

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Correlation between Cloud Point and Wax Concentration

In order to prepare the model systems of wax and oil used in the cold finger experiments a cross-polarized light microscope coupled with temperature-control device was used to determine the cloud point temperature of various wax-oil mixtures. Figure 4.1 shows the values of cloud point of Wax No. 1 and Wax No. 2 in dodecane at various concentrations, respectively. For both wax samples, an increase in wax concentration resulted in increasing cloud point.

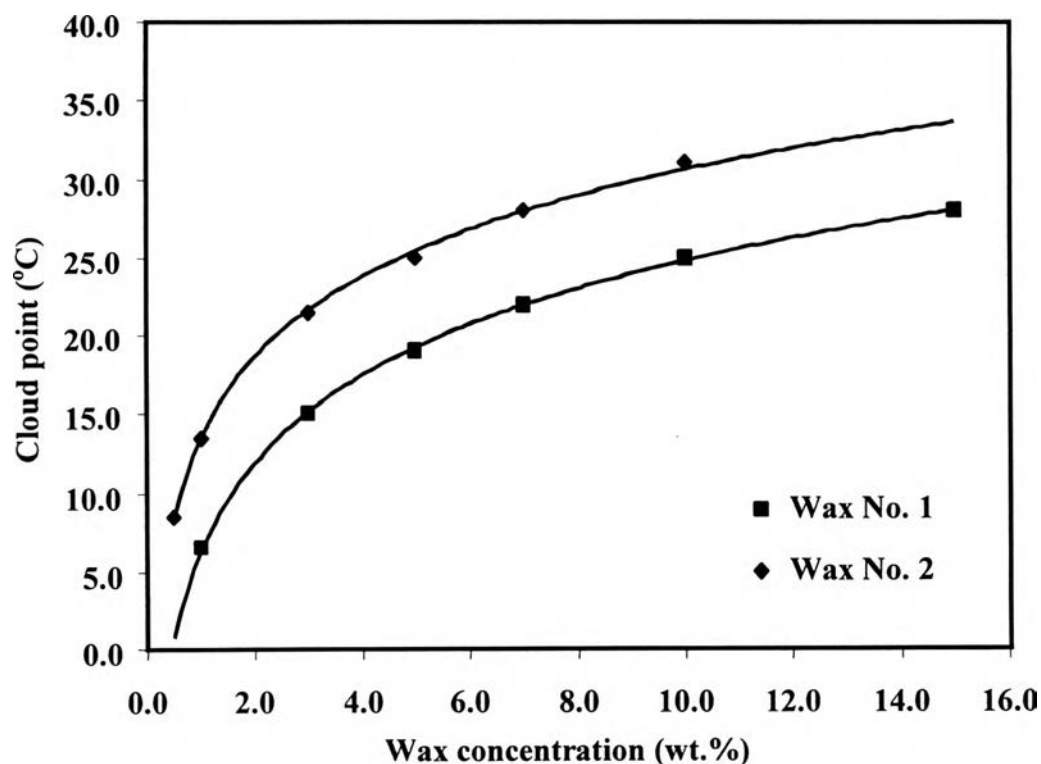


Figure 4.1 Cloud points of waxes in dodecane at various wax concentrations

The results also indicated that the solubility of both waxes in dodecane solvent was a strong function of temperature. For any given wax concentration, Wax No. 2 had higher cloud point temperature than Wax No. 1. This is due to the larger amount of higher molecular weight components in Wax No. 2 resulting in having higher melting point.

4.2 Critical Carbon Numbers of Studied Oil Systems

The cold finger experiments are used to simulate wax deposition on a cold surface under negligible shear force. Since, there is no mechanical compressive force on the wax-oil gel deposit layer, the aging of the deposit is expected to be caused only by the thermal gradient present across the gel layer.

