# CHAPTER IV
# RESULTS AND DISCUSSION

## 4.1 Potentiometric Titration Results

As mentioned in experimental section, pKa measurements were performed at -0.33 mol asphaltene/mol alkylbenzene for 3 times. Table 4.1 shows half-neutralization point and calculated pKa results of considered alkylbenzenes at 2.5 mM from potentiometric titrations.

**Table 4.1** Half-neutralization point and pKa value of considered alkylbenzenes at 2.5 mM from potentiometric titrations in tetrahydrofuran

| **Alkylbenzenes** | **Half-neutralization point (HNP)** | **pKa** |
|---|---|---|
| Nonylacetophenone (NNAP) | 131.25 ± 1 | 4.78 ± 0.01 |
| Octyloxybenzonitrile (OOBN) | 119.75 ± 5.26 | 4.97 ± 0.08 |
| Nonylphenol (NP) | 25.08 ± 25.04 | 6.57 ± 0.42 |
| Nonylaniline (NNAL) | -45 ± 4.27 | 7.76 ± 0.07 |
| Dodecyloxybenzaldehyde (DDBD) | -62.91 ± 7.28 | 8.06 ± 0.12 |

The pKa values of five alkylbenzenes which have different functional groups were obtained from potentiometric titrations in the following order: nonylacetophenone < octyloxybenzonitrile < nonylphenol < nonylaniline < dodecyloxybenzaldehyde. The concentration of alkylbenzene should not be excessively high because the homoconjugation will be occurred. Homoconjugation is an association between a base and its conjugate acid, therefore, it masks the intrinsic acid-base properties of acids and bases. Basicity of alkylbenzene was compared to their degree of destabilization in section 4.2.2. However, DBSA is not used in this work because DBSA is the only one commercially available acidic alkylbenzene and very strong acid. Then there is no acidic titrant which has greater acidity than DBSA.

## 4.2 Microscopy Results

### 4.2.1 Ideal concentration of all alkylbenzenes for destabilization effect

The concentrations of alkylbenzenes need to be chosen to be not extremely high to solvate asphaltenes and not inadequately low to detect destabilization effect. From pKa measurement results, nonylphenol has medium pKa among all alkylbenzenes. Hence, nonylphenol was chosen as a representative alkylbenzene to perform microscopy experiments. Three sets of microscopy experiments were performed as shown in Figure 4.1, 4.2, and 4.3.

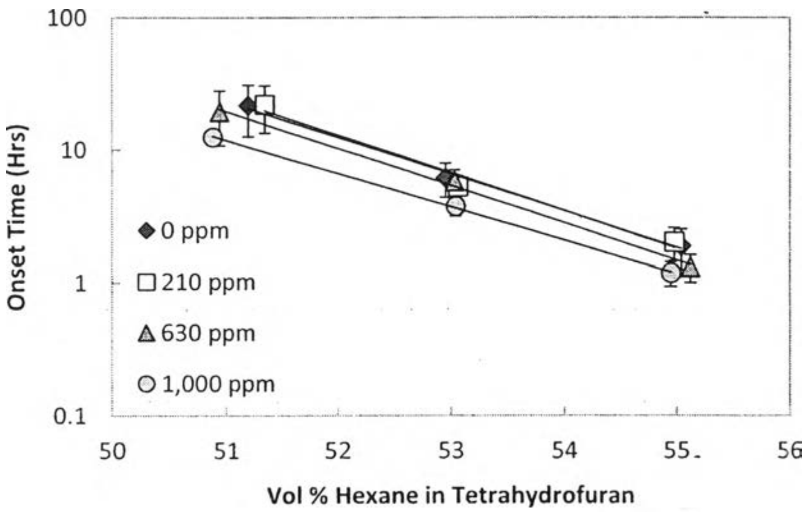

**Figure 4.1** Detection time as a function of hexane concentration of 0, 210, 630, and 1,000 ppm of nonylphenol with 1 wt% asphaltene in tetrahydrofuran.

From Figure 4.1, the differences in stability of nonylphenol between no chemicals, 210, and 630 ppm are very small to detect. Nonylphenol 210 ppm almost have the same detection time with no chemicals, and 630 ppm made a slightly difference compared to no chemicals. However, 1,000 ppm of nonylphenol obviously stabilizes asphaltenes. Destabilization effect of nonylphenal has never found because all of previous work used extremely high nonylphenol concentrations.

