

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Asphaltenes

Asphaltenes are the heaviest and most complex fraction of crude oil. They are defined as a solubility class and are insoluble in light alkanes, such as heptane, and soluble in aromatics, such as toluene. Extracted asphaltenes are brown and black powdery solids. Structurally, asphaltenes consist of polyaromatic cores surrounded by alkyl side chains. Asphaltenes contain small amounts of heteroatoms (S, N, and O), and traces of vanadium, nickel and iron (Wattana, 2004).

2.2 Asphaltene Precipitation

Asphaltene precipitation and deposition result in huge economic losses. Asphaltene precipitation can be induced by changes in temperature, pressure or composition and occurs during oil production, enhanced oil recovery or any part of the production process. This can damage reservoirs by blocking pore space, plug tubing and transportation facilities, and cause fouling in downstream equipment causing a reduction in capacity and productivity (Wattana, 2004).

In the laboratory, the precipitation of asphaltene is normally induced by precipitant addition. The amount of precipitant required to initiate asphaltene precipitation is defined as the onset of precipitation. Many techniques such as refractive index, light absorbance and optical microscopy have been used for studying asphaltene precipitation as a function of heptane concentration. Onset experiments were conducted on asphaltenes mixed with toluene by Maqbool et al. These results confirmed that slow kinetics can significantly influence the reported onset point in crude oils mixed with heptane. Maqbool also defined the time required for asphaltene particles to be detectable by microscopy after adding heptane as detection time, represented in Figure 2.1 (Maqbool, 2009). The longer detection times of asphaltene systems are indicated more stable asphaltenes than the shorter detection times.

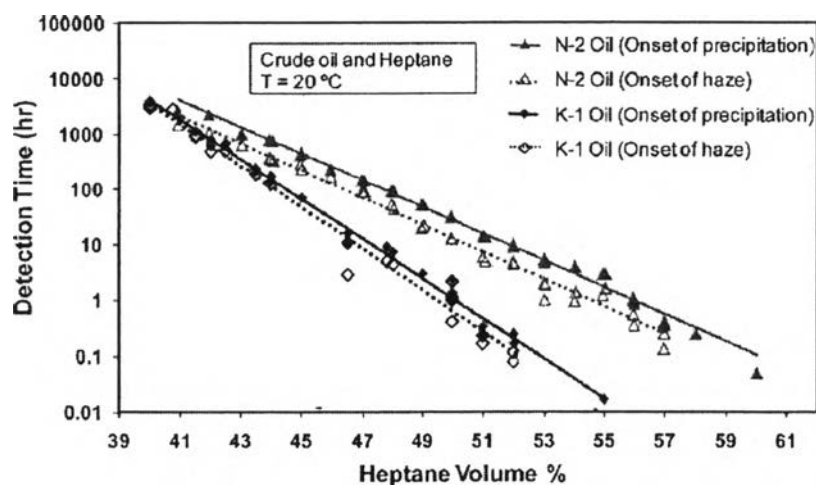


Figure 2.1 Detection times for onset of precipitation and onset of haze for varying heptane concentrations using K-1 and K-2 crude oils (Maqbool, 2009).

2.3 Amphiphilic Molecule on Asphaltene Precipitation

In order to remediate asphaltene precipitation problems, dispersants are injected to stabilize asphaltene systems at concentrations of 1,000 to 10,000 ppm (Schantz, 1991). Naturally, asphaltene molecule can be dispersed and stabilized in crude oil by another polar fraction of crude oil, called resins. These resin molecules form micelle-like aggregates with asphaltene molecules. It was found that once resins were separated from crude, the remaining crude oil will no longer solubilize asphaltenes (Chang, 1994). Hypothetically, molecules with chemical structures that are resin-like could stabilize asphaltene systems. The peptization of asphaltene by alkylbenzenes was first studied by Gonzalez and Middea in 1991, and they found that the effectiveness of amphiphiles on asphaltene stabilization was influenced by the head group of alkylbenzenes (Östlund, 2004).