The cold finger experiments were carried out for two model oils containing different types and concentrations of wax in order to keep the cloud point temperature of the mixtures to be 20°C. The wax-oil gel deposit was collected from the finger after each experiment and was analyzed using High Temperature Gas Chromatography (HTGC). The carbon number distributions of gel deposits collected from cold finger experiments on Model Oil No. 1 at the cold finger temperature of 5°C and at different times as well as that of the original oil sample are shown in Figure 4.2. It showed that the weight fractions of all components did not increase with deposition time. In fact, the weight fractions of low carbon numbers did not change with deposition time but the weight fractions of carbon number greater than a certain value known as the critical carbon number increased with deposition time. From Figure 4.2, the critical carbon number of Model Oil No. 1 is approximately C23.

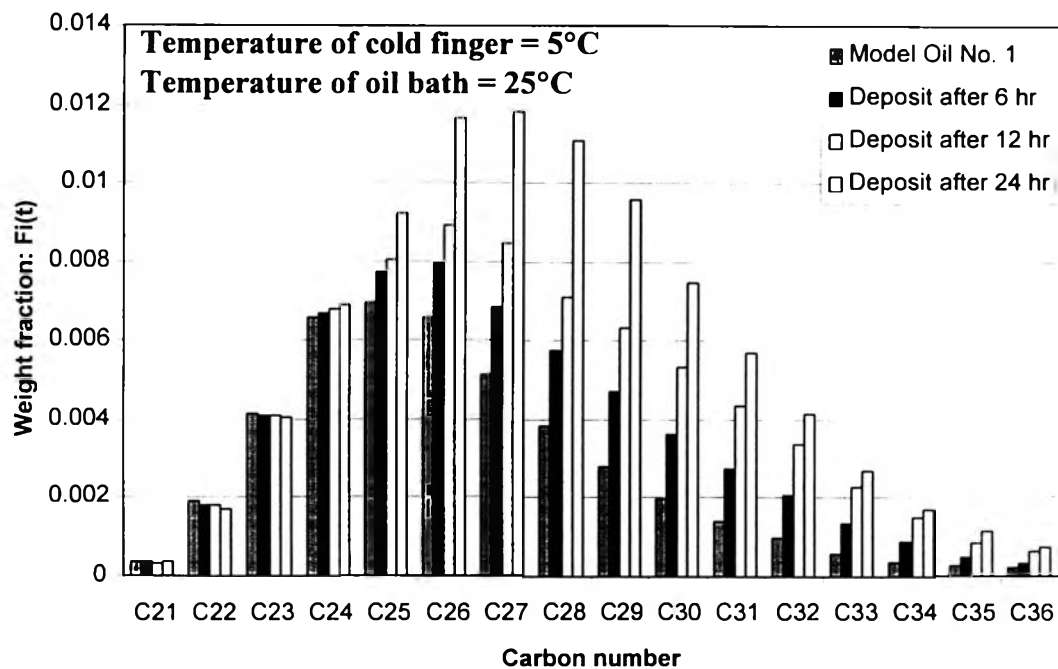


Figure 4.2 Carbon number distribution of gel deposits collected from cold finger experiments on Model Oil No. 1 at various deposition times

