Asphaltene Dispersion in Mixed Poor Solvents

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A good binary solvent for asphaltene was identified using Hansen solubility parameter (HSP) analysis, and aggregation behaviors were determined by small-angle X-ray scattering (SAXS) measurements. The pure solvents showed poor performance in dissolving asphaltene, whereas a mixed solvent system of 83 vol% benzyl benzoate and 17 vol% hexane dissolved up to ~16 wt% asphaltene. SAXS profiles at 10,000 mg/L of asphaltene in the binary solvent showed disappearance of nanoaggregates. These findings will be useful when developing mechanisms for controlling asphaltene aggregation/disaggregation in the crude oil industry.

Keywords: Asphaltene dispersion, Hansen solubility parameter, SAXS

1. Introduction

Asphaltene is an undesirable component of crude oil that can cause fouling and catalyst deactivation during the petroleum recovery and conversion processes ¹). Asphaltene is defined as the insoluble fraction after heptane extractions. Understanding the effects of solvent on the aggregation and disaggregation behaviors of asphaltene is essential for the full utilization of petroleum and heavy crude resources. In addition, understanding these solvent effects is important for determining the various mechanisms underlying molecular interactions. Asphaltene molecules aggregate through a combination of chemical mechanisms, including electrostatic and Van der Waals forces, Brønsted acid–base interactions, hydrogen bonding, metal coordination complexes, and hydrophobic effects ²).

Our previous study of the heptane-insoluble asphaltene in Canadian oil sand bitumen (CaAs) used Hansen solubility parameter (HSP) analysis to identify bromobenzene as one of the best pure solvents for relaxing asphaltene aggregation ³, ⁴). HSPs measure the dispersive, polar, and hydrogen-bonding forces as functions of the square root of cohesive energy density,
and are represented by $\delta_d$, $\delta_p$, and $\delta_h$ MPa$^{0.5}$, respectively. Theoretically, every compound has a unique set of HSP values and two compounds with similar HSP values typically exhibit good affinity for each other. The differences in HSP values between a solute and a solvent, $R_a$, can be used to evaluate this similarity, as shown in Eq. (1).

$$R_a^2 = 4(\delta_{d,solvent} - \delta_{d,solute})^2 + (\delta_{p,solvent} - \delta_{p,solute})^2 + (\delta_{h,solvent} - \delta_{h,solute})^2$$ (1)

The $\delta_d$, $\delta_p$, and $\delta_h$ of CaAs are 19.1, 4.2, and 4.4 MPa$^{0.5}$, whereas those of bromobenzene are 19.2, 5.5, and 4.1 MPa$^{0.5}$, respectively. These differences correspond to an $R_a$ as low as 1.3 MPa$^{0.5}$. Small-angle X-ray scattering (SAXS) analyses showed that bromobenzene can disperse CaAs nanoaggregates. Therefore, we may be able to identify a mixed solvent with the same set of HSPs as asphaltene. The HSPs of a binary solvent system are given by:

$$[\delta_{d,\text{mix}}, \delta_{p,\text{mix}}, \delta_{h,\text{mix}}] = [\alpha \delta_{d1} + (1 - \alpha) \delta_{d2}, \alpha \delta_{p1} + (1 - \alpha) \delta_{p2}, \alpha \delta_{h1} + (1 - \alpha) \delta_{h2}]$$ (2)

where $\alpha$ is the volume fraction of solvent 1. Equations (1) and (2) suggest that a good binary solvent might consist of two solvents along a straight line across the target solute values in the three-dimensional HSP plot, as shown in Fig. 1.

This study found that a mixture of 83 vol% of benzyl benzoate and 17 vol% of hexane exhibited $\delta_d$, $\delta_p$, and $\delta_h$ values of 19.1, 4.2, and 4.3 MPa$^{0.5}$, respectively, which are nearly the same as those of CaAs, resulting in an $R_a$ of 0.1 MPa$^{0.5}$. The effects of this benzyl benzoate/hexane mixture on asphaltene solubility and disaggregation behavior were examined using SAXS analyses. Note that asphaltene is insoluble in either benzyl benzoate or hexane at room temperature, because asphaltene powder mixed into the solvent at 1000 mg/L remains even after 1 day.

2. Experimental

This study refers to a mixed solvent of benzyl benzoate and hexane with a volume ratio of x/y using the abbreviation BH-x/y.

