

CHAPTER II

BACKGROUND

2.1 Asphaltenes

2.1.1 Asphaltene Structures

Crude oils and petroleum products are complex mixtures of hydrocarbon compounds which can be classified and separated into four major fractions: saturates, aromatics, resins, and asphaltenes. (T.Zerlia,1990)

Resins and asphaltenes are often referred to as polar materials of the heavy end of crude (i.e.asphalt fraction) which cannot be distilled without thermal cracking. Their specific chemical structures are still unclear due to their complexity. Generally, their molecules are large polyaromatic and polycyclic condensed ring structures containing hetero-atoms such as nitrogen, oxygen, sulfur, and other metals such as nickel and vanadium. These properties cause them to interact readily with rock surfaces.

The differentiation between resins and asphaltenes is based on the solubility in normal paraffin. (S.Kokal et.al,1995) Asphaltenes are often defined as the fraction of crude insoluble in light normal alkanes (for example,

n-pentane, heptane, and decane), but soluble in an aromatic solvent (for example, benzene, toluene, and xylene). While resins are assumed to be insoluble in liquid propane, but soluble in n-pentane. (Vivtorov and Firoozabadi,1996) Figure 2.1 shows the fractionation and classification scheme for asphalt fractions.

It is recognized that asphaltenes are dispersed in the crude oil due to resins. The degree of dispersion depends on the aromaticity and the chemical composition of oil. In highly aromatic oils, asphaltenes are dispersed colloiddally, but, in the presence of excess paraffinic hydrocarbons, they are coagulated and precipitated. These precipitated asphaltenes can be re-peptized by addition of aromatics. This peptization of adsorbed resins is the basis of the thermodynamic-colloidal model proposed earlier by Leontaritis and Mansoori in 1987. These resins and asphaltenes together are called micelles as shown in Figure 2.2. The asphaltene fraction has been proposed to aggregate in reversed micelle. The polar moieties will be associated in the center of the micelle, surrounded by the nonpolar moieties of the same molecules. Many works have reconfirmed the formation of micelles in asphaltenes and resin-containing crudes. (Pfeiffer and Saal,1940; Koots and Speight,1975; Leontaritis,1987; Anderson and Birdi, 1991; F.Carnahan et.al,1993). The addition of an adequate amount of flocculant, for example n-pentane, causes the destruction of the micelle and may result in irreversible flocculation of asphaltenes. (S.Kokal et.al,1995)

2.1.2. Asphaltene Flocculation and Deposition

In general, asphaltene flocculation is dependent on the thermodynamics of the system (i.e., temperature, pressure, and composition). Flocculation due to composition changes can occur when secondary or tertiary oil recovery is applied to the oil production. The reservoir fluid composition can be changed by two common ways, normal depletion during the lighter components of the fluid being produced in higher proportion and the injection of fluids for enhanced oil recovery.

Asphaltene Deposition Envelope (ADE) is a term defined as the boundary of the thermodynamic space at which the onset of asphaltene flocculation occurs. Figure 2.3 shows a typical P, T, X thermodynamic phase diagram with the ADE superimposed. The severity of asphaltene flocculation increases as the fluid conditions move from the boundary to the center of the envelope. This thermodynamic phase diagram was calculated using a model tuned to only a few data points. The shape of a true, complete ADE of an oil is unknown because it has never been measured due to the nonavailable technology required for measuring the onset of asphaltene flocculation in live fluids. (Leontaritis et.al, 1992)

It is important to note that flocculation and in-situ deposition are two separate phenomena. It is possible to have flocculation without substantial

in-situ deposition, depending on the flow dynamics and the nature of the flocculated materials. However, asphaltene is deposited only after its flocculation, so the best way to prevent asphaltene-induced formation damage is to avoid asphaltene flocculation. If it is not possible then the next goal is to minimize the asphaltene drop (Leontaritis et.al,1994).

Generally aromatic-based liquids are the most reliable and economical solvents used for removing asphaltene deposition, but due to their hazard to the environment, there is a need in development for the effective substitutes.

