

CHAPTER V

RESULTS AND DISCUSSION



5.1 Measured Cloud Point Temperatures

The cloud point temperatures of octacosane (n -C28) in different solvents were measured at the n -C28 mol fraction equal to 0.025. Figure 5.1 shows the measured values of cloud point temperature of octacosane in three different types of solvents.

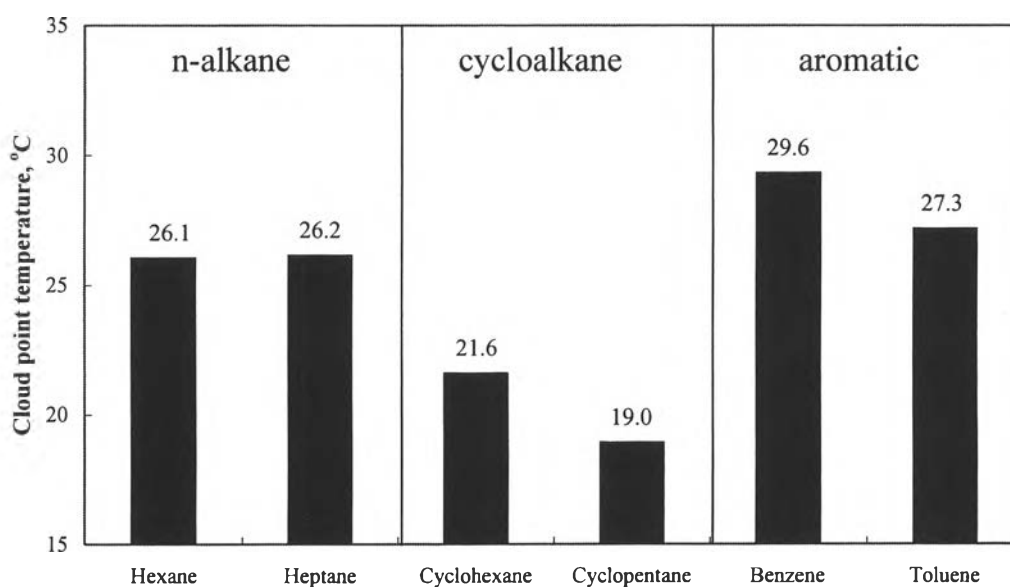
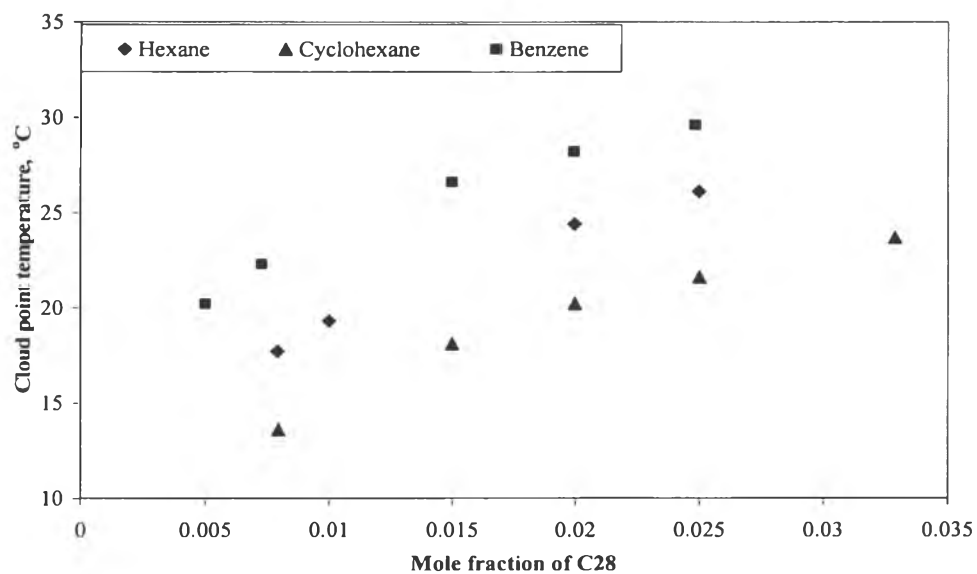


