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A Study of the Predictive Thermodynamic Models for the Wax Deposition of Synthetic Fuels

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Abstract: Local composition models (UNIQUAC, Wilson and NRTL) and regular solution models (Won and Pedersen) were applied to predict the cloud point temperature of systems with n-alkanes and acceptable results were obtained by these models. The prediction of wax formation and the composition below cloud point temperature were done by UNIQUAC model using two different structural parameter for solid phase activity coefficient (UNIQUAC10 and Coutinho 2000). The results that are more accurate for calculating the wax content and the composition at different temperatures below cloud point were obtained using UNIQUAC10.

Keywords: Cloud point, model, solid-liquid equilibrium.

INTRODUCTION

The majority of petroleum fluids contain heavy hydrocarbons, which at low temperatures may precipitate as a wax phase. The presence of wax phase causes problems during oil production, transport and use of both crude oil and refined products. This phenomenon is responsible for losses of billions of dollars per year in the petroleum industries. Under-standing the wax phase and modeling this behavior are fundamental in dealing with this problem. Thermodynamically, this problem treated for along time as solid liquid equilibria models. Different models are presented in the literature. The models differ in the approach for describing the non-ideality of solid and liquid phases. In this study, computer programs have been developed on the basis of thermodynamic models.

The main purpose of this paper is to apply some thermodynamic models that can be used to predict cloud point temperature based on literature experimental data. A comparison between the predictions of these models and experimental data is presented. The models selected in this study are regular solution models (Won and Pedersen) and local composition models (UNIQUAC, Wilson, and NRTL).

THERMODYNAMIC MODELS

The cloud point is defined as the temperature at which the first crystal appears in petroleum fluids. The formation of wax is treated as solid liquid equilibrium between a solution (liquid phase) and solid phase (wax) in a hydrocarbon mixture.

The general solid-liquid equilibrium equation relates the composition in both phases with the non ideality of the phases and the pure component thermophysical properties.

The equilibrium equation relating the composition in the liquid and solid phases with the non ideality of the phases and the thermophysical properties of the pure components can be written for each component i present at equilibrium as[1]:

$$\left(\frac{x_i^s\gamma_i^s}{x_i^l\gamma_i^l}\right)=\frac{\Delta h_{m,i}}{RT_{m,i}}\left(\frac{T_{m,i}}{T}-1\right)+\frac{\Delta h_{tr,i}}{RT_{tr,i}}\left(\frac{T_{tr,i}}{T}-1\right)-\frac{\Delta cp_{m,i}}{R}\left(\ln\left(\frac{T}{T_{m,i}}\right)+\frac{T_{m,i}}{T}-1\right) \quad (1)$$

Where $\Delta h_{m,i}$ is the enthalpy of melting for component i, $T_{m,i}$ is the melting temperature, $\Delta h_{tr,i}$ is the transition enthalpy of component i, $T_{tr,i}$ is the transition temperature of component i, ΔCp_m is the heat capacity at melting temperature, and γ_i^s, γ_i^l are the activity coefficients for both liquid and solid phases respectively.

Regular solution models: Won and Pedersen

Won model

Two simplifications in equation (1) were done by Won[2]. First the heat capacity differences were neglected in the equilibrium ratio. Secondly, the melting temperatures and solid-solid transition

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temperatures are considered as equal, and then the general expression can be written as:

$$\ln\left(\frac{x_i^s\gamma_i^s}{x_i^l\gamma_i^l}\right)=\frac{\Delta h_{m,i}}{RT_{m,i}}\left(\frac{T_{m,i}}{T}-1\right) \qquad (2)$$