In order to fully study the effect of nonylphenol and locate the point when nonylphenol starts solvating asphaltenes, the second set of microscopy experiment was conducted. Nonylphenol was performed at 2500 and 5,000 ppm, and the results are shown in Figure 4.2.

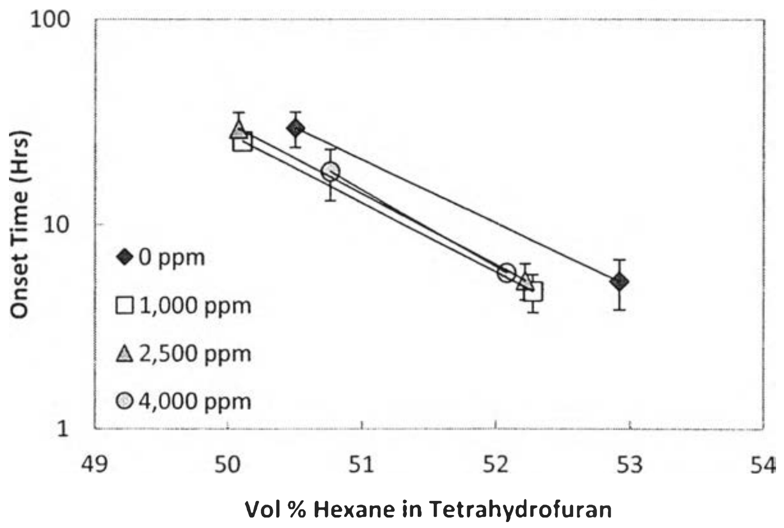

**Figure 4.2** Detection time as a function of hexane concentration of 0, 1,000, 2,500, and 4,000 ppm of nonylphenol with 1 wt% asphaltene in tetrahydrofuran.

The microscopy results from Figure 4.2 suggest that adding additional nonylphenol has no effect between concentrations 1,000, 2,500, and 4,000 ppm. These concentrations of nonylphenol destabilize asphaltene at the same degree.

Higher concentrations of nonylphenol were added to 5,000 and 10,000 ppm in the third set of microscopy experiment and the results are shown in Figure 4.3.

The results from Figure 4.3 suggest that at concentration 5,000 and 10,000 are more stable than 1,000 ppm. This means physical dispersion begins to become important at concentration higher than 4,000 ppm. However, 5,000 and 10,000 ppm of nonylphenol is still less stable than no chemicals.

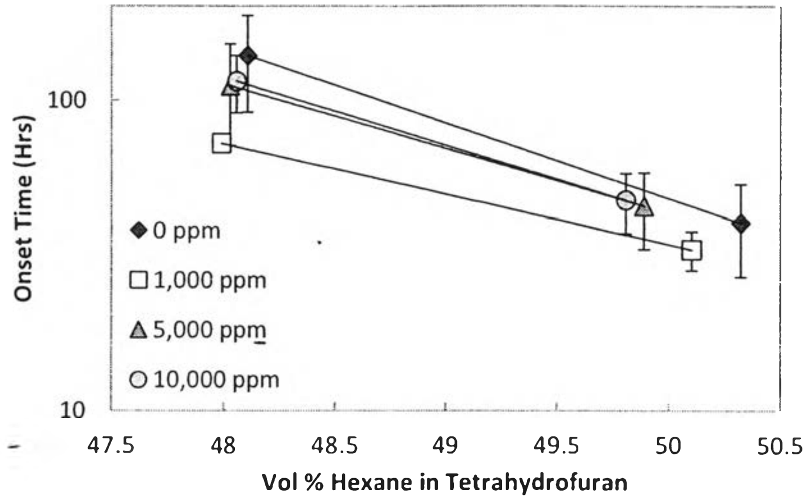

**Figure 4.3** Detection time as a function of hexane concentration of 0, 1,000, 5,000, and 10,000 ppm of nonylphenol with 1 wt% asphaltene in tetrahydrofuran.

To prove that nonylphenol will be more stable than no chemicals at some point as illustrated by the literature, microscopy experiments of nonylphenol at extremely high concentration were conducted. Therefore, the fourth set of microscopy experiment was performed at 30,000 and 50,000 ppm of nonylphenol and the results are shown in Figure 4.4.

