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SOLUTION PROPERTIES OF COLLOIDS FORMED BY PETROLEUM VACUUM RESIDUES

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SUMMARY

We briefly reviewed the historical research on VR colloids, and its impact on VR upgrading. We then reported our study of VR/solvent systems, in which we (1) directly characterized the self-association phenomenon of VR molecules, (2) explicitly determined the colloidal structure and quantitatively estimated the colloid-solvent interaction, (3) determined the detailed particle shape, polydispersity, and the surface roughness, (4) identified the type of intermolecular interaction, which is responsible for self-associations, and (5) characterized the colloidal dynamics and their slowing down, as a function of concentration and temperature.

INTRODUCTION

It is well known that yields of refining products such as gasoline depend on the crude oil being processed. In the first step approximately 60 - 75% of the crude oil is separated into easily refinable fractions by distillation. The residual material is called vacuum residue (VR). Since VR is composed of hydrocarbons, there is of course a significant economic incentive to also refine this subfraction into gasoline, jet fuel, diesel, and home heating oil. Unfortunately difficulties are encountered with current technology and these difficulties appear to be related to the chemistry of a group of ill-defined molecules called asphaltenes. The most elemental piece of information about this group, the average molecular weight, is not known. Some results suggest they are polymer-like consisting of large polynuclear aromatics having high molecular weights[1]. Other workers have argued that the molecules are actually much smaller, but appear to be bigger, because they form aggregates[1] in solvents, and in petroleum fractions[1-4]. It is important to resolve this question. If the molecules are indeed polymer-like, then the best course of action would be to gasify VR to make electricity. If, on the other hand, the molecules are actually small, then refining will be a more efficient way to utilize this hydrocarbon source.

Since VR contains several classes of materials having very different chemical constituents, most studies separate VR into serval fractions. In most known vacuum residues, the light and heavy ended fractions (pentane soluble and heptane insoluble fractions respectively) comprise approximately 90% of the VR. These two fractions naturally become the two most important fractions for characterization studies. In particular, the heavy ended fraction (or asphaltene) is suspected to hinder refining and initiate coking formation.

In this article, a chronicle of the colloidal studies on these two classes of molecules from VR in both solvents and in petroleum will be reviewed briefly. In addition, we will present results from our rheological, structural, and dielectric studies for these two fractions dissolved in various organic solvents.

I. History and Literature Review

Since VR is usually separated into several fractions for characterization study, we shall briefly describe VR fractionation, before reviewing the literature. The conventional method for VR fractionation is by a stepwise separation procedure based on polarity. In the first step, VR is mixed with a low polarity solvent, like pentane, according to a mixing ratio of one part VR to 40 parts solvent. The soluble portion so extracted is defined as oil (or the light ended material). The insoluble portion is further fractionated using a higher polarity solvent, such as heptane, with the same mixing ratio. The soluble portion extracted from this stage is defined as resin and the insoluble portion is referred to as asphaltene (or the heavy ended material).

To the best of our knowledge, the aggregation model (sometime called the micellar model) for VR colloids was proposed by Mack to interpret the rheological data[2]. Since no sufficient scientific evidence was given in this work to support the proposed model and the data analysis was possibly misinterpreted[3], this micellar model did not draw much attention at the time. In 1940, Pieffer and Saal adopted this concept to interpret their rheological data[4]. They also determined the molecular weight of asphaltenes, derived from asphalts, to be between 8,000 and 14,000 using monomolecular film balance measurements[4]. Based on this work they hypothesized that asphaltenes are the centers of spherical micelles formed by adsorption, or even by absorption of part of the maltenes onto the surfaces, or into the interiors of the asphaltene particles. However, certain properties could not be explained, unless a diffused molecular interface, either within a micelle or between them, was assumed[5]. In 1941, Höppler studied the rheology of asphalts in solvents[6]. The result not only supported the micellar model but also determined the micellar structure to be spherical. In 1949, Eiler studied solubility and rheology of asphalts and crude oil[7]. The result suggested that there were colloidal particles in these systems. In 1957, Ray et. al. showed that colloidal particles could be separated from crude oil by ultracentrifiguation[8]. The molecular weight of the particles were in the range of 20,000 to 30,000. Eldib et al later showed that if the crude oil was deasphalted first, no significant separation of particles was observed during the untracentrifugation experiment[9]. This result implies that asphaltenes may have correlation with formation of colloidal particles in oil.

The works mentioned above are very suggestive that asphaltenes are colloidally dispersed in crude oil. However, interest in the micellar model for asphaltenes in crude oil waned over the years, because (1) one could not establish a direct link between the presence of the asphaltene and the observed colloidal behavior (i.e., there was no way to systematically vary the asphaltene concentration in the crude oil, and show the number of particles is a function of asphaltene concentration), and (2) the existence of colloids in crude oil does not necessarily mean that they are formed by self-associations (colloid is defined by its size, not how it is formed[10]).