Alkylbenzenes are a family of organic compounds with the formula with at least a benzene ring and an alkyl tail. In addition to these basic structural features, alkylbenzenes may have one or more polar head groups attached to the benzene ring, heteroatom substitutions in the alkyl chain, or multiple benzene or alkyl groups (Östlund, 2004). The chemical structure of alkylbenzene is shown in Figure 2.2.

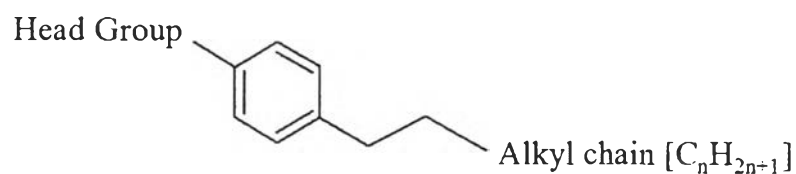


Figure 2.2 Schematic of the chemical structure of alkylbenzene molecules used in this study. -

Different head groups and alkyl tail lengths alter the properties of alkylbenzenes. The alkylbenzenes used in this study are listed in Table 2.1.

Table 2.3.1 List of all alkylbenzenes used in this study

Head group	n	Name	Abbreviation	Structural Formula
-OH	9	Nonylphenol	NP	
None	9	Nonylbenzene	NB	
-NH ₂	9	Nonylaniline	NA	
-NH ₂	12	Docecylaniline	DA	
-COH	12	Dedecyloxybenzaldehyde	DOBA	
-COOH	12	Dodecylbenzoic Acid	DBA	
-COCH ₃	9	Nonylacetophenone	NAP	
-CN	8	Octyloxybenzotrile	OONB	
-SO ₃ H	12	Dodecylbenzenesulfonic Acid	DBSA	

To study the effect of changing the chemistry of the alkylbenzene's head group, Chang and Fogler used four alkylbenzenes: dodecylbenzenesulfonic acid (DBSA), nonylphenol (NP), p-[(hydroxyethoxy)ethoxy]nonylbenzene (NBDO), and nonylbenzene (NB) (Östlund, 2004). The adsorption of four alkylbenzenes to asphaltene experiments was performed to investigate the stability of each alkylbenzene. Excessive amounts of 4 wt % asphaltene were mixed with stock solutions of 1 wt% alkylbenzene and alkane. The solution was filtered, and the supernatant was separated from the precipitated asphaltenes. The concentration of alkylbenzene in supernatant was measured by FT-IR spectrophotometry by quantifying the absorption peaks. Then, the concentration of solubilized asphaltene in the supernatant was measured from the absorbance of light using UV-vis spectrophotometry. The results shown in Figure 2.3a indicate that the polarities directly affect the ability of alkylbenzenes to stabilize asphaltene systems, as there is a direct correlation between effectiveness and polarity.

