CHAPTER V

DISCUSSION

5.1 Kinetic Study of Asphaltene Dissolution by Amphiphile/Alkane Solutions.

The dissolution of deposited asphaltene particles in the amphiphile solution could be described by 3 steps in series: the diffusion of amphiphile solution on the asphaltene surface, the dissociation of asphaltene molecules through a surface reaction, and the subsequent diffusion of the disintegrated asphaltene toward the bulk liquid phase. The diffusion is considered as mass transfer reaction . Depending on the operating conditions, the rate of dissolution may be controlled by one of these processes. (Hsu and Lin,1991; Hsu and Liu,1993)

The rate of diffusion of amphiphile solution is considered as mass transfer reaction which can be expressed by

$$r_a = k_d \ S \ (C_i - C_b)$$

when	k_d	=	mass transfer coefficient
	C_i , C_b	=	concentration of amphiphile at the solid-liquid interface and in the bulk liquid phase respectively.
	S	=	surface area of particle.

The rate of dissociation of asphaltene (Surface reaction) can be expressed by

$$r_x = k_r \ S \ (M_e - M_o)^n$$

when k_r =   empirical rate constant

M_e , M_o =   Mass of asphaltene at equilibrium and at the initial stage of experiment.

n   =   constant

The rate of diffusion of dissolved asphaltene into bulk phase (Mass transfer reaction) can be expressed by

$$r_d \quad = \quad k_d \ S \ (M_i - M_b)$$

M_b =   Mass of asphaltene in bulk phase.

Note that since the molecular weight of asphaltene was unknown, its concentration was represented in term of mass.

Assuming that the dissolution was first order reaction and a pseudo-steady state was achieved, then the rate of solute released through surface reaction was equal to the rate of solute diffused to the bulk phase.

In other words,

$$r_a = r_x = r_d = r = dM/dT = kM$$

When   k = reaction rate constant

M = mass of asphaltene at t= t

By integral method, the integration of the combined mole balance and rate law, with the limit M = Mo at t = 0, gave

$$\ln (M/Mo) \quad = \quad -k\,t \qquad\qquad (5.1)$$

By fitting the experimental data to the first order rate law and plotting the curves of [ln (M/Mo)] as a function of time, the linear curves with slope -k were obtained as shown in Figure 5.1 to 5.10. From the well-behaved linearity obtained for all experimental data, we could conclude that the dissolution of asphaltene in this study was the first order reaction. Another interesting observation found in Figure 5.3 was that when the system approached equilibrium, the curves gradually became nonlinear. These results could be attributed to the structure complexity of asphaltene.

In all cases, the dissolution of asphaltenes decreased monotonically as a function of time and eventually reached an equilibrium. The equilibrium value was found to be a function of temperature and amphiphile concentration. These relationships were identified in the following paragraph.

The temperature dependence of the reaction rate constant (k) was studied. An Arrhenius plot of the reaction rate constant versus 1/T was reported in Figure 5.11 to 5.14. These figures were obtained by a linear regression fit. It could be seen that the model fitted the experimental data reasonably. Therefore, the temperature dependence of the reaction rate constant could be represented by an Arrhenius equation. Activation energy, Ea, were calculated from the slope of curves and found to be approximately 8.80, 9.19, and 15.91 kcal/mol for the dissolution of asphaltene by 5wt% DBSA in dodecane media, 20 wt% NP in heptane, and in dodecane media respectively.

The relationship between the reaction rate constant and the concentration of amphiphile was then identified. Assume the reaction was single site reaction, i.e. one of amphiphile molecule adsorbed on one of asphaltene molecule, and the reaction was
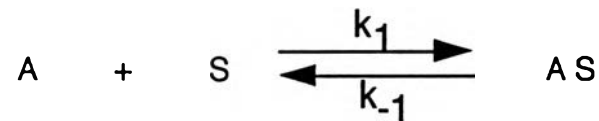
$$A \quad + \quad S \quad \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \quad A S$$

Where   A   represents   asphaltene molecules

S   represents   amphiphile molecules

A S   represents   dissolved asphaltene.

Rate of adsorption   = $k_1 [A] [S]$

Rate of desorption   = $k_{-1} [AS]$

At equilibrium,

Rate of adsorption =   Rate of desorption

$k_1 [A] [S]$ = $k_{-1} [AS]$ (5.2)

let k_1 / k_{-1} = K_1 = adsorption equilibrium constant.

$[A] [S]$ = $[AS] / K_1$

Since $[A]_{total}$ = $[A] + [A S]$

Substitute [A] into eq (5.2)

$$[A S] \quad = \quad \frac{K_1 [S] [A]_{total}}{1 + K_1 [S]} \qquad (5.3)$$

Equation (5.3) gives concentration of dissolved asphaltene, [AS] as a function of amphiphile concentration,[S]. This particular form of equation is called Langmuir form.

Since reaction rate constant calculated by integral method, k, was proportional to [AS, it was used to represent [AS].

Figure 5.14 and 5.15 showed the plot of k versus concentration of DBSA and NP amphiphiles in both heptane and dodecane media respectively. It was found that when the experimental data was fitted by the equation 5.3, the shape of fitted curves were similar to that of Langmuir form. Therefore, the Langmuir equation could be used to describe the relationship between the concentration of amphiphile and the reaction rate constant.

To reconfirm that the equation in Langmuir form could predict the behavior of the experimental data, equation 5.3 was rearranged in the form

$$\frac{1}{[A\,S]} = \frac{1}{K_1\,[S]\,[A]_{total}} + \frac{1}{[A]_{total}} \qquad (5.4)$$

Figure 5.16 and 5.17. showed the plot of 1/k versus (1/ concentration of amphiphile). The obtained straight line with reasonable linear regression supported that the relationship between the specific rate constant and the concentration of amphiphile could be expressed by the equation in Langmuir form.

