Temperature and solvent effect on molecular size and shape of heavy oil fractions

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For studying the diffusion and hindrance effect of heavy oil molecules on catalytic upgrading process, it is necessary to understand the transport and equilibrium properties of heavy oil molecules in the pore of catalyst. However, these properties depend on the molecular size and shape of heavy oil fractions. Therefore, a thorough knowledge of molecular size and shape is foundational to develop catalyst and catalytic upgrading process. The molecular size and shape of heavy oil fractions also influence their elution characteristics in gel permeation chromatography, hence understanding molecular size and shape is necessary for the accurate interpretation of information obtained from this chromatographic process [1].

Since intrinsic viscosity reflects the hydraulics volume of molecule that molecular weight is known, intrinsic viscosity is measured to characterize the molecular shape and size of heavy oil fractions. In our previous work [2], Tahe atmosphere residue (THAR) was fractioned into eight fractions by Liquid-Solid Adsorption Chromatography and the solution and solvent viscosity were measured using Ubbelohde capillary viscometer. The relative viscosity versus concentration curve for dilute solution of each fraction was plotted and the curve agrees well with Einstein law. The slope of relative viscosity versus concentration curve is the value of intrinsic viscosity.

In this study, the molecular size and shape of THAR fractions in three kinds of organic solvent were determined at different temperature by intrinsic viscosity measurement. Take saturate for instance, with temperature increasing, the slope of relative viscosity versus concentration curve for toluene solution decreases, as shown in Fig.1. Therefore, the molecular size decreases as the temperature increases, which consist with the conclusion derived from Fluorescence Correlation Spectroscopy measurement [3]. Compared to the pyridine and nitrobenzene solutions, the intrinsic viscosity of THAR fractions in toluene solution is higher at 333.15K. According to Equation (2), the sphere equivalent hydrodynamic diameter of THAR fractions in toluene solution was estimated to be 1.2-4.0nm. The molecular size of asphaltene is much larger than other fractions. With molecular weight increasing, the molecular size also increases.

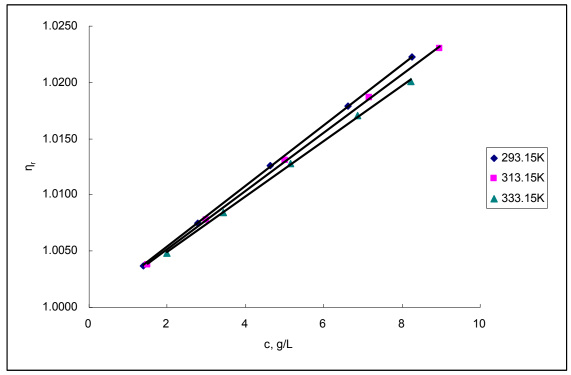

Fig. 1. The relative viscosity versus concentration curve for toluene solution of THAR saturate at different temperature.

Equations

Einstein law is represented by the following equation:

$$\eta_r = 1 + [\eta]\,c \qquad (1)$$

where η_r, $[\eta]$ and c denote relative viscosity, intrinsic viscosity and concentration respectively.

$$[\eta] = \frac{2.5N_A}{M}\left(\frac{1}{6}\pi D^3\right) \qquad (2)$$

where N_A is the Avogadro's number, M is the solute molecular weight and D is the sphere equivalent hydrodynamic diameter.

References

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[3] Schneider, M.H., Andrews, A.B., Mitra-Kirtley, S., Mullins, O.C. (2007) E&F 21, 2875-2882.