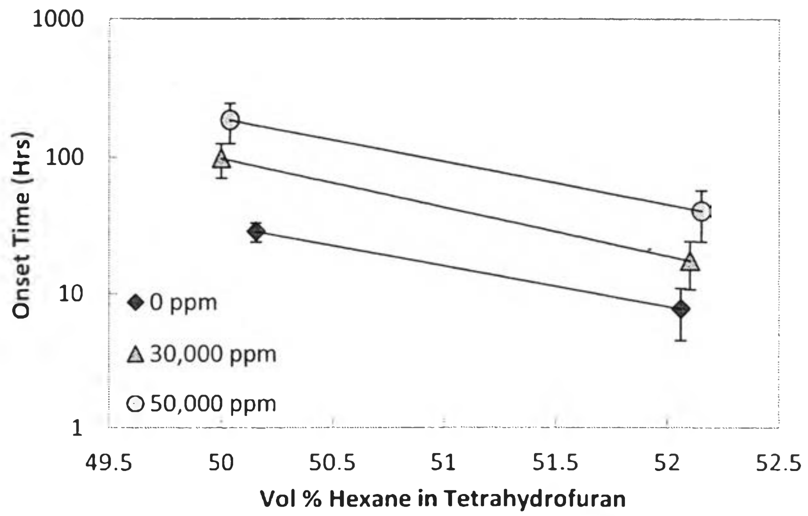

**Figure 4.4** Detection time as a function of hexane concentration of 0, 30,000, and 50,000 ppm of nonylphenol with 1 wt% asphaltene in tetrahydrofuran.

Figure 4.4 shows that 30,000 ppm and 50,000 ppm obviously stabilizes asphaltene as shown in all literature. If the asphaltene molecular weight is assumed to be 750 (Mullin, 2007), the concentration 30,000 and 50,000 will equal to 3 wt% and 5 wt% of nonylphenol or 10.26 and 17.1 mol nonylphenol/ mol asphaltene, respectively; it means nonylphenol has 10-time greater amount than asphaltenes in the system.

From three sets of microscopy experiments, we are able to conclude that nonylphenol between 210-630 ppm does not affect the degree of stabilization of asphaltene. While 1000-4000 ppm of nonylphenol stabilizes. However, at 5,000-10,000 ppm, physical dispersion begins to become important. Moreover, at 30,000 and 50,000 ppm, nonylphenol completely stabilizes the asphaltene system.

In this work, the goal is to study the effect of alkylbenzenes on asphaltene destabilization. Hence, from three sets of microscopy experiments of nonylphenol, concentration at 1,000 ppm was chosen to be the ideal concentration for all alkylbenzenes. Nonetheless, all alkylbenzenes have to be compared in the same amount or molar basis which concentration 1,000 ppm of nonylphenol equals to 0.33 mol alkylbenzene/mol asphaltene.

### 4.2.2 Degree of destabilization of all alkylbenzenes

All alkylbenzenes were performed in microscopy experiments at 0.33 mol alkylbenzene/mol asphaltene with 1 wt% asphaltene. Five concentrations of hexane concentration were chosen at these experiments; 46, 48, 49, 50, and 52 wt% hexane. The results are demonstrated in Figure 4.5.

From Figure 4.5, pKa values from potentiometric titration were added after the names of alkylbenzenes. The color bar was added showing the degree of basicity from purple which is the strongest base and orange is the weakest base.

The degree of destabilization from Figure 4.5 was found to be in order: nonylacetophenone (pKa = 4.78) > octyloxybenzonitrile ( pKa = 4.97) > nonylphenol (pKa = 6.47) > nonylaniline (pKa = 7.76) > dodecylbenzaldehyde (pKa = 8.06). The results demonstrate the relationship between basicity and degree of destabilization of alkylbenzenes. The weakest bases were found to be the most destabilizing and the strongest bases were the least destabilizing. A correlation was found between the pKa and the degree of destabilization.