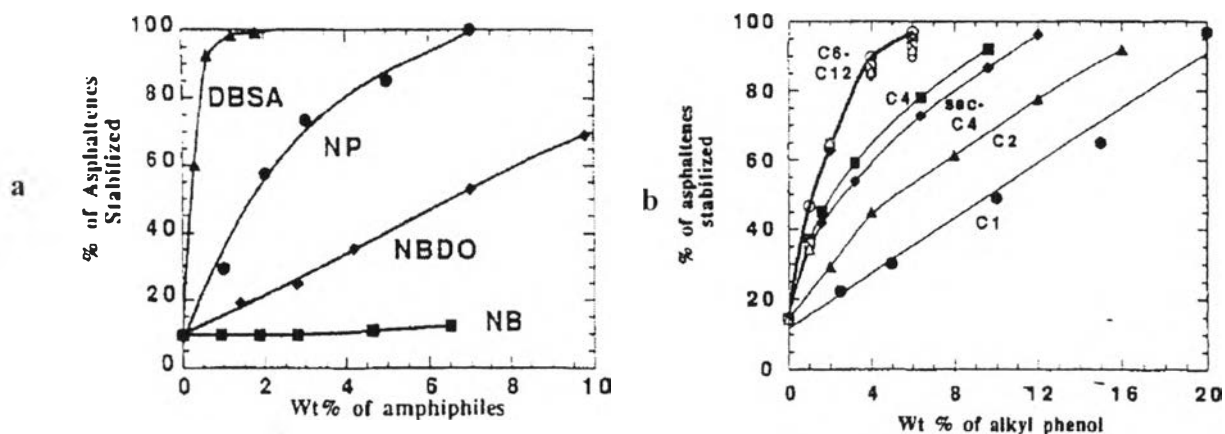


Figure 2.3 (a) Percentage of asphaltenes stabilized in the heptane solutions containing different head groups of dispersants. (b) Percentage of asphaltenes stabilized in the heptane solutions containing alkylphenol with different tail lengths (Chang, 1994).

Additional experiments were conducted to determine the effect of alkylbenzene tail length on asphaltene stability. Derivatives of p-alkylphenol were used with tail lengths ranging from one to twelve carbons. The results were shown in Figure 2.3b. This trend suggests that the minimum chain length for alkylbenzenes is about six, and a tail with a carbon number greater than 6 can only induce very little effect to the stabilization of asphaltenes (Chang, 1994).

All previous alkylbenzene-asphaltene studies show that the presence of alkylbenzene stabilizes asphaltene systems. However, those experiments were conducted at high alkylbenzene concentrations that exceeded the asphaltene concentration (Östlund, 2004), (Low, 1998), (Gonzalez, 1990). This limits the industrial viability of alkylbenzenes because high alkylbenzene concentrations may be significant potential risks to health and the environment (Östlund, 2004). In addition, the price of alkylbenzenes as inhibitors is costly for large quantities. Hence, using very low concentration of alkylbenzenes to stabilize asphaltene systems will reduce the risks to environment and the cost of production operation appreciably.

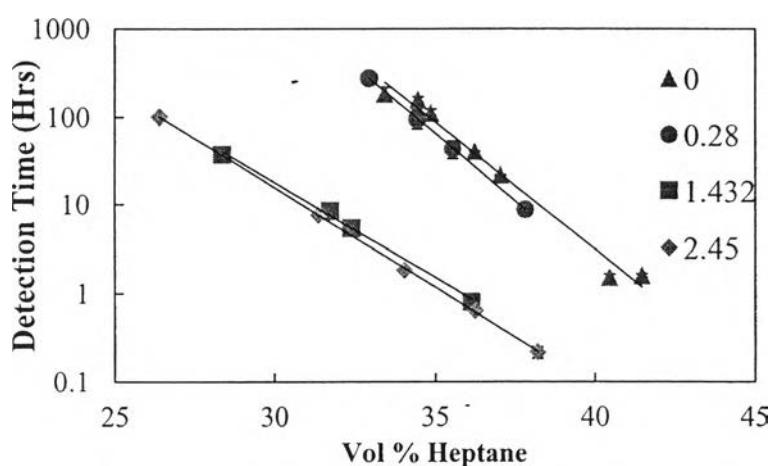


Figure 2.4 Onset curves for 2.35, 1.432, 0.28 mmol DBSA/mol.

Therefore, onset experiments at low concentrations of DBSA, corresponding to 0.28, 1.432 and 2.450 mmol DBSA/mol asphaltene, have been conducted in our lab; the results of these findings are shown in Figure 2.4. The

results demonstrate that the more alkylbenzene there is in solution, the more instable the asphaltenes are. The detection times between 1.432 and 2.45 mmol DBSA/mole asphaltene are not significantly different, which suggests a possible depletion of reactive sites on the asphaltene surface or a DBSA solubility limitation; further work will have to be done to discern this nature of this result.

