CHAPTER IV
EXPERIMENTAL

4.1 Materials

4.1.1 Oil Solvents

Six solvents of three different types (n-alkane, cycloalkane and aromatic) were used in this study to investigate the effect of solvent type on wax precipitation. Table 4.1 shows the list of solvent purities, formulations and suppliers.

Table 4.1 Solvent specifications

Type	Solvent	Purity	Chemical formular	Supplier
n-alkanes	n-Hexane	99.50%	C_6H_{14}	Fluka
	n-Heptane	99+% HPLC	C_7H_{16}	Aldrich
cycloalkanes	Cyclopentane	99+%	C_5H_{10}	Sigma-Aldrich
	Cyclohexane	HPLC	C_6H_{12}	Acros
Aromatics	Benzene	99.9% HPLC	C_6H_6	Aldrich
	Toluene	99.8% HPLC	C_7H_8	Aldrich

4.1.2 High Molecular Weight Paraffin Solutes

Pure n-alkane and multiparaffinic wax were used as model solutes in this study. In binary systems, octacosane (n-C28) was used as a solute. Octacosane was obtained from Aldrich with 99% purity. For multicomponent systems, food grade wax was used as a solute and food grade wax composition is shown in the Figure 4.1.
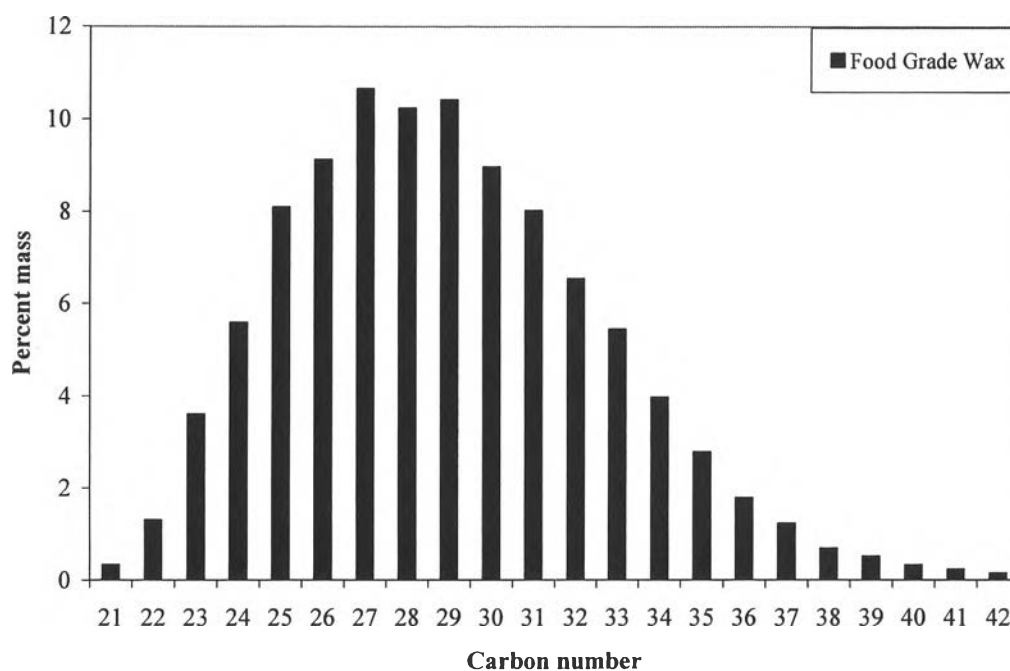
Figure 4.1 Paraffin distribution of food grade wax.