In 1964, Dwiggins reported the first direct observation of colloidal particles in crude oil by using small angle X-ray scattering to study these particles in their undisturbed, natural state[11]. A slight polydispersity in size was observed. The average particle size did not change with increasing temperature, or with the addition of solvents. In 1967, Dickie and Yen[1] reported their X-ray diffraction study for precipitated asphaltenes. They proposed an aggregation model to interpret the data. This aggregation model is structurally different from that proposed by Pieffer and Saal[4]. This model suggested that the macrostructure of asphaltics consisted of elemental units (approximately spherical) formed by randomly stacked asphaltenic molecules.

Due to Yen's work and the increasing capability of microscopic measurement, the micellar concept for VR colloids has become popular again: A qualitative study of asphaltenes in various solvents by vapor pressure osmometry (VPO) was reported by Al-Jarrah and Apikian[12] in 1987. By using tetrahydrofuran (THF) at 60 °C as the reference condition (assuming asphaltenes to be in monomer form in this solvent at this temperature), they found that the degree of association for asphaltene changed, both with respect to temperatures and to the various solvents. However, the minimum molecular weight reported is similar to a colloid, suggesting that the association they observed may be between colloidal particles. Thus, whether the particle of minimum molecular weight is a monomer or an aggregate was still not resolved in this study. In fact, in Dwiggins' work, the macromolecular size was found to be independent of temperature. If the size Dwiggins observed corresponded to the minimum molecular weight obtained by Al-Jarrah and Apikian, and the minimum particle is indeed a monomer, then, one would expect this molecular weight to be retained, even at high temperature. If this is the case, the basic asphaltenic molecule has an average molecular weight of ~6000. Alternately, the colloidal particles could be aggregates formed by a strong association of smaller molecules, and thus can not be easily dissociated via heating. In 1988, Herzog et. al.[13] and Ravey et. al.[14] reported their respective small angle X-ray and Neutron scattering results for structural determination of asphaltenes dispersions. Both studies found that a flat sheet structure was the best model for describing their data. A slight dependence of the particle size on solvents was observed, shedding light on the micellar argument of these colloidal particles. In 1989 Overfield et. al.[15] reported their small angle neutron scattering results for asphaltenes in toluene at various temperature and found that the size was greatly reduced at 250 °C after one hour. The size then slowly increased to about half of the initial size after cooling to room temperature for 20 hours. This experiment indicated that (1) the micellar picture is very likely correct in solvents and (2) the self-association kinetics is very slow. The latter point is understandable, since individual asphaltenic molecule can have a different molecular structure, thereby slowing the packing process. If the particles at 250 °C are monomers, this work would be the first direct measurement of the aggregating process. Unfortunately, the average molecular weight of the particles at 250 °C was not reported. Recently, Storm et. al.[16] showed that the average molecular weight of asphaltenes is the order of thousand, considerably lower than the minimum molecular weight reported by Al-Jarrah and Apikian. This suggests that VR colloids are aggregates, although direct micellization evidence is not yet available.

In our study of this topic, we took three steps to characterize the VR colloids dispersion systems. First, we employed surface tension measurement to directly detect the micellization of the light and heavy ended VR molecules respectively. Secondly, we studied the rheological properties of these colloids in different solvents. We then applied various theories to interpret the viscosity data, from which we extracted the colloidal structure and the colloid-solvent interactions. Moreover, we used small angle neutron and X-ray scattering to confirm the structure determined from the rheological study and to investigate the particle size distribution of these colloids. Finally, we performed conductivity and dielectric response measurements, by which we identified the type of interaction between the asphaltenic molecules within an aggregate. In addition, we evaluated the dynamic slowing down of the particle diffusion upon heating. The rationale of this three-step procedure is as follows: (1) in order to disperse these colloids one needs to ensure that they are aggregates, (2) structure and polydispersity information are needed for evaluating the strength of the molecule-molecule interaction within aggregates, and (3) one needs to know the interaction type, in order to develop appropriate technology for refining the bottom of the barrel. In the following sections, we shall systematically report the results of our studies.

