

CHAPTER III EXPERIMENTAL



3.1 Asphaltene Precipitation

The asphaltenes used in this study were heptane-insoluble fractions of crude oils. The crude oils, named NM1, NM5, Col-2, and CHA, from PDVSA-Intevep Company, Venezuela, Mesa, Cold Lake, and BRB, from Conoco Oil Company, and Villano Creek, from Arco Company, were used to precipitate asphaltenes. Technical grade n-heptane was used as solvent for precipitating asphaltenes from these crude oils.

Crude oil from the Cold Lake reservoir was also used to precipitate asphaltenes for studying the effect of aging under air, oxygen, or nitrogen on the solubility of asphaltenes.

Samples were prepared from crude oils in accordance with a modified procedure contained in ASTM 2007D. In brief, one volume of crude oil was mixed with forty volumes of heptane for 45 minutes at 65°C. The mixture was allowed to settle 8 hours and then was filtered through a 0.45 μm membrane to obtain the asphaltene sample. The precipitated asphaltenes obtained from different crude oils were washed in the soxhlet apparatus with heptane until the washed solvent was colorless. The washed asphaltenes were allowed to dry overnight in vacuum desiccators at room temperature and the mass of asphaltenes was determined when the sample had a constant weight.

3.2 Aging Procedure

The air aged, oxygen aged and nitrogen aged asphaltenes were prepared by precipitating asphaltenes from Cold Lake crude oil that were aged under air, oxygen and nitrogen, respectively, for 3 days.

3.3 Fractionation Procedure

One of the objectives of this work was to demonstrate that different asphaltenes from different sources contain different amounts of specified polar fractions. The asphaltene sample obtained from precipitation was first completely dissolved in pure CH_2Cl_2 . Sufficient pentane was then added to precipitate the first asphaltene fraction. As the amount of n-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 n-pentane.

The original asphaltene was completely dissolved with 10 times by weight of CH_2Cl_2 . Pentane was added in the discrete increments of 10 vol% until the first fraction was precipitated out. The first asphaltene fraction precipitated at a pentane-to-methylenechloride ratio of 60/40 was termed F60/40. The precipitate was separated by centrifugation at 3500 rpm for 30 minutes. Additional pentane was then added to the supernatant to achieve a pentane-to-methylenechloride ratio of 70/30. The asphaltene precipitated from this solvent system was separated by centrifugation and were termed F70/30. This process of adding pentane to the supernatant and then separating the asphaltenes by centrifugation was repeated. The asphaltene sample was collected at pentane-to-methylenechloride volume ratios of 80/20 (F80/20) and 90/10 (F90/10). All asphaltene precipitates were dried in vacuum desiccators overnight and the mass of each asphaltene precipitate was determined (Nalwaya et al, 1999).

3.4 Asphaltene Solubility Measurement

Solvents used in the solubility study were composed of the mixture of aromatic/alkane solvent. HPLC grade toluene and heptane were obtained from Fisher and decalin and 1-methyl naphthalene were obtained from Sigma-Aldrich. Toluene, and 1-methyl naphthalene were used as aromatic solvents, decalin was used as dicyclohexane solvent, and heptane was used as alkane solvent.

Solubility of asphaltenes was determined by adding asphaltene powder with 3 ml of mixture of aromatic/alkane solvent having 60 vol% toluene and 40 vol% heptane. Afterwards, the sample mixture was put in the sonicator bath to completely dissolve the asphaltenes. If all the asphaltene powder dissolved, then more heptane was added until the solution reached the solubility limit of asphaltene in 50 vol% toluene and 50 vol% heptane. The sample was left to reach equilibrium for 12 hours and then centrifuged at 3500 rpm for 30 minutes. The supernatant was analyzed for asphaltenes using UV-Vis spectroscopy at a wavelength of 400 nm. Additional heptane was added to the solution in order to determine the solubility of asphaltene in the toluene/heptane mixture. When heptane was added to the solution, asphaltenes precipitated out of the solution due to the reduced asphaltene solubility in heptane. The solubility of asphaltenes in various concentrations of toluene and heptane was observed. The solubility of asphaltenes in decalin/heptane, and 1-methyl naphthalene/heptane mixtures at the different temperatures were then determined in the same manner as described above.

3.5 Characterization Technique of Asphaltenes

The chemical compositions of two types of crude oils, NM1 and NM5, were analyzed by SARA analysis (Saturates, Aromatics, Resins, and Asphaltenes). These data were provided from PDVSA-Intevep Company, Venezuela.