

## CHAPTER IV

### RESULTS

#### 4.1 Kinetic Study of Asphaltene Dissolution by Amphiphile/Alkane Solutions.

The results of this experiment were described as belowed.

##### 4.1.1 Effect of Amphiphile Concentration

The influence of the concentration of amphiphiles in the alkane-based fluid on the rate of dissolution of asphaltene deposits was studied using two types of amphiphiles, DBSA and NP, and two types of alkane medium, heptane and dodecane. The rate of fluid flow was fixed at 1 ml/minute and the experimental temperature maintained at 22°C.

Figures 4.1 and 4.2 shows the profile of asphaltene dissolution as a function of NP concentration in heptane and dodecane, respectively. Both figures shows that the rate of asphaltene dissolution in general increases with increasing the concentration of NP amphiphile. However, the trend of asphaltene dissolution with respect to NP concentration appeared quite different at the concentrations of NP above and below 7 wt%. When the NP concentration was less than 7 wt%, asphaltene deposits were apparently not completely dissolved in the fluid. For example, the percent of asphaltene dissolved in the first 50 ml of the injected fluid increased gradually from 15%, 30% to 80% as the concentration of NP increased from 0 wt%, 2 wt% to 4

wt% of NP. This result indicated that the asphaltene sample used in this study had a distribution of solubility, and the less soluble fraction could only be dissolved in the fluid with higher NP concentrations. When the NP concentration was above 7 wt%, asphaltene deposits could be dissolved completely in the fluid. The rate of asphaltene dissolution seemed to increase slightly with increasing the concentration of NP amphiphile, indicating that the concentrated NP amphiphilic molecules in alkane media expedited the process of dissolution of asphaltene deposits.

Figure 4.3 and 4.4 shows the profile of asphaltene dissolution as a function of the concentration of dodecylbenzene sulfonic acid in heptane and dodecane, respectively. Both figures shows that the rate of asphaltene dissolution in general increased with increasing the concentration of DBSA amphiphile. Nevertheless, similar to the results of NP amphiphiles shown in Figures 4.1 and 4.2, the trend of asphaltene dissolution with respect to DBSA concentration appeared quite different at the concentrations of DBSA above and below 3 wt%. When the DBSA concentration was less than 3 wt%, asphaltene deposits were apparently not completely dissolved in the fluid. For example, the percent of asphaltene dissolved in the first 50 ml of the injected fluid increased gradually from 15% to 33% as the concentration of DBSA increased from 0 wt% to 1 wt%. When the DBSA concentration was above 3 wt%, asphaltene deposits could be dissolved completely in the fluid. The rate of asphaltene dissolution apparently increased gradually with increasing the concentration of DBSA amphiphile, indicating that the concentrated DBSA amphiphilic molecules in alkane media expedited the process of dissolution of asphaltene deposits.

#### 4.1.2 Effect of the Type of Amphiphiles.

Two amphiphiles, nonylphenol and dodecylbenzene sulfonic acid, were used in the alkane media for the dissolution of asphaltene deposits. As illustrated in Figures 4.1 to 4.4, both amphiphiles were effective to the dissolution of asphaltene deposits. However, the minimum concentration of NP and DBSA for completely dissolving asphaltene deposits were 7 wt% and 3 wt%, respectively. These results were very consistent with the stability of asphaltenes in the amphiphile/alkane solutions studied previously by Chang and Fogler in 1994, and they could be explained by the strength of the associative interaction between amphiphiles and asphaltenes.

According to the structure of asphaltenes which consisted of not only aromatic compounds, but also a variety of acidic and basic functional groups, it was believed that asphaltenes were stabilized by amphiphiles through the acid-base interaction. The polar headgroup of the amphiphiles would attach to the asphaltene micelles and stretched their aliphatic groups outward to form a steric-stabilization layer around asphaltene. (Chang and Fogler, 1994)

The DBSA-asphaltene association is significantly stronger than the NP-asphaltene association because DBSA is such a strong acid which can readily undergo an acid-base reaction resulting in the irreversible attachment of its sulfonic acid group to asphaltenes. For nonylphenol, it is less acidic than DBSA even though its aromatic benzene group can delocalize the electrons bonded between O and H elements of the hydroxyl group and makes the phenol more acidic than the common alcohol. The lower acidity of

NP than DBSA causes NP to be a weaker asphaltene stabilizer than DBSA. Therefore, a higher concentration of NP amphiphilic molecules in solution is needed to provide a sufficient attractive interaction with asphaltene particles in order to dissociate them from asphaltene deposits. Figures 4.1 to 4.4 also shows that when the concentration of amphiphiles is higher than the minimum value for completely dissolving asphaltenes, the rates of asphaltene dissolution by NP solution and by DBSA solution appear similar.