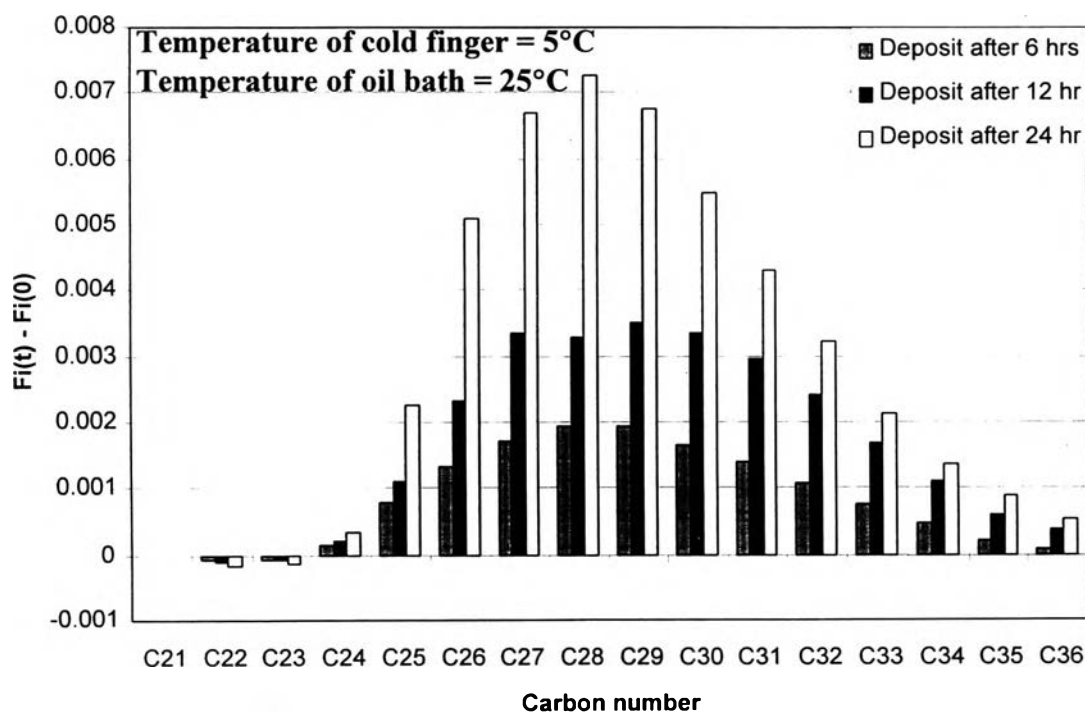


Figure 4.3 Changes in carbon number distribution of gel deposits collected from cold finger experiments on Model Oil No. 1 at various deposition times

In order to determine the value of the critical carbon number more precisely, the difference between the weight fraction of each carbon number at any deposition time and that at initial time is plotted as shown in Figure 4.3. Figure 4.3 obviously shows that the weight fractions of hydrocarbons having carbon number greater than C23 increase with increasing time and weight fractions of those having carbon number less than C23 decrease with deposition time. The critical carbon number of this system was C23. This finding implies that the hydrocarbons having carbon number greater than C23 diffuse into the gel deposit and those having carbon number less than C23 diffuse out of the gel deposit. These results indicate that the aging process of the gel deposit is a counter diffusion phenomenon.

For the cold finger temperatures of 10°C and 15°C, the critical carbon numbers of Model Oil No. 1 were C23 and C24. For Model Oil No. 2, the critical carbon numbers were C24, C24, and C25 for the cold finger temperatures of 5°C, 10°C and 15°C, respectively. All of the results are shown in Appendix B and Appendix C.

4.3 Effect of Temperature on Critical Carbon Number

The wall of cold finger was set at three temperatures of 5°C, 10°C, and 15°C for each experiment to investigate the temperature effect on the critical carbon number while the model oil was kept in the bath at the constant temperature of 25°C.

Figure 4.4 illustrates the effect of gel deposit temperature (T_{gel}) on the systems of both model oils. It was found that the critical carbon number increased with increasing temperature as a step function from C23 at 285.5 K to C24 at 290.5 K for Model Oil No. 1 and from C24 at 285.5 K to C25 at 290.5 K for Model Oil No. 2. As discussed earlier, the solubility of wax-oil mixture is a strong function of temperature. An increase in

temperature causes the larger wax molecules to be dissolved in the gel deposit resulting in the higher critical carbon number.