II. Macromolecules or Aggregates?

We determined if the VR colloid is a molecule or an aggregate by measuring the surface tension of a VR colloidal solution as a function of concentration. Surface tension measurement is a common technique used in surfactant chemistry for determining the critical micelle concentration (CMC). This technique is based on Gibb's adsorption equation[17]. Usually, the surface tension of a surfactant solution will be linearly reduced upon addition of the surfactant molecules, until micelles are formed, where the surface tension becomes independent of concentration. This critical surfactant concentration is defined as CMC. If we assume that there exists a component in VR, which serves as a surfactant molecule when the proper solvent is selected, then the "CMC" of this VR/solvent system can be obtained by a simple surface tension measurement. We have measured the surface tensions for both light and heavy ended fractions (referred to as C5S and C7I respectively from what follows) of Ratawi VR (Neutral Zone) using pyridine and nitrobenzene as solvents. The results are given in Fig. 1. A discontinuity in the surface tension gradient (with respect to concentration) was observed for all of the cases investigated. This provides direct evidence that self-association occurs for both C5S and C7I fractions.

III. Characterization of VR Colloids - A Rheological Study

A Brookfield viscometer with 0 to 1000 centipoise working range was used to measure the viscosities of C5S in a series of n-alkane solvents and C7I in toluene at room temperature. The accuracy is approximately 0.1% of the selected scale. Fig. 2a. shows the reduced viscosity of C5S in four different n-alkane solvents. The intrinsic viscosities vary from 1.8 to 5.5 depending on the carbon chain length. This means that the degree of solvation varies for solvents of different carbon chain length. To prove this view point, we adopted a recent theory derived by Pal and Rhodes[18]. They followed the derivation procedure proposed by Roscoe[19]. In this derivation, Pal and Rhodes explicitly took into account the effect of particle solvation. The equation they arrived at was a simplified form of Krieger and Dougherty's equation[20],

$$\eta_r = [1 - K\Phi]^{-2.5} \text{ or } (1/\eta_r)^{0.4} = 1 - K\Phi, \qquad (1)$$

where K represents the solvation of the dispersed particles. In Krieger and Dougherty's equation the exponent of Eq.(1) was replaced by $[\eta]/K$ ($[\eta]$ is the intrinsic viscosity), instead of 2.5. Since Pal and Rhodes used Eq.(1) to interpret their data from flocculated emulsions (including flocs) droplets of spherical shape, this exponent was taken to be 2.5 directly. We applied Eq.(1) to

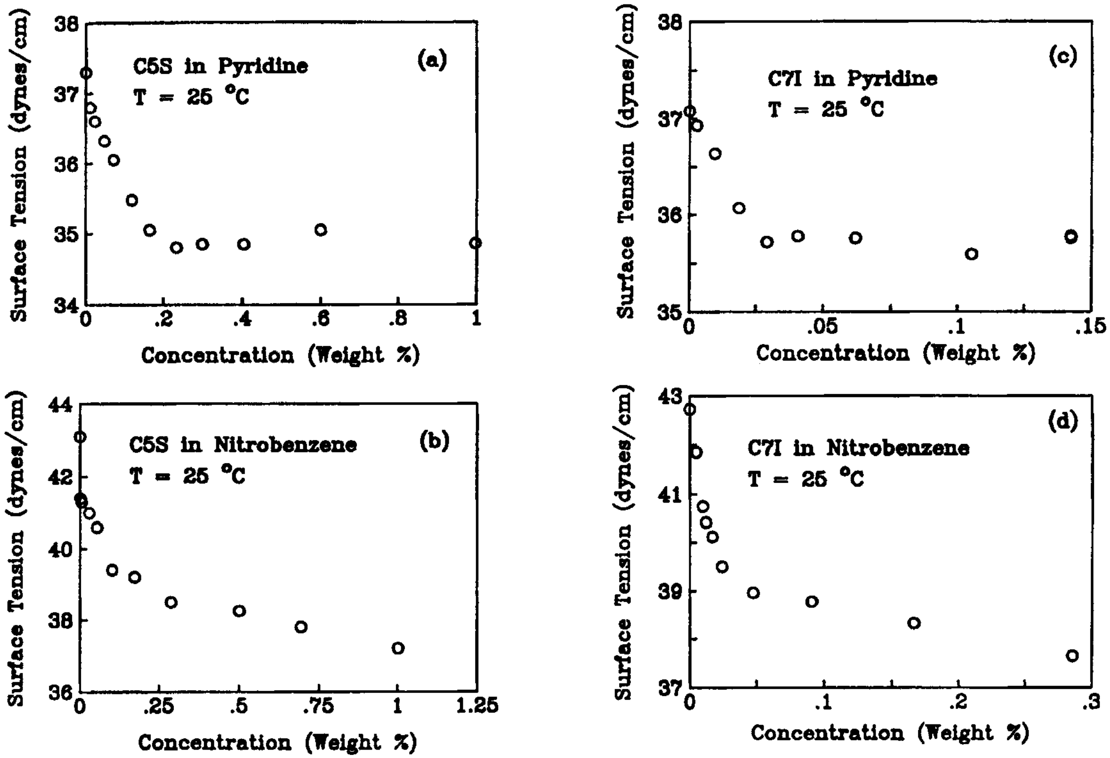

Fig. 1. Surface tensions of C5S and C7I as a function of concentration in various solvents.

