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SOLID-LIQUID EQUILIBRIA OF BINARY SYSTEMS CONTAINING *n*-TETRACOSANE WITH NAPHTHALENE OR DIBENZOFURAN

Prediction with UNIFAC model

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A differential scanning calorimeter (DSC) was used to determine binary solid-liquid equilibria (SLE) for dibenzofuran+*n*-C24 and naphthalene+*n*-C24 mixtures. Results obtained with this technique were compared with those predicted by two modified UNIFAC (Universal Functional group Acitivity Coefficients) versions. This model is employed with the idea to extensively investigate the validity of UNIFAC (Larsen and Gmehling versions). The corresponding activity coefficients were calculated and applied to the prediction of non-electrolyte mixtures real behavior. Reasons of prediction without success in the case of using original interaction parameters, were analysed and discussed. Interesting representation of solubility diagrams was obtained using partly readjusted UNIFAC interaction parameters. The two systems selected can be used for contributing to develop the data base using group contribution methods. For practical purposes, SLE are of interest in chemical process design, especially when process conditions must be specified to prevent precipitation of a solid.

Keywords: *activity coefficients, n-alkanes, polycyclic aromatic, SLE, UNIFAC prediction*

Introduction

SLE are of great technical interest in the petroleum industry, particularly in light of present trends to heavier feedstocks. Precipitation of polycyclic aromatics during the hydrocracking process is of prime interest in the refining industry. These components tend to reduce the heat exchange in these units. Studies of conditions of solubility and precipitation of polycyclic aromatics are thus of great importance. The study of solid-liquid equilibrium of binary mixtures provides information on both the intermolecular forces between solvent and solute and also on the nature of the intermolecular compounds in the solid phase. The understanding of the real behavior of fluid mixtures plays an important role in different fields of application, particularly for the optimization of the separation procedures or the calculation of chemical equilibrium compositions. This method is worldwidely used for the synthesis and design of the separation processes.

Systems containing polycyclic aromatic and long chain normal alkane can be considered as precursors of complex systems present in fluid reservoirs. Thermodynamic properties of these heavy molecules are strongly dependent of the nature of the heavy components. It is important to have informations about this type of components, in order to carry out a contribution to measure and estimate the thermodynamic properties of heavy hydrocarbon substances and their mixtures.

The representation of the thermodynamic properties of these fluids requires the taking into account the binary interactions between the various involved molecules. However, studies on the binary mixtures related to the size of these molecules, either of two light components or of asymmetric mixture between heavy and light components. In the literature, measurements of thermodynamic properties concerning binary mixtures – formed by long chain normal alkanes with HAP compounds – are practically limited. We can find measurements of Djordjevic [1], on mixtures formed by polycyclic aromatic hydrocarbons such as naphthalene, acenaphthene, anthracene, phenanthrene and pyrene, in solution in the *n*-octadecane, those of Aoulmi [2] for the mixtures containing HAP compounds in solution in long chain *n*-alkanes and finally measurements of Mahmoud [3] concerning the mixtures formed by polycyclic heteropolyaromatics and long chain *n*-alkanes.

SLE remains the way giving access to the excess functions for this type of mixtures. So as to show the thermodynamic functions of studied mixtures, we considered measurements of solubilities by using a PerkinElmer DSC 7 calorimeter. We obtained experimental measurements for the systems formed by dibenzofuran or naphthalene, in solution in *n*-tetra-

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cosane. Differential scanning calorimetry is a rapid and sensitive technique mainly used for the characterization of any kind of phase of change [4, 5].

The thermodynamic treatment of these experimental results is carried out by a group contribution method [6]. As the experimental data concerning heavy hydrocarbon materials is weak, it is obvious that the importance of these methods is large. The central question in the case of the pure substances or in the mixtures, concerns the possibility of applying general methods for which parameters are given for molecules of low or average size to the case of molecules with significant size.

Experimental

The choice of the substances consdered was deliberately carried out for a more fundamental analysis of the phase diagrams. The *n*-alkane and the aromatic hydrocarbon are completely miscible in the liquid state. Experimental methodology was checked by comparison with the data of SLE obtained for a system formed by naphthalene in solution in *n*-octacosane, already measured by Aoulmi [2]. The apparatus was calibrated using indium (purity=99.99%, T_m=429.78 K, ΔH_f=28.45 J g^{-1}). For a given molar fraction of aromatic in each mixture, the absolute average error was of 0.73 K (Fig. 1). Measurements of the solubilities were taken under inert atmosphere (20 mL min^{-1}) and heating at 1°C min^{-1}. The mixture was heated while agitating until fusion of the lowest volatile component and the sample was heated very slowly inside a glass cell. After melting, the cell was immersed immediately in liquid nitrogen bath to solidify the mixture completely. A small amount of solid was taken and sealed in a pan; the capsule was crimped and placed in the calorimetric block for the analysis. Chemical substances purchased from Fluka were used as delivered without further purification. The purity was better than 99% excepting dibenzofuran (98%).

