Acid-base chemistry enables reversible colloid-to-solution transition of asphaltenes in non-polar systems

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Supplemental Information

UV-vis spectroscopy on DBSA in heptane

We measure the UV-vis spectra of DBSA in heptane, to confirm that signatures in the asphaltene systems arise from asphaltene-DBSA complexation rather than from DBSA alone. DBSA has a strong signature in the region below $\lambda = 280$ nm, as show in Figure S1(a). The signature in the region $240 < \lambda < 280$ nm reveals the fine structure of electronic transitions in DBSA at $c \leq 2,500$ ppm. The average absorption $\langle A \rangle$ in this region increases linearly with c up to nearly 10,000 ppm, and then saturates, as seen in Figure S1(b). No significant signatures appear above 300 nm. This observation confirms that the protonation observed in the UV-vis spectra of asphaltenes with DBSA (Figure 2 in the manuscript) arises directly from the asphaltene-DBSA interaction.

Critical micelle concentration of DBSA in heptane

We measure c_c, the critical micelle concentration, of DBSA in heptane by monitoring the normalized intensity of scattered light I/I_0 at a wave vector $q = 0.02320$ nm^{-1} (ALV Instruments). Figure S2 shows $I/I_0(c)$ in DBSA solutions in heptane with 3% by weight tolune, to mimc the solvent conditions of the asphaltene suspensions. The increase in I/I_0 at $c \sim 100$ ppm indicates the formation of micelles, which scatter more light than individual DBSA molecules. We find $c_c \sim 100$ ppm. Above c_c, dynamic light scattering gives an average micellar size of 33 ± 4 nm.
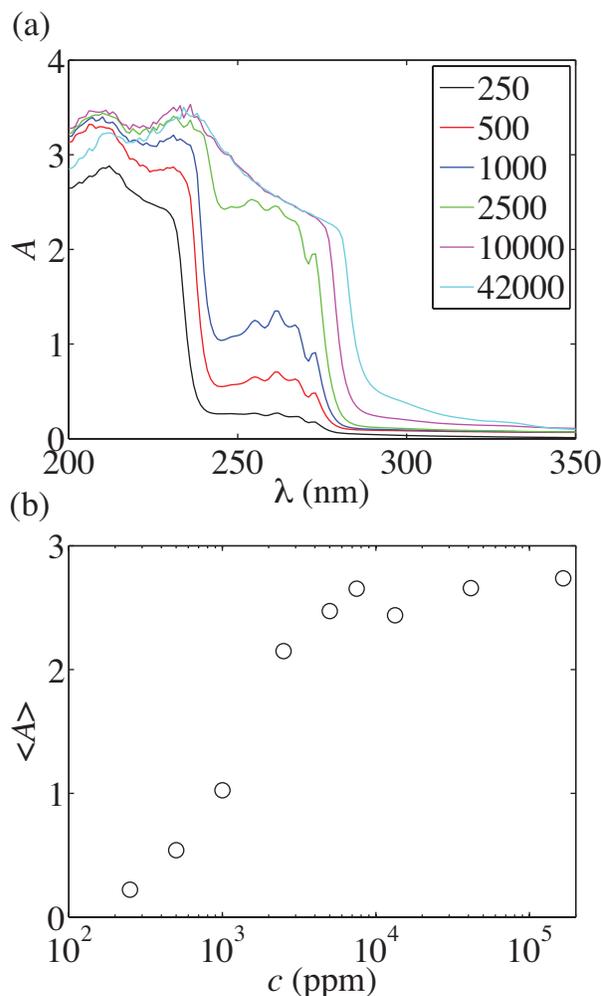

Figure S 1 UV-vis spectroscopy of DBSA in heptane. (a) shows spectra at various concentrations as listed in the legend, and (b) shows the average absorption $\langle A \rangle$ in the range $240 < \lambda < 280$ nm as a function of c.

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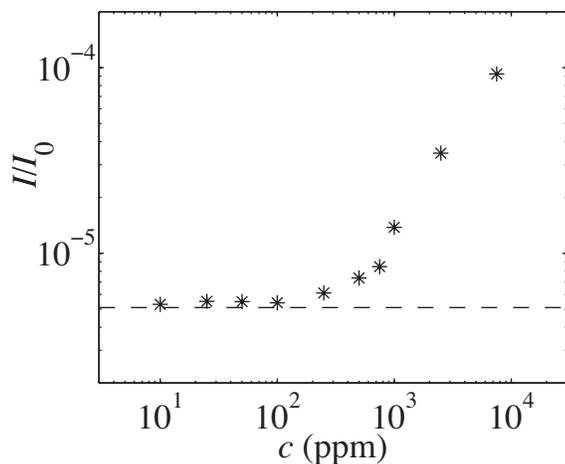
Figure S 2 Scattered light intensity of DBSA solutions in heptane with 3% toluene by weight, showing the cmc at 100 ppm. The dashed line indicates I/I_0 in heptane with 3% toluene by weight.

Dissolution screening for DLS measurements

While UV-visible spectroscopy measures the absorption of light, DLS measures the amount of light scattered at a fixed angle and wavelength, in our case $\alpha = 90^0$ and $\lambda = 658$ nm. The increasing darkness of the superantants with the addition of DBSA as seen in Figure 1(a) means that less light is available to either transmit or scatter through the suspensions. Only at DBSA concentrations which leave a sufficiently transparent supernatant can allow for effective measurements to be obtained by scattering. In order to assess the appropriate DBSA concentration range over which scattering is an effective tool, we first monitor the scattered light intensity from asphaltene suspensions over a wide range of DBSA concentrations. Indeed we see the darkness gradation of Figure 1(a) mirrored in the quantity $I/I_{max}(c)$, the normalized light intensity scattered by the model asphaltene suspensions. As c is increased, the asphaltenes begin to dissolve to the molecular scale, absorb an increasing amount of light, and cause I/I_{max} to decrease. DBSA causes I/I_{max} to decrease below $\sim 80\%$ at $c \sim 1000$ ppm for model suspensions of both SB and QAB. Model suspensions of CV require $c > 2500$ ppm before I/I_{max} falls below $\sim 80\%$. As the model asphaltene suspensions become model asphaltene solutions, the samples become nearly opaque to light, and the amount of scattered light dimishes to 0. This behavior is shown in Figure S3.
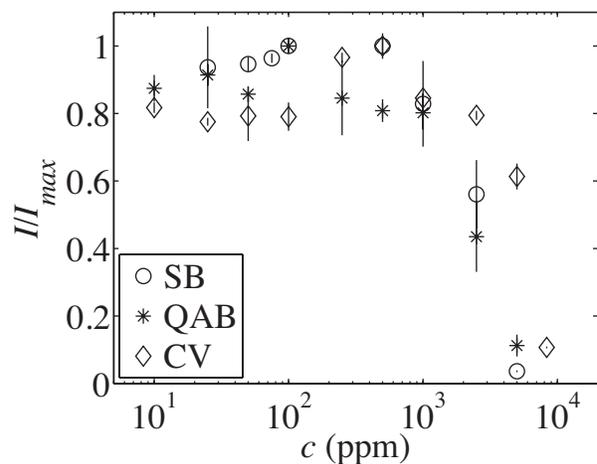

Figure S 3 Scattered light intensity from the three types of model asphaltene suspensions as a function of DBSA concentration.