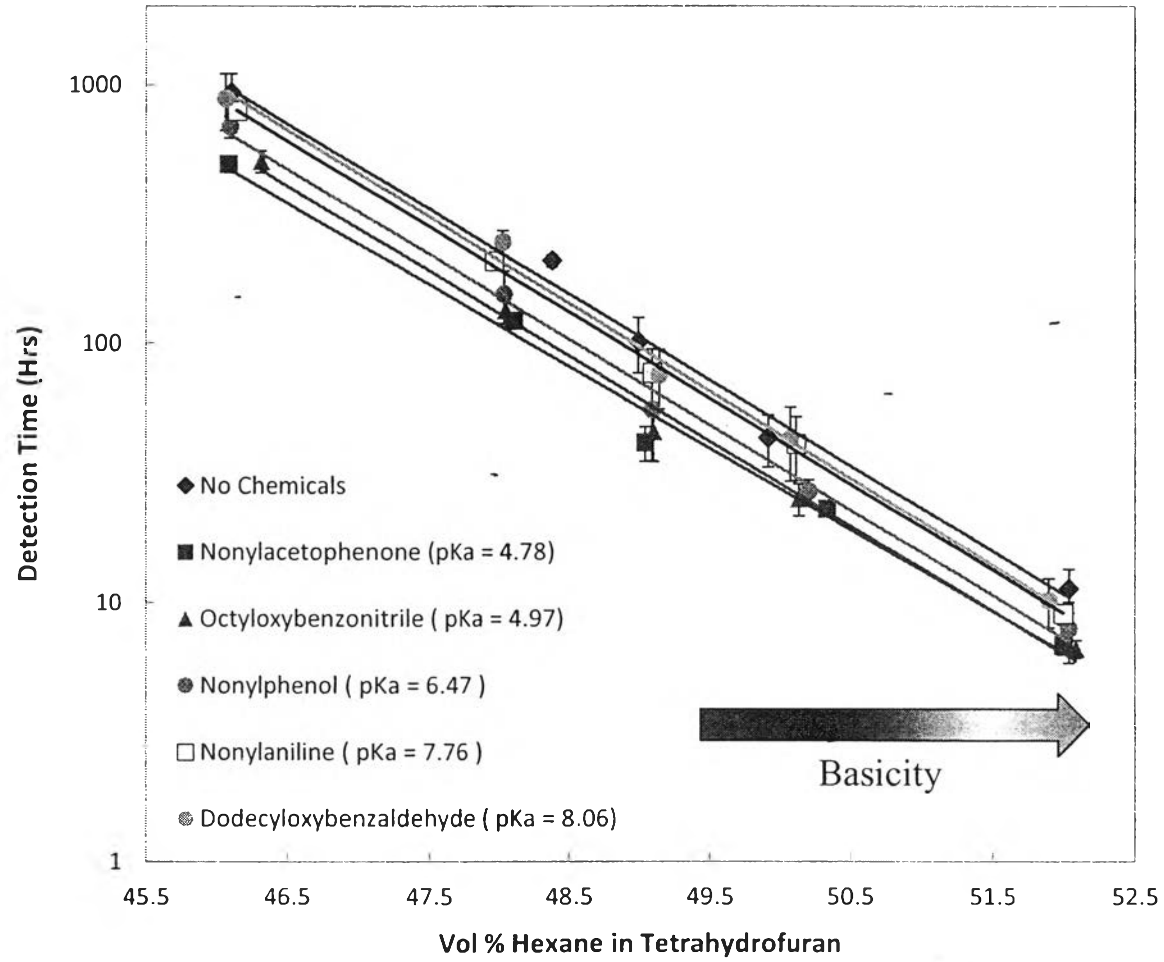

**Figure 4.5** Detection time as a function of hexane concentration of no chemicals, nonylacetophenone, octyloxybenzonitrile, nonylphenol, nonylaniline, and dodecyloxybenzaldehyde at 0.33 mol alkylbenzene/ mol asphaltene with 1 wt% asphaltene in tetrahydrofuran.

## 4.3 Solubility Parameter Results

In this work, we assumed that alkylbenzene reacts with asphaltene via chemical reactions at low alkylbenzene concentrations as shown in Figure 4.6.

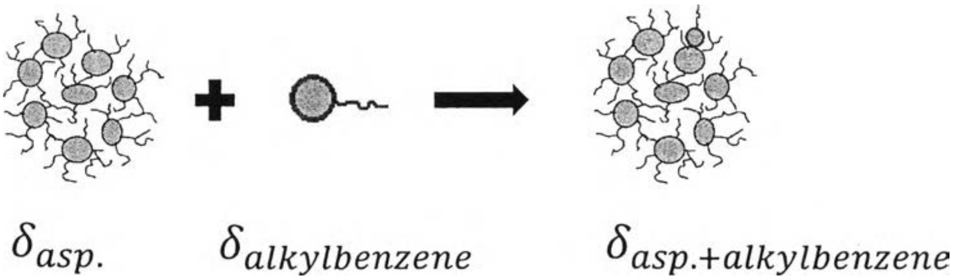

**Figure 4.6** Simulated reaction between alkylbenzene and asphaltenes.

In the work of Haji Akbari Balou 2012, it discussed about a unified model for asphaltene aggregation. In this work, this model can be supported for the better explanation of asphaltene-alkylbenzene interaction. By using the model, the solubility parameter of the reacted asphaltenes can be calculated by equation 4.3.1 (Akbari, 2013).