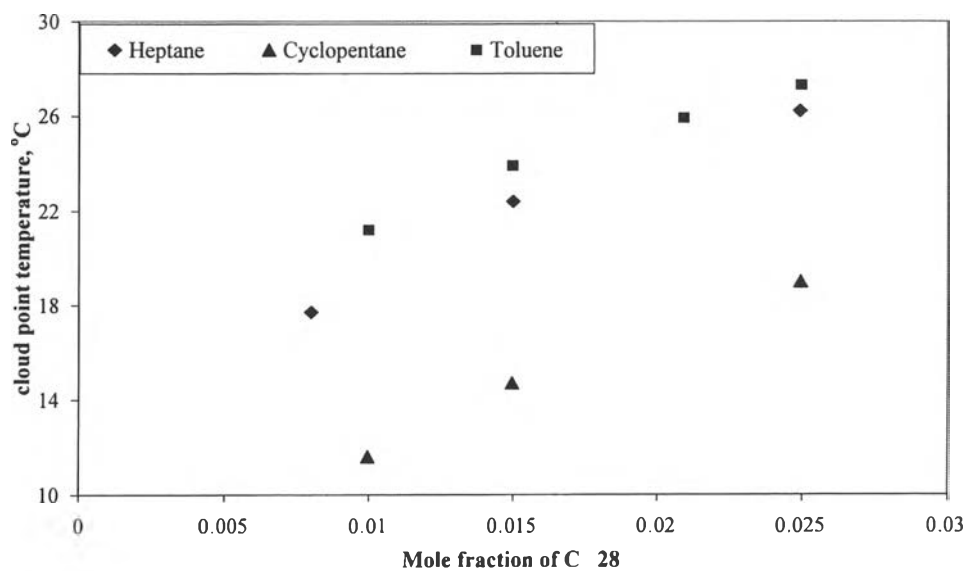
Figure 5.1 Cloud point temperatures of octacosane in various solvents at $x_{n-C28}=0.025$.

The results indicate that cloud point temperatures of octacosane in solvent are highly dependent upon solvent type. It was found that cloud point temperatures of n -C28 in n -alkane solvents are higher than those in cycloalkane solvents but lower than those in aromatic solvents. Figure 5.2 shows the measured cloud point temperature of food grade wax (FGW) in various solvents which have the same trends as those of

octacosane. Figure 5.2 also shows that cloud point temperature increases with increasing mole fraction of food grade wax.



(a)



(b)

Figure 5.2 Cloud point of food grade wax (FGW) in various solvents and concentrations; a) in hexane, cyclohexane and benzene b) in heptane, cyclopentane and toluene.

The effect of different solvents on cloud point temperature can be explained by considering differences in shape and chemical bond or the intermolecular between solvent and wax. It was found experimentally that the differences in solvent size do not play an important role as evidenced by the cloud point temperatures in hexane and heptane solvents as shown in the Figure 5.1. In contrast the difference in shape between *n*-alkane and cycloalkane may provide insight why cyclohexane gives lower cloud point temperatures than hexane. Because cycloalkanes consist of CH₂ groups similar to *n*-alkane, the differences in the intermolecular interactions among solute-solute, solvent-solvent and solute-solvent molecules are considerably small. However, Tancrede and coworker (1977) used a light scattering technique to demonstrate that globular in shape solvent such as cyclohexane destroys the orientational order among *n*-C16 solute molecules more than hexane. The orientational order present in liquid *n*-alkane molecules, as illustrated in Figure 5.3, results from the anisotropy of a polarizability of the *n*-alkane molecule (Bothorel, 1968). The destruction of orientational order leads to a higher entropy of mixing, lower free energy, higher solubility and, lower cloud point temperature. Hence, cloud point temperature of *n*-alkane in cyclohexane is lower than in hexane. According to the cloud point temperature results, one can conclude that cyclopentane destroys the orientational order in liquid *n*-alkanes more than cyclohexane.