Won[2] used the regular solution theory in order to describe the nonideality in the oil (liquid) and wax (solid) which means that the activity coefficients are determined from the solubility parameters of the individual components

$$\ln\gamma_i = V_i\frac{(\bar{\delta}-\delta_i)^2}{RT} \qquad (3)$$

$$\bar{\delta} = \sum \Phi_i\delta_i \qquad (4)$$

$$\Phi_i^l = \frac{x_i v_i}{\sum x_i v_i} \qquad (5)$$

$$\Phi_i^s = \frac{S_i v_i}{\sum S_i v_i} \qquad (6)$$

Where v_i is the molar volume, δ_i is the solubility parameter, Φ_i is the volume fraction of component i, is the average solubility parameter of the mixture, S_i and Xi are the mole fractions for solid and liquid phases. Won used the following expression to determine for the melting enthalpy (cal/mol) of component i:

$$\Delta H_{m,i} = 0.1426\,Mw_i T_{m,i} \qquad (7)$$

Where Mw_i is the molecular weight and $T_{m,i}$ the melting temperature in Kelvin and has the following expression:

$$T_{m,i} = 374.5 + 0.02617\,Mw_i - \frac{20172}{Mw_i} \qquad (8)$$

The molar volume, v_{i-} in the equations 5 and 6 was calculated by the following correlation[2]:

$$V_i = \frac{Mw_i}{d} \qquad (9)$$

Where:

$$d = 0.8155 + 0.6272*10^{-4}Mw_i - \frac{13.06}{Mw_i} \qquad (10)$$

The solubility parameters, for both liquid and solid phases of the normal paraffin up to C_{40}, which were used by Won[2] are presented in Table (1).

Table 1. Solubility Parameters (cal/cm^3)$^{0.5}$ for paraffinic components used in Won's model(2).

COMPONENT	δ^L	δ^S
C_{10}	7.71	9.17
C_{11}	7.78	9.32
C_{12}	7.83	9.44
C_{13}	7.88	9.55
C_{14}	7.92	9.64
C_{15}	7.96	9.72
C_{16}	7.99	9.79
C_{17}	8.02	9.86
C_{18}	8.05	9.92
C_{19}	8.07	9.97
C_{20}	8.09	10.0
C_{21}	8.11	10.1
C_{22}	8.13	10.1
C_{23}	8.15	10.1
C_{24}	8.17	10.2
C_{25}	8.18	10.2
C_{26}	8.20	10.3
C_{27}	8.21	10.3
C_{28}	8.22	10.3
C_{29}	8.24	10.3
C_{30}	8.25	10.4
C_{31}	8.26	10.4
C_{32}	8.27	10.4
C_{33}	8.28	10.4
C_{34}	8.29	10.4
C_{35}	8.30	10.5
C_{36}	8.31	10.5
C_{37}	8.32	10.5
C_{38}	8.33	10.5
C_{39}	8.34	10.5
C_{40}	8.35	10.6

Pedersen model

Pedersen et al.[3] have made two modifications of Won's model. The first modification takes the heat capacity difference into account in the equilibrium equation, and has the following form:

$$\Delta Cp_i = (0.3033Mw_i - 4.635*10^4 Mw_i T) \qquad (11)$$

The second is that the solubility parameters are function of carbon number of components according to[3]:

$$\delta_i^l = 7.41 + 0.5914(\ln C_n - \ln 7) \qquad (12)$$

$$\delta_i^S = 8.5 + 5.763(\ln C_n - \ln 7) \qquad (13)$$

Where: C_n is carbon number.

Local composition models: UNIQUAC, Wilson, and NRTL

These models are based on the concept that the composition of the system in the neighborhood of a given molecule is not the same as the bulk composition and presumed to account for the shortrange order and nonrandom molecular orientations that result from differences in molecular size and intermolecular forces. The heat capacity term of equation (1) is neglected and is not used in the modeling of the local composition model[4,5].

The Liquid Phase Nonideality

The activity coefficient model used for the liquid phase can be described as:

$$\gamma_i^l = \ln \gamma_i^{res} + \ln \gamma_i^{comb-fv} \tag{14}$$

Where the residual contribution for the activity coefficient, γ^{res}, is estimated by UNIFAC model and the Flory-free volume equation[6,7] were used to provide the combinatorial term

$$\gamma_i^{comb-fv} = \ln \frac{\Phi_i}{x_i} + 1 - \frac{\Phi_i}{x_i} \tag{15}$$

with:

$$\Phi_i = \frac{x_i (v_i^{0.333} - v_{wi}^{0.333})^{0.333}}{\sum_{j=1}^{n} x_j (v_j^{0.333} - v_{wj}^{0.333})^{0.333}} \tag{16}$$

Where v_i is the molar volume, and v_{wi} is the van der waals volume of component i

The Solid Phase Nonideality

The solid phase non-ideality was described using three different predictive local composition models: UNIQUAC, Wilson, and NRTL[8,9].