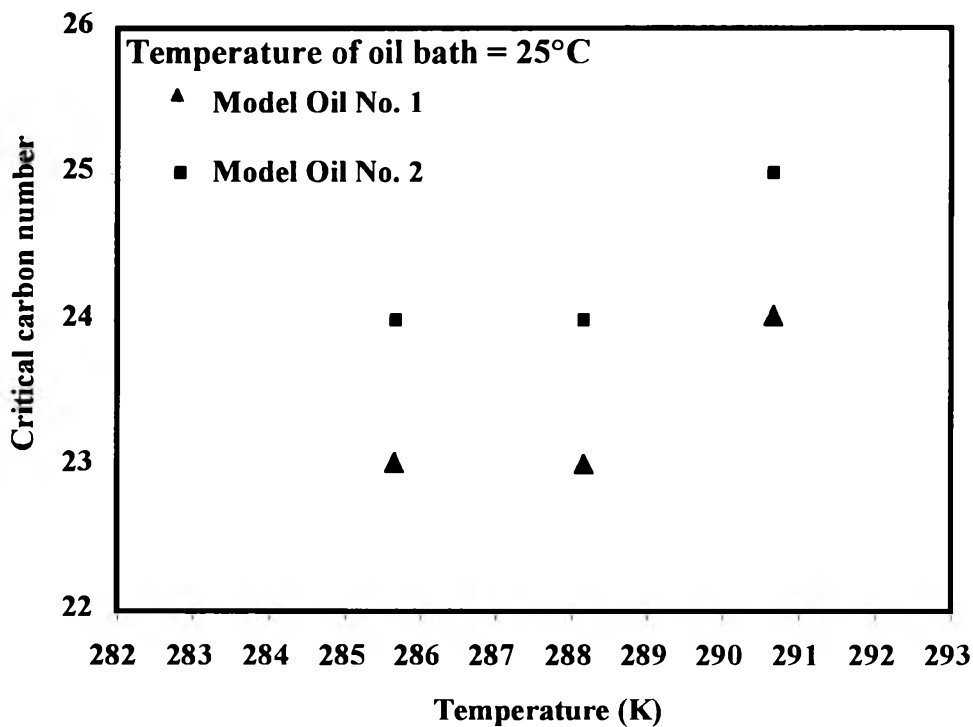


Figure 4.4 Critical carbon number of model oils as a function of gel deposit temperature

4.4 Verification of Proposed Thermodynamic Model

In solid (wax)-liquid (oil) equilibrium, the liquid phase molar fraction and solid phase molar fraction of all the components in the mixture can be predicted using the thermodynamic model. The gel deposit in the cold finger experiment is not in the equilibrium condition; however, because of the rapid precipitation of wax molecules in the gel deposit, it is assumed that the gel deposit is reasonable in thermodynamic equilibrium. Continuous diffusion of wax molecules into the gel deposit causes an increase in solid wax content of the gel deposit. With the following assumptions, the composition of gel

deposits can then be constructed using thermodynamic equilibrium data obtained from the developed model as shown in Table 4.1.

Assumptions:

1. Solid wax content of the gel deposit *increases* with increasing time.
2. Critical carbon number does *not* change with time.
3. All components in gel deposit increase/decrease *uniformly*.

The carbon number distributions of gel deposits constructed using the theoretical data were obtained for three different deposition times. The carbon number distribution of the original model oil was subtracted with those of deposits as discussed in section 4.2. The changes in carbon number distributions were observed and the critical carbon number was determined.

Table 4.1 Construction of gel deposits using theoretical data

Deposition Time	Solid Wax Content	Gel Deposit Composition
t_1	w_1	$w_1*s + (1-w_1)*x$
t_2	w_2	$w_2*s + (1-w_2)*x$
t_3	w_3	$w_3*s + (1-w_3)*x$

where s and x are fraction of solid phase and liquid phase, respectively.

Since the thermodynamic model is used for prediction of the equilibrium data. The developed model in this work has to be verified with the equilibrium data in the literature. The literature data of solid phase compositions at six different system temperatures taken from Dauphin *et al.* (1999) were used to verify the thermodynamic model developed in this study.