#### 4.1.3 Effect of Alkane Solvent.

Five types of alkane solvents as listed in Table 3.2 were used to prepare micellar fluids for the dissolution of asphaltene deposits. Figures 4.5 and 4.6 shows that for both NP and DBSA amphiphiles, the rate of asphaltene dissolution was in general faster when the solvent was changed from hexane to hexadecane. For example, to completely dissolve asphaltene deposits required 25 ml of hexane media with 5 wt% DBSA while it required 40 ml of dodecane media containing 5 wt% DBSA. Similarly, the amount of solution with 20 wt% NP required to dissolve 80% asphaltene deposits was 4 ml for hexane media and 15 ml for dodecane media. In general, it required 30 - 50 ml of NP amphiphile solutions and 25 - 40 ml of DBSA amphiphile solutions to completely dissolve asphaltene deposits in the differential reactor.

#### 4.1.4 Effect of Temperature.

The effect of temperature on the rate of dissolution of asphaltene deposits by micellar fluids was illustrated in Figures 4.7 to 4.10. Figure 4.7

shows the time evolution profiles of asphaltene dissolution by a dodecane-based fluid containing 20 wt% NP amphiphile at the flow rate of 1 ml/minute. It was clear that the rate of asphaltene dissolution increased significantly with increasing the temperature of fluids and asphaltene deposits. For example, when temperature increased from 6°C, to 22°C and to 58°C, the volume of the injected micellar fluid required to dissolve 80% asphaltene deposits decreased from 40 ml, to 16 ml and to 8 ml. Similarly, as illustrated in Figure 4.8, the rate of asphaltene dissolution by a dodecane-based fluid containing 5 wt% DBSA amphiphile also increased clearly with increasing temperature.

Figure 4.9 and 4.10 shows the time evolution profiles of asphaltene dissolution by a heptane-based fluid containing 20 wt% NP amphiphile and 5 wt% DBSA at the flow rate of 1 ml/minute respectively. The trend of asphaltene dissolution with increasing temperature was also similar to that of Figure 4.7 and 4.8.

#### 4.1.5 Effect of Flow Rate of Micellar Fluid.

The effect of the flow rate of micellar fluids on the rate of asphaltene dissolution was illustrated in Figure 4.11. Under two different rates of flow of a heptane-based fluid containing 20 wt% NP amphiphiles, 0.1 and 1 ml/minute, the profiles of asphaltene dissolution appeared much more closely overlapped with each other if they were plotted as a function of the dissolution time rather than as a function of the accumulated elution volume of micellar fluids. This result indicated that the flow rate of micellar fluids in

this flow rate range did not significantly affect the rate of asphaltene dissolution.

#### **4.2 Study of Stability of Different Asphaltene Fractions in Selected Amphiphile/Alkane Solutions**

The results of stability studies of different asphaltene fractions in selected micellar fluid were described below.

The stability of 2 different asphaltene fractions and Mobil asphaltene (without further fractionation) in heptane solution with NP and DBSA amphiphiles was illustrated in Figure 4.12 and 4.13 respectively. It could be seen from Figure 4.12 that the stability of asphaltene fractions decreased from 1 wt% NP to 10wt% and to 20 wt% for Fraction 4, Mobil asphaltene and Fraction 1 respectively. Similar to the result of NP amphiphiles, the trend of the stability of asphaltene fractions in heptane-based solution containing DBSA amphiphile shown in Figure 4.13 decreased from 0.5 wt% DBSA for Fraction 4 to 1.5 and 10 wt% for Mobil asphaltene and Fraction 1 respectively. The results supported the idea that asphaltenes were composed of a large number of different molecules of different molecular weight and polarity. The results also indicated that asphaltene precipitation could be correlated with the solvent used as precipitant. These results were discussed in detail in chapter V.