UNIQUAC model for solid phase activity coefficient: The UNIQUAC model for solid phase used has the following form:

$$\text{In}\ \gamma_i^s = \ln\frac{\Phi_i}{x_i^s} + 1 - \frac{\Phi_i}{x_i^s} - Z/2q_i\left[\ln\frac{\Phi_i}{\theta_i} + 1 - \frac{\Phi_i}{\theta_i}\right] + q_i - q_i \ln\left[\sum_{j=1}^{n}\theta_j\tau_{ji}\right] - q_i \ln\sum_{j=1}^{n}\frac{\theta_j\tau_{ij}}{\sum_{k=1}^{n}\theta_k\tau_{kj}} \tag{17}$$

With:

$$\Phi_i = \frac{x_i r_i}{\sum_{j=1}^{n} x_j r_j} \tag{18}$$

$$\theta_i = \frac{x_i q_i}{\sum_{j=1}^{n} x_j q_j} \tag{19}$$

τ_{ji} is the interaction parameter.

Subscript i identifies species and j is a dummy index. All summations are over all species.

The structural parameters r_i (relative molecular volume) and q_i (a relative molecular surface area) are function of paraffin chain length. The correlations used for r and q are[10,11]:

$$r_i = 0.0148C_n + 0.0096 \tag{20}$$

$$q_i = 0.0185C_n + 0.0211 \tag{21}$$

***Wilson model for solid phase activity coefficient*:** The Wilson equation used to predict the nonideality of solid phase is a modification of the original Wilson equation, where the contribution of the molar volumes to the local compositions is not taken into account and q_i (area parameter) was added to the interaction parameter.

$$\gamma_i^s = 1 - \ln\sum_{j}^{n} x_j A_{ij} - \sum_{k}^{n}\frac{x_k A_{ki}}{\sum_{j}^{n} x_j A_{kj}} \tag{22}$$

Where: $A_{ij} = \exp\left(-\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right)$

***NRTL model for solid phase activity coefficient*:** The NRTL model for solid phase was used without modifications of the original NRTL model and has the following form:

$$\gamma_i^s = \frac{\sum_{j=1}^{n}\tau_{ij}G_{ij}x_j^s}{\sum_{k=1}^{n}G_{ki}x_k^s} + \sum_{j=1}^{n}\left[\frac{x_j^s G_{ij}}{\sum_{k=1}^{n}G_{kj*}x_k^s}\left(\tau_{ij} - \frac{\sum_{k=1}^{n}x_k^s\tau_{kj}G_{kj}}{\sum_{k=1}^{n}G_{kj}x_k^s}\right)\right] \tag{23}$$

Where: $G_{ij} = \exp(-\alpha_{ji}\tau_{ji})$

Where á is a measure of the non-randomness of the mixture and for the solid phase has a value of $\alpha = 2/Z$, and Z is the coordination number for solid phase having a value of 6.

For these three models studied, the estimation of the local compositions is based on the interaction energies between pairs of molecules, λij. The pair interaction energies between two identical molecules were predicted using the enthalpy of sublimation of the orthorhombic crystalline phase of the pure component:

$$\lambda_{ii} = -\frac{2}{z}\left(\Delta_{sub,i}H - RT\right) \tag{24}$$

Where *z* is the coordination number with a value of 6 for the n-alkanes in the orthorhombic crystals[11] and is the enthalpy of sublimation of the pure n-alkanes defines as:

$$\Delta_{sub,i}H = \Delta H_{vap} + \Delta H_{fus} + \Delta H_{tr}. \tag{25}$$

THERMOPHYSICAL PROPERTIES FOR THE N-ALKANES

The following correlations were used to calculate the parameters needed to obtain the the thermophysical properties of the n-alkanes in local composition models used in this paper[12]:

$$T_{fus,i}[K] = 421.63 - 1936412\exp\left(-7.8945(Cn_i - 1)^{0.07194}\right) \quad (26)$$

$$T_{tr,i}[K] = 420.42 - 13487\exp(-4.344\left(Cn_i + 1)^{0.14627}\right) \quad (27)$$

and

$$\Delta H_{tot,i}[KJ/mol] = 3.7791 Cn_i - 12.654 \quad (28)$$

$$\Delta H_{fus,i}[KJ/mol] = 0.0035 Cn_i^3 - 0.2376 Cn_i^2 + + 7.400 Cn_i - 34.814 \quad (29)$$

with

$$\Delta H_{tr,i} = \Delta H_{tot,i} - \Delta H_{fus,i}$$

Where C_{ni} is the number of carbon atoms in n-alkanes.

Morgan and Kobayashi correlations were used to predict the heat of vaporization[13].

$$\frac{\Delta H_{vap,i}}{RT} = \Delta H_v^{(0)} + \omega \Delta H_v^{(1)} + \omega^2 \Delta H_v^{(2)}$$

With

$$\Delta H_v^{(0)} = 5.2804X^{0.3333} + 12.865X^{0.8333} + + 1.171X^{1.2083} - 13.116X + 0.4858X^2 - 1.088X^3 \quad (30)$$

$$\Delta H_v^{(1)} = 0.80022X^{0.333} + 273.23X^{0.8333} + + 465.08X^{1.2083} - 638.51X - 145.12X^2 + 74.049X^3 \quad (31)$$

$$\Delta H_v^{(2)} = 7.2543X^{0.3333} - 346.45X^{0.8333} - 610.48X^{1.2083} + + 839.89X + 160.05X^2 - 50.711X^3 \quad (32)$$

where: $X = \left(1 - \frac{T}{T_C}\right)$

The acentric factor is a function of the carbon number, C_{ni},

$$\omega = -0.000185397\, Cn_i^2 + 0.0448946\, Cn_i - - 0.0520750 \quad (33)$$

The critical properties are obtained from the correlations of Twu[14]:

$$\theta = \ln(Mw)$$

$$T_b[K] = \left[\exp\left(5.71419 + 2.71579\theta - 0.28659\theta^2 - - \frac{39.8544}{\theta} - \frac{0.122488}{\theta^2}\right) - 24.7522\theta + 35.3155\theta^2\right]/1.8 \quad (34)$$

$$T_C[k] = T_b\left(0.533272 + 0.343831 \times 10^{-3} T_b + 2.52617 \times 10^{-7} T_b^2 - - 1.65848 \times 10^{-10} T_b^3 + \frac{4.60774 \times 10^{24}}{T_b^{13}}\right)^{-1} \quad (35)$$

$$P_C[atm] = \left(1.0 + 0.312\left(1 - \frac{T_b}{T_C}\right)^{0.5} + 9.1\left(1 - \frac{T_b}{T_C}\right) + + 9.4417\left(1 - \frac{T_b}{T_C}\right)^2 + 27.1793\left(1 - \frac{T_b}{T_C}\right)^3\right)^2 \quad (36)$$

Ideal solution model

The simplest model also has been tested in which liquid and solid phases are assumed an ideal solution,

$$\gamma_i^l = 1, \quad \gamma_i^s = 1 \quad (37)$$

RESULTS AND DISCUSSION

Experimental data of synthetic fuel[15] have been used to test the predictive capabilities of these various models for predicting the cloud point temperature. Also UNIQUAC model was used to predict the composition and contents of wax below this point. This synthetic fuel, Table(2) consists of five synthesis paraffinic systems. These systems were made up of

Table 2: Composition in mass % of the paraffinic system.

