Soft Matter

PAPER

Field- and concentration-dependence of electrostatics in non-polar colloidal asphaltene suspensions

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Electrostatic stabilization has recently been found to be an important factor in non-polar colloidal asphaltene suspensions. However, the nature of charging in asphaltene systems may be quite different than in other non-polar colloid systems. For instance, the origin of charging in asphaltene colloids arises from both positive and negative charges native to the asphaltenes. In part due to this bimodality of surface charge, some dispersants are shown to stabilize asphaltene colloids at concentrations below their cmc. This effect does not arise from ionic effects of the dispersant, but rather from preferential dispersant adsorption onto charged sites on the colloidal asphaltene surface. Due to the long-range nature of electrostatics in non-polar systems, electrophoretic mobility can depend on both electric-field and particle volume fraction. We investigate the field- and concentration- dependence of electrophoretic mobility in non-polar colloidal asphaltene suspensions. Our results suggest that colloidal asphaltene suspensions stabilized by non-ionic dispersants can exhibit large screening lengths even in the presence of dispersant micelles. Due in part to the large screening length, a decrease in electrophoretic mobility can occur even at low colloidal particle concentrations.

Introduction

The destabilization and precipitation of asphaltenes from petroleum fluids begins with a liquid–liquid phase separation from the molecular scale and, in the absence of any preventative measures, continues to complete phase separation.[1] Asphaltene molecules consist of fused benzene rings with aliphatic chains: π–π bonding of the benzene rings facilitates asphaltene association and destabilization in unfavorable conditions. During the precipitation process, the association and aggregation of asphaltene molecules generates colloidal scale particles. Colloids in non-polar suspensions are typically difficult to stabilize, as evidenced by the inherent instability of asphaltene colloids toward aggregation, deposition and sedimentation.[2–4] One reason for the inherent instability of colloids in non-polar suspensions is the high energetic cost of charge separation in low-dielectric constant liquids. Electrostatics have recently been shown to play an important role in colloidal asphaltene suspensions: asphaltene colloids exhibit both positive and negative surface charges, rendering them highly susceptible to aggregation.[5] The control of surface charge characteristics by dispersants converts native asphaltene charges from a liability to an asset. Through surface adsorption covering the negative charges found on the asphaltene colloids, the use of dispersants

results in uniformly positive charged particles which effectively repel each other.

The origin of charge in non-polar colloidal systems remains a topic of lively discussion in the literature. Charge is thought to arise due to the presence of additives, sometimes called charge-control agents, in concentrations beyond their critical micelle concentration in the non-polar liquid. While there is total charge neutrality in the system, the interaction of neutral micelles can result in a pair of charged micellar ions; the non-polar tails of the molecules transiently stabilizing the charged micelles against neutralization.[6,7] Depending on the surface chemistry of the colloids, the charged micelles can then adsorb onto the colloids or induce acid–base interactions or ion exchange at the surface.[8–10] Only a few such "charge disproportionation" events are sufficient to effectively charge colloids in non-polar systems.[6] While charge-control agents are mainly ionic surfactants or dispersants at concentrations above their cmc, non-ionic dispersants can be effective at concentrations below the cmc.[5,11] In the unique case of non-polar colloidal asphaltene suspensions, the charge arises from the asphaltenes themselves: asphaltene colloids in non-polar suspension exhibit both non-zero electrophoretic mobility and significant conductance even in the absence of dispersants.[5]

Several caveats are associated with observations of electrostatic phenomenon in non-polar systems. Due to the long-range nature of electrostatics in low-dielectric liquids, non-polar colloidal suspensions can exhibit electrostatic behavior which is dependent on particle volume fraction.[12,13] Varying the electric

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field strength used to measure mobility can lead to non-monotonic behavior, as has been reported in suspensions of PMMA particles in hexane.[11] These effects have yet to be quantified in non-polar colloidal asphaltene suspensions. In this study we investigate the dependence of colloidal asphaltene electrophoretic mobility on electric field strength, colloidal volume fraction, and dispersant concentration. We find that the Hückel limit of long screening length applies in the colloidal asphaltene suspensions. While estimates of the surface charge and zeta potential are comparable to other non-polar colloidal suspensions, asphaltene suspensions exhibit interesting effects, such as low-concentration charge regulation and destabilization by moderate electric fields.