In order to determine the effect of alkylbenzene head group on asphaltene stability at low alkylbenzene concentrations, onset experiments were conducted using model oil solution with concentration of 2.35 mmol alkylbenzene/mol asphaltene. Three alkylbenzenes were used and the results are shown in Figure 2.5. All of three alkylbenzenes DOBA, OOBN, and DBSA destabilize asphaltene.

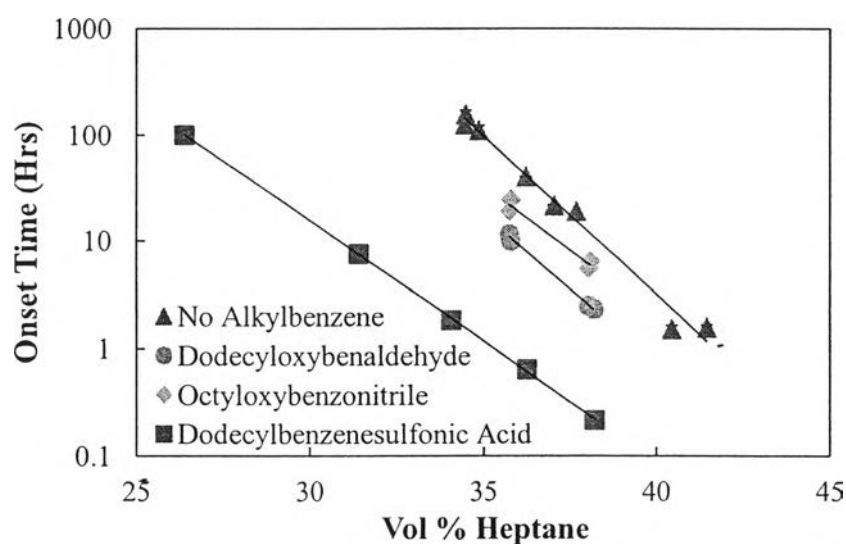


Figure 2.5 Onset curves for DOBA, OOBN, DBSA, and no alkylbenzene at 2.35 mmol alkylbenzene/mole asphaltene.

Insight into the mechanism of interaction between asphaltenes and alkylbenzenes suggests that an acid-base reaction is occurring. Figure 2.6 shows the results from FT-IR spectra (Chang, 1994). After adding 2 wt% of asphaltenes, the band between $2000 - 2800 \text{ cm}^{-1}$, which represents DBSA's SO-H stretching band

decreases. This decrease indicates that asphaltene is protonated by the proton from the SO-H group.

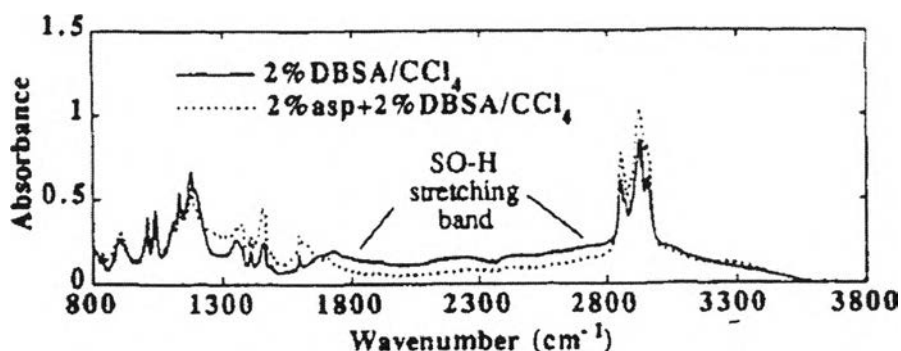


Figure 2.6 FT-IR spectra of DBSA in solution before and after the addition of 2wt% asphaltenes (Chang, 1994).

From the acid-base evidence from previous work, the destabilization effect between alkylbenzenes and asphaltenes were assumed to be acid-base reaction in this work.