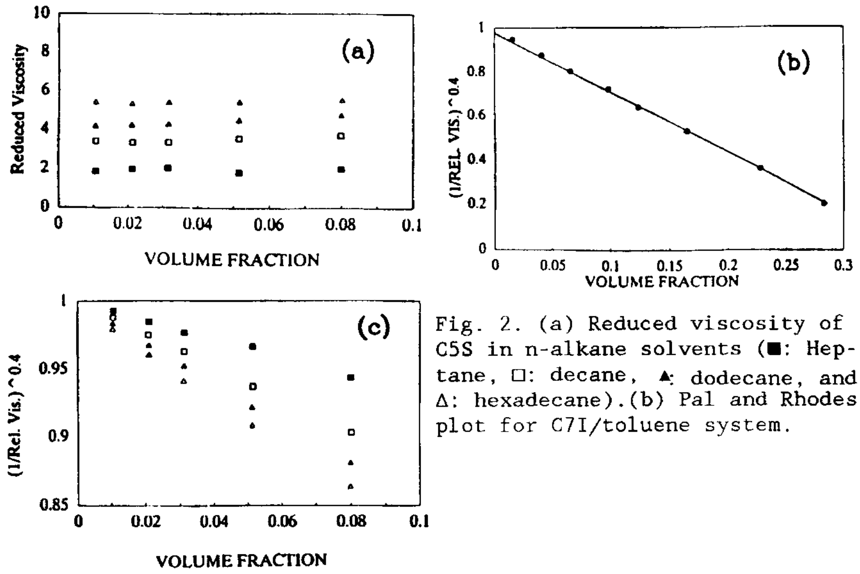

Fig. 2. (a) Reduced viscosity of C5S in n-alkane solvents (■: Heptane, □: decane, ▲: dodecane, and Δ: hexadecane).(b) Pal and Rhodes plot for C7I/toluene system.

explain our data and found that the $(1/\eta_r)^{0.4}$ vs Φ plots for both C5S series (Fig. 2b) and C7I (Fig. 2c) cases exhibited linearity. This means that Eq.(1) is an appropriate equation to use, and the particles are approximately spherical. The K values obtained increased monotonically as the solvent carbon chain length increased, indicating an increasing solvation effect. This is qualitatively consistent with the trend of their intrinsic viscosities. It also agrees with a recent study by Ali and Saleem[21] using solvent fractionation. In order to quantitatively estimate the amount of solvation from the extracted K values, the assumption made by Pal and Rhodes, that the particles are hard spheres, should be met. Unfortunately, in our systems this was not the case. Instead of being hard spheres, the VR colloids exhibit significant surface roughness (to be described in the next section). We thus adopted an equation developed by Eiler[22], which allowed us to estimate the maximum packing volume fraction Φ_m. The difference between this extracted Φ_m and that of an ideal hard sphere system would then provide the degree of solvation. The Eiler's equation reads

$$\eta_r = [1 + k(\Phi/\Phi_m)/(1 - \Phi/\Phi_m)]^2$$

or

$$(\eta_r^{1/2} - 1)/\Phi = [\eta]/2 + (1/\Phi_m)(\eta_r^{1/2} - 1). \qquad (2)$$

We followed Eq.(2) by plotting $(\eta_r^{1/2}-1)/\Phi$ vs $(\eta_r^{1/2}-1)$ and found the plots to be linear for all C5S (Fig. 3a) and C7I (Fig. 3b)

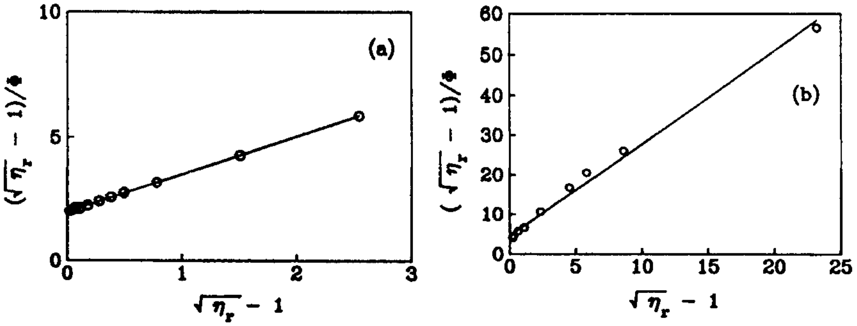

Fig. 3. Eiler plots for (a) C5S/dodecane and (b) C7I/toluene.