Materials and methods

We obtain a proprietary non-ionic dispersant of the polyolefin alkeneamine class with molecular weight $\sim$2000, which we call BA (Lubrizol Corporation). We use the dispersant as received. The critical micelle concentration c_c of the dispersant BA in heptane has been previously reported: $c_c = 10$ ppm by weight.[5] We prepare stock solutions of BA in heptane at a range of normalized concentrations $\bar{c} = c/c_c$ from 0 to 10.

We obtain a petroleum fluid, SB, from Abu Dhabi, and characterize its asphaltene content by filtration with an asphaltene precipitant. We precipitate asphaltenes by adding heptane, and define the heptane ratio χ, with units mL g^{-1}, indicating the number of mL of heptane (Fisher) mixed with 1 g of oil. The asphaltene content of SB is measured by mixing the oil with heptane at $\chi = 40$ mL g^{-1}.[4] The mixtures are sonicated for 1 min, allowed to equilibrate for several hours, and filtered through 0.2 μm pore-size cellulose nitrate membrane filters (Whatman). The filtrate is collected, dried and weighed to give a fraction of asphaltenes in the oil $f = 0.007$ g g^{-1}. We measure the density of the petroleum fluid to be $\rho = 0.865 \pm 0.005$ g mL^{-1} (Anton Paar). By dissolving the asphaltene filtrate in toluene as previously described, we measure the density of the asphaltenes to be $\rho_a = 1.1 \pm 0.09$ g mL^{-1}.[5]

Samples are prepared by adding heptane solutions of varying concentrations of the BA dispersant to the SB oil, for a total sample volume of 3 mL. Samples are sonicated for 1 min after mixing and the properties of the resultant asphaltene colloids are measured immediately thereafter. Samples are prepared with a given volume of heptane per mass of the SB oil, between $\chi = 30$ and 300 mL g^{-1}. The asphaltene volume fraction ϕ is obtained by $\phi = f/(\chi \rho_a)$. While $\bar{c}$ refers to the normalized concentration of BA in heptane, the ratio of BA to oil is also known: for instance, when $\bar{c} = 1$ at $\phi = 2 \times 10^{-4}$, the ratio of BA to oil is 200 ppm.

Phase analysis light scattering (ZetaPALS, Brookhaven) is used to measure the electrophoretic mobility μ of the colloidal asphaltenes as a function of electric field strength E, particle volume fraction ϕ, and normalized dispersant concentration $\bar{c} = c/c_c$. The electric field dependence of μ is measured at $\phi = 9 \times 10^{-5}$ and at $\bar{c} = 0.1$, 1, and 10, over a range $E = 1.4$ to 55.6 kV m^{-1}. To measure $\mu(\phi)$ and $\mu(\bar{c})$, we fix the voltage at 10 V across an electrode gap of 0.36 cm, giving $E = 2.8$ kV m^{-1}. To investigate dependence on $\bar{c}$, we prepare samples at $\phi = 9 \times 10^{-5}$ and $\phi = 2 \times 10^{-4}$, with $\bar{c}$ ranging from 0.01 to 10. To investigate the dependence on ϕ, we prepare samples at $\bar{c} = 5$ and 10, varying ϕ

from 2×10^{-5} to 2×10^{-4}. Between 5 and 10 measurements were taken for each sample, and 3–10 samples are measured at each combination of E, ϕ and $\bar{c}$. Phase analysis light scattering can detect mobilities as low as 10^{-10} m^2/Vs.[14,15]

We use dynamic light scattering (ZetaPALS, Brookhaven) at a wave vector $q = 0.01872$ nm^{-1} to investigate the dependence of particle diameter a on both ϕ and $\bar{c}$. Dependence of a on $\bar{c}$ is measured at $\phi = 9 \times 10^{-5}$ and $\phi = 2 \times 10^{-4}$, while dependence on ϕ is measured at $\bar{c} = 5$ and 10. DLS measurements for each sample are collected every 30 s for approximately 20 min.

All measurements are taken at room temperature.