To describe the effect of those variables from the kinetics point of view, diffusion process was discussed as below.

According to the fundamental of diffusion, the rate of diffusion depends on the concentration gradient and mass transfer coefficient which is defined as

$$kd = 0.6 \left[\frac{(D_{AB})^{3/2}}{\gamma^{1/6}} \right] \left[\frac{U^{1/2}}{dp^{1/2}} \right]$$ (5.5)

(Term1)   (Term2)

when D_{AB} =   diffusivity of solution

γ =   kinematic viscosity, m^2/s

d_p =   diameter of pellet, m

U   =   free-stream velocity

Term 1 is a function of temperature and pressure only while as term 2 is a function of flow conditions and particle size. Therefore the effect of all variables on the dissolution rate could be described as followed.

Effect of Alkane Solvent

The fact that the rate of asphaltene dissolution in light alkane was faster than that in the heavy ones could be attributed to the different fluidity of these five alkane solvents. The viscosity of light alkanes such as hexane and heptane were significantly lower than that of heavy alkanes such as dodecane and hexadecane. As a result, the mass transfer coefficient, i.e , the rate of diffusion, of light alkanes were much higher than that of heavy alkanes. Therefore, light alkanes could penetrate into the porous asphaltene deposits to mobilize the deposits more quickly and easily than heavy

alkanes. Overall, the results of this study indicated that the type of alkane solvents had a significant effect on the rate of asphaltene dissolution.

Effect of Flow Rate of Micellar Fluid

Because the mass transfer coefficient is a function of the flow condition as shown in equation 5.4 , thus increasing flowrate resulted in the higher mass transfer coefficient and thus the overall rate of reaction . Since the results indicated that the flow rate of micellar fluids in this flow rate range (0.1-1ml/minute) did not significantly affect the rate of asphaltene dissolution, it could be concluded that the rate of dissolution of deposited asphaltene was weakly dependent on the external fluid flows. On the other hand, the internal diffusion of micellar fluids in the porous asphaltene deposit could play an important role in the dissolution process.

Effect of Temperature

The cause of higher rate of asphaltene dissolution at higher temperature could be due to the enhancement of mass transfer coefficient. At higher temperature, the diffusivity of micellar fluid increased and the viscosity of solution decreased, leading to the faster rate of movement of fluid into the deposit and the faster rate of dissolved asphaltenes diffusing into the bulk phase. The temperature dependence of the rate of asphaltene dissolution in this study fitted reasonably to an Arrhenius equation. The activation energy, E_a, of asphaltene dissolution by different micellar fluids were calculated to be approximately 8.80, 9.19, and 15.91 kcal/mol for the

dissolution of asphaltene by 5wt% DBSA in dodecane media, 20 wt% NP in heptane, and in dodecane media respectively.

Effect of Amphiphile Concentration

It was clearly shown that the increase in the concentration of amphiphiles resulted in the higher concentration gradient and thus the mass transfer coefficient. However, when the concentration of amphiphiles was very high, the increase in the rate of dissolution increased more slowly and finally became constant. This fact was corresponded to the behavior predicted by the equation 5.3, relating the rate of dissolution and the concentration of the amphiphile in Langmuir form.

5.2 Study of Stability of Different Asphaltene Fractions in Selected Amphiphile/Alkane Solutions

On the basis of the weight percentage of amphiphile, Figure 4.12 and 4.13 showed that the stability of different asphaltene fractions in micellar fluid was in the order Fraction 4 > Mobil asphaltene > Fraction 1. These results could be due to the fact that asphaltene aggregated into micelles which were kept peptized or dispersed by resins which formed a kind of adsorbed covering sheath and as the distance from the micelles center increased, there was a gradual transition to the less aromatic resins and to the oily dispersion medium. (Anderson and Birdi, 1991)

Therefore a minimum requirement for a solvent to dissolve an oil is an ability to penetrate the asphaltene micelle, or the solvent must have a high solvent power. Thus, if the solvent power of such solvent is not high enough to overcome the force of micelle, asphaltenes will start to precipitate.

Hildebrand related the solvent power of non-polar solvents, expressed as a solubility parameter. This solubility parameter was used as a measurement of the energy of the solution to overcome the association forces of micelle.

The solubility parameter of methylene dichloride is 7.1 dyn $mol^{1/3}$ cm^{-2} (9.8 $cal^{1/2}$ $mol^{1/2}$ $cm^{-3/2}$) and the solubility of pentane is 3.2 dyn $mol^{1/3}$ cm^{-2} (7.0 $cal^{1/2}$ $mol^{1/2}$ $cm^{-3/2}$). It is clearly seen that the solvent power of CH_2Cl_2 is very high compared with the one of pentane and falls within the area of the solvent power of the aromatics which is considered as the good solvent to dissolve asphaltene. Therefore, the solvent power of the mixture of CH_2Cl_2 and n-pentane is decreased when the proportion of CH_2Cl_2 is decreased from 25 vol% to 18 and to 10 vol%.

According to the fact mentioned above, Fraction 1 was considered being the most polar fraction as it was precipitated by the solvent with the highest solvent power Therefore, it required higher concentration of amphiphile to stabilize. On the other hand, Fraction 4 or the residual asphaltene was considered being the least polar one, so it could be stabilized by the solution with low concentration of amphiphile such as 0.5 wt% DBSA and 1 wt%NP.

The stability of Mobil asphaltene was in between Fraction 1 and Fraction 4. This result could cause by the wide distribution of polarity in asphaltene molecules. To completely stabilize Mobil asphaltene, the higher concentration of amphiphile was therefore needed to dissolve the more polar molecules which was surrounded by the less polar ones.