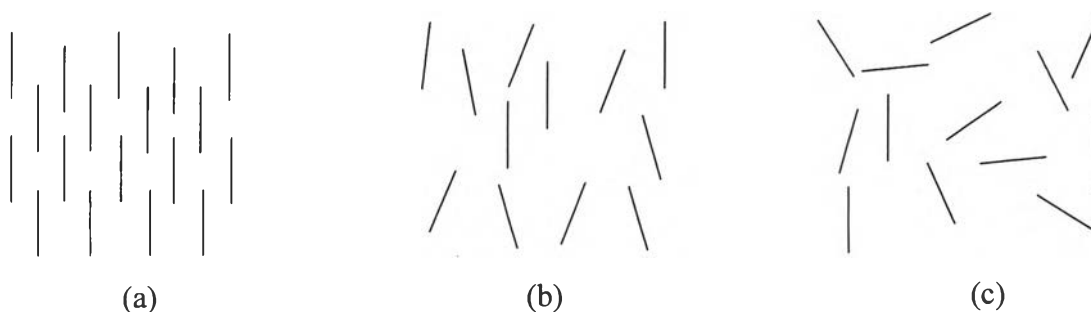


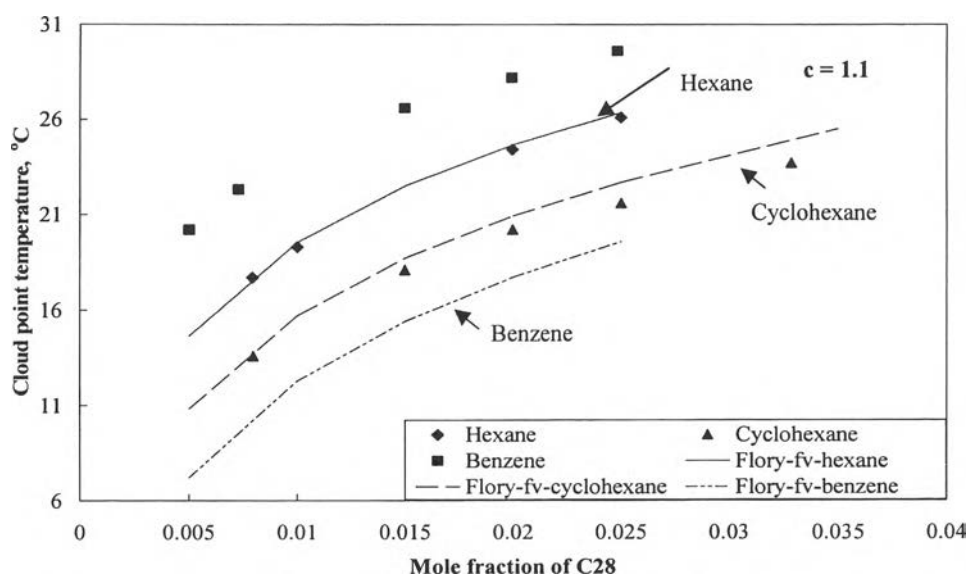
Figure 5.3 Schematic illustration of (a) solid (b) liquid with an orientational order (c) liquid without an orientational order. The slender sticks represent the molecules.

The results show that the cloud point temperatures of both *n*-C28 and FGW in benzene are the highest. The highest cloud point temperatures of both solutes in benzene suggested that both solutes have the lowest solubility in benzene solvent. This low solubility behavior can be explained by considering dissimilarities of intermolecular interaction which are caused by the differences in the nature between the aromatic double bonds in benzene and aliphatic single bonds in *n*-alkane. The weak intermolecular interaction between solute and solvent molecules comparing to solute-solute interaction and solvent-solvent interaction leads to a lower solubility and a higher cloud point temperature. In other word, a strong solute-solvent interaction compare to solute-solute and solvent-solvent interactions leads to a lower cloud point temperature. From the results, one can conclude that intermolecular interactions between *n*-alkane solute and aromatic solvent are relatively weak compared to the like pair interactions. It was observed that the cloud point temperature of *n*-C28 and FGW in toluene is lower than in benzene. The lower cloud point temperatures of the toluene-wax mixture as compared to those in the benzene-wax mixture can be explained by the decrease in surface area fraction for aromatic CH group.