Figure 4.5 shows the relationship between carbon number and weight fraction of solid phase from the experimental and theoretical data at 283.25 K. The results show that the experimental data match very well with the theoretical values especially in the high hydrocarbon range.

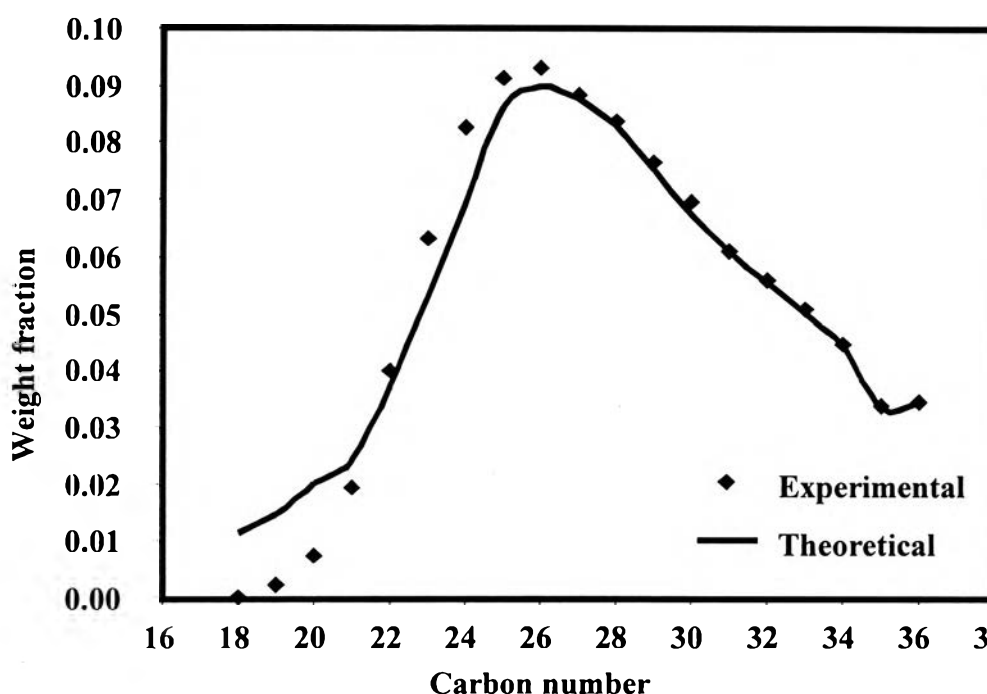


Figure 4.5 Comparison of experimental and theoretical solid phase composition at 283.25 K (data from Dauphin *et al.*, 1999)

Figure 4.6 shows the relationship between system temperature and the critical carbon number from the experimental and the theoretical data. The results showed that there was an excellent agreement between the experimental and theoretical data. The results confirm that the developed model in this study can be used reasonably to predict the critical carbon number of the model oils in the cold finger experiment.

