenes (or other solids). The scattering peak from concentrated asphaltenes can be considered spinodal decomposition, arrested as a microphase-separated structure.

The morphological characteristics of these systems are also consistent with this picture. The fractal appearance of precipitated asphaltenes is due to the fact that they phase separate into a highly viscous glasslike state. Tuning composition toward lower molecular weight and solubility parameter or higher temperature, results in a liquidlike appearance to the asphaltene phase. The high (and strongly temperature dependent) viscosity of bitumen and asphaltenic mixtures is then understood to be related to their proximity to the glass transition.

While micellar and colloidal models provide simple pictures to explain particular behaviors, we have shown the dangers in extending colloidal analogies too far for asphaltene-containing systems. Solution behavior of associating molecules can explain many features too often uncritically attributed to colloid behavior. By freeing ourselves from taking these analogies too seriously, we can potentially make substantial progress toward understanding the role of asphaltenes in effecting the phase behavior, morphology, and viscosity.

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