The dispersion of asphaltenes in heptane by different oil soluble amphiphiles was studied by Gonzalez and Middea (1991). It was found that the effectiveness of amphiphiles on the stabilization of asphaltenes was influenced by the headgroup of the amphiphiles and alkylphenols showed good peptizing properties. Deboer and coworkers also found that alkylbenzene sulfonic acid could effectively reduce the precipitation of asphaltenes in near-wellbore regions.

In a later study, Chang and Fogler (1994) used a series of alkylbenzene-derived amphiphiles to investigate the asphaltene-amphiphile interaction and the stability behavior of asphaltene in amphiphile/alkane solutions. It was concluded that the criteria for amphiphile molecules effective to stabilize asphaltenes in apolar media were the association of amphiphiles to asphaltene surfaces by the headgroups of amphiphiles and

the establishment of a steric layer around asphaltenes by the tail group of amphiphiles. A mechanistic study on the interaction between asphaltenes and two types of alkylbenzene-derived amphiphiles, namely, p-alkylphenol and p-alkylbenzene sulfonic acid, was carried out by using Fourier infrared transform spectroscopy to characterize the acid-base interactions between asphaltenes and amphiphiles and Small-angle X-ray scattering techniques to study the physical structure of asphaltene colloids in these amphiphiles solution.

A study of the kinetics of dissolution of asphaltene deposits by fluid composed of amphiphiles and alkane solvent presented in this report is a part of the research work on the stabilization and dissolution of asphaltenes conducted to design and to evaluate new chemical treatments using surfactant/micellar technology alone or in combination with other chemicals methods to prevent, alleviate, and minimize damage resulting from asphaltene deposition in oil production reservoirs and oil pipelines

2.2 Analysis of Rate Data

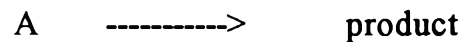
2.2.1 Integral Method

The integral method is one of the methods used to find the rate law or the kinetic expression that relates the rate of reaction to the species concentration from experimental data.

First the reaction order was guessed and the differential equation used to model the batch system was then integrated. If the assumed order is correct, the appropriate plot of concentration-time data should be linear.

The integral method is desired to evaluate the specific reaction rate constant at different temperatures and to determine the activation energy. (Fogler, 1992)

For the reaction



If the reaction is a first-order reaction, integration of the combined mole balance and rate law will be,

$$-dC_A/dt = k C$$

with the limits $C_A = C_{A0}$ at $t = 0$ gives

$$\ln(C_{A0}/C_A) = k t$$

$$\text{or } \ln(C_A / C_{A0}) = -k t$$

Consequently, the linear plot of $[\ln(M/M_0)]$ as a function of time is obtained with slope k .

2.2.2 Arrhenius Equation

The rate constant for elementary reactions is almost always expressed as

$$k(T) = k_0 T^m \exp[-E_a/RT] \quad (2.1)$$

Where $m = 0, 1/2, 1$, depending on the specific theoretical model being used.

E_a = activation energy, J/mol or cal/mol

R = gas constant = 8.314 J/mol.K = 1.987 cal/mol.K

T = absolute temperature, K

Equation (2.1), known as the Arrhenius equation, has been verified empirically to give the temperature behavior of most reaction rate constant within experimental accuracy over fairly large temperature ranges.

The activation energy is determined experimentally by carrying out the reaction at several different temperatures. After taking the natural logarithm of equation (2.1),

$$\ln k = \ln A - E_a/RT$$

when $A = k_0 T^m$ = preexponential factor or frequency factor.

A plot of $(\ln k)$ versus $(1/T)$ should be a straight line whose slope is proportional to the activation energy (Fogler, 1992).