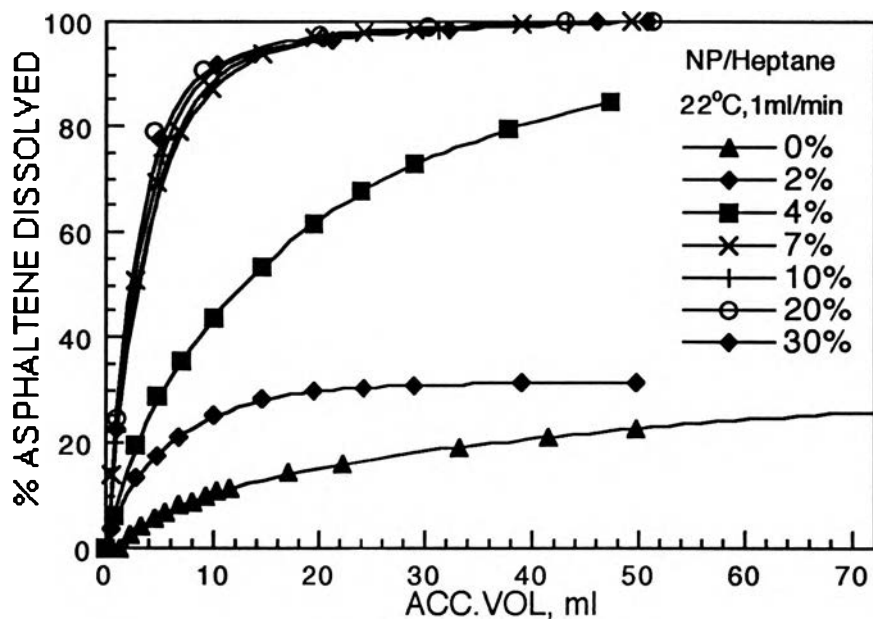


Figure 4.1 The profile of asphaltene dissolution by heptane-based fluids containing different concentrations of NP amphiphile.

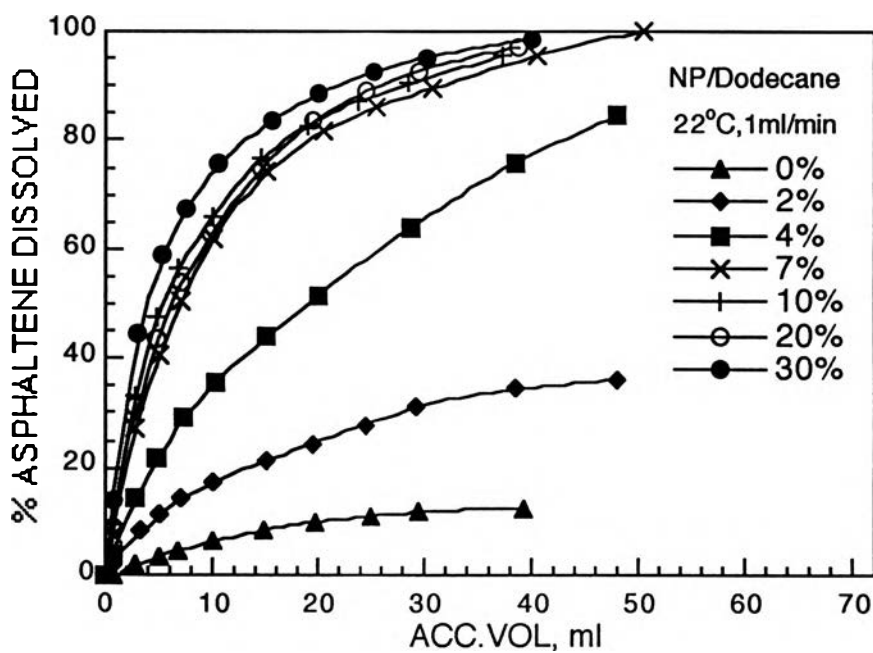


Figure 4.2 The profile of asphaltene dissolution by dodecane-based fluids containing different concentrations of NP amphiphile.