2.1. Solubility Tests

The solubility of CaAs in BH-95/5, 83/17, 70/30, 60/40, or 50/50 was determined using a membrane filter and thermogravimeter (TG; TGB8121; Rigaku Corp.). CaAs was added to each mixed solvent system at about 30 wt%, dispersed using ultrasonication for 15 min, and then shaken mechanically in a water bath at 25 °C for 1 day. Then, the sample was ultrasonicated for an additional 5 min and filtered through a membrane filter with a pore size of 0.2 $\mu$m. The asphaltene content in each solution was determined from the residual weight after solvent evaporation at 350 °C for 30 min using the TG.

2.2. SAXS Experiments

SAXS data of CaAs at concentrations of 10,000 mg/L (−1 %) in BH-95/05, 83/17, 70/30, 60/40, and 50/50 were obtained using a membrane filter and beamline BL6A of the Photon Factory (PF) at the High Energy Acceleration Research Organization (KEK). The asphaltene concentration was lower than the maximum solubility determined and sufficiently low to prevent the effects of interparticle interference. Prior to each measurement, the samples were shaken by hand, ultrasonicated for 10 min, and then allowed to stand for 1 week. SAXS measurements were acquired using an 8.27-keV monochromatic X-ray beam with a wavelength ($\lambda$) of 1.50 Å, using a sample cell with single-crystal diamond windows. A two-dimensional detector (PILATUS3 1M; Dectris Ltd.) was positioned 2021 mm from the cell. The exposure...
time was 2 min. The range of the observable scattering parameter, $q = 4\pi \sin \theta / \lambda$, where $2\theta$ is the scattering angle, was 0.07–3.0 nm$^{-1}$. SAXS data of the asphaltene solutions were corrected by subtracting the data of the solvent system.

### 3. Results and Discussion

#### 3.1. Asphaltene Solubility

The ratio of benzyl benzoate and hexane in the mixed solvent system drastically influenced asphaltene solubility. Table 1 summarizes the asphaltene solubility and HSPs of the mixed solvents. The solubilities of CaAs in BH-95/5, 83/17, 70/30, 60/40, and 50/50 were about 3, 16, 7, 8 and 6 wt%, respectively. The relative amounts of benzyl benzoate or hexane did not directly influence the asphaltene solubility, so that the solubility was presumably controlled by the properties of the mixed solvent. The $R_a$ values of these solvents relative to CaAs ($R_a$CaAs) were 1.4, 0.1, 1.6, 2.8, and 4.1 MPa$^{0.5}$, respectively. Solubility is maximized under the set of conditions with a minimum $R_a$CaAs. Note that these data show that a mixture of poor solvents can dissolve as much as 16% asphaltene as the HSP of the mixed solvent approaches that of asphaltene. These results demonstrate that applying the HSP concept to a binary mixture is effective for asphaltene solubilization, even for otherwise poor solvents. For comparison, benzene and toluene showed solubilities of 12 wt% and 26 wt%, respectively, under the same test conditions.

#### Table 1  HSPs of CaAs and Solvents and Solubility of CaAs in Mixed Solvents

|             | HSP / MPa$^{0.5}$ | Solubility /wt% |
|-------------|------------------|-----------------|
|             | $\delta_d$ | $\delta_p$ | $\delta_h$ | $R_a$CaAs |
| CaAs        | 19.1        | 4.2         | 4.4        |   -   |   -   |
| Benzyl benzoate | 20.0        | 5.1         | 5.2        | 2.2   |   -   |
| Hexane      | 14.9        | 0.0         | 0.0        | 10.4  |   -   |
| BH-95/5     | 19.7        | 4.8         | 4.9        | 1.4   | 2.9   |
| BH-83/17    | 19.1        | 4.2         | 4.3        | 0.1   | 15.7  |
| BH-70/30    | 18.5        | 3.6         | 3.6        | 1.6   | 7.1   |
| BH-60/40    | 18.0        | 3.1         | 3.1        | 2.8   | 7.8   |
| BH-50/50    | 17.5        | 2.6         | 2.6        | 4.1   | 5.7   |