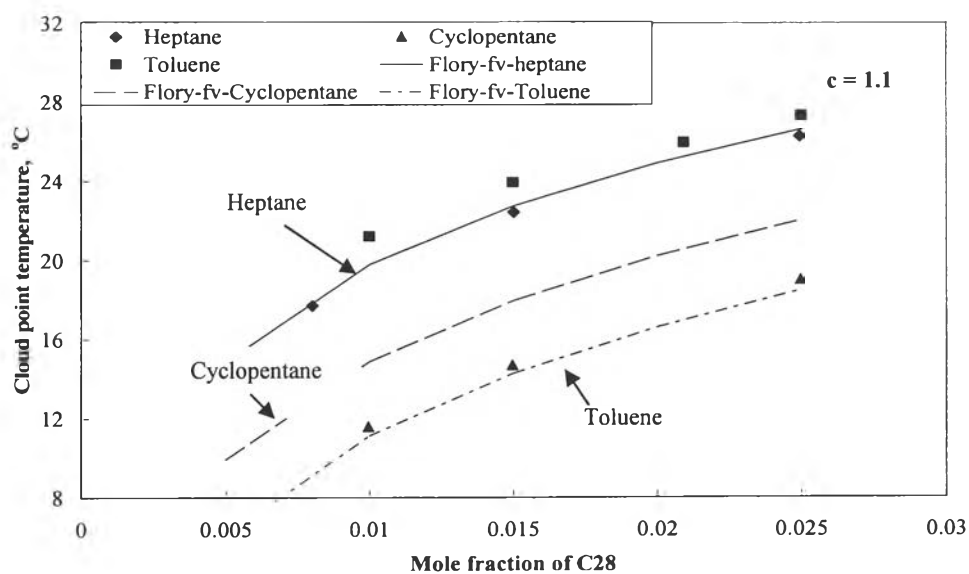
5.2 Predicted Cloud Point Temperature

5.2.1 Binary Systems

Pure octacosane was used as a solute in different types of solvents, namely *n*-alkanes, cycloalkanes and aromatics. Combinatorial-free volume and residual activity coefficients are needed to be calculated, in order to determine liquid phase activity coefficients, from Equation (3.2). The Flory-free volume model (Flory-fv), Equations (3.3) and (3.4), with an external degree of freedom (*c*) equal to 1.1 (Coutinho, 1995) was used to calculate the combinatorial-free volume activity coefficients while the residual activity coefficients were assumed to be negligible ($\gamma^{res} = 1$). The solid phase activity coefficient of solute is equal to one since the precipitated solid is a pure octacosane. The cloud point temperature predictions and experimental results are shown in Figure 5.4.



(a)



(b)

Figure 5.4 The comparison between the experimental and calculated cloud point temperatures using only combinatorial term with c -value is set to be equal to 1.1 for octacosane-solvents mixtures; a) in hexane, cyclohexane and benzene b) in heptane, cyclopentane and toluene.

The results indicate that the model provides an excellent cloud point temperature predictions only for *n*-alkane solvents, while cloud point temperature predictions are higher than the experimental values on the average of 1°C for cyclohexane and by 3°C for cyclopentane. For the aromatic systems, the model greatly underpredicts the cloud point temperatures with 14 °C and 9 °C for benzene and toluene system, respectively.

In order to minimize the differences between the calculated values and the experimental data, the *c*-value was adjusted. The experimental and predicted cloud point temperatures with adjusted *c*-values are shown in Figure 5.5. Cloud point temperatures of octacosane in cyclohexane and cyclopentane solvents were predicted by the model with changing the *c* values to 1.16 and 1.27, respectively. However, the model fails to accurately correlate the cloud point temperatures of *n*-C28 in benzene solvent. For aromatic solvents, the *c*-value is needed to be reduced (from 1.1) in attempt to correlate the experimental data. Figure 5.5 shows that cloud point temperature predictions at *c* = 0.1 for both benzene and toluene have the same values. Further reduction of the *c*-value from 0.1 does not significantly improve predictions even *c*-value has a negative value.

Combinatorial-free volume activity coefficient alone does not provide an accurate prediction in the system that has different intermolecular interactions, such as *n*-C28 in aromatic solvents. In order to account for the differences in intermolecular interaction between solute and solvent, the residual activity coefficients are needed to be included. For the systems that have no differences in intermolecular interactions, such as *n*-alkane solute in *n*-alkane solvent, the use of combinatorial-free volume activity coefficient alone is sufficient to predict cloud point temperatures ($\gamma^{res} = 1$). As shown in the Figure 5.4, cloud point temperatures of octacosane in both hexane and heptane can be accurately predicted using only the combinatorial-free volume term with a *c*-value equals to 1.1. Therefore, in this work, the *c*-value was set to be equal to 1.1. The group interaction parameters, a_{mn} , used for calculating the residual activity coefficient were obtained from the Modified UNIFAC. The values of a_{mn} were estimated by fitting with experimental vapor-liquid equilibrium data (Larsen *et al*, 1987). The modified UNIFAC model does not

distinguish between CH_2 group in *n*-alkane and cycloalkane. As a result, the residual activity coefficient of octacosane in cycloalkane solvents becomes unity ($\gamma^{res}=1$). Therefore, the model still overpredicts the cloud point temperatures of octacosane in cyclohexane and cyclopentane as shown in Figure 5.4.