	BIM0	BIM3	BIM5	BIM9	BIM13	Purity
$n.C_{10}$	63.84	64.25	64.65	65.59	66.65	>99.0
$n.C_{18}$	4.276	4.872	5.383	6.958	10.57	>99.0
$n.C_{19}$	3.871	4.411	4.874	6.301	9.571	99.0
$n.C_{20}$	3.494	3.981	4.400	5.688	8.641	99.0
$n.C_{21}$	3.149	3.587	3.963	5.124	-	>98.0
$n.C_{22}$	2.828	3.221	3.561	4.603	-	99.0
$n.C_{23}$	2.536	2.889	3.193	-	-	99.0
$n.C_{24}$	2.270	2.586	2.858	-	-	>99.0
$n.C_{25}$	2.028	2.310	-	-	-	>98.0
$n.C_{26}$	1.811	-	-	-	-	>99.0
$n.C_{27}$	1.612	-	-	-	-	>98.0
$n.C_{28}$	1.441	-	-	-	-	>98.0
$n.C_{29}$	1.274	1.451	-	-	-	>99.5
$n.C_{30}$	1.130	1.290	1.424	-	-	>99.0
$n.C_{31}$	1.004	1.142	1.262	-	-	>97.0
$n.C_{32}$	0.887	1.011	1.119	1.444	-	>98.0
$n.C_{33}$	0.788	0.895	0.989	1.280	-	>99.5
$n.C_{34}$	0.695	0.790	0.873	1.129	1.716	>98.0
$n.C_{35}$	0.522	0.698	0.771	0.998	1.516	>99.5
$n.C_{36}$	0.541	0.616	0.682	0.881	1.337	>98.0

a solvent (n-decane) plus synthetic wax in the proportion of 4 moles of n-decane to 1 mole of wax. The composition of waxes is essentially made up of heavy n-paraffins whose carbon number varies from 18 to 36.

Comparison between predicted values using the various models and experimental values is reported in Table (3).

It can be clearly seen from this table that the use of local composition models in general provides satisfactory prediction of the cloud point temperatures with the deviation less than experimental error. In the regular solution models, the results were satisfactory for Pedersen model. This model gave better prediction than Won model as shown in Table (3). This can be attributed to the fact that Pederson model considered the difference between solid and liquid heat capacities, a term has been neglected in Won model. Also it seemed the estimation values of solubility parameter necessary to increase the values of the solid phase solubility parameters as compared with Won model.

The large deviation was clear in an ideal solution model, this leads to a clear indication of the importance of using a description of the non-ideality in the solid-liquid equilibrium.

Composition of solid phase at cloud point

The composition of the solid phase at cloud point for the synthetic fuel were predicted by the models carried out in this work, and exponential decay of normal alkanes can be seen clearly from Figures 1 and 2 for BIM0 system .

A study of solid deposit at cloud point, by these different models leads to similar prediction. The heavy components are present in the first solid bulk, whereas the lightest do not precipitate. This means that only the heaviest components are contained in the solid phase at the cloud point temperature.

Table 3: Deviation "T" between experimental and calculated cloud points.

MODEL	BIM0	BIM3	BIM5	BIM9	BIM13
Texp/K	308.75	309.65	310.37	311.33	312.31
Won	-4.51	-3.71	-1.02	-1.71	4.42
Pedersen	-0.1	0.17	0.67	0.93	1.85
UNIQUAC	-1.94	-1.72	-1.23	-1.03	0.35
Wilson	0.05	-0.07	0.16	-0.17	-0.01
NRTL	-1.91	-1.04	0.03	1.75	3.73
Ideal solution	-7	-6.33	-5.55	-4.75	-4.45

Wax solid content and liquid- solid equilibrium

Solid liquid equilibrium model at temperatures below cloud point was calculated using UNIQUAC model. The solution of the model was based on the methodology prepared by Leivobici and Neoschil(16).

To test the UNIQUAC model ability to predict liquid-solid phase composition below cloud point, experimental data, Table (2), were used[15]. In the prediction, two different structural parameters r and q of the solid phase have been used; the first is mentioned above in equations 20, 21 and its named as Coutinho 2000[10]. The second is UNIQUAC10[17], it has the following form:

$$r_i = 0.1C_n + 0.0672 \tag{38}$$

$$q_i = 0.1C_n + 0.1141 \tag{39}$$

Figures 3 to 6 show the comparison between the experimental and calculated composition in the solid phase at different temperatures. Also Figure 7 shows the comparison between the experimental wax solid composition content and that predicted by the two different structural parameters. It can be seen that the UNIQUAC 10 gives better results in comparison with Coutinho 2000[10].