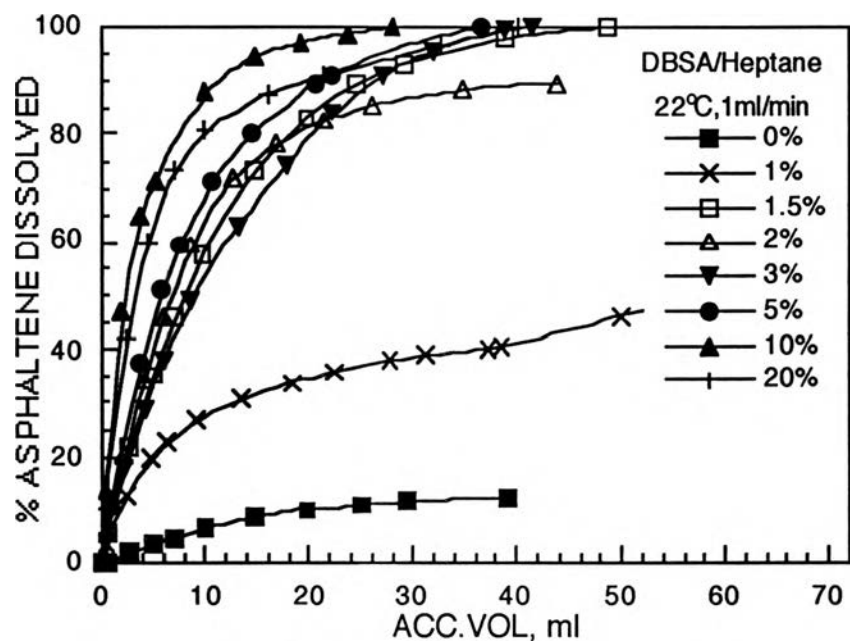


Figure 4.3 The profile of asphaltene dissolution by heptane-based fluids containing different concentrations of DBSA amphiphile.

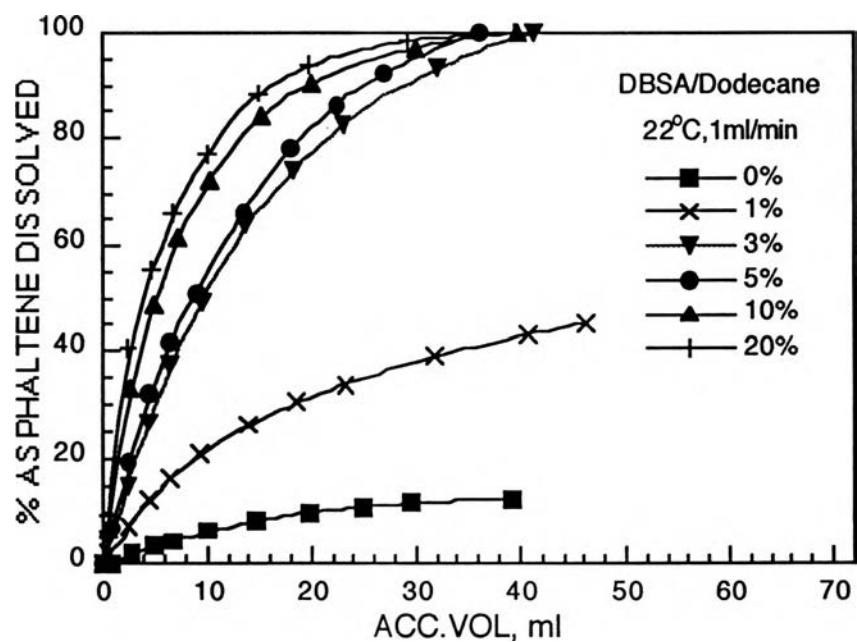


Figure 4.4 The profile of asphaltene dissolution by dodecane-based fluids containing different concentrations of DBSA amphiphile.



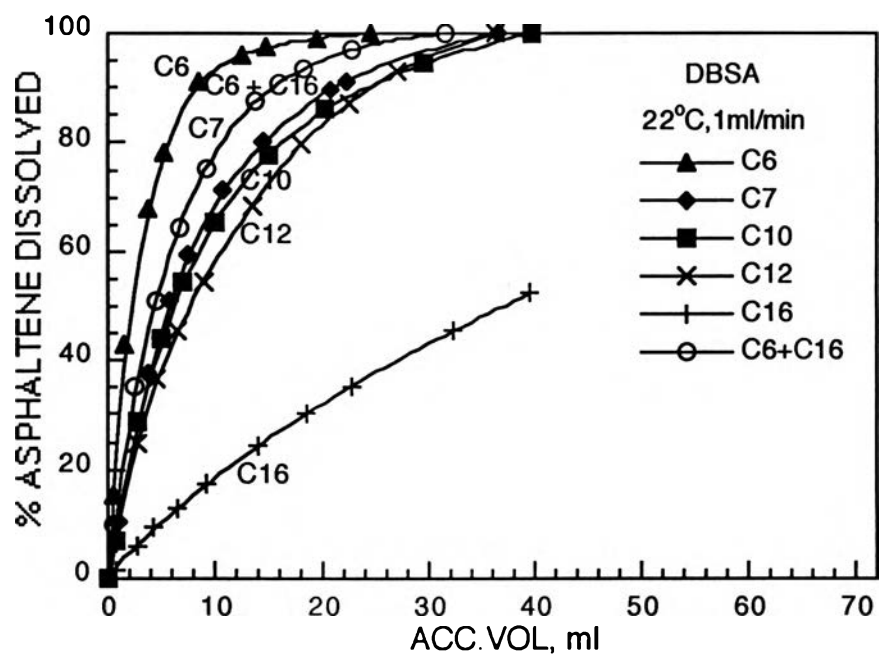


Figure 4.5 The profile of asphaltene dissolution by 5% DBSA amphiphile different alkane media.