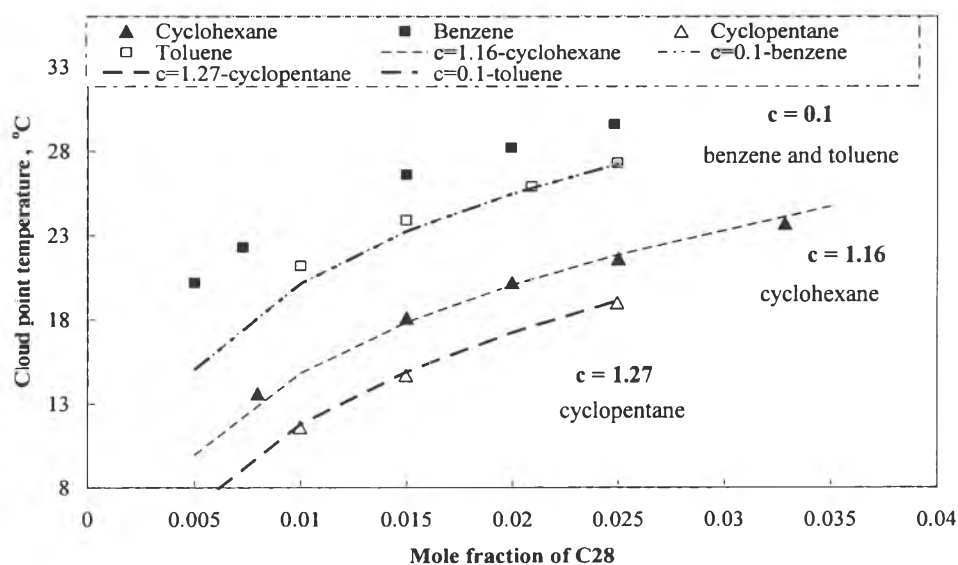


Figure 5.5 The comparison between the experimental and calculated cloud point temperatures using only combinatorial-free volume term with adjusted *c*-value for octacosane-solvents mixtures.

The cloud point temperature predictions of octacosane in aromatic solvents using Larsen's group interaction parameters are shown in the Figure 5.6. The results show that by adding the term of the residual contribution the accuracy of predictions can be improved as seen from the differences between the experimental and predicted values from 14°C to 6.7°C for benzene and from 9°C to 0.7°C for toluene systems. The remaining discrepancies are originated from the values of interaction parameters used in the calculation. Larsen and coworker (1987) determined group interaction parameters from the vapor-liquid equilibrium data while wax precipitation is a solid-liquid equilibrium. The group interaction parameters obtained by Larsen and coworker do not take the effect of order/disorder

phenomenon of high molecular weight *n*-alkane into account because the systems used to fit group interaction parameters in Larsen's work are mostly for low molecular weight compounds. In order to improve the cloud point temperature prediction, the solid-liquid equilibrium group interaction parameters for *n*-alkane in nonparaffin solvents were determined in this work using the cloud point temperature data obtained from the present experiments.