For liquid phase, the UNIQUAC model provides an excellent description of the experimental data for all of the systems studied using these two structural parameter correlations, equations. Figures 8 to 11 show the comparison between the experimental and calculated composition in the liquid phase at different temperatures for the different systems.

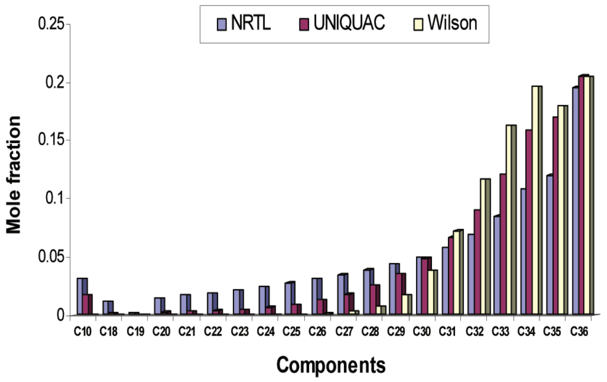

Fig. 1. Solid phase composition at cloud point for BIM0 system by local composition models.

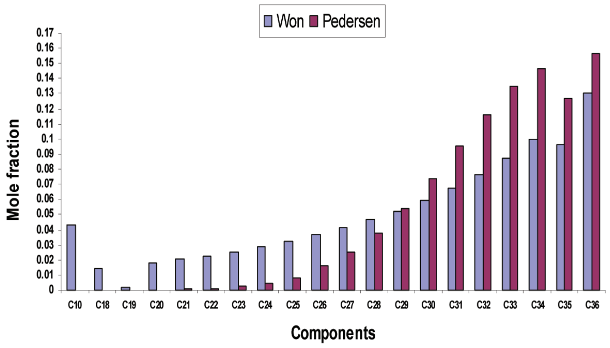

Fig. 2. Solid phase composition at cloud point for BIM0 system by regular solution models.

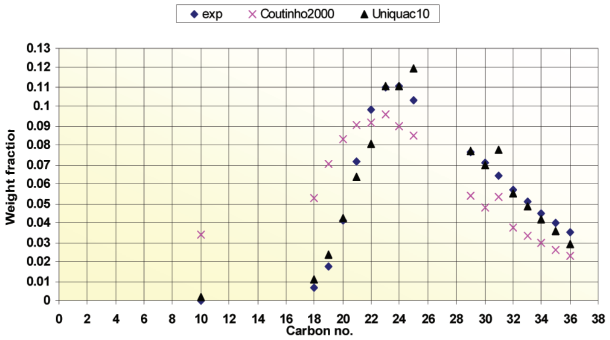

Fig. 3. Comparison between experimental[15] and predicted solid phase composition of BIM3 system at 278.35K by two different structural parameters.

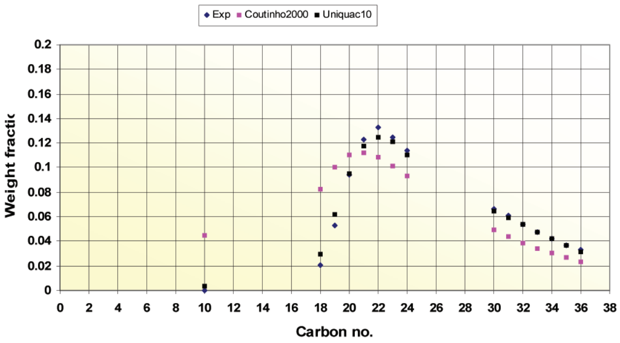

Fig. 4. Comparison between experimental[15] and predicted solid phase composition of BIM5 system at 273.45K by two different structural parameters.