Results and discussion

We use phase analysis light scattering (PALS) to measure the electrophoretic mobility $\mu = v/E$ of colloidal asphaltenes in suspension, where v is the particle velocity given an electric field strength E. Similar to laser Doppler electrophoresis, PALS measures the phase shift of a laser signal compared to a reference signal which does not pass through the electric field. Given the balance of hydrodynamic drag and electrostatic forces, mobility measurements reflect both the total number of surface charges Q and the particle size a: $\mu \sim Qe/(3\pi\eta a)$, where η is the solution viscosity and e the elementary charge. This relationship between μ, Q, and a is strictly true only in dilute suspensions and in the unscreened bare Coulomb interaction limit.[15]

Because μ in non-polar suspensions can be quite small, we obtain several measurements in the absence of electric field to determine how PALS interprets instantaneous velocities due to Brownian motion alone. We prepare asphaltene suspensions by mixing the petroleum fluid SB with heptane to achieve a volume fraction ϕ between 2×10^{-4} and 2×10^{-5}. We discard measurements below 10^{-10} m^2/Vs, the nominal noise floor of the instrument[14,15] The value of artificially interpreted μ due to Brownian motion ranges between -0.029 to 0.031×10^{-8} m^2/Vs over a selection of six samples at $\bar{c} = 0$, with an average magnitude of 0.016×10^{-8} m^2/Vs. A histogram of these results is shown in Fig. 1(a). This measurement establishes $\mu \sim 0.03 \times 10^{-8}$ m^2/Vs as a more appropriate "diffusive" noise floor for the PALS technique; smaller magnitudes cannot be interpreted as being due to the presence of surface charges: they could result simply from Brownian motion of the asphaltene colloids.

To measure the true value of μ due to electrophoresis, we choose several samples at $\bar{c} = 0$ measured with electric field. Of these, 70% of the measurements fall outside the range obtained due to diffusion alone. A histogram of the mobilities for $\sim$90 measurements at three combinations of asphaltene concentration and field strength is shown in Fig. 1(b). Approximately 50% of the measurements give negative results, with an average $\langle \mu_- \rangle = -0.043 \times 10^{-8}$ m^2/Vs. The magnitude of the positive measurements averages $\langle \mu_+ \rangle = 0.049 \times 10^{-8}$ m^2/Vs. The magnitudes of the measurements are larger than the diffusive noise floor of the technique, and therefore can be interpreted as arising from surface charge on the asphaltene colloids.
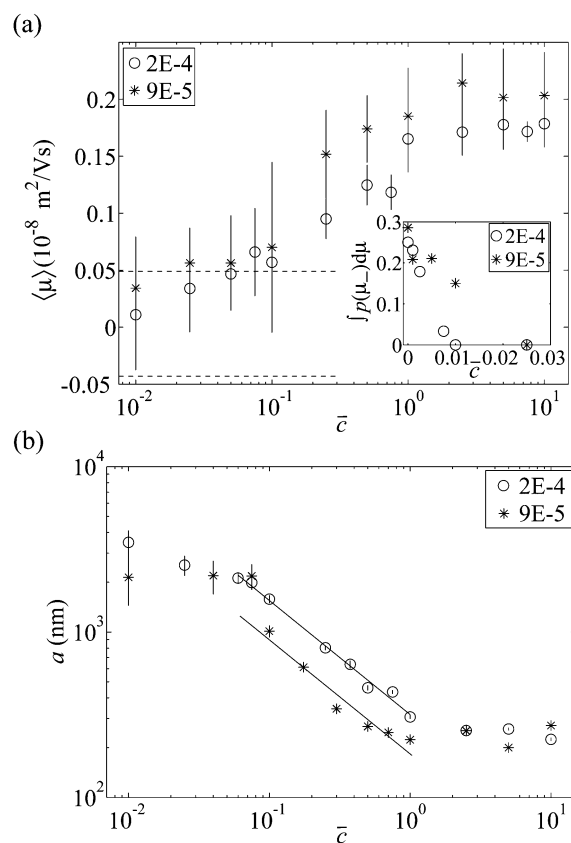
The result suggests that asphaltene colloids carry both positive and negative surface charges. One interpretation of this result is that some particles may have a small net positive charge, while others have a small net negative charge, resulting in the bimodal distribution of μ. This bimodality may explain previously