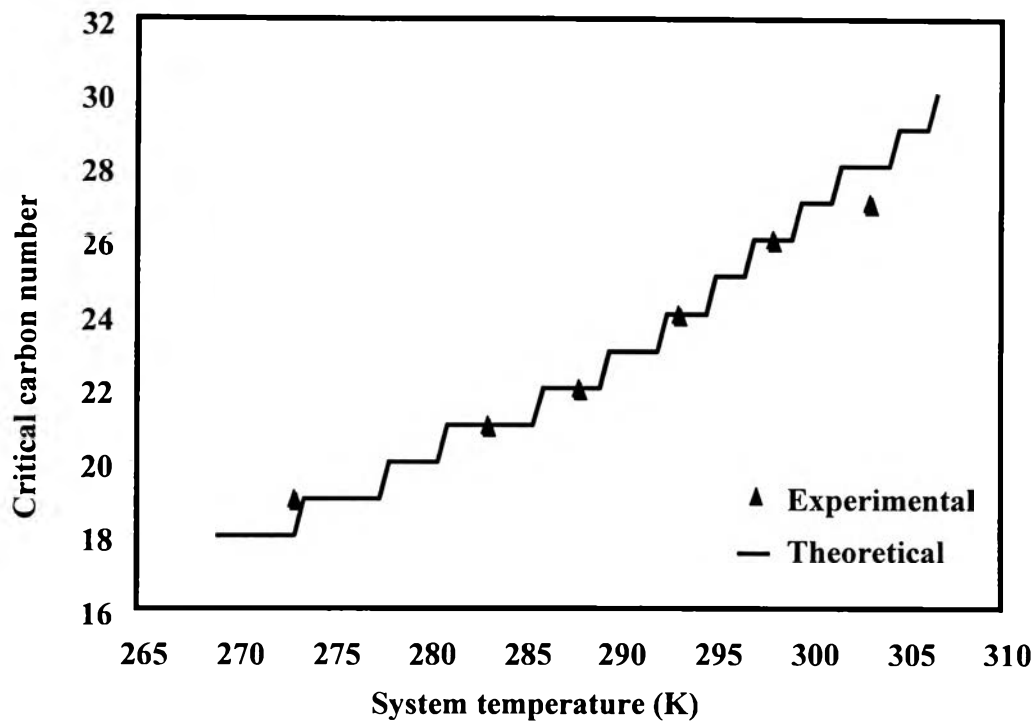


Figure 4.6 Comparison of experimental and predicted critical carbon number as a function of temperature (data from Dauphin *et al.*, 1999)

Figure 4.7 shows the comparison of the experimental and theoretical cloud points of mixture of Wax No. 1 in dodecane (model oil No. 1). It has been shown that the thermodynamic model proposed a significant deviation of the theoretical value from the experimental value is observed clearly at a high wax concentration.

Figure 4.9 shows the comparison of experimental and theoretical cloud points of mixture of Wax No. 2 in dodecane (model oil No. 2). It could be seen that the theoretical data were fitted well with the experimental data for whole range of wax concentration.

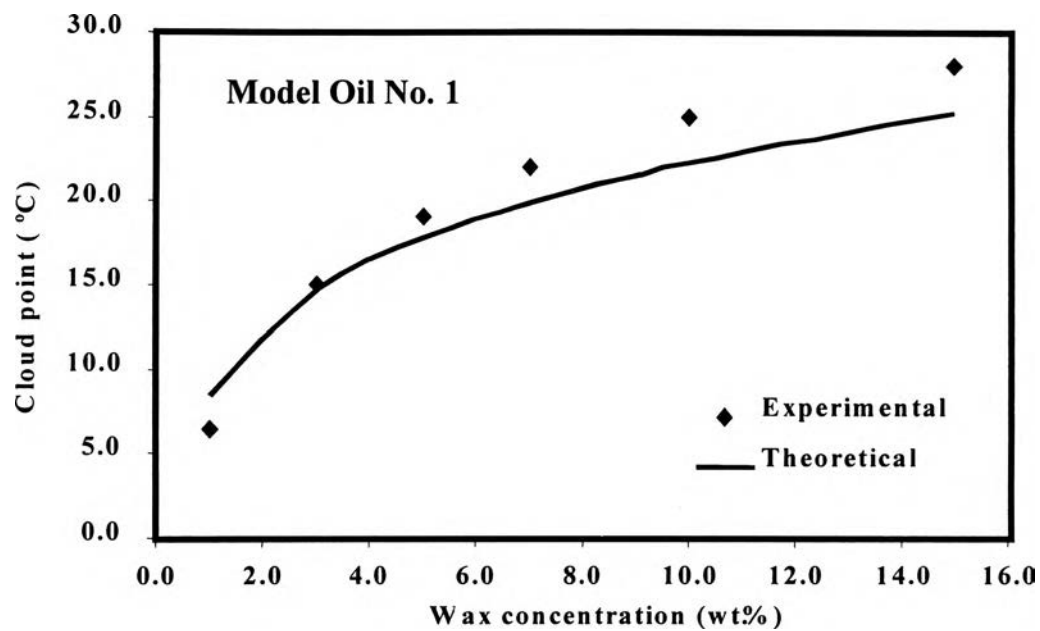


Figure 4.7 Comparison of experimental and theoretical value of cloud points of mixture of Wax No. 1 in dodecane