In addition, as mentioned earlier that fraction 1 appeared as dark solid, so its particle size was much bigger compared to that of Mobil asphaltene and Fraction 4, therefore, it required higher concentration of amphiphile in the solution to overcome the associative force between particles. .
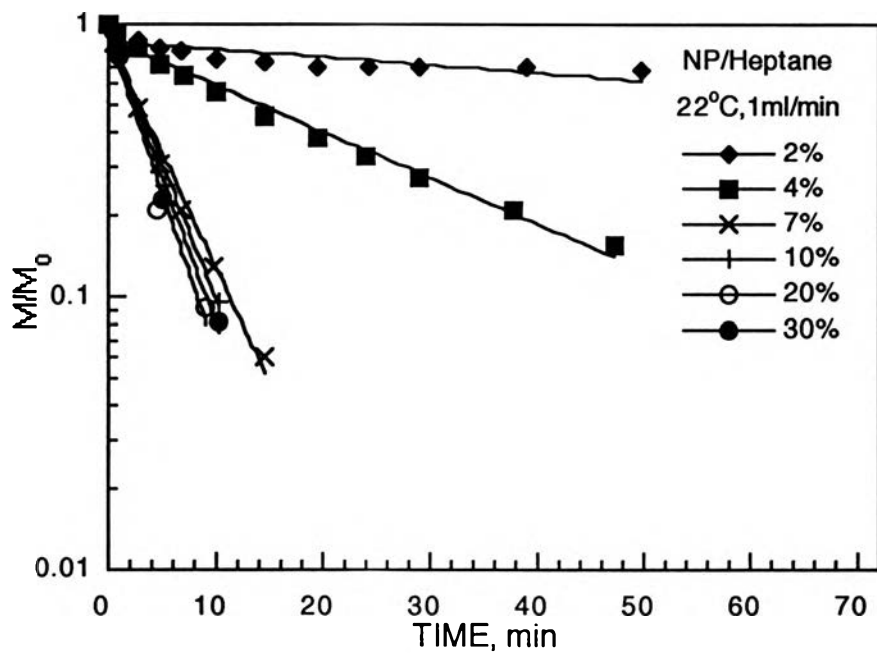
Figure 5.1 Analysis plot of Figure 4.1 according to equation (5.1).