(a)

(b)
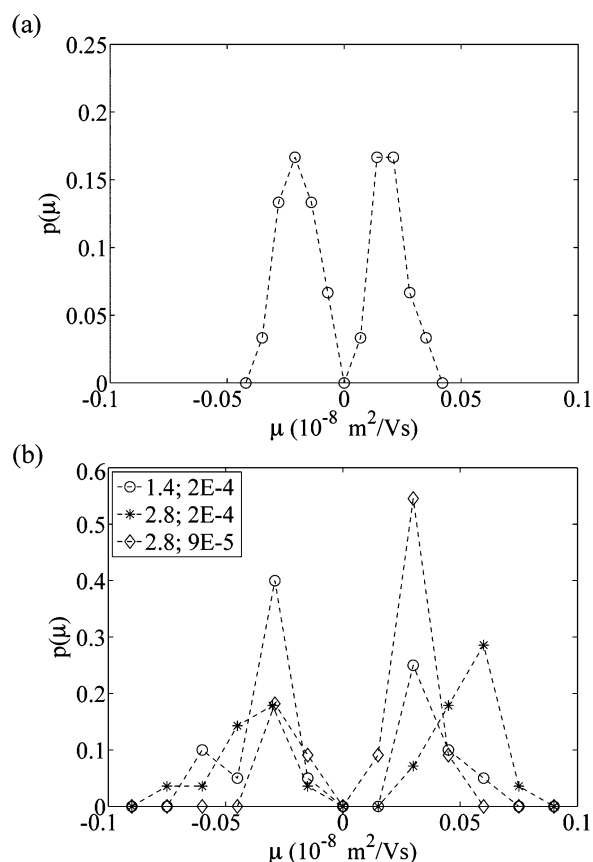
Fig. 1 Bimodal surface charge at $\bar{c} = 0$: (a) shows a histogram $p(\mu)$ of mobilities measured with $E = 0$ kV m^{-1}. (b) shows $p(\mu)$ measured at $\phi = 2 \times 10^{-4}$ at $E = 1.4$ and 2.8 kV m^{-1}, and at $\phi = 9 \times 10^{-5}$ at 2.8 kV m^{-1}, as shown in the legend.

(a)

(b)

Fig. 2 Variation of colloidal properties with $\bar{c}$: (a) shows $\langle\mu\rangle(\bar{c})$ at both $\phi = 2 \times 10^{-4}$ and 9×10^{-5}. The dashed lines indicate $\langle\mu_-\rangle$ and $\langle\mu_+\rangle$ at $\bar{c} = 0$. (b) shows $a(\bar{c})$ at $\phi = 2 \times 10^{-4}$ and 9×10^{-5}; the solid lines are fits to the data.

reported electrodeposition results, which indicate that asphaltenes are charged entities that can deposit on either anode or cathode, and sometimes on both anode and cathode from within a single suspension.[16–18] While the origin of the charges is not fully understood, the aliphatic tails in molecular asphaltenes are known to contain metallic components which influence the stability of asphaltenes in non-polar systems.[19,20] These same metallic components could contribute to positive charges in the system. Negative charges might arise from the π electron clouds. Zwitterions and acid–base surface groups have also been proposed as a source of charge on asphaltenes.[21,22]

Once dispersant is added to the system, the total fraction of negative measurements $\int p(\mu_-)d\mu = 0.3$ at $\bar{c} = 0$ and decreases to 0 at or before $\bar{c} = 0.025$, at which concentration all subsequent measures are fully positive, as seen in the inset to Fig. 2(a). The average mobility $\langle\mu\rangle$ as a function of $\bar{c}$ has three regions: at low $\bar{c}$, the average mobility is roughly constant, and low compared to the average positive value found in the absence of dispersant. Beginning at approximately $\bar{c} = 0.1$ of dispersant, $\langle\mu\rangle$ begins to rise. This is true both for suspensions at $\phi = 2 \times 10^{-4}$ and 9×10^{-5}. In between $\bar{c} = 0.1$ and 1, asphaltene colloids in the more dilute suspensions exhibit slightly higher mobilities by ~40%. In each case, the mobility reaches a plateau value at $\bar{c} = 1$. For $\phi = 2 \times 10^{-4}$, $\langle\mu\rangle = 0.173 \pm 0.005 \times 10^{-8}$ m^2/Vs. When $\phi = 9 \times 10^{-5}$, approximately half the volume fraction of asphaltenes,