**Fig. 2  SAXS Profiles of CaAs in Mixed Solvents of Benzyl Benzoate/hexane**
3.2. Asphaltene Dispersion Behavior

The SAXS data in Fig. 2 show that the ratio of benzyl benzoate to hexane significantly affected the aggregation behavior of asphaltene. Higher proportion of benzyl benzoate reduced the SAXS intensity at $q > 0.2 \text{ nm}^{-1}$, indicating that the number of nanoaggregates decreased. Therefore, benzyl benzoate molecules facilitate the dispersion of asphaltene nanoaggregates. In contrast, at $q < 0.2 \text{ nm}^{-1}$, power law profiles indicated increasing proportions of benzyl benzoate. Power law profiles in the low-$q$ region corresponded to the presence of larger aggregates which might be micro-scale insoluble clusters, and the slope corresponded to the distribution of matter either inside or on the surface of a particle \(^9\). Further experiments using ultra-small-angle X-ray scattering (USAXS) are needed to analyze the low-$q$ region in detail.

To elucidate the disaggregation mechanism of asphaltene nanoaggregates based on these SAXS data at $q > 0.2 \text{ nm}^{-1}$, Zimm approximation analysis \(^9, 10\) was applied to obtain the radii of gyration ($R_g$) for the aggregates. $R_g$ was extracted from the SAXS profiles by curve-fitting using the following Eq. (3):

$$I(q) = I(0) \left(1 + q^2 R_g^2 \right)^{-\frac{1}{2}}$$

where $I$ is the SAXS intensity. Fig. 2 includes the resulting fits for BH-95/5, 83/17, 70/30, 60/40, and 50/50, and the calculated $R_g$ values of aggregates were 1.4, 2.2, 2.9, 3.0, and 4.5 nm, respectively, smaller than those in toluene (~5 nm) at the same concentrations using the same asphaltene source \(^3\). It is interesting that aggregate size in a mixture of poor solvents can be much smaller than that in a good solvent. $R_g$ decreased with higher proportions of benzyl benzoate in the mixed solvents, indicating that benzyl benzoate molecules helped to reduce the size of asphaltene nanoaggregates.

4. Conclusions

A novel binary mixture of poor solvents was shown to optimally disperse asphaltene nanoaggregates at a specific mixing ratio (83 % benzyl benzoate and 17 % hexane) by volume. The solvent combination and optimal mixing ratio were determined by HSP analyses, resulting in asphaltene solubility as high as ~16 wt%. The SAXS data at 10,000 mg/L indicated that the mixed solvent dispersed nanoaggregates in smaller sizes. This study demonstrated the utility of HSP analysis for identifying good solvent systems for asphaltene using a binary mixture of poor solvents. These findings will be useful for developing mechanisms for controlling asphaltene aggregation/disaggregation in the crude oil industry.

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References

1) Mullins, O. C., Sheu, E. Y., Hammami, A., Marshall, A. G., “Asphaltenes, Heavy Oils, and Petroleomics,” Springer Science+Business Media, LLC, New York (2007).
2) Gray, M. R., Tykwinski, R. R., Stryker, J. M., Tan, X., Energy & Fuels, 25, 3125 (2011).
3) Morimoto, M., Imamura, H., Shibuta, S., Morita, T., Nishikawa, K., Yamamoto, H., Tanaka, R., Takanohashi, T., Energy & Fuels, 29, 5737 (2015).
4) Morimoto, M., Sato, T., Araki, S., Tanaka, R., Yamamoto, H., Sato, S., Takanohashi, T., Energy & Fuels, 29, 2808 (2015).
5) Hansen, C. M., “Hansen solubility parameters : a user's handbook.” 2nd ed., CRC, Boca Raton (2007).
6) Sato, T., Araki, S., Morimoto, M., Tanaka, R., Yamamoto, H., Energy & Fuels, 28, 891 (2014).
7) Takagi, H., Igarashi, N., Mori, T., Saijo, S., Ohta, H., Nagatani, Y., Kosuge, T., Shimizu, N., AIP Conference Proceedings, 1741, 030018 (2016).
8) Hoepfner, M. P., Yang, Y., “Chemistry Solutions to Challenges in the Petroleum Industry,” ed. by Rahimi, P., Ovalles, C., Zhang, Y., Adams, J. J., Vol. 1320, ACS, Washington (2019), pp 67-87.
9) Zimm, B. H., The Journal of Chemical Physics, 16, 1093 (1948).
10) Barré, L., Jestin, J., Morisset, A., Palermo, T., Simon, S., Oil & Gas Science and Technology, 64, 617 (2009).