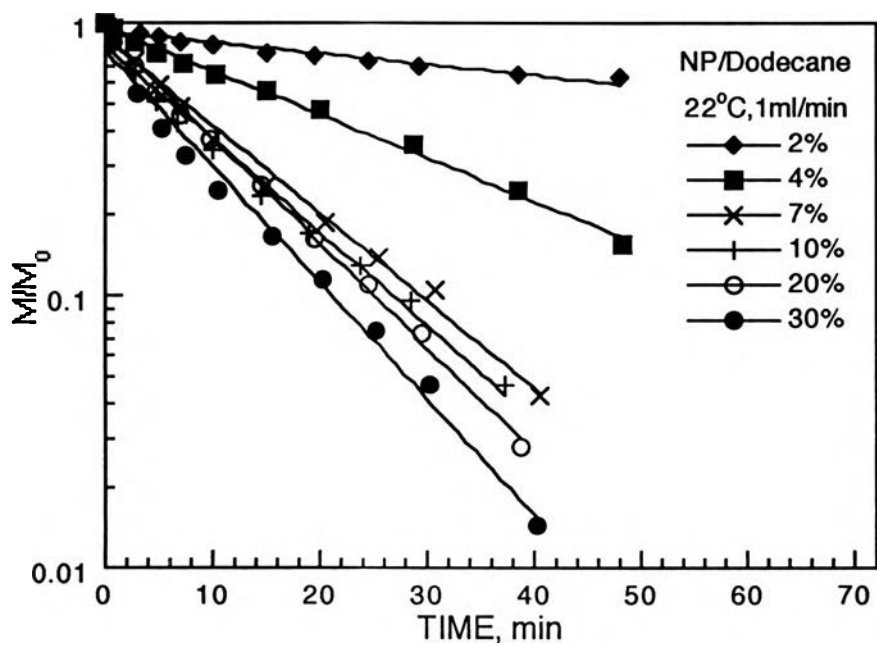
Figure 5.2 Analysis plot of Figure 4.2 according to equation (5.1).
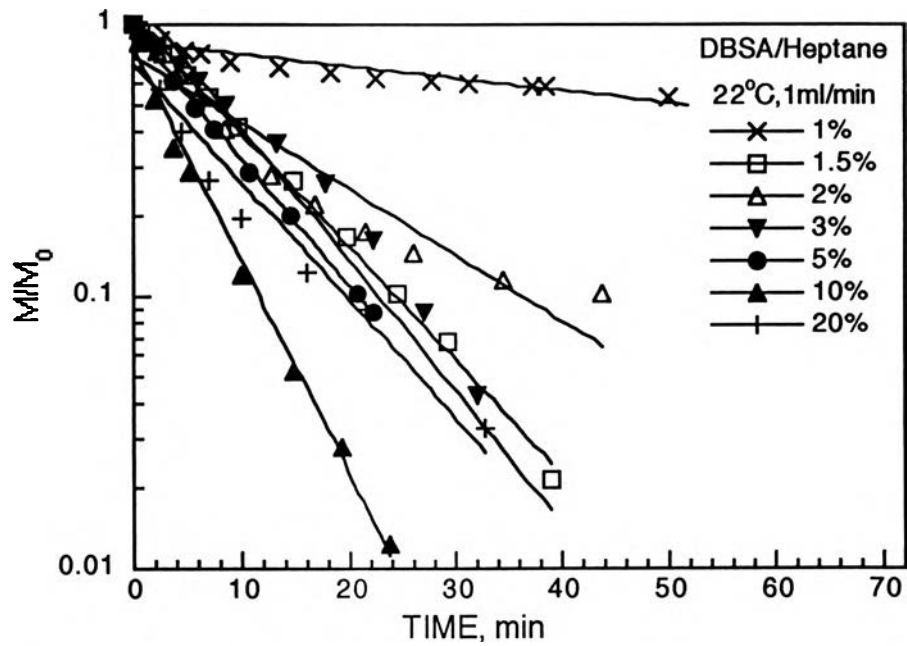
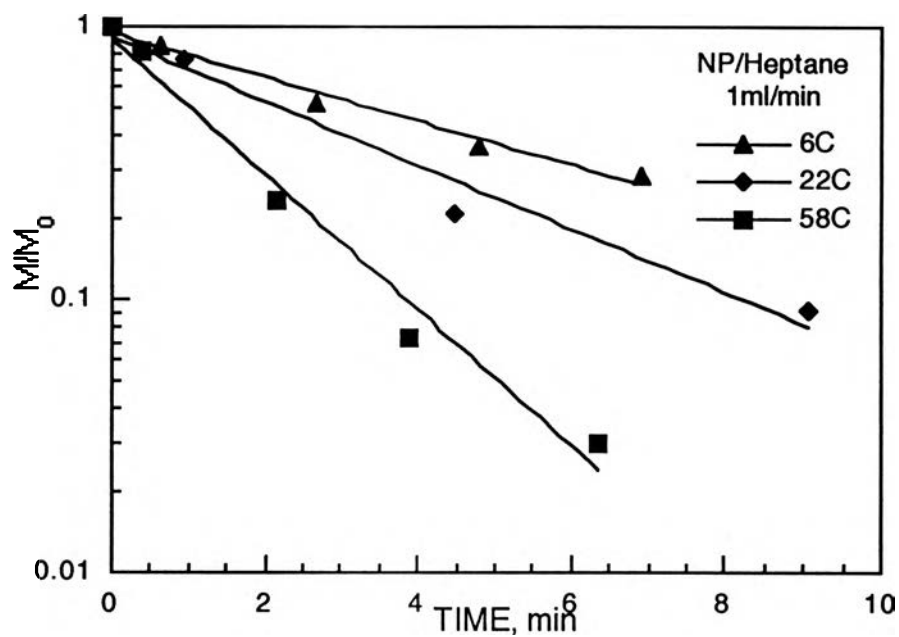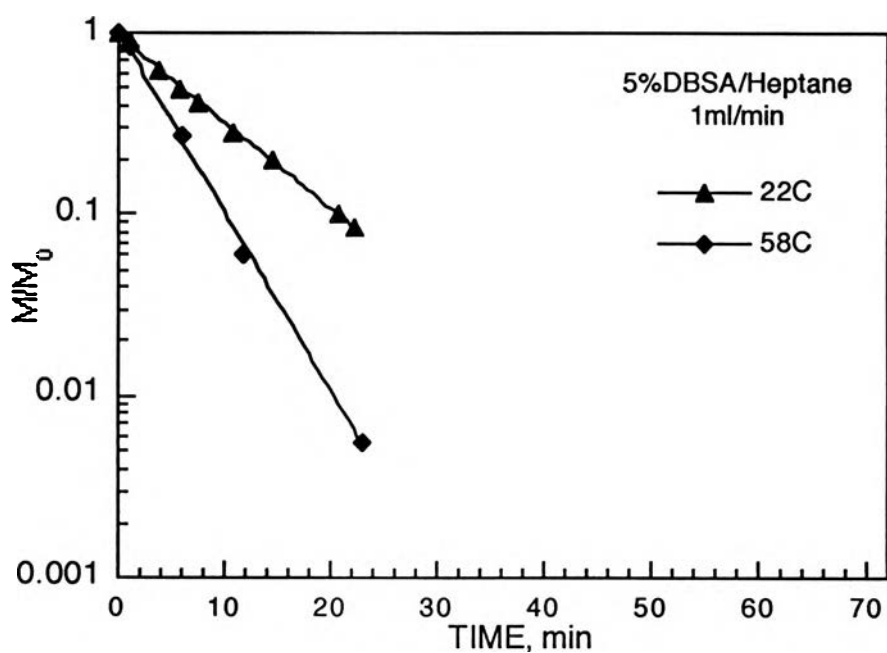Figure 5.3 Analysis plot of Figure 4.3 according to equation (5.1).
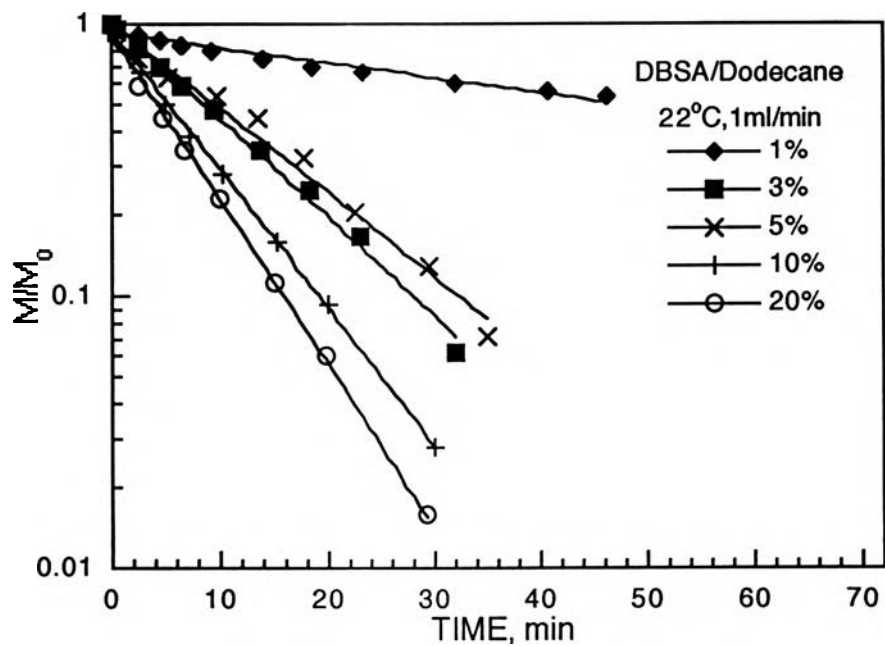