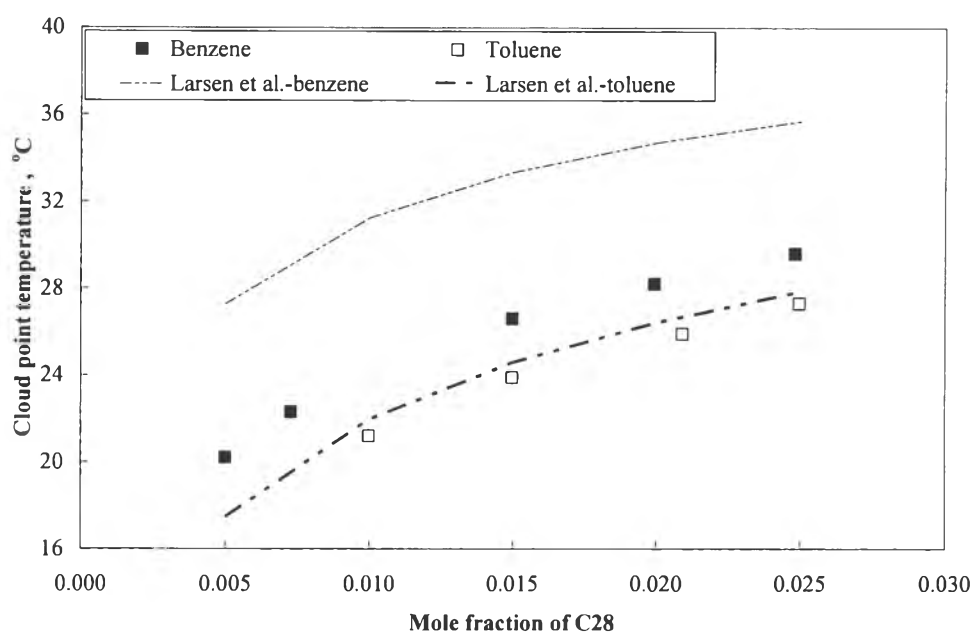


Figure 5.6 Comparison between experimental and calculated cloud point temperatures using Larsen and coworker's interaction parameters.

In order to differentiate *n*-alkane and cycloalkane, CH_2 groups in *n*-alkane and CH_2 groups in cycloalkane are considered as different molecular groups. Cloud point temperatures of octacosane in cyclohexane, cyclopentane and benzene were used to optimize the group interaction parameters, following the schematic shown in Figure 4.5. Table 5.1 shows the values of group interaction parameters estimated in this work.

The interaction parameter of group ACH (2) to group CH_2 (1), A_{21} , in this work has the negative values corresponding to the values reported in the

UNIFAC and the modified UNIFAC (Fredenlund *et al.*, 1977; Larsen *et al.*, 1987). The intermolecular interaction of pure component can be qualitatively estimated using solubility parameter (Hildebrand, J. H. and Scott, R. L., 1950). The solubility parameter of hexane is less than that of benzene so the intermolecular interactions between CH₂ groups in *n*-alkane are weaker than that between ACH group in aromatic ($u_{11} < u_{22}$). From Equations (3.9.1) and (3.9.2), one can see that a_{12} is lower than a_{21} . Therefore, The value of A_{12} is expected to be negative instead of A_{21} . The physically-corrected interaction parameters may needed to obtaine from the estimation with both cloud point temperatures and heats of mixing data. The group interaction parameters estimated from only cloud point temperature as shown in Table 5.1 were used in this work for the prediction of wax precipitation.

Table 5.1 Group interaction parameters A_{mn} and B_{nm} optimized in this work

Group	A_{12}	A_{21}	$B_{12} = B_{21}$
Cyclopentane CH ₂	82.75	-82.77	-0.0636
Cyclohexane CH ₂	73.31	-69.03	-0.1627
Aromatic ACH and AC	249.73	-138.21	-0.6192

where 1 is a CH₂ group in *n*-alkane solute and 2 are the CH₂/ACH groups in the solvents.

The group interaction parameters for aromatic groups, obtained from benzene data, can be successfully extended to predict cloud point temperatures for toluene systems. The cloud point temperature predictions for cyclopentane solvent systems were improved by using the cyclohexane group interaction parameters. However, the predictions remained higher than the measured values by 2.5 °C on average; suggesting that the CH₂ group in cyclohexane affects the cloud point temperature reduction to a lesser extent compared with CH₂ in cyclopentane. The reason for this behavior may be the order/disorder effect which has a higher magnitude in cyclopentane than cyclohexane. Hence, the correlated group interaction parameters for CH₂ group in both cyclohexane and cyclopentane were separately determined. Our group interaction parameters provide accurate predictions for all solvents and concentrations as shown in Figure 5.7.