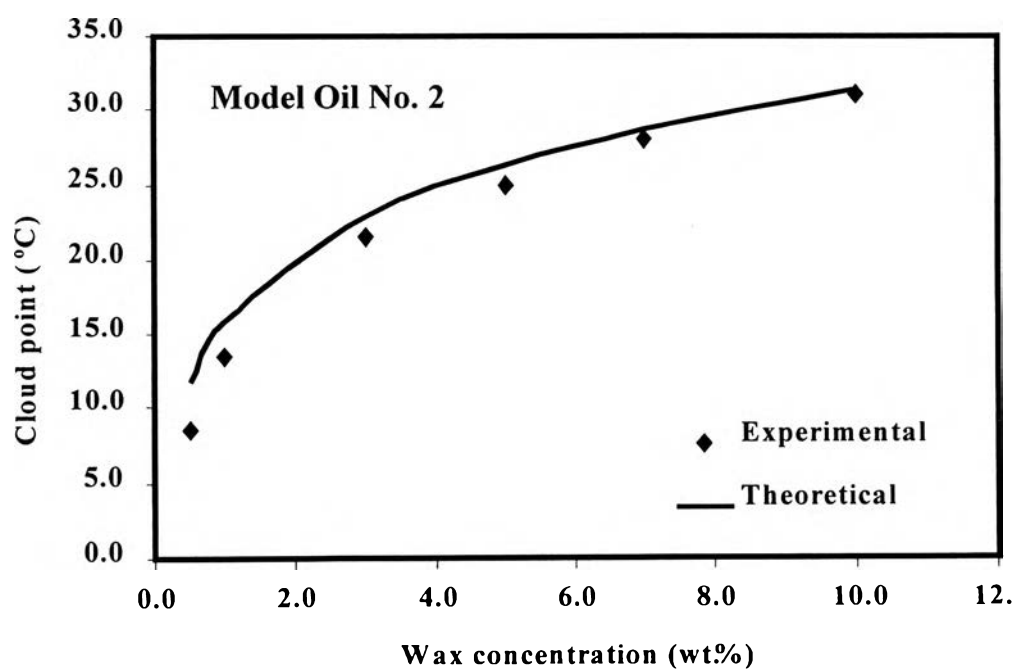


Figure 4.8 Comparison of experimental and theoretical cloud point of mixture of Wax No. 2 in dodecane

Figures 4.9 and 4.10 show the comparison of experimental and theoretical critical carbon numbers of Model Oils No. 1 and No. 2, respectively. It could be seen that the theoretical data were in good agreement with the experimental data for both model oils except at the lowest gel temperature of (278 K).