cases. The intrinsic viscosities obtained (from the y-axis interceptions) were consistent with those obtained from reduced viscosity plots (Fig. 2a). The Φ_m's extracted are tabulated in Table I. In order to relate Φ_m to the degree of solvation, we made the following assumptions: (1) a colloid and its nearest neighboring colloids form a face center cubic (fcc) structure[23,24], and (2) the solvated molecules form a layer of thickness ΔR on the VR colloidal surface. With the first assumption, the expected Φ_m will be 0.74 for a ideal hard sphere system. Thus, the difference between Φ_m extracted from Eiler analysis and 0.74 can be used to calculate the solvated volume. The second assumption allows us to estimate the solvated layer thickness by the following equation, which can be derived in a straight forward manner,

$$\Delta R/R = (0.74/\Phi_m)^{1/3} - 1. \tag{3}$$

R in Eq.(3) represents the unsolvated core radius. From the slopes of Fig. 3a and 3b and Eq.(3) we obtained $\Delta R/R$ to be 0.05 and 0.2 respectively. Apparently, the degree of solvation for C7I/toluene is much higher than C5S/dodecane system. This result can be justified by the small angle neutron scattering study, to be described in the next section.

If we assume the particles are hard spheres and use K to estimate $\Delta R/R$ ($\Phi_m = 1/K$, and Eq.(3), according to Krieger[16]), we obtain $\Delta R/R = 0.03$ for C5S/dodecane and 0.26 for C7I/toluene, different from Eiler's analysis. This difference reflects the effect of surface roughness. In order to compare with a hard sphere system, we simulated the relative viscosity of a hard sphere system for volume fraction higher than the percolation concentration[25], according to Campbell and Forgacs[26]. Fig. 4a and 4b show the results. As one can see, our systems are only "similar" to a hard system within certain volume fraction ranges. It is thus dangerous to calculate $\Delta R/R$ using K directly.

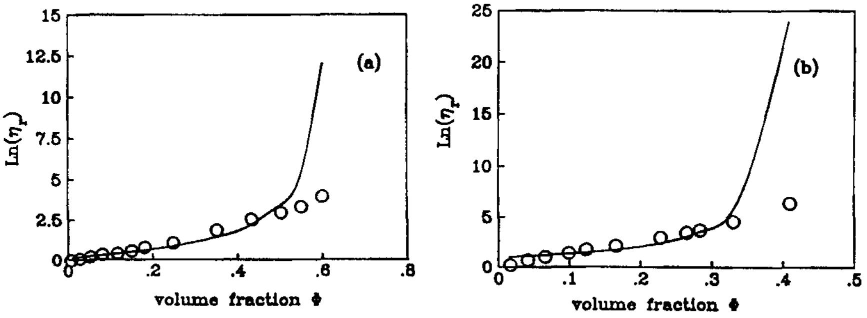

Fig. 4. (a) Viscosities for C5S/dodecane and its corresponding hard sphere system. (b) Same plot for C7I/toluene.

IV. Structure, Polydispersity, and Surface - A Small Angle Neutron Scattering Study

Small angle neutron scattering (SANS) has been applied to study structure of micellar systems[27-29], microemulsions[30-32], and polymeric systems[33-34]. It measures the differential cross section per unit volume of the scatterer. In a dispersed system, the suspended particles can be treated as the disperse phase. In this case, the whole system can be treated as a two-component fluid. For a polydispersed two-component fluid, the scattering intensity can be written as,

$$I(Q) = N_p(\Delta\rho)^2 \langle V_p^2 \rangle \langle P(Q) \rangle \langle S(Q) \rangle . \qquad (4)$$

N_p is the number density of the dispersed particles, $\Delta\rho$ is the particle-solvent contrast, V_p is the particle volume, $P(Q)$ is the form factor representing the particle structure, and $S(Q)$ is the structure factor governed by interparticle correlations. $\langle\ \rangle$ represents the average over the particle polydispersity. Since the continuous phases of our systems were oil-like, and the interparticle interactions are short-ranged, the structure factor was neglected (by taking $\langle S(Q) \rangle = 1$) in our SANS analysis. In addition, the contrast term is very difficult to compute for our cases. This is due to the complicated chemical constituents of VR. We thus used an amplitude factor A to represent the prefactors. By this, Eq.(4) becomes

$$I(Q) = A \cdot \langle P(Q) \rangle . \qquad (5)$$

The SANS experiment for VR colloids was performed on Small Angle Diffractometer (SAD) of Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory. The spectrometer was set to cover a scattering vector range, Q, from 0.007 to 0.35 Å^{-1}, which corresponds to a resolution of approximately 10 to 500 Å.