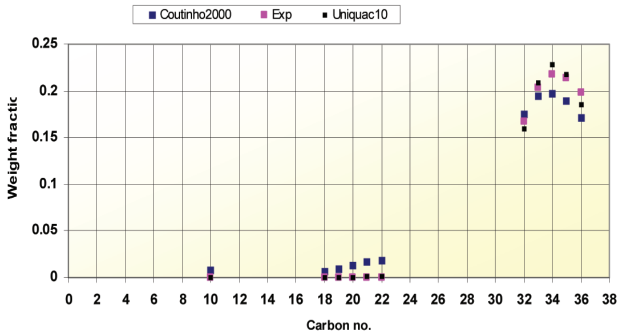

Fig. 5. Comparison between experimental[15] and predicted solid phase composition of BIM9 system at 303.15K by two different structural parameters.

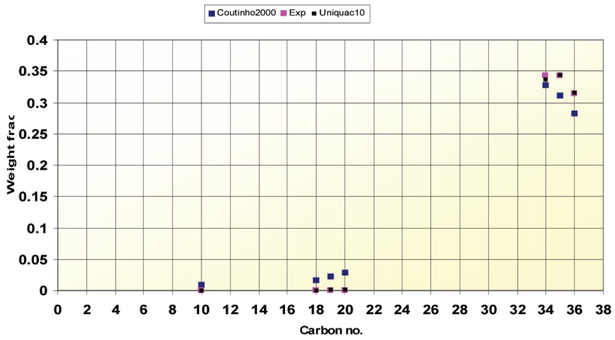

Fig. 6. Comparison between experimental[15] and predicted solid phase composition of BIM13 system at 299.15K by two different structural parameters.

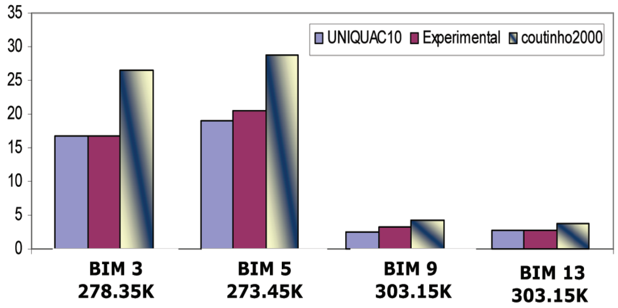

Fig. 7. Wax solid content at some temperatures for the studied system.

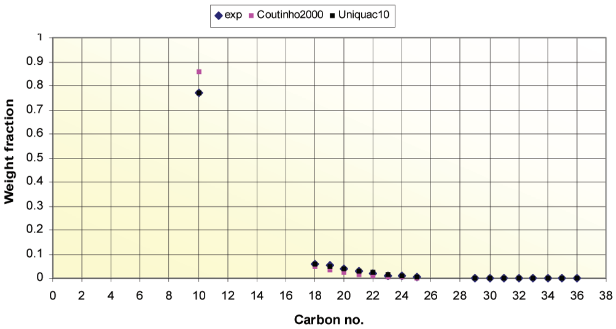

Fig. 8. Comparison between experimental[15] and predicted liquid phase composition of BIM3 system at 278.35K by two different structural parameters.

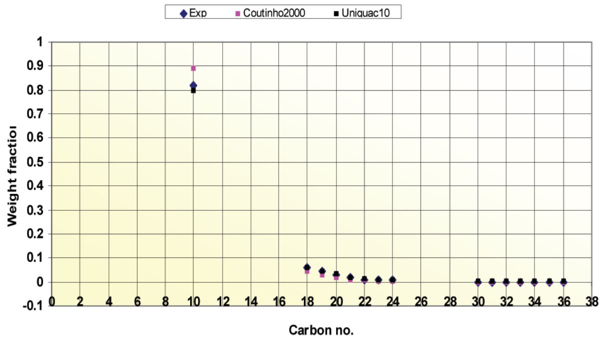

Fig. 9. Comparison between experimental[15] and predicted liquid phase composition of BIM5 system at 273.45K by two different structural parameters.