$\langle\mu\rangle = 0.201 \pm 0.012 \times 10^{-8}$ m^2/Vs. The shape of $\langle\mu\rangle(\bar{c})$ is the same for both values of ϕ, but the entire curve is shifted to slightly higher values at smaller ϕ. The plateau $\langle\mu\rangle$ in the more dilute suspensions is ~14% larger, as seen in Fig. 2(a). The dashed lines indicate $\langle\mu_-\rangle$ and $\langle\mu_+\rangle$ at $\bar{c} = 0$.

Because mobility reflects both particle size as well as surface charge, we measure the colloidal particle size as a function of $\bar{c}$. In samples with little to no added dispersant, initial measurements reveal particles a few μm in size. These particles are prone to aggregation after ~15–20 min, and we report a, their size prior to aggregation.[4] Less than $\bar{c} = 0.1$ in suspension prevents colloidal asphaltene aggregation, and the size distribution of particles at $\bar{c} > 0.1$ is monomodal, with standard deviations less than 10%. With increasing dispersant, a decreases an order of magnitude to $a \sim 260$ nm at $\bar{c} = 1$ and beyond. Between $\bar{c} \sim 0.06$ and 1, the decrease in a follows a power law: $a \sim (\bar{c})^s$, where the slope $s = -0.69$ fits the data with $R^2 = 0.992$. The power law decrease in a with $\bar{c}$ occurs in suspensions at $\phi = 2 \times 10^{-4}$ and 9×10^{-5}. However, at $\phi = 9 \times 10^{-5}$, a in the power law region is ~50% smaller than a in the suspensions at $\phi = 2 \times 10^{-4}$, as shown in Fig. 2(b).

The power law decrease of a with $\bar{c}$ can be explained by dispersant adsorption on the colloidal asphaltene surface.[5] Dispersant adsorption during precipitation truncates the growth of asphaltenes at sub-micron length scales, generating a larger

number of smaller particles with an increase in $\bar{c}$. The size of the asphaltene colloids in suspensions at $\phi = 9 \times 10^{-5}$ reaches a minimum size plateau at $\bar{c} = 1$, while at $\phi = 9 \times 10^{-5}$ the minimum size plateau is reached closer to $\bar{c} = 0.5$. The increased ratio of BA to SB oil at lower ϕ may explain this: at $\phi = 2 \times 10^{-4}$ and $\bar{c} = 1$ there is ~200 ppm BA with respect to SB oil, while at $\phi = 9 \times 10^{-5}$, a concentration of ~200 ppm BA with respect to SB is reached at $\bar{c} \sim 0.5$.

Smaller particle sizes may lead to the increased mobilities in the more dilute colloidal asphaltene suspensions between $\bar{c} = 0.1$ and 1. The observed decrease in a between $\bar{c} = 0.1$ and 1 at the lower value of ϕ may explain the corresponding increase in $\langle\mu\rangle$ $(\bar{c})$. However, the difference in the plateau mobility values at $\bar{c} > 1$ is not accompanied by a size difference in suspensions at $\phi = 2 \times 10^{-4}$ and 9×10^{-5}. In order to investigate the dependence of μ and a on colloidal asphaltene volume fraction at $\bar{c} > 1$, we vary ϕ from 2×10^{-5} to 2×10^{-4} at $\bar{c} = 5$ and 10. For small ϕ, $\langle\mu\rangle$ has an average value 0.213×10^{-8} m²/Vs for both $\bar{c} = 5$ and 10. Above $\phi = 9 \times 10^{-5}$ at $\bar{c} = 10$, μ decreases from this plateau, as seen in Fig. 3(a). At $\bar{c} = 5$ the decrease occurs above $\phi = 1.6 \times 10^{-4}$. At both dispersant concentrations, $\langle\mu\rangle$ decreases nearly 20% below its plateau value at low ϕ. Because μ depends on size as well as surface charge, we also measure $a(\phi)$. At $\bar{c} = 5$ and 10, $a = 240 \pm 14$ nm, a variation of <6% over an order of magnitude change in ϕ, as seen in Fig. 3(b). At dispersant concentrations above $\bar{c} = 1$,

the decrease in $\langle\mu\rangle$ with increasing ϕ cannot be explained by any corresponding systematic decrease in a.