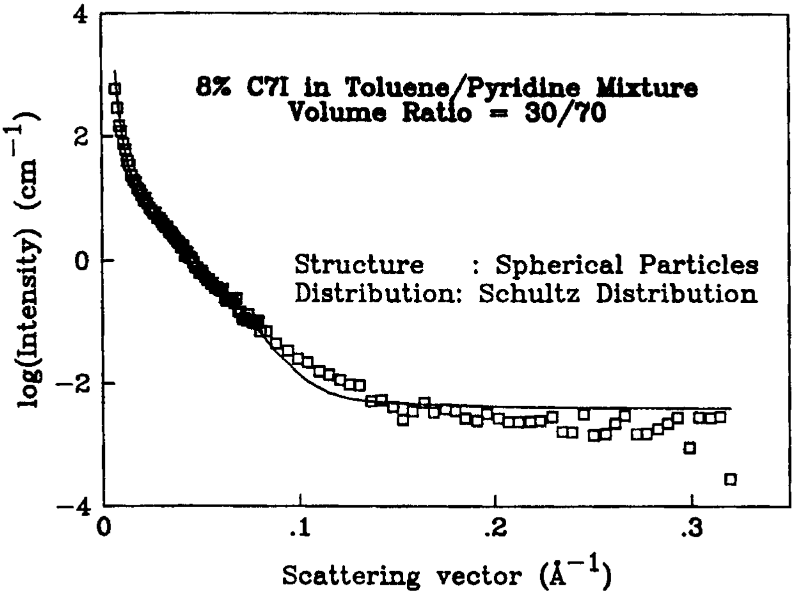

Fig. 5. A typical SANS intensity distribution I(Q). The solid line is the fitted curve.

In the experiment, we measured C5S/n-alkane solvents for n = 7, 10, 12, 14, and 16 at T = 22 °C to investigate the chain length effect. The other series measured was C7I in various toluene/pyridine mixtures for studying the effect of solvent permittivity.

The scattering intensity distributions for all the samples showed pronounced small angle scattering, indicating the existence of colloidal-like particles. In order to properly analyze the SANS data, we employed a self-consistent mechanism, recently proposed by Sheu[35]. A typical analysis is depicted in Fig. 5. The particles were found to be spherical (consistent with our rheological study). The size distribution was found to follow a Schultz distribution, which has the following form,

$$f(R) = [(z+1)/\bar{R}]^{z+1} \cdot R^{z}/\Gamma(z+1) \cdot \exp[-(z+1)R/\bar{R}]. \qquad (6)$$

The parameter z is a width parameter, characterizing the polydispersity. The polydispersity, defined as,

$$p = \sqrt{R^{2} - \bar{R}^{2}} \,/\, \bar{R}, \qquad (7)$$

($\bar{R}$ is the average particle radius) can be expressed in term of z as $p = 1/\sqrt{z+1}$. We extracted both $\bar{R}$ and p for C5S/n-alkane and

Table I. Maximum packing fraction extracted from Eiler's plot

Carbon Length	7	10	12	14
Φ_m	0.68±0.01	0.65±0.01	0.64+0.01	0.6±0.01
ΔR/R	0.029	0.044	0.05	0.072

Table II. Extracted parameter from SANS analysis

Conc. (%)	Toluene/Pyridine *	Radius (Å)	Polydispersity (%)
8	100/0	32.4 ± 0.4	17.6
8	85/15	31.3 ± 0.3	19.2
8	70/30	30.4 ± 0.3	20.4
8	55/45	30.8 ± 0.3	20.5
8	30/70	30.1 ± 0.3	21.7
4	80/20	30.8 ± 0.4	18.6
4	60/40	31.6 ± 0.3	19.7
4	40/60	31.1 ± 0.3	20.4
4	20/80	30.7 ± 0.4	21.3
2	80/20	31.6 ± 0.4	19.0
2	60/40	31.8 ± 0.3	19.4
2	40/60	31.3 ± 0.4	19.6
2	20/80	30.8 ± 0.3	20.2
1	80/20	31.6 ± 0.4	19.7
1	60/40	31.5 ± 0.4	19.0
1	40/60	32.0 ± 0.5	19.7
1	20/80	31.0 ± 0.4	19.0

* The toluene/pyridine is in volume ratio.

C7I/(toluene/pyridine mixture) systems. The results are given in Table II. The average radius of C5S colloids decreased as a function of solvent carbon chain length, implying increasing solvent quality. This agrees with our rheological study. No appreciable dependence of C7I colloidal size was observed when the toluene/pyridine ratio or C7I concentration was varied. This indicates that C7I molecules have an association energy substantially higher than the van der Waal forces, otherewise, a strong size dependence on the toluene/pyridine ratio would be observed. This is because pyridine has a much higher dielectric constant (12 compared to 2.4 for toluene). The sizes of C5S colloids obtained were much smaller than those for C7I (this comparison is plausible because the solvent effect does not seem to be essential). This indicates that the C5S molecules have lower molecular weight, as reported by DeCanio et. al.[36]. With this structural information, one can easily explain why the solvation of C7I is much higher than C5S (see the previous section). A possible scenario is as follows: the C7I molecules are larger and possibly more complex than C5S molecules. They naturally create more cavity space, while packing themselves into an aggregate. Since these cavities are filled with solvent molecules, the degree of solvation for C7I molecules is higher.