4.2 Determination of Experimental Cloud Point Temperatures

Cloud point temperatures of mixtures were measured in order to study the precipitation of wax since cloud point temperature is the temperature at which a first paraffin molecule precipitates out from the fluid. Predetermined amounts of solute and solvent were placed in a 20 mL vial. The mixtures in the vial were heated to dissolve the solid solute and it was then emerged in a water bath for 30 minutes at the setting temperature (T_1). After 30 minutes, the mixtures were visually examined for the formation of crystals or for a change in turbidity. If a crystal or turbidity change was observed, the bath temperature was increased (T_2) and the procedure repeated. Similarly, if a crystal or turbidity change was not observed, the bath temperature was reduced (T_2). A final temperature change increment of 0.1° C was used in this study. The cloud point temperature was reported as the highest temperature that a crystal or a turbidity change was observed. Figure 4.2 graphically shows the cloud point temperature determination procedures.
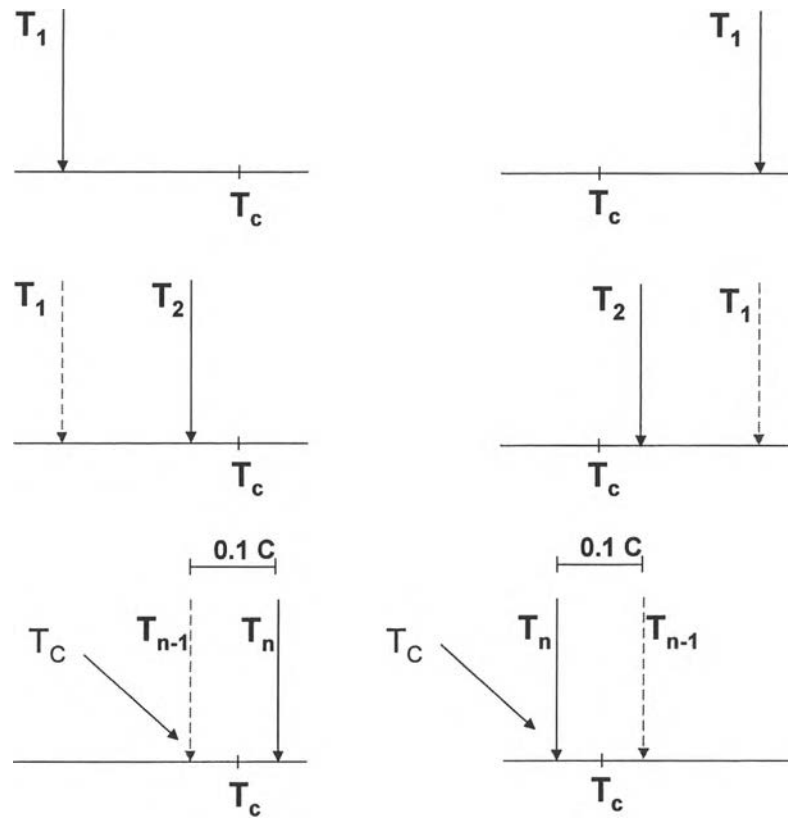
Figure 4.2 Cloud point temperature measurement procedures.

Two sets of experiments were conducted. First, the cloud point temperatures were measured in Food grade wax-solvent mixtures. Second, the cloud point temperatures were measured in octacosane-solvent mixtures.

4.3 Procedures of Cloud Point Temperature Prediction

Figure 4.3 shows the schematic of the predicted cloud point temperature calculation procedure. The mixture composition and the temperature, T_{input}, are the input data to calculate the solid phase fraction (f_s). The solid phase fractions at equilibrium were calculated at various temperatures with the temperature increment of 0.1°C. Theoretical cloud point temperature of the mixture (T_c^{cal}) was determined

by plotting f_s versus T_{input} and extrapolating the total amount of solid phase to zero. Total solid phase fractions of at least five different temperatures were used for extrapolation. Figure 4.4 shows the extrapolation to determine a theoretical cloud point temperature.
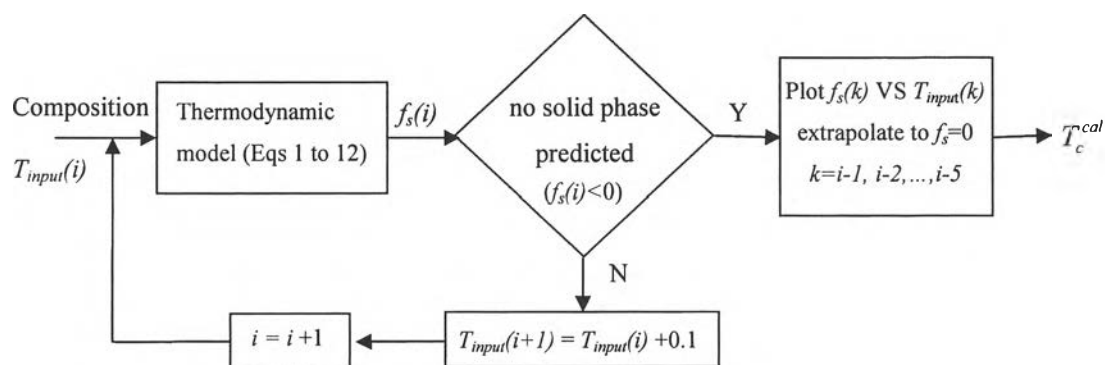