Figure 5.4 Analysis plot of Figure 4.4 according to equation (5.1).
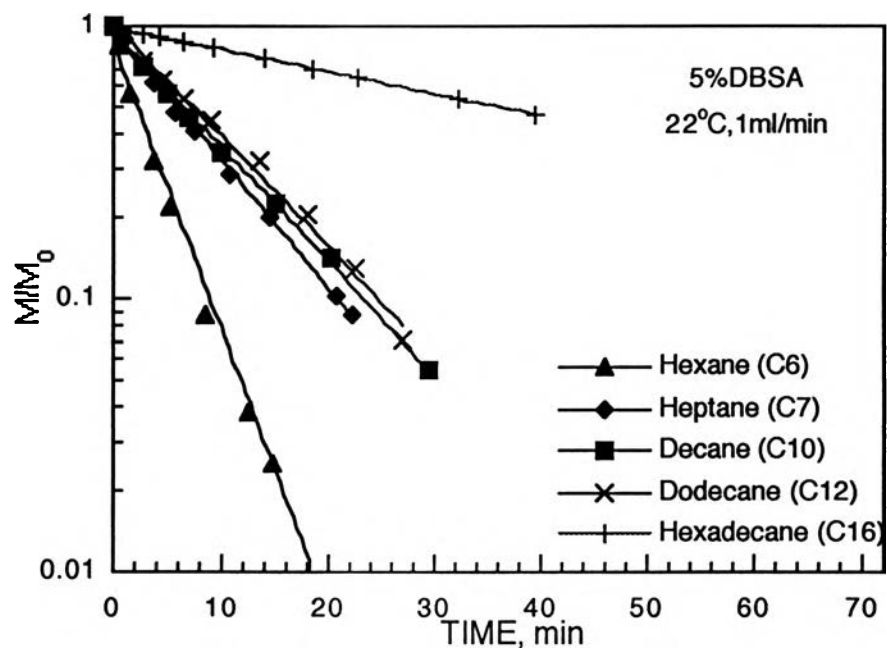
Figure 5.5 Analysis plot of Figure 4.5 according to equation (5.1).
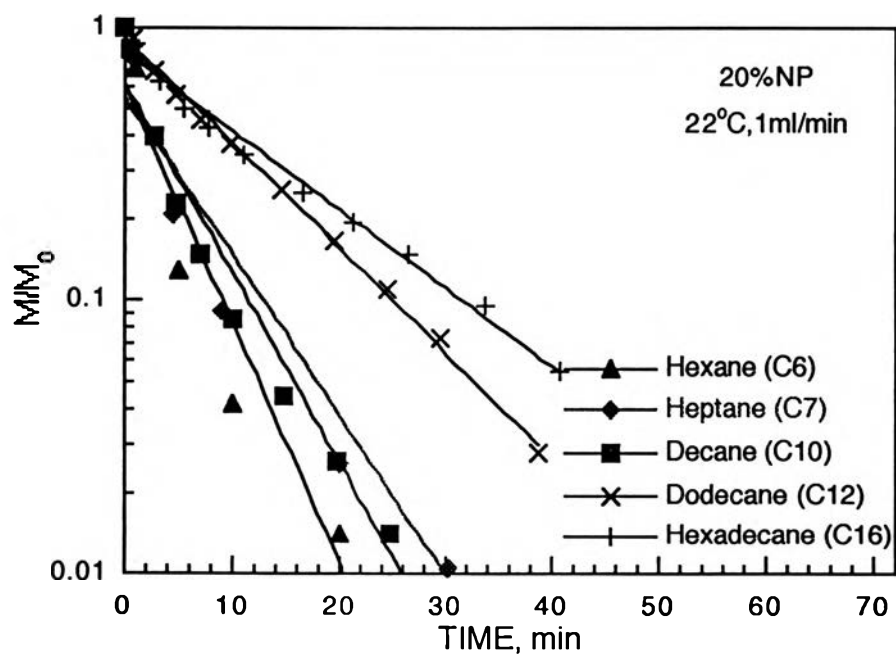
Figure 5.6 Analysis plot of Figure 4.6 according to equation (5.1).
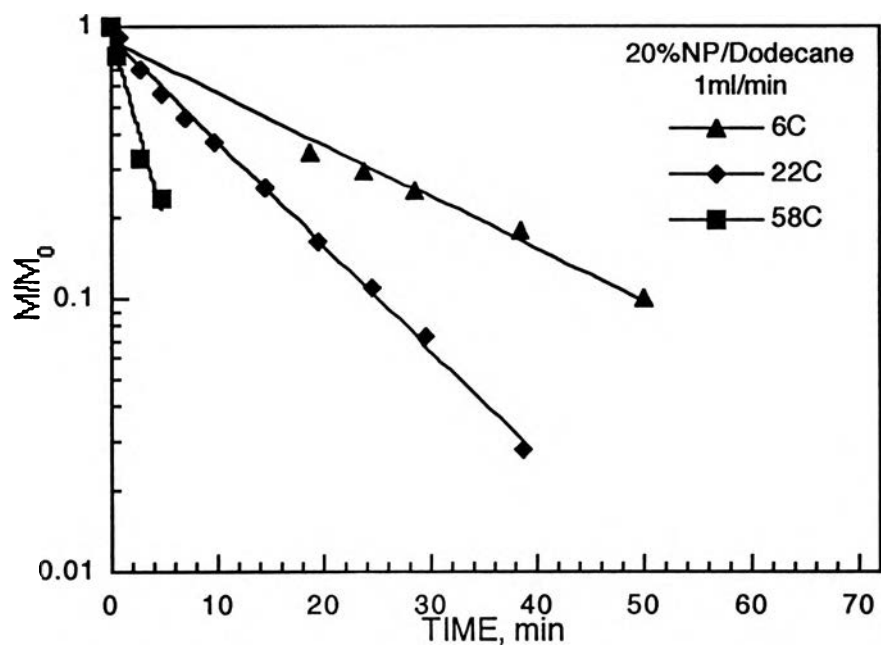
Figure 5.7 Analysis plot of Figure 4.7 according to equation (5.1).
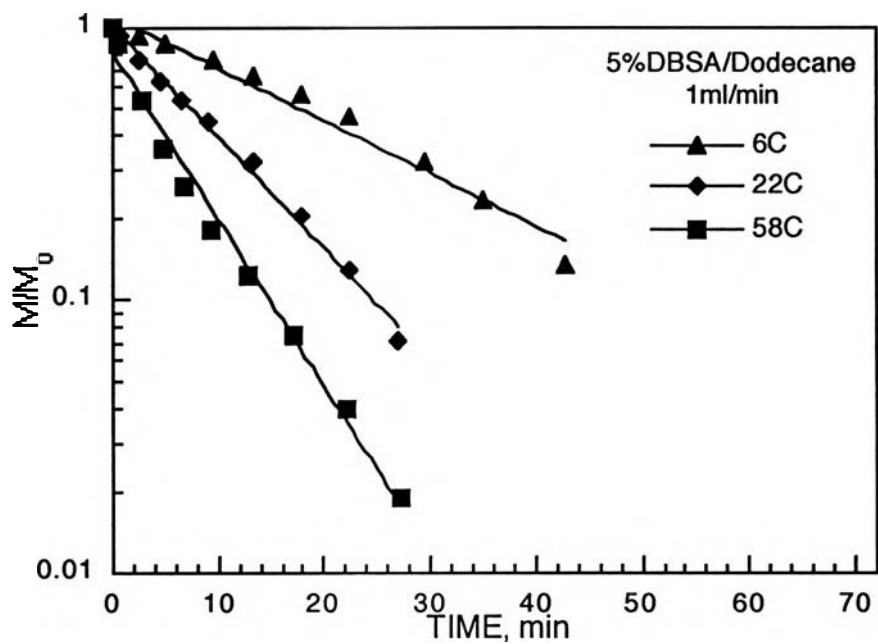
Figure 5.8 Analysis plot of Figure 4.8 according to equation (5.1).