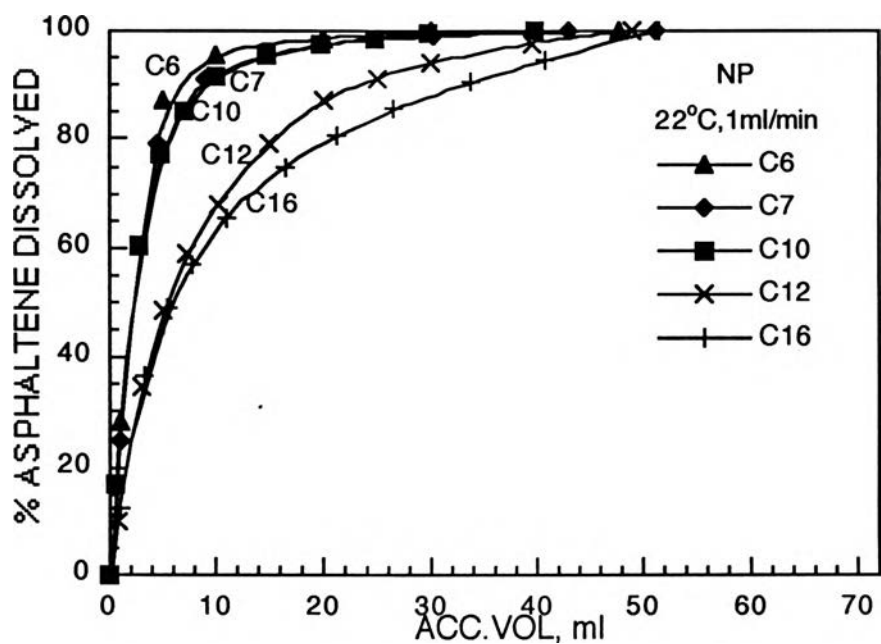


Figure 4.6 The profile of asphaltene dissolution by 5% DBSA amphiphile different alkane media.

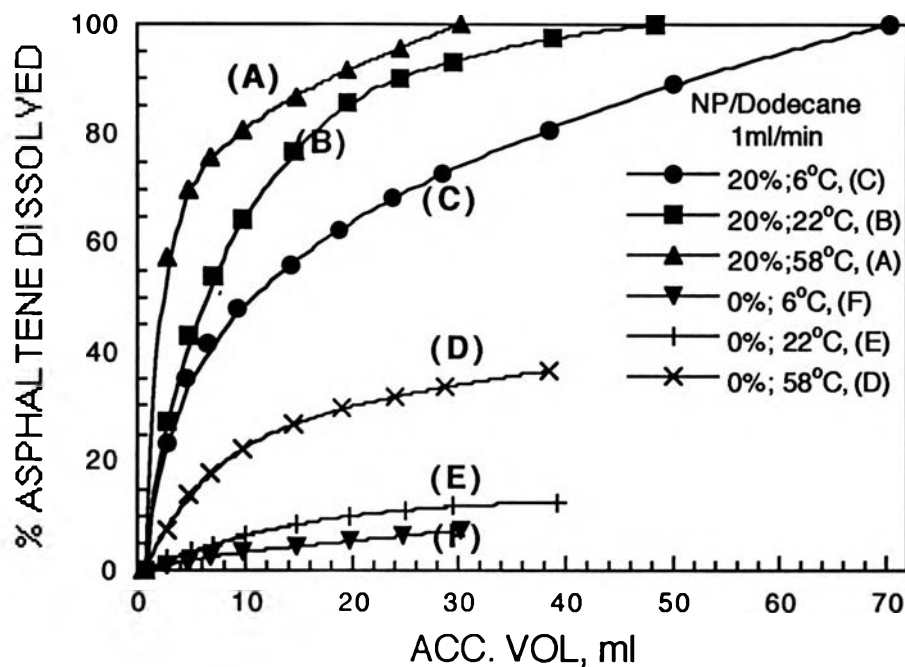


Figure 4.7 The profile of asphaltene dissolution at different temperatures by the dodecane-based fluid containing 20 wt% of NP amphiphile.