2.3 pKa measurement

Acid-base theory was discovered since 1880, by Arrhenius. Then, the theory that acids are substances which can dissociate protons and bases are substances which can receive the protons was found by Brønsted and Lowry in 1923 (Kütt, 2008). There are no bases without acids, likewise, no acids without bases. For example, water can be both acidic and basic depending on react substances. The ability to receive protons will judge the substance to be likely acidic or basic; bases can receive protons more strongly than acids. Many methods can measure the ability to receive and donate protons which is the strength of acids and bases.

2.3.1 Selection of Method

Many methods have been developed to study acid-base equilibria. In this section only the main methods are discussed and briefly analyzed. We have used potentiometric titration for this work because there are many advantages compared to other methods. Firstly, it is applicable to measure pK_a in low permittivity non-aqueous solution (Gunduz, 1987). Secondly, no complex equipment is required; only pH meter, electrode, and micropipette are required for titration. Lastly, there is no need to measure the acidity of the medium or concentrations of samples (Kütt, 2008). Another method, UV-vis spectrophotometry has been widely used in the literature. It was used in this work for the first time; however, the signals were scattered and the equilibrium points were not found for all experiments. Moreover, it requires repeated measurements to make ladders of pK_a results between couples of chemicals. Another problem with this approach for our work is that we are impossible to guess that where the pK_a of considered alkylbenzenes should locate at. Another method is gas-phase measurements, which yield intrinsic acidities and have the added benefit of being free of all medium effects. An absolute scale of acidity in the gas phase has been published, ranging almost 90 orders of magnitude (Leivens, 2012). However, if very strong acids are used, gas-phase measurements often fail (Leito, 2006). This is because strong acids are not typically volatile enough and tend to undergo fragmentation in the course of the experiments (Leito, 1998).

2.3.2 Selection of Solvents

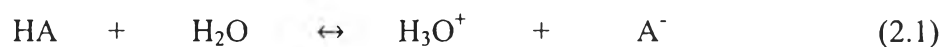
Both the physical and chemical properties of a solvent significantly influence the strength of an acid-base reaction. Water is the most common media and has been used for thousands of pK_a measurements. However, water is amphoteric and has a high acidity and basicity. Thus, it tends to solvate anions and causes the leveling effect, which means the strength of a strong acid or strong base will be limited by the basicity or acidity of the solvent, respectively. Water also forms H-bond complexes with acids or bases and, therefore, changes the true acid-base properties of acids and bases. Furthermore, water is a polar solvent which is not a good solvent for nonpolar molecules (Kütt, 2008).

Toluene is widely used as solvents for asphaltene experiments, but toluene is non-polar solvent and has extremely low dielectric constant which is 2.3 to conduct pK_a measurements. Many solvents are typically used in previous work to

perform potentiometric titration such as acetonitrile and nitrobenzene having dielectric constant as 37.5 and 35.74, respectively. However, asphaltenes are completely insoluble in these two solvents even after sonication. Among these non-aqueous solvents, tetrahydrofuran is found to have moderate dielectric constant around 7.52 and asphaltenes are soluble in it.

2.3.3 Potentiometric Titration in Non-aqueous Media

In general, acid-base reaction consists of acid, base, conjugate base, and conjugate acid. By the definition of Brønsted–Lowry acid–base theory, the typical acid-base reaction is shown below in equation 2.1.



(acid) (base) (conjugate acid) (conjugate base)

In the Brønsted–Lowry acid–base theory, an acid is defined as a proton donor and a base as a proton acceptor. The substances that are related to acid and base by donating and gaining of a proton are called a conjugate acid and conjugate base (Ege, 1984).