The decrease in μ with ϕ may suggest charge regulation, which occurs when particles become crowded enough that nearest neighbors are closer than the screening length κ^{-1}.[12,13,23] An overlap of the ion clouds surrounding the particles effectively lessens the surface charge on all of them to maintain a constant potential.[24,25] As observed in PMMA suspensions in hexadecane, the effects of charge regulation can become even more pronounced as κa decreases toward 0.[25] In the asphaltene suspensions, we obtain the interparticle distance l from the effective total volume per particle: $4\pi l^3/3 = 0.64V/N$, where V is the total sample volume, N the total number of particles, and 0.64 the random hard sphere packing limit. The total number of particles N is related to ϕ: $4\pi a^3/3 = \phi V/N$. We estimate the interparticle distance using $(l/a)^3 = 0.64/\phi$. The effects of charge regulation appear in asphaltene suspensions denser than $\phi > 9 \times 10^{-5}$, when $l/a \sim 20$. At this concentration, $l > \kappa^{-1}$ to enable overlapping screening lengths, suggesting that the screening length is much larger than the particle size: $\kappa a \sim 0.05$. As a comparison, in several literature studies of non-polar colloidal suspensions, κa ranges from 0.05 to 2, and increases with increasing $\bar{c}$.[8,9,11,25,26] Even at $\bar{c} = 10$ in the non-polar asphaltene suspensions, κa remains small. Furthermore, charge regulation in colloidal asphaltenes occurs at a low particle concentration; in other non-polar colloidal systems this effect has been reported at concentrations as high as $\phi = 0.1$.[25]

Given that $\kappa a \sim 0.05$ in the asphaltene suspensions, the Huckel limit $\kappa a \ll 1$ applies. We use μ to estimate the zeta potential of the asphaltene colloids $\zeta = (3\mu\eta)/(2\varepsilon\varepsilon_0)$, where ε is the dielectric constant of heptane and ε_0 the permittivity of free space. The measured range of $\langle\mu\rangle$ between 0.05 and 0.21×10^{-8} m²/Vs gives ζ between approximately 17 and 70 mV. The values of $\zeta \sim 70$ mV at $\bar{c} > 1$ are comparable to measurements in other non-polar suspensions.[8,11,26]

The effects of screened electrostatic interactions usually appear through a decrease in the magnitude of μ as the concentration of ions increases, as is commonly observed in aqueous suspensions at high ionic strength. In non-polar colloidal suspensions stabilized by ionic dispersants, decreases in both μ and ζ have been observed at ionic strengths greater than the cmc of the surfactant.[10,26,27] The effect of screened electrostatics in non-polar suspensions with non-ionic dispersants, on the other hand, is observed at concentrations lower than the cmc, as low as $\bar{c} = 0.2$.[11] In the colloidal asphaltene suspensions with the non-ionic dispersant BA, μ is not observed to decrease with dispersant concentration, even at $\bar{c} = 10$. The lack of evidence of screening in the mobility measurements, coupled with the estimate that $\kappa a \sim 0.05$, suggests that interactions in the asphaltene suspensions may approach the bare Coulomb limit.