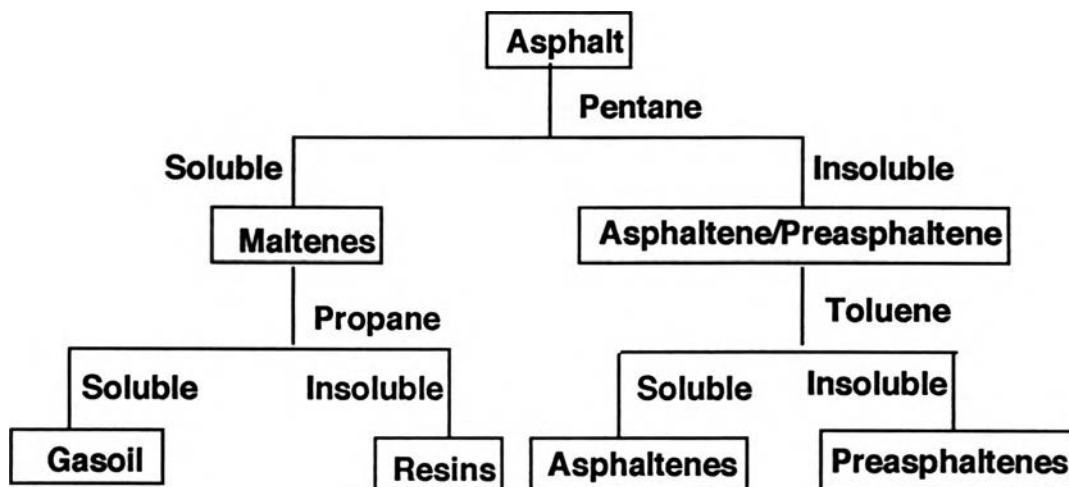


Figure 2.1 Fractionation and classification scheme for asphalt fractions.

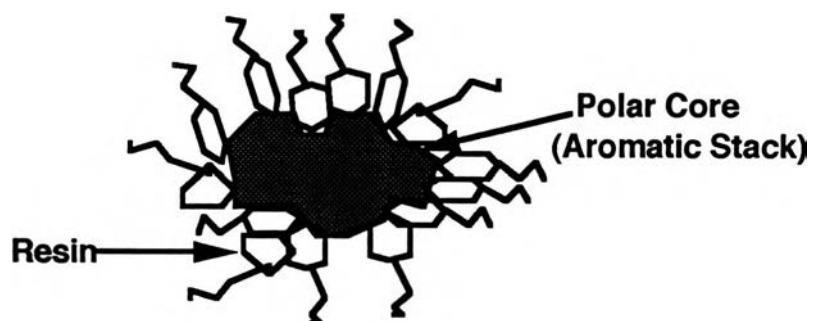


Figure 2.2 Structure of asphaltenes.

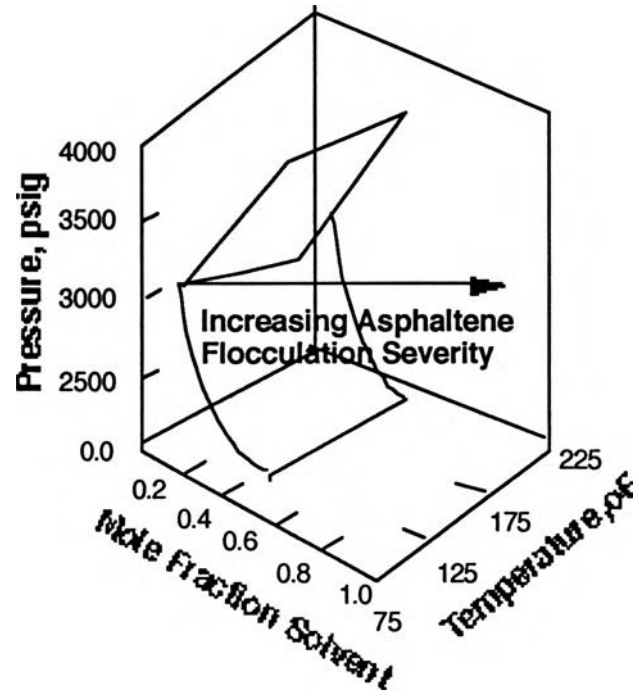


Figure 2.3. P-T-x Asphaltene Deposition Envelope.