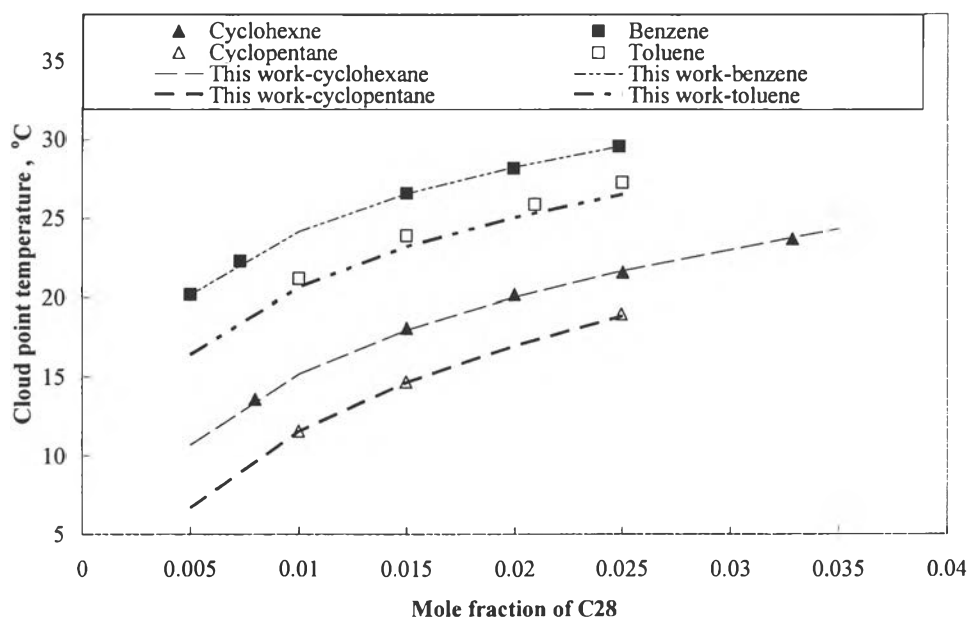
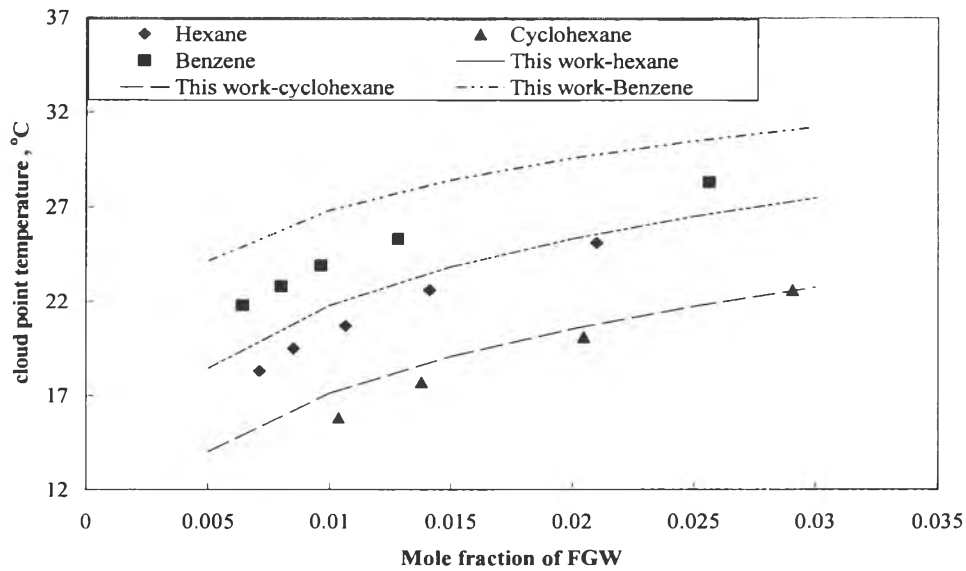


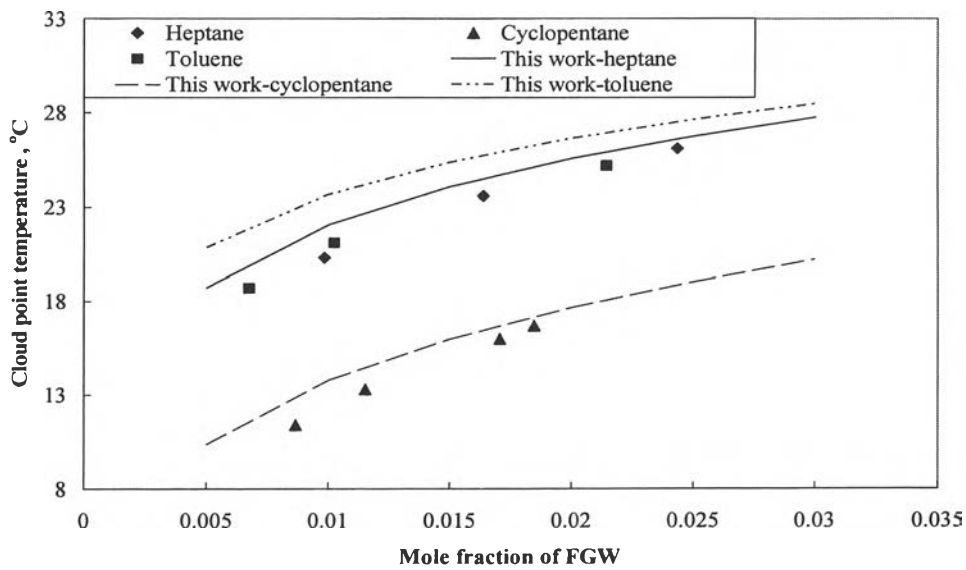
Figure 5.7 The comparison between the experimental and calculated cloud point temperatures for octacosane in non-normal alkane solvents.