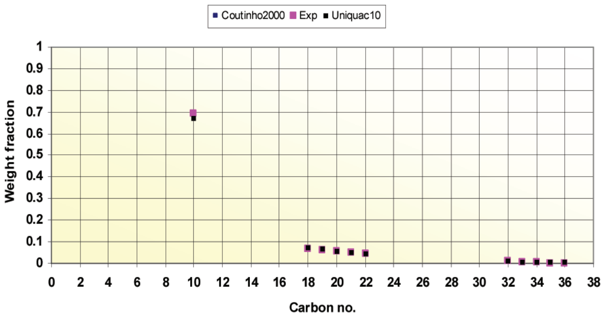

Fig. 10. Comparison between experimental [15] and predicted liquid phase composition of BIM9 system at 303.15K by two different structural parameters.

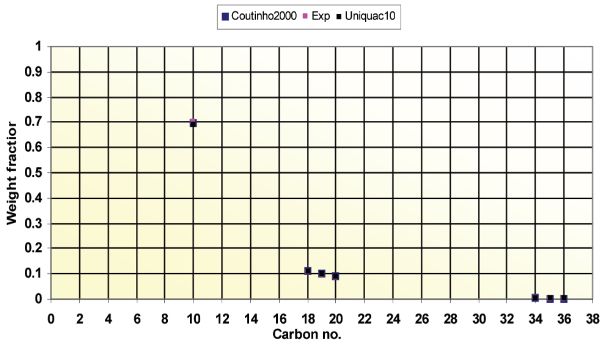

Fig. 11. Comparison between experimental [15] and predicted liquid phase composition of BIM13 system at 299.15K by two different structural parameters.

CONCLUSION

Six thermodynamic models namely, Won, Pedersen, UNIQUAC, Wilson, NRTL and ideal solution have been used to predict the cloud point temperature of defined liquid mixtures (synthetic fuel). The predicted cloud point temperatures have been compared with the literature experimental cloud point data. Good agreement between the predicted and experimental values was obtained using models that are based on solid activity coefficients as compared with those that neglect the non-ideality in the solid phase. Also, the UNIQUAC model was applied to predict the wax formation and the composition of liquid and solid phase below the cloud point temperature. This model was found to provide a remarkably good description of the low-temperature phase behavior for different types of synthetic fuel in broad temperature region.

NOMENCLATURE

A_{ij} is the binary interaction parameter for pair ij in the Wilson model.

C_{ni} is carbon number, i=10 to 40

d density of the component, g/cc

G_{ij} is the binary interaction parameter for pair ij in the NRTL model.

Mw_i is the molecular weight.

q_i relative molecular surface area of the paraffinic constituent.

P_c is the critical pressure in atm.

r_i relative molecular volume of the paraffinic constituent.

S_i is the mole fraction for solid phase.

T_b is the boiling point temperature in Kelvin.

T_c is the critical temperature in Kelvin.

$T_{m,i}$ the melting temperature in Kelvin.

$T_{tr,i}$ is the transition temperature of component i in Kelvin.

$T_{fus,i}$ is the fusion temperature of component i in Kelvin.

v_i is the molar volume of component i cc/gmol

V_{wi} is the van der waals volume of component i cc/gmol.

Xi is the mole fraction for liquid phase.

Z is the coordination number for solid phase.

α is a measure of the non-randomness of the mixture.

λij. The pair interaction energies between two identical molecules, area the activity coefficients for both liquid and solid phases respectively

δ_i is the solubility parameter

Φ_i is the volume fraction of component i

is the average solubility parameter of the mixture

γ^{res} residual part of the activity coefficient

$\gamma^{comb\text{-}fv}$ combinatorial part of the activity coefficient.

is the interaction parameter for the UIQUAC model.

ΔCp_m is the heat capacity at melting temperature

$\Delta h_{m,i}$ is the enthalpy of melting for componenti

$\Delta h_{tr,i}$ is the transition enthalpy of componenti

is the enthalpy of sublimation of the pure n-alkanes

“H_{vap} heat of vaporization, kJ/mol

“H_{fus} heat of fusion, kJ/mol

“H_{tr} heat of transition, kJ/mol

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