In the limit of bare Coulomb interactions, as $\kappa a \to 0$, the balance of electrostatic and hydrodynamic forces allows us to relate μ to both surface charge and particle size, $\mu = Qe/(3\pi\eta a)$. Using the plateau values for $\langle\mu\rangle$ and a, we find $Q \sim 12$ charges per asphaltene colloid. Interestingly, the results suggest that Q remains constant even with the addition of dispersant. The variation of $\langle\mu\rangle(\bar{c})$ seen in Fig. 2(a) could indicate changing Q between $\bar{c} = 0.1$ and 1. However, a decreases with $\bar{c}$ over the same concentration range. Between $\bar{c} = 0.1$ and 1, $\langle\mu\rangle$ increases by
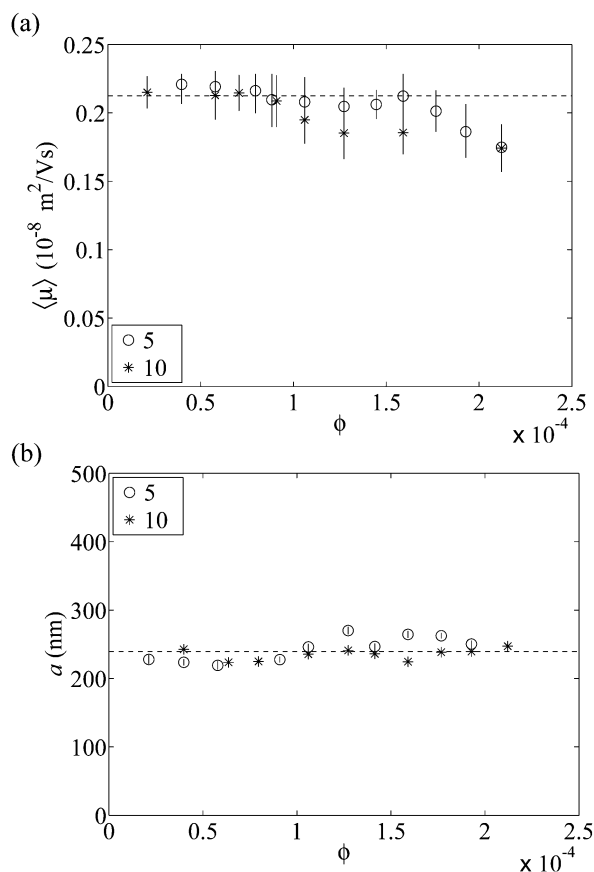
Fig. 3 Variation of colloidal properties with ϕ: (a) shows $\langle\mu\rangle(\phi)$ and (b) shows $a(\phi)$, each at both $\bar{c} = 5$ and 10.

a factor of 3, while a decreases by somewhat less than a factor of 5, suggesting that Q remains relatively constant despite the adsorption of dispersant. Over this same range of $\bar{c}$, even the difference between $\langle\mu\rangle$ at $\phi = 2 \times 10^{-4}$ and 9×10^{-5} can be explained by the difference in particle size. As ϕ is halved over the range $\bar{c} = 0.1$ to 1, a decreases by $\sim 50\%$ while $\langle\mu\rangle$ increases by $\sim 40\%$. The estimate $Q \sim 12$ is somewhat less than that measured on amine-modified latex particles in both hexane and hexadecane.[8,11]

One basic assumption must be confirmed to validate the present results: electrophoretic measurements are obtained as a reliable measure of colloidal surface charge given that the mobility is independent of the applied field. However, in non-polar suspensions this assumption may break down even at moderate field strengths.[28] Field dependence of electrophoretic mobility has been hypothesized to be due to the polarization or even complete detachment of the electric double layer from the particle as it drifts through the electric field.[28,29] For PMMA particles in hexane with the non-ionic dispersant Span 85, as little as 10 kV m^{-1} is sufficient to cause field-dependent results in the measurement of μ.[11,30] In such instances, an extrapolation to the zero-field mobility may be necessary to properly assess compositional effects.[11]

We investigate the importance of electric field strength in the asphaltene suspensions by measuring μ at E between 1.4 and 55.6 kV m^{-1}. For these measurements we use suspensions at $\phi = 9 \times 10^{-5}$, dilute enough to fall before the onset of charge regulation seen in Fig. 3(a). We find that $\langle\mu\rangle$ does not strongly depend on E below ~ 20 kV m^{-1}. Fig. 4 shows results for $\phi = 9 \times 10^{-5}$ and $\bar{c} = 0.1$, 1 and 10. In the case of the colloidal asphaltene suspensions, extrapolation to the zero-field mobility may not be necessary. The composition dependent effects $\langle\mu\rangle(\bar{c})$ and $\langle\mu\rangle(\phi)$, shown in Fig. 2(a) and 3(a), are all obtained at $E = 2.8$ kV m^{-1}, within the region where $\langle\mu\rangle$ is independent of E. At larger E, however, the field-independence breaks down. At $\bar{c} = 0.1$, μ decreases at $E > 20$ kV m^{-1}, signifying a possible degradation of the sample. As $\bar{c}$ is increased, the critical field strength E_c increases to 42 and 50 kV m^{-1} for $\bar{c} = 1$ and 10, respectively. We anticipate that sample degradation can occur once the applied field strength surpasses ζ/a. At $\bar{c} = 0.1$, $\zeta/a \sim 19$ kV m^{-1}, very close to the observed value $E_c \sim 25$ kV m^{-1}. Due to the decrease in particle size with $\bar{c}$, we expect