$$\ln\left(\frac{t_{detection}\sqrt{C_1(0)}}{\mu}\right) \sim \frac{1}{\left(\delta_{asphaltene+alkylbenzene} - \delta_{solution}\right)^2} \qquad (4.1)$$

The actual concentrations of precipitant and detection time from microscopy experiments were substituted into aggregation model. The calculated solubility parameters of each alkylbenzene are shown in Table 4.2.

Solubility parameter can define the ability of the system to be soluble with asphaltenes by using detection times and precipitant concentrations from microscopy experiments. The deviation of the solubility parameter in the presence of chemicals from pure-asphaltene system makes the differences in asphaltene stability. The greater of solubility parameter represents less stable system; likewise, the smaller solubility parameter represents more stable system (Haji Akbari *et al.*, 2013).

**Table 4.2** Solubility parameters of alkylbenzenes at 0.33 mol alkylbenzene/mol asphaltene in tetrahydrofuran

| **Alkylbenzenes** | **Solubility Parameter ($Pa^{1/2}$)** |
|---|---|
| No chemicals | 23,990 |
| Nonylacetophenone | 24,023 |
| Octyloxybenzonitrile | 24,020 |
| Nonylphenol | 24,012 |
| Nonylaniline | 23,999 |
| Dodecyloxybenzaldyhyde | 23,995 |

In this case, the solubility parameter of asphaltene in tetrahydrofuran is 23,990. The presence of alkylbenzenes reduces solubility parameter and the results were obtained as follows: nonylacetophenone (24,023) > octyloxybenzonitrile (24,020) > nonylphenol (24,012) > nonylaniline (23,999) > dodecyloxybenzaldehyde (23,995)

The calculated solubility parameters and pKa values of alkylbenzene were plotted in Figure 4.7.

As can be seen from Figure 4.7, the weakest bases increased the solubility parameter of the reacted asphaltene-alkylbenzene complex the most and the strongest bases increased the least. There appearts to be a linear correlation between the pKa of the alkylbenzene and the solubility parameter.

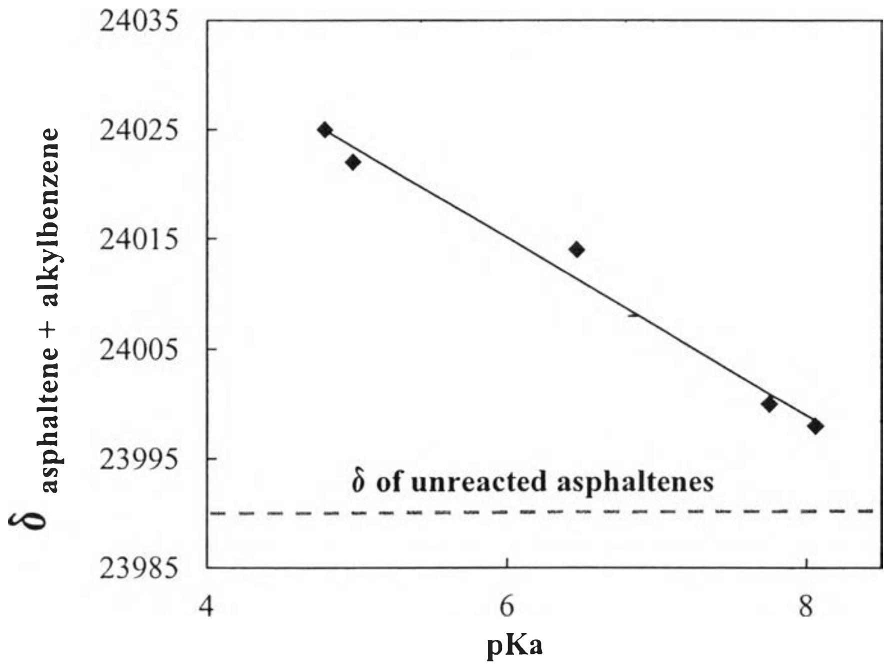

**Figure 4.7** Plot of solubility parameter versus pKa for five different asphaltene samples.