5.2.2 Multicomponent systems

Food grade wax was used as a solute for multicomponent systems. Liquid phase activity coefficients were calculated using both combinatorial and residual terms, as described earlier in the binary systems section. The values of group interaction parameters obtained from the binary systems are listed in Table 5.1 were extended to calculate the residual activity coefficients in multicomponent systems. For multicomponent systems, solid phase activity coefficients are not equal to one and needed to be determined. The solid phase activity coefficients were calculated from UNIQUAC model, Equation (10) and Equation (11). Predicted cloud point temperatures were are shown in the Figure 5.8.



(a)



(b)

Figure 5.8 The comparison between experimental and calculated cloud point temperature of food grade wax –solvent mixtures; a) in hexane, cyclohexane and benzene b) in heptane, cyclopentane and toluene.

The predicted cloud point temperatures are higher than the measured values for all solvents. The highest average deviation is 2.8 °C for the benzene system. The deviations from the experimental results for each solvent are expressed by sum-square of error per one data point (SSE).

$$SSE = \sum_{i=1}^N \frac{(T_{c,i}^{\text{exp}} - T_{c,i}^{\text{cal}})^2}{N}$$

N is the number of experimental data point. The cloud point temperature predictions accounting only the combinatorial term (Flory-fv) and accounting both combinatorial and residual terms were compared. Figure 5.9 shows the SSE values of different solvents. The SSE values of every solvents are the lowest when this work's group interaction parameters were used. Therefore, the cloud point temperature predictions were greatly improved when our group interaction parameters were used in the residual activity coefficient calculations.

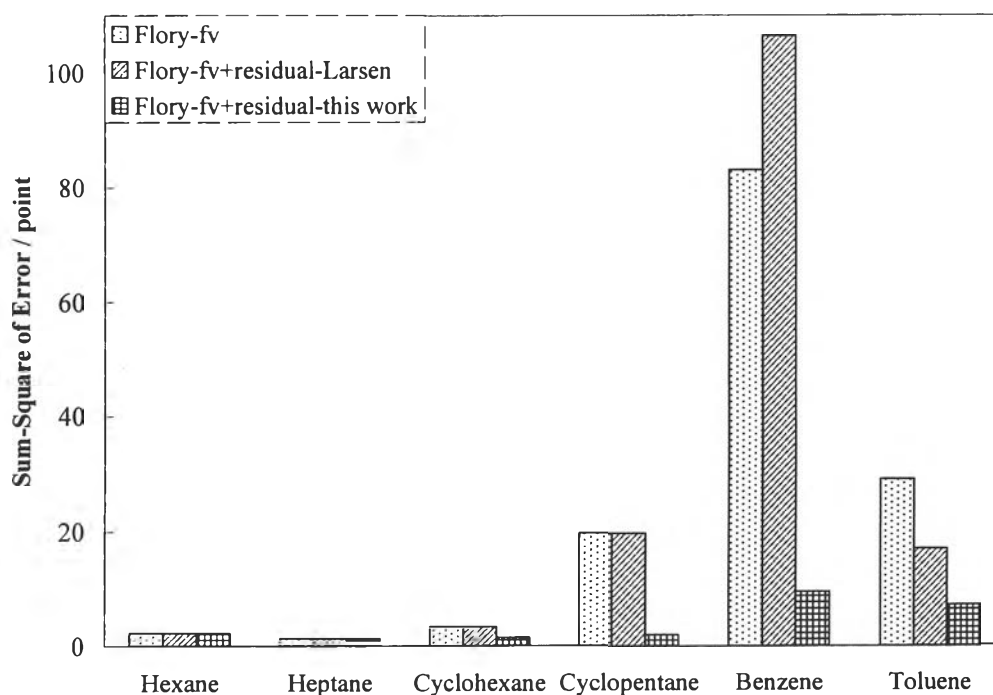


Figure 5.9 Mean deviation between experimental and calculated cloud point temperatures.