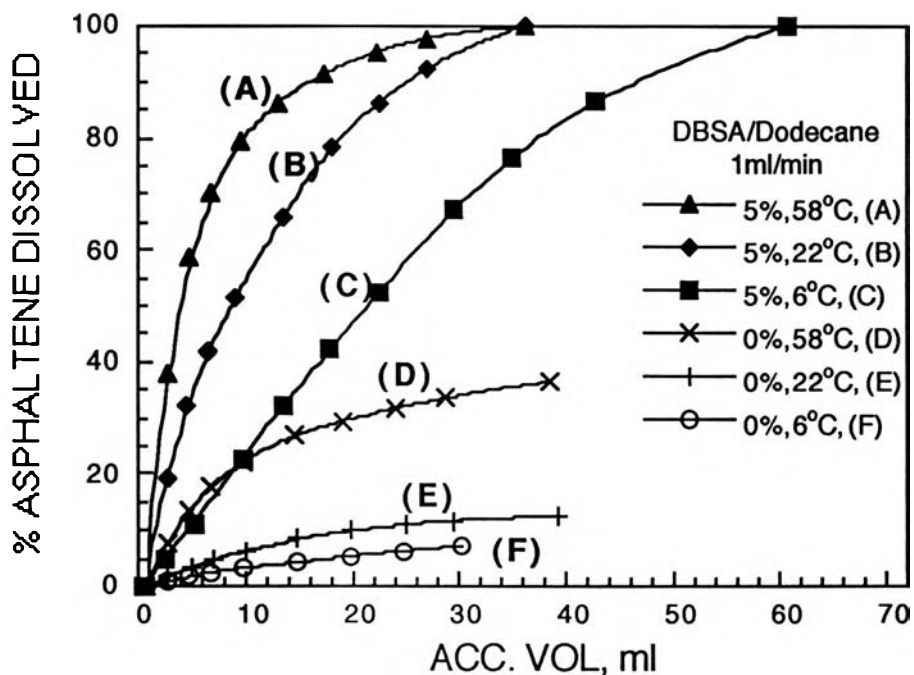


Figure 4.8 The profile of asphaltene dissolution at different temperatures by the dodecane-based fluid containing 5 wt% of DBSA amphiphile.

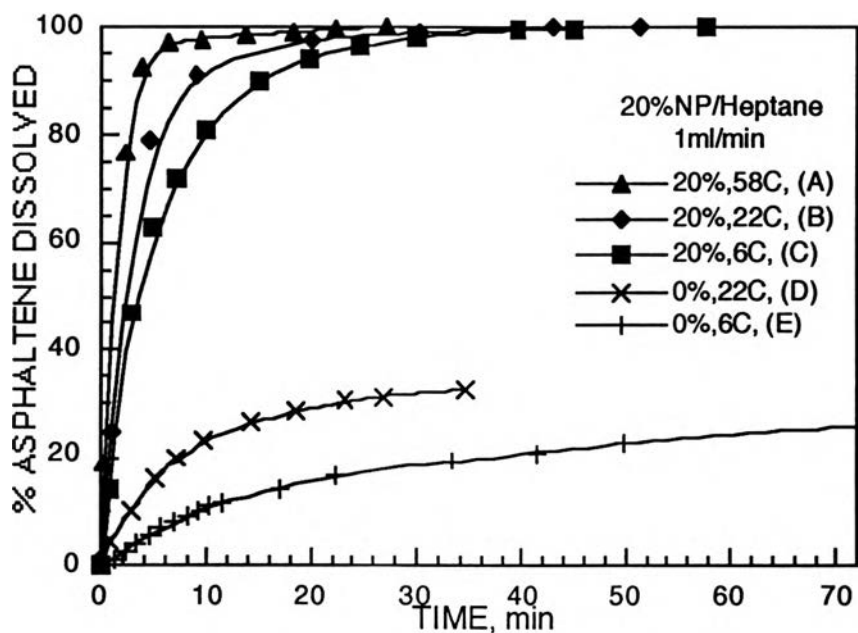


Figure 4.9 The profile of asphaltene dissolution at different temperatures by the heptane-based fluid containing 20 wt% of NP amphiphile.

