

CHAPTER III

EXPERIMENTAL

3.1 Materials

The asphaltenes studied in this work were precipitated from crude oil obtained from Cold Lake reservoir. The asphaltenes used in this study were heptane-insoluble fractions of crude oil. Cold Lake crude oil was supplied by Conoco Inc. Toluene, heptane and acetone used in solubility studied were HPLC grade and obtained from Fisher Scientific. Methyl alcohol was 99.8% and purchased from Fluka.

3.2 Asphaltene Precipitation

Asphaltene samples were prepared from Cold Lake crude oil with the modified ASTM 2007D procedure. In brief, one volume of crude oil was mixed with 40 volumes of n-heptane for 45 minutes at 65 °C. The mixture was allowed to settle for 8 hours at room temperature, and then was filtered through a 0.45 µm membrane. The precipitated asphaltenes were washed with n-heptane in soxhlet apparatus until the washed solvent was colorless. The washed asphaltenes were then dried in a vacuum desiccator at room temperature until the sample's weight was constant.

3.3 Asphaltene Fractionation

Asphaltenes were fractionated into different polar fractions using binary mixtures of polar (methylene chloride) and nonpolar (n-pentane) solvents (Nalwaya *et al*, 1999). An asphaltene sample was completely dissolved with 10 times by weight of CH₂Cl₂. Pentane was added in a discrete increment of 10 vol% until the first fraction was precipitated. The first asphaltene fraction precipitated at a pentane-methylene chloride volume ratio of 60/40, and was referred to as the F40/60 Fraction. The precipitate was separated by centrifugation at 3500 rpm for 30

minutes. Pentane was further added to the supernatant to achieve a pentane-methylene chloride volume ratio of 70/30. The asphaltene precipitated from this solvent system was separated by centrifugation, and was referred to as the F30/70 Fraction. This process of adding pentane to the supernatant and then separating the asphaltenes by centrifugation was repeated. The asphaltene samples were collected at pentane-methylene chloride volume ratios of 80/20 (F20/80) and 10/90 (F10/90). All asphaltene precipitates were dried in vacuum desiccators until the sample's weight were constant (Nalwaya *et al.*, 1999). As the amount of pentane (nonpolar solvent) was increased in the binary mixture, the polar effect of CH_2Cl_2 decreased. The asphaltene fraction precipitated out first is the most polar fraction, followed by precipitation of less polar fractions upon the addition of more pentane.

3.4 Density Measurement

The measurement of asphaltene densities were done at 25 °C in various concentrations in toluene using 10 ml calibrated volumetric flasks. The flasks with the solution were weighted by using a 0.0001 g sensitive balance. The density of solution at each concentration was determined by ratio of mass and volume (density of solution = mass of solution/volume of solution) in the unit of kg/m^3 .

3.5 Solubility Measurement

3.5.1 Precipitation Method

A stock solution of asphaltene in toluene was prepared. This stock solution was distributed in vials, and then heptane was added to each vial to achieve the necessary volume percentage of toluene in solvent mixtures in the range of 5%-30%. Then, the samples were placed in the sonicator bath for 30 minutes, and were left outside the sonicator bath until they reached the equilibrium. After 10 days of mixing at a constant temperature, the solid samples were separated by centrifugation at 3000 rpm for 45 minutes, and the supernatant was then analyzed for the concentration of asphaltenes using a UV-Visible spectroscopy at a wavelength of 450 nm.

3.5.2 Solubility Method

Saturated solutions of asphaltene samples in the binary solvent mixture of toluene-heptane were prepared by mixing an excess amount of solid asphaltene in solvent mixture. In all experiments, the sample mixtures were placed in a sonicator bath to ensure the maximum amount of asphaltene dissolved in the solution. The samples were left for 10 days to reach equilibrium after which, the solid samples were separated by centrifugation and supernatant was then analyzed in the same way as the precipitation method.

Non-agitated and agitated systems of solubility measurement were investigated. For the non-agitated system, the samples were left on the bench until reached the equilibrium time while, in the agitated system; the samples were placed in a shaker for the same period time as non-agitated system.

3.6 Chemical Analysis of Asphaltenes

Elemental analysis data of unfractionated Cold Lake asphaltene and its fractionated components which represented amounts of elements (C, H, O, N and S) in the asphaltene were obtained from Galbraith Laboratories Inc., Knoxville, Tennessee, USA while the metal (Al, Cr, Cu, Fe, Ni, V and Zn) contents of asphaltene using ICP 90 method were obtained from the XRAL Laboratories, Ontario, Canada.

3.7 Molecular Size Analysis of Asphaltenes

NMR self-diffusion data of asphaltene which expressed the size of asphaltene molecule were obtained from the Department of Applied Surface Chemistry, Chalmers University of Technology, Göteborg, Sweden.