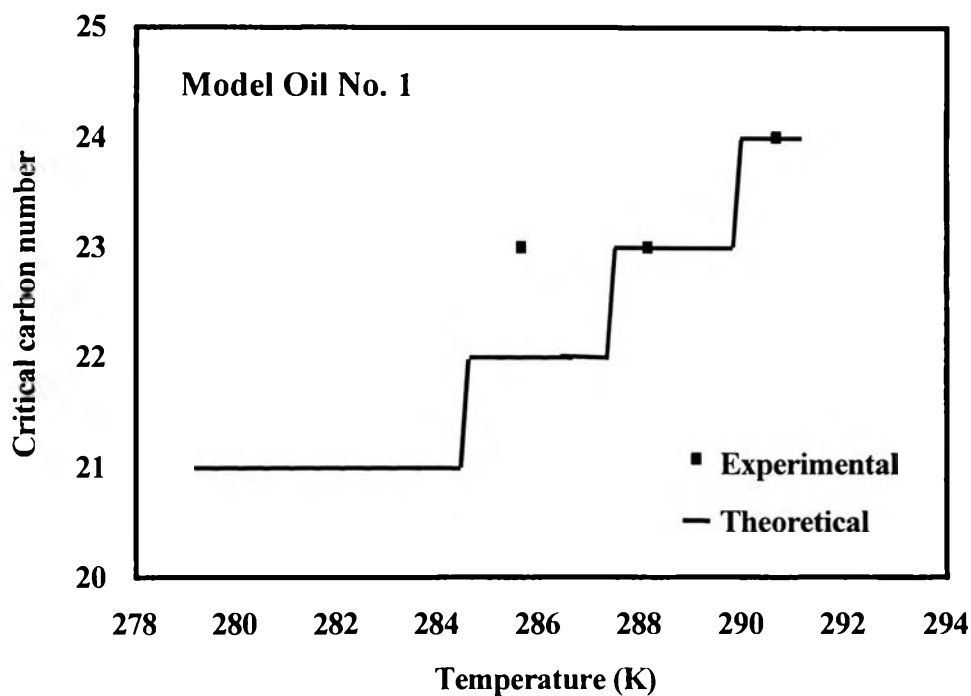


Figure 4.9 Comparison of experimental and predicted critical carbon numbers of Model Oil No. 1 as a function of temperature

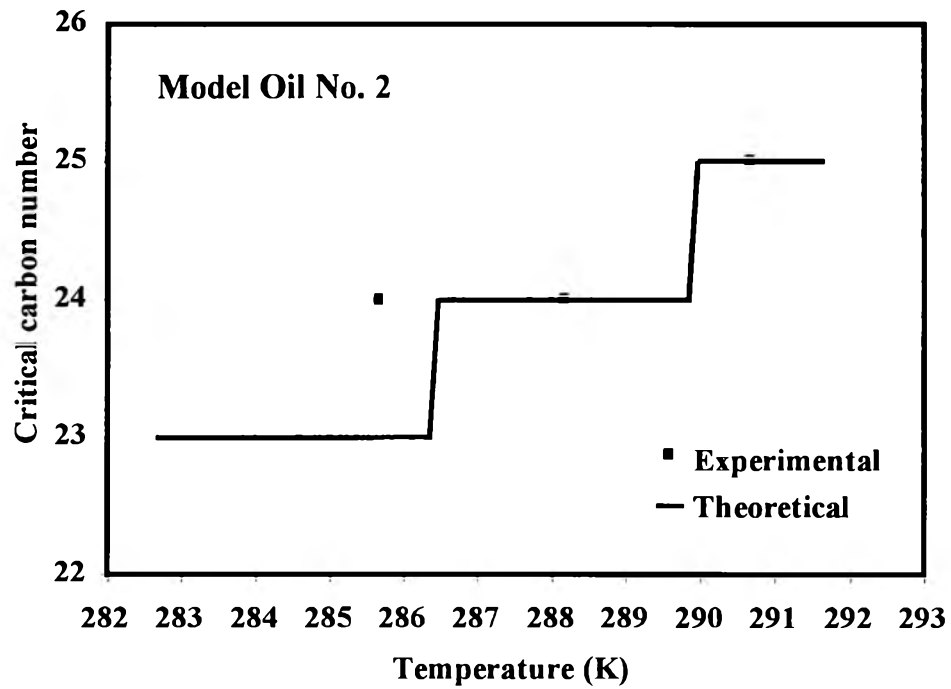


Figure 4.10 Comparison of experimental and predicted critical carbon numbers of Model Oil No. 2 as a function of temperature