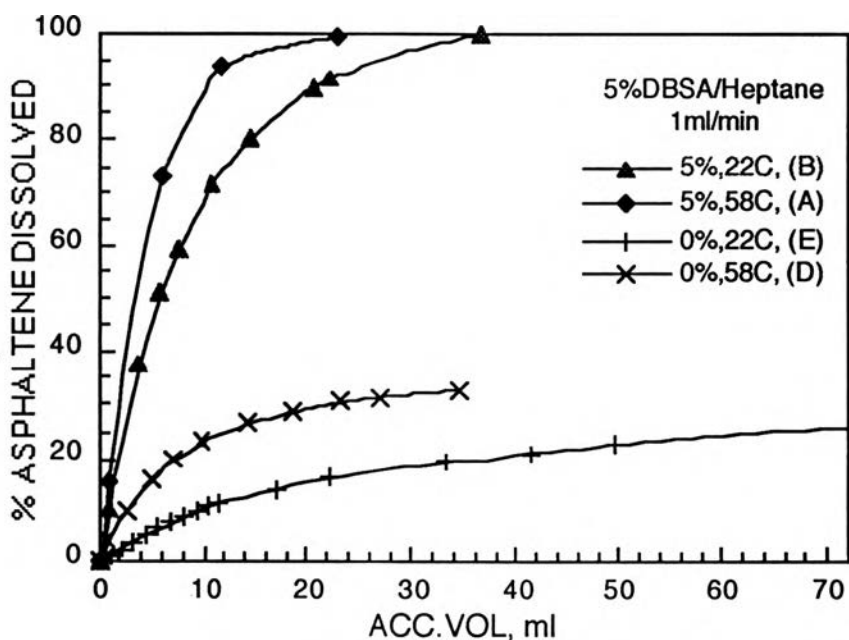


Figure 4.10 The profile of asphaltene dissolution at different temperatures by the heptane-based fluid containing 5 wt% of DBSA amphiphile.