Figure 5.9 Analysis plot of Figure 4.9 according to equation (5.1).

Figure 5.10 Analysis plot of Figure 4.10 according to equation (5.1).
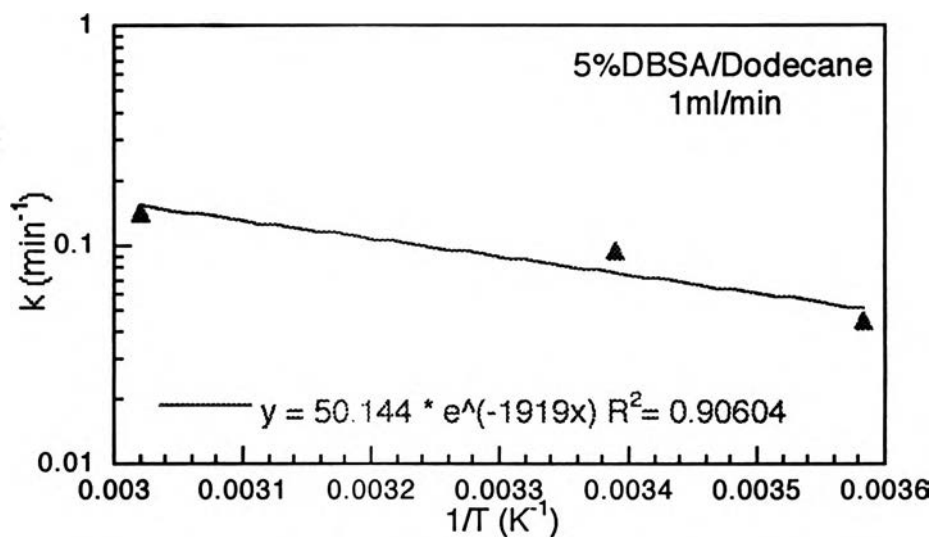
Figure 5.11 Arrhenius plot for asphaltene dissolution by dodecane-based