It is also interesting to note that the Schultz distribution determined from SANS study is very similar to the molecular weight distribution obtained from the MS study of Storm et. al.[16].

SANS data can also be used to calculate the colloidal surface area. Porod[37] derived an equation for this purpose based on Debye's scattering function[38],

$$\frac{S}{V} = \Pi \cdot \lim_{Q\to\infty} I(Q)\cdot Q^4 \Big/ \int Q^2 \cdot I(Q)\, dQ \qquad (8)$$

This equation is valid only when the interface is well defined. Eq.(8) is not expected to converge at $Q \to \infty$, if the colloids have diffused boundaries. Fig. 6a and 6b show the analyses for C5S/n-alkane and C7I/(toluene/pyridine) systems respectively. Some striking features were found in this analysis. First, the surfaces for all systems were rough (no convergence at large Q limit in Porod's plot). Secondly, no observable effect for either the carbon chain length on C5S (Fig. 6a) or the solvent permittivity on C7I (Fig. 6b) interfacial area and surface roughness (all curves overlap for nearly the entire Q range for both cases). Finally, for a given volume fraction, C5S colloids form a total interfacial area of approximately 3 time larger than those of the C7I colloids (a representative C5S case (+) was shown in Fig. 6b for comparison). Based on the last feature, we can compare the surface "roughness" of C5S and C7I colloids. Since both C5S and C7I colloids are spherical and their radius ratio is approximately 0.6 (see Table II), the corresponding surface area ratio was expected to be 5/3 (if $N_1R_1{}^3 = N_2R_2{}^3$, then, $N_1 \cdot 4\Pi R_1{}^2 / N_2 \cdot 4\Pi R_2 = R_2/R_1$). This will be true if their surface roughness is the same. However, our analysis showed a ratio of about twice the expected value. This suggests that C5S colloids have much "rougher" surfaces.

V. Conductivity

As we mentioned in section I, it is necessary to understand the type of interaction that initiates the molecular association, in order to evaluate the intermolecular association forces. To achieve this, we performed a series of AC conductivity measurements for a C7I/toluene system at various temperatures. The rationale for selecting the conductivity measurement was based on our SANS

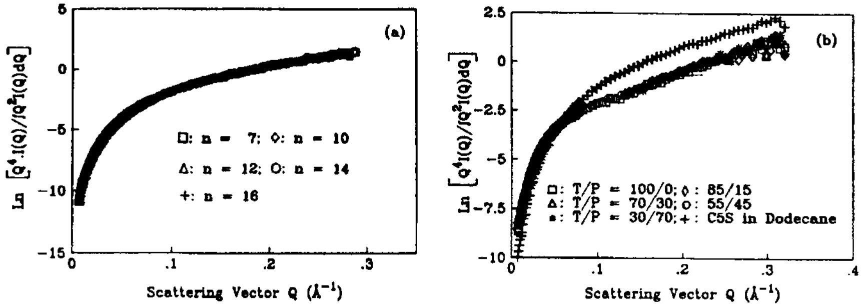

Fig. 6. Surface roughness analysis using Porod's equation. (a) C5S/n-alkane series, and (b) C7I in toluene/pyridine series.

study. The SANS results showed that the structure factor, S(Q), was negligible for concentrations up to ~15 weight percent. This means that the inter-colloidal interaction is very short-ranged. The results also showed that the molecular association is much stronger than can be attributed to van der Wall forces[39]. Otherwise, there would be an appreciable dependence of size on both solvent dielectric constant and concentration. Thus, this strong association force is likely related to intermolecular charge transformation, which can be verified by conductivity measurements.

The conductivity measurements were performed using a Hewlett Packard 4192 low frequency impedance analyzer. The cell used contained four-plate platinum black electrodes. The conductivity and the permittivity were measured simultaneously for each C7I/toluene sample in a frequency range of 100 to 1.3×10^6 Hz.

In Fig. 7 we give the AC conductivity measurements for 20% C7I/toluene at various temperatures. Noting that the AC conductivities remained nearly unchanged initially, but suddenly increased when the frequency exceeded a certain threshold. This unusual frequency response indicates that the charges move freely only within a small spatial domain (high frequency corresponds to short time, or short length scale). A logical interpretation of this phenomenon is that the charges move nearly freely within a colloid, but do not hop between colloids frequently. If this is true, then, the charge transformation energy would likely be the free energy that induces the molecular associations.