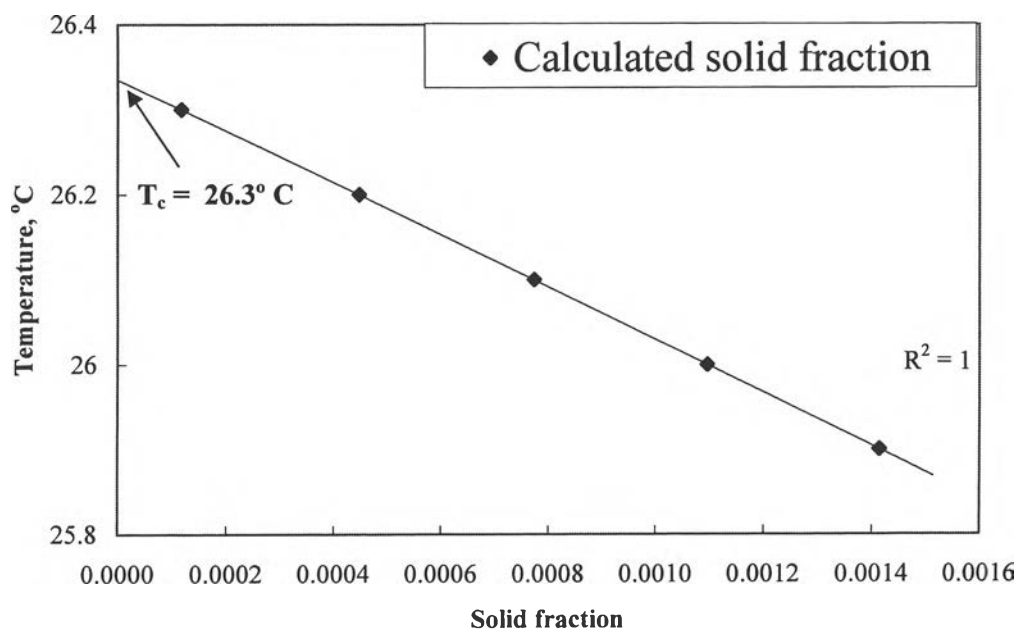**Figure 4.3** Cloud point temperature prediction procedures.

Figure 4.4 The extrapolation of theoretical cloud point temperature.

4.4 Estimation of Group Interaction Parameters in Non-normal Alkane Solvents

Cloud point temperatures of octacosane in non-normal alkane solvents can not be accurately predicted using the group interaction parameters from a literature; therefore, group interaction parameters for octacosane in non-normal alkane solvent were estimated. Group interaction parameters used in Equations (3.8) and (3.9) were adjusted to fit the experimental cloud point temperatures. Experimental cloud point temperatures of octacosane at various concentrations were used to estimate the group interaction parameter (a_{mn}). The term of group interaction parameter is used to describe the difference in the intermolecular interaction between m-n pair and n-n pair. For example of octacosane-benzene mixture, m represents the CH_2 group in n-C28 and n represents the aromatic-CH group (ACH) in benzene. Figure 4.5 shows the estimating procedure to estimate group interaction parameters where N is a number of experimental data points.
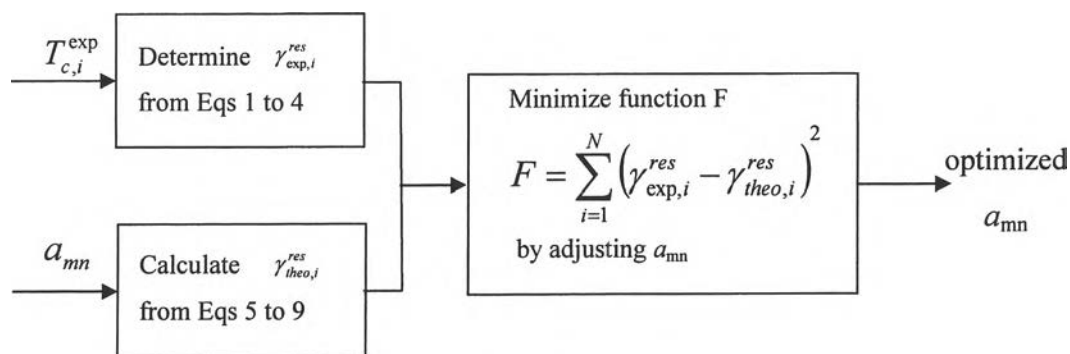

Figure 4.5 Group interaction parameters determination.

The experimental residual activity coefficients in liquid phase for octacosane in the solvent (γ_{exp}^{res}) were calculated from Equations (3.1) to (3.4) at a mixture temperature equal to the measured cloud point temperature $(T_{input} = T_c^{exp})$. Theoretical residual activity coefficients (γ_{theo}^{res}) were calculated from Equations (3.5)

to (3.9). Group interaction parameters were adjusted to minimize the difference between experimental and theoritical residual activity coefficients. Two simplifications were made on the interaction parameters estimation. First, Equation (3.9) was simplified by neglecting the last term ($C_{mn} = 0$). Second, the temperature-dependent interaction parameters for group m and n were assumed to have the same value or $B_{mn} = B_{nm}$. The nonlinear least-square method in MATLAB software was used to optimize the interaction parameters by minimizing the objective function (F).

$$F = \sum_{i=1}^{N} \left(\ln \gamma_{exp,i}^{res} - \ln \gamma_{theo,i}^{res} \right)^2 \qquad (4.1)$$