fluids containing DBSA amphiphile.
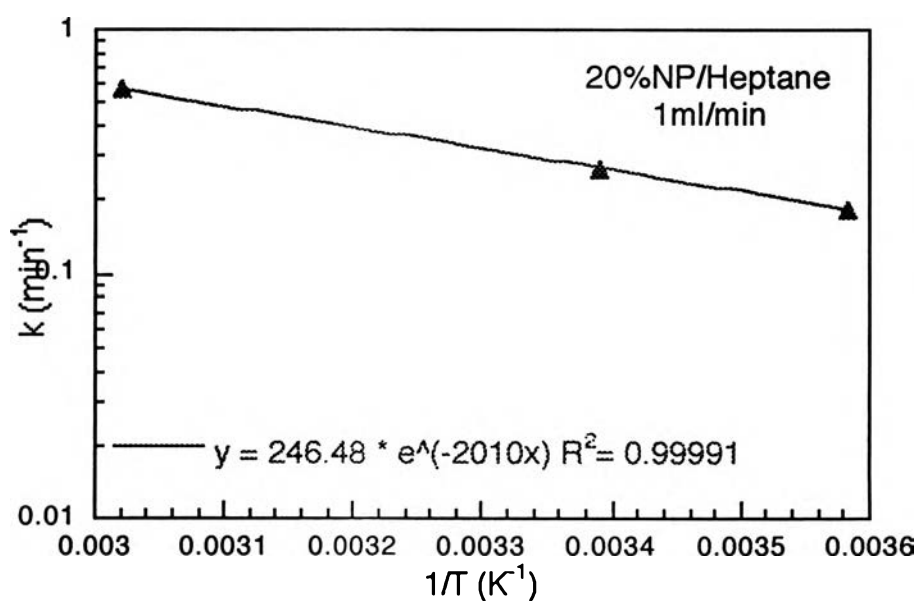
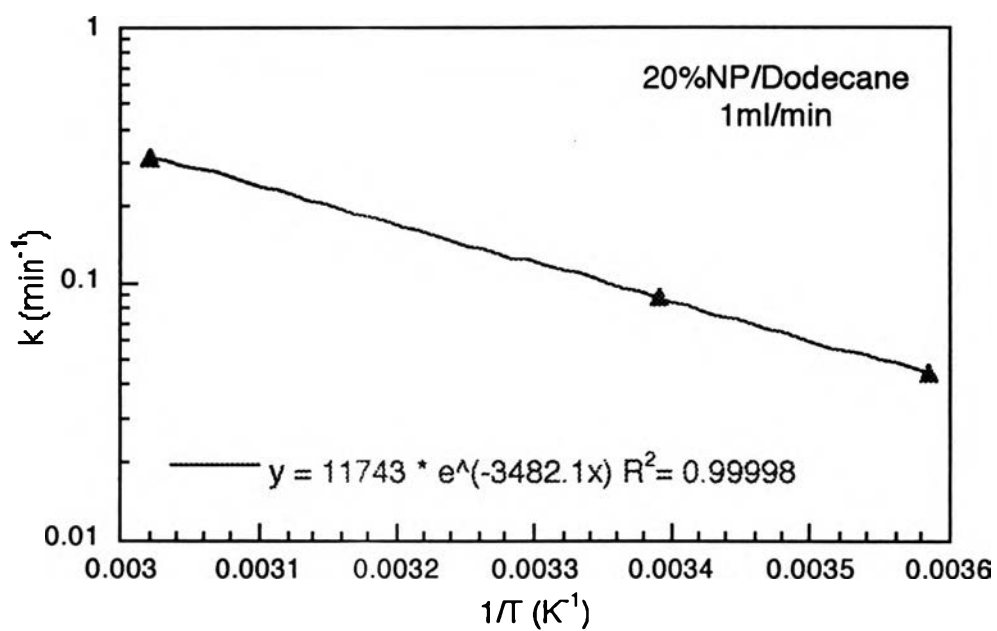Figure 5.12 Arrhenius plot for asphaltene dissolution by heptane-based
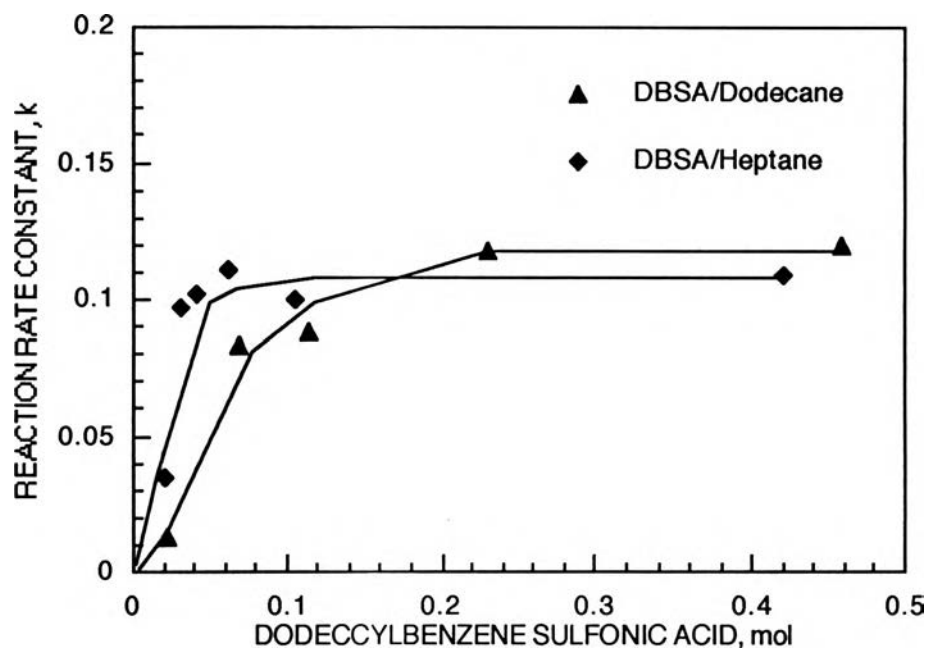fluids containing NP amphiphile.