E_c to increase with $\bar{c}$, as is observed. Interestingly, the observed E_c is nearly an order of magnitude less than anticipated by ζ/a at both $\bar{c} = 1$ and 10. This observation coupled with the fact that $\langle\mu\rangle$ decreases above E_c suggests that the electric field degradation causes an increase in particle size, possibly by inducing aggregation.

Conclusions

Our investigation of the field- and concentration-dependence of colloidal asphaltene mobility reveals several interesting features of non-polar colloidal asphaltene suspensions. The main features of the electrostatics in non-polar asphaltene suspensions are robust despite changes in electric field strength and colloidal volume fraction. In the absence of dispersant, colloidal asphaltenes display a bimodal surface charge, with roughly equal fractions of positive and negative surface charges. The addition of dispersant to the system suppresses the negative measurements and increases the average mobility. The shape of $\mu(\bar{c})$ remains constant at different volume fractions. However, the magnitude of μ increases with a decrease in ϕ. Over a certain concentration range, $\bar{c}$, this increase is explained by a corresponding decrease in particle size. However, measurements of $\langle\mu\rangle(\phi)$ at $\bar{c} > 1$ indicate the presence of charge regulation, a phenomenon that occurs when particles are closer to each other than the screening length. Despite the presence of dispersant micelles, the screening length in the system is large compared to the particle size. Given $\kappa a \ll 1$, we estimate that the asphaltene colloids used in this study can have large ζ, up to 70 mV, and carry approximately 12 unit surface charges.
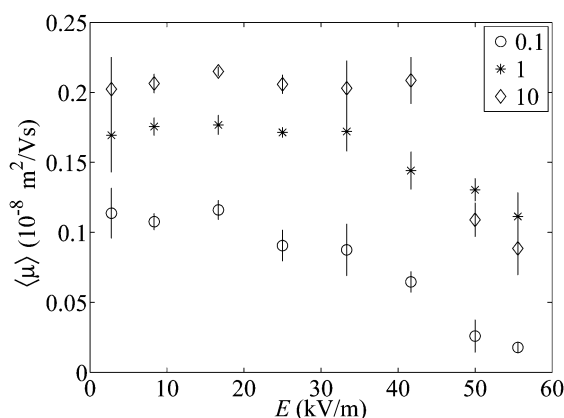
Although the estimates for both Q and ζ in the colloidal asphaltene suspensions are comparable to those in other non-polar colloidal suspensions from the literature, charging in asphaltene suspensions presents some departures from several commonly-held views on charging in non-polar suspensions. Despite the presence of dispersant micelles above the cmc, no effects of screening are observed in the behavior of μ with $\bar{c}$ either below or above the cmc. The screening length remains long even at $\bar{c} = 10$, where we estimate $\kappa a \sim 0.05$. This suggests the use of asphaltene colloids as a model system for studying long-range electrostatics in non-polar suspensions, perhaps even down to the limit of bare Coulomb interactions. Interestingly, Q remains constant despite the adsorption of dispersant at $\bar{c} < 1$, suggesting that asphaltenes provide the charges in the system, and not dispersant micelles. This observation and the possibility that electric fields may induce asphaltene aggregation could provide an additional pathway to approach electric-field mediated assembly in non-polar suspensions.

Acknowledgements

Fig. 4 Electric-field dependence of mobility at $\phi = 9 \times 10^{-5}$ and three values of $\bar{c}$ as indicated in the legend.

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