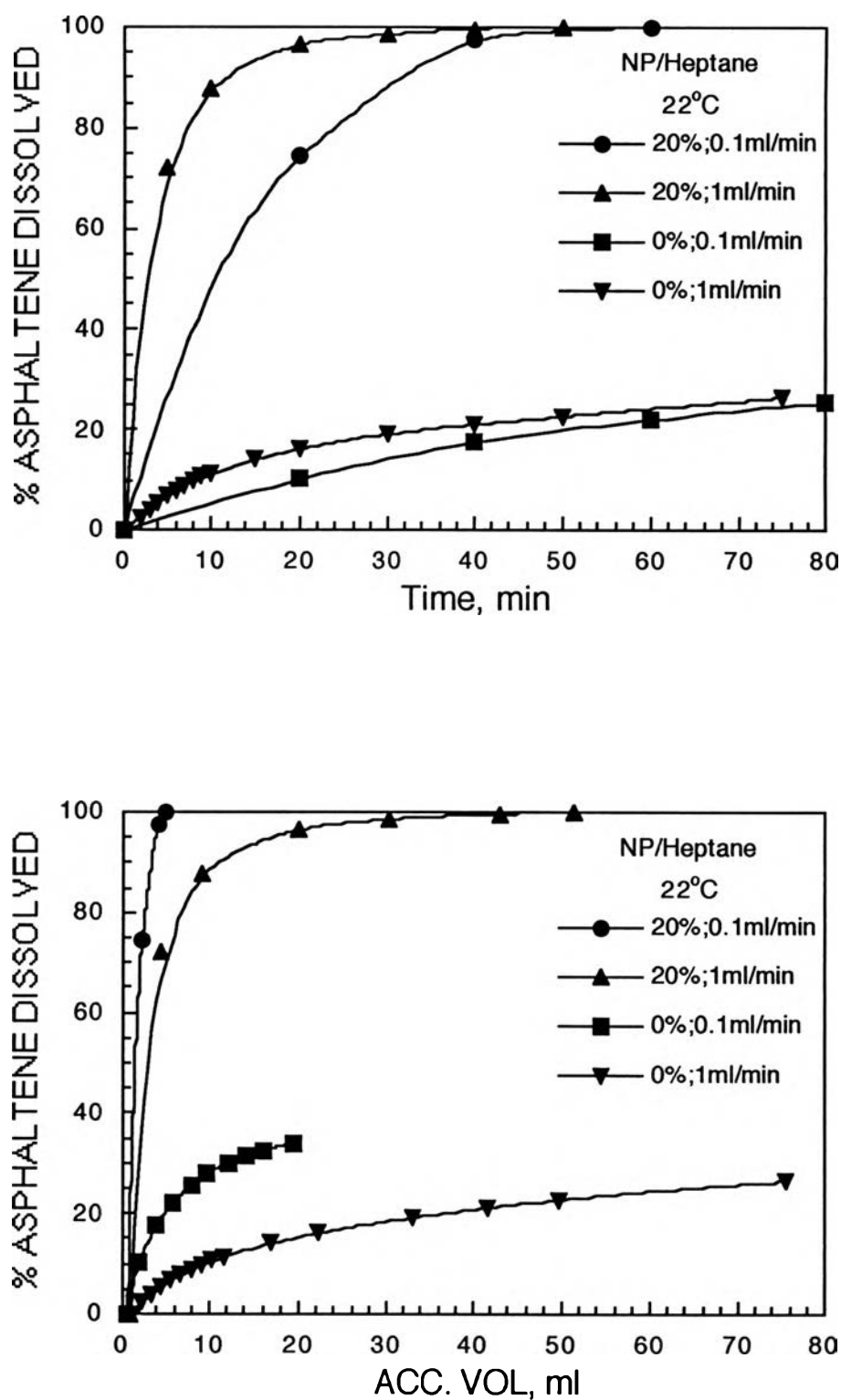


Figure 4.11 The profile of asphaltene dissolution by the heptane-based fluid containing 20 wt% of NP amphiphile at different flow rates. (upper) The dissolution profile is plotted as a function of both the time of dissolution (up) and the volume of effluent (bottom).

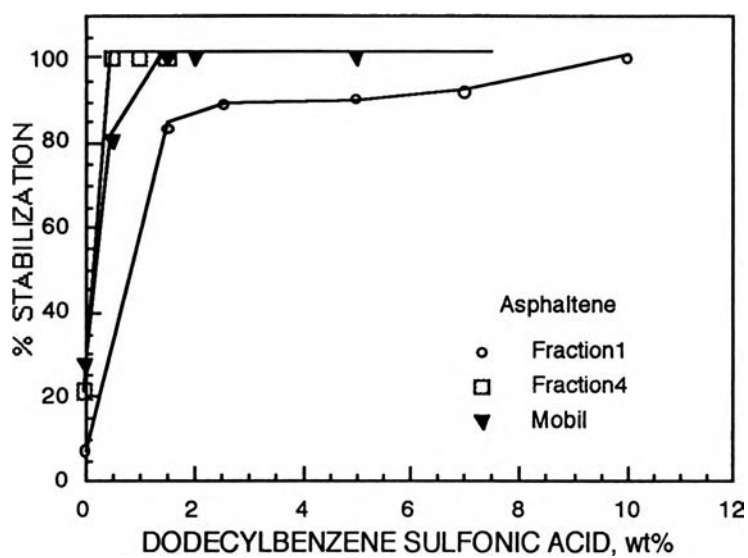


Figure 4.12 Stability of asphaltene fraction in fluids containing 5wt% DBSA amphiphile.

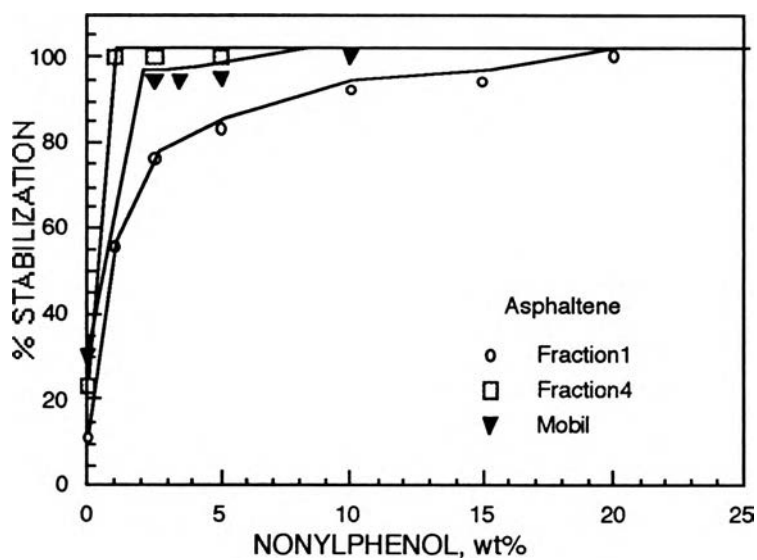


Figure 4.13 Stability of asphaltene fraction in fluids containing 20wt% NP amphiphile.