Figure 5.13 Arrhenius plot for asphaltene dissolution by dodecane-based
fluids containing NP amphiphile.

Figure 5.14 Reaction rate constant for asphaltene dissolution as function
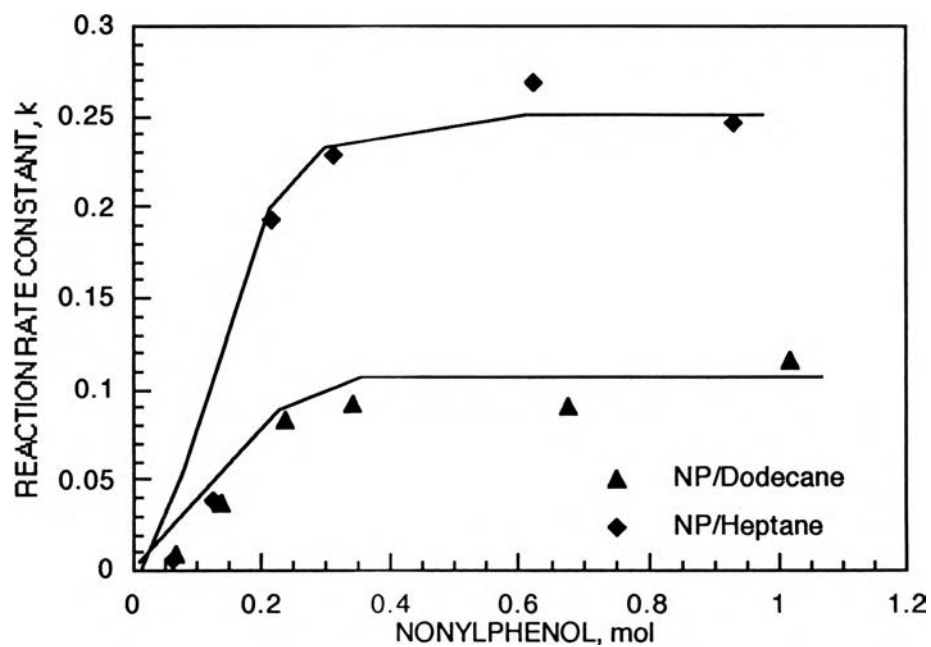of DBSA concentration.

Figure 5.15 Reaction rate constant for asphaltene dissolution as function
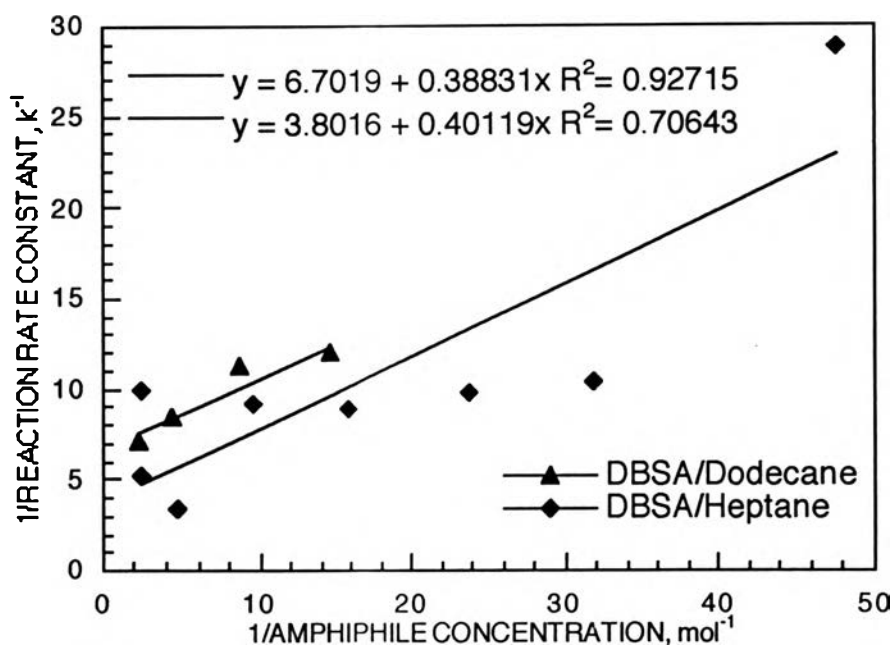of NP concentration.

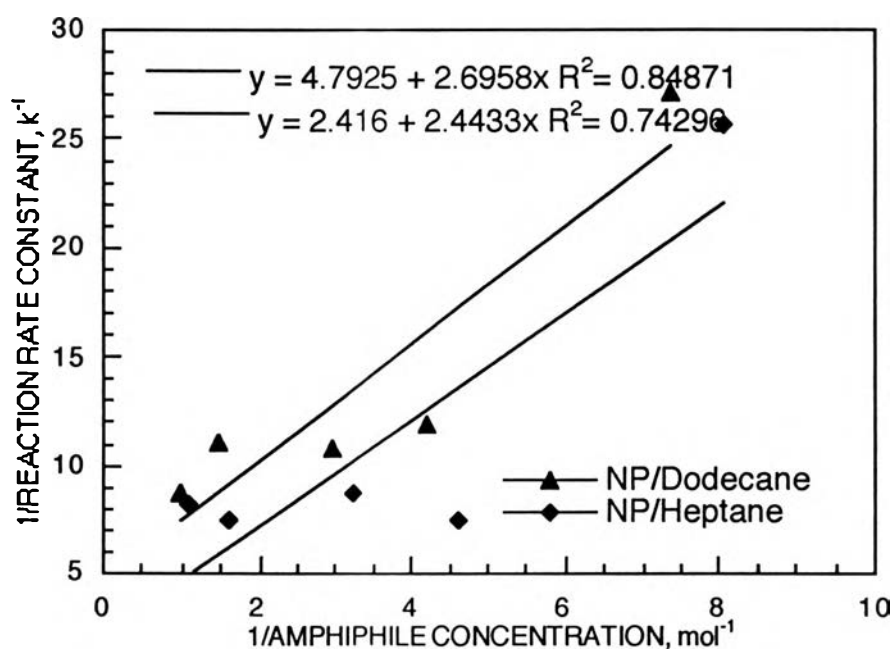Figure 5.16 Replotted curve of figure 5.14 according to equation (5.4).

Figure 5.17 Replotted curve of figure 5.15 according to equation (5.4).