In the following section, we shall discuss the dynamics of the colloids and their dielectric responses upon heating.

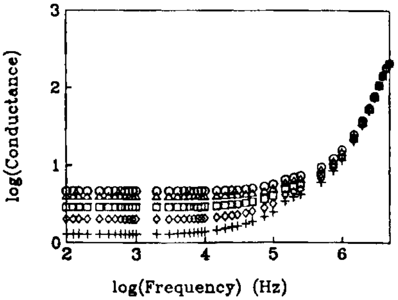

Fig. 7. Conductivity for C7I/toluene at various temperatures (+: 10 °C, ◇: 20 °C, □: 35 °C, Δ: 50 °C, and o: 60 °C).

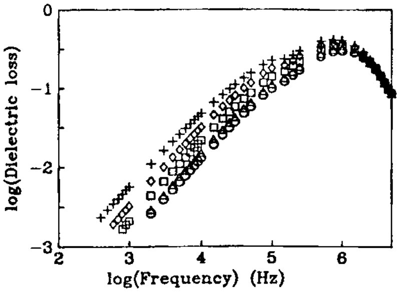

Fig. 8. The corresponding dielectric loss as a function of frequency (see Fig. 7).

VI. Dynamic Slowing Down - Dielectric Relaxation Study

Fig. 8 shows the dielectric loss of a 20% C7I/toluene system at various temperatures. We analyzed the data using Cole-Cole equation[40]

$$\epsilon''(\omega) = \epsilon_\infty + \Delta\epsilon/[1 + (i\omega\tau)^{1-\alpha}] \tag{9}$$

where ϵ'' is the dielectric loss, ω the frequency, ϵ_∞ the dielectric constant at high frequency limit, τ the relaxation time, and α the frequency spread parameter, representing the slowing down of the system relaxation ($\alpha = 0$ corresponds to the standard Debye relaxation with no slowing down). The α values extracted were non-zero, reflecting an effect of dynamic slowing down of particle diffusion. For lower temperatures the effect became more significant, similar to microemulsion systems. We attributed this slowing down of diffusion dynamics to the structural caging effect, with strength depending on inter-colloidal correlations. Apparently, this effect is significant, even at 20% concentration.

DISCUSSION

Speight et. al.[41] showed a hypothetitcal curve of VR molecular weight evolution as a function of concentration, and suggested that if this curve can be measured, it would provide direct proof for VR molecular self-association. In our study, we took an alternative route. Since the molecular weight measurement is too difficult for such a dilute system, we "made" the VR molecules serve as surfactants via properly selecting a solvent. Under this circumstance, one part of the VR molecules exhibit solvent affinity, while the other part does not. Thus, we can measure the surface tension to see if "micellization" occurs. Since a phenomenon similar to the micellization process was observed, we believed that VR molecules self-associate to form colloidal-like particles.

In interpretation of our viscosity data, we combined three theories, by which we determined the VR colloidal structure and the degree of solvation. We also compared our systems to a hard sphere system and found that their similarity only lies within a narrow concentration range. The structure agrees with our SANS results, and the solvation of C5S/n-alkane systems agrees qualitatively with the previously reported results[21]. The size distribution, determined by SANS, closely follows a Schultz distribution function. It is similar to the molecular weight distribution of an asphaltene system reported by Storm et. al.[16]. The surface roughness of the VR colloids was determined from SANS data using Porod's formula[37]. The results showed that both C5S and C7I colloids have diffused surface boundaries and C5S colloids have rougher surfaces. In addition, the SANS results show that the colloidal sizes are nearly independent of concentration, unlike most micellar systems. This independence is likely due to the packing constraint, since individual VR molecule can be structurally different. Every VR colloid can be viewed as the final packing product with a strong intermolecular interaction. Hence, they do not grow as a function of concentration.

In the AC conductivity study, we identified that charge transfer energy may be the main interaction that induces VR molecular associations. This was concluded from the conductivity responses to the applied frequency. The dielectric response measurement allows us to characterize the dynamics of the C7I/toluene systems. The results suggests that for 20% concentration, the interparticle interaction is significant enough to build structural cages. These structural cages greatly reduce the free diffusion of the colloidal particles.

PERSPECTIVE

In order to develop efficient technology for upgrading the bottom of the barrel fraction of crude oil, we need to establish that asphaltenes are the species colloidally dispersed in crude oil, and these colloidal particles are formed by aggregation of small molecules (molecules about the same size as the other molecules in crude oil). Additionally, studies of asphaltenes in solvents will help identify the origin of the forces responsible for the association. Furthermore, it will be useful to develop an understanding of the phase behavior exhibited by these complex fluids, because molecular association forces strongly depend on the phase of the system. This information will perhaps provide the key to avoid current difficulties associated with refining the bottom of the barrel.

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