From Henderson-Hasselbalch equation, equilibrium constant of reaction from equation 2.1 can be expressed as (Ege, 1984):

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \quad (2.2)$$

$$\text{Or} \quad [\text{H}_3\text{O}^+] = K_a \left(\frac{[\text{HA}]}{[\text{A}^-]} \right) \quad (2.3)$$

Where $[H_3O^+]$ is denoted as concentration of conjugate acid, $[HA]$ is concentration of acid, and $[A^-]$ is concentration of conjugate acid in the solution. By taking logarithm of both sides, equation 2.3 became Equation 2.4:

$$\log[H_3O^+] = \log K_a + \log \left(\frac{[HA]}{[A^-]} \right) \quad (2.4)$$

By the definition, $pH = -\log[H_3O^+]$ and $pK_a = -\log K_a$. Then, equation 2.4 will become equation 2.5 (Ege, 1984):

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \quad (2.5)$$

From equation 2.5, pH will be equal pKa when the concentration of acid equals its own conjugate base.

Potentiometric methods are used to measure the acidity or basicity strength and based on the difference in potential between 2 electrodes in an electrochemical cell. Combination electrode has been widely used recently; it consists of an indicator electrode and a reference electrode inside. The measure potential in electrode is given by equation 2.6 (Ege, 1984):

$$E_{cell} = E_{ind} - E_{ref} + E_j \quad (2.6)$$

Where E_{cell} is the potential of whole cell, E_{ind} is the potential of indicator electrode, E_{ref} is the potential of the reference electrode, and E_j is the liquid junction potential.

The typical result from potentiometric titration is shown in Figure 2.1.

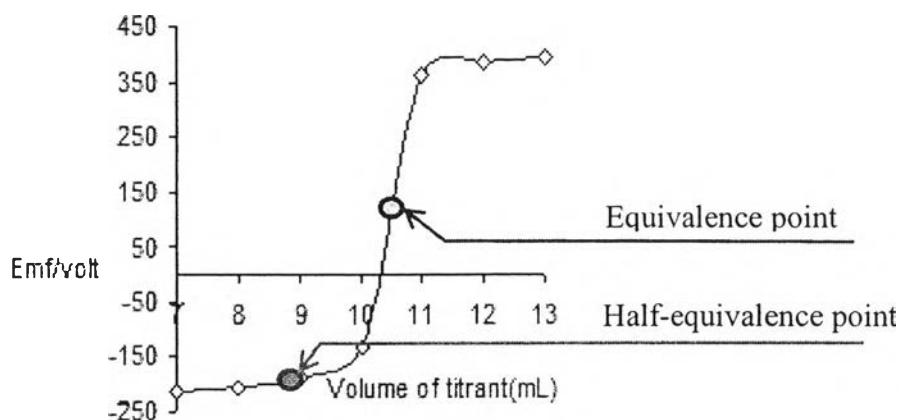


Figure 2.7 Typical results from potentiometric titration of potential values versus volume of titrant showing the location of equivalence point and half-equivalence point.

From Figure 2.7, there is slightly little change in potential when the titrant is initially titrated until the equivalence point is approached. The potential values are changed rapidly at equivalence point means all moles of bases or acids in the system are completely reacted with acidic or basic titrant. At the halfway point in the titration, precisely half of the base originally present is neutralized. Therefore, at half-equivalence point, the concentration of acid or base will be equal to concentration of their own conjugate base or conjugate acid, respectively. Hence, at half-equivalence point the value of pH will be equal to pKa.

Output from electrode at half-equivalence point can be converted to pKa values by Nernst equation:

$$E = E_0 + 2.3 \frac{RT}{nF} \log(H^+) \quad (2.7)$$

Where E is the mV output obtained from pH meter, E_0 is zero offset constant for the electrode, R is the gas constant, F is the Faraday constant, T is the temperature in K and n is the ionic charge. By solving the Nernst equation, the calculated ideal slope value has a change in output of 59.16 mV per pH unit as shown in Table 2.1.

Table 2.2 pH or pKa electrode output at 25°C at half-equivalence point

pH or pKa at half-equivalence point	mV
1	+354.96
2	+295.80
3	+236.64
4	+177.48
5	+118.32
6	+59.16
7	0
8	-59.16
9	-118.32
10	-177.48
11	-236.64
12	-295.80
13	-354.96