The thermodynamic properties of these pure compounds are given in Table 1; these properties are in good agreement with literature data [3, 7–9]. Experimental SLE data are given in Table 2 and typical DSC curves are shown in Figs 2 and 3. It was found out that the two diagrams are simple eutectic systems.

Thermodynamic treatment

SLE data can be used to calculate activity coefficients of components in mixtures. In the case of the studied

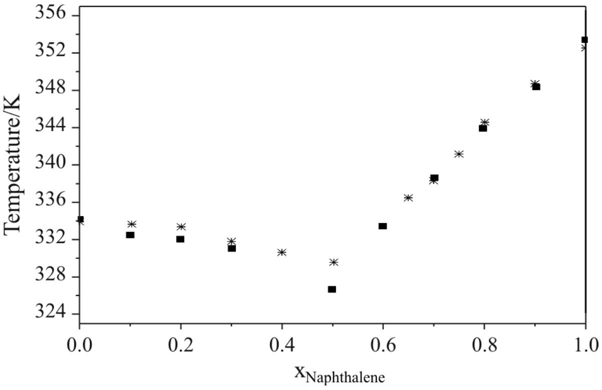

Fig. 1 Solubility of naphthalene in *n*-octacosane: ■ – Experimental results, ∗ – Literature results [2]

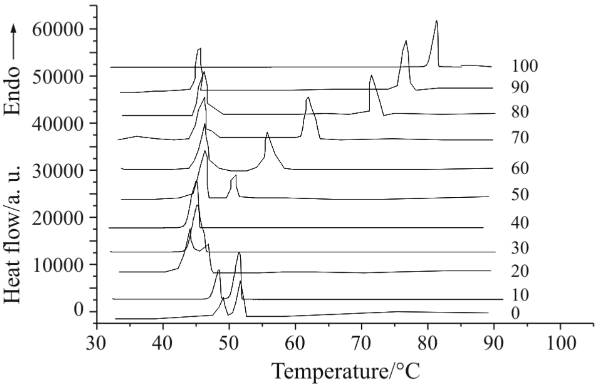

Fig. 2 DSC curves of naphthalene (1) + *n*-C24 (2). Proportions (%) of naphthalene in the mixture

Table1 Thermodynamic properties of considered pure components

Compound	T_m/K	ΔH_m/J mol^{-1}	T_{tr}/K	ΔH_{tr}/J mol^{-1}
n-Tetracosane	324.10^h	59305^h	321.03^h	33176^h
	323.75^k	54840^k	321.25^k	31270^k
n-Octacosane	333.91^s	64690^s	331.15^k	36010^k
	334.20^m	64600^m	331.20^m	35460^m
	334.20^h	67383^h	329.57^h	31522^h
Naphthalene	352.55^c	18238^c	–	–
	353.42^h	16440^h	–	–
Dibenzofuran	355.20^m	18600^m	–	–
	355.10^h	19405^h	–	–

m: Mahmoud [3], s: Schaerer [7], k: Kniaz [8]; c: McLaughlin [9], h: This work

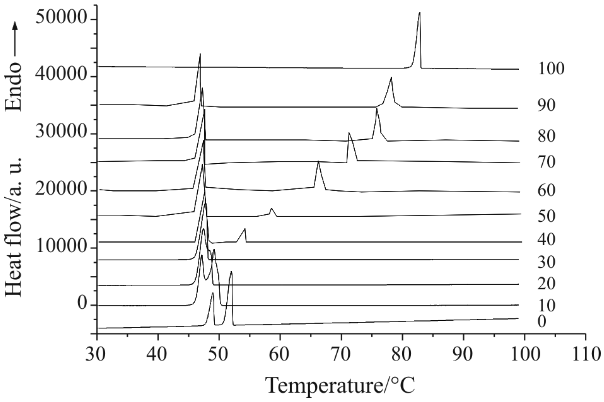

Fig. 3 DSC curves of dibenzofuran (1) + *n*-C24 (2). Proportions (%) of dibenzofuran in the mixture

systems, the components are not miscible in the solid phase. The activity coefficient γ_i of a component i in the liquid phase can be calculated according to the following equation:

$$\ln x_i \gamma_i = -\frac{\Delta H_{m,i}}{RT}\left(1-\frac{T}{T_{m,i}}\right)+ \frac{\Delta C_{p,i}}{R}\left(\ln\frac{T}{T_{m,i}}+\frac{T_{m,i}}{T}-1\right)-\frac{\Delta H_{tr,i}}{RT}\left(1-\frac{T}{T_{tr,i}}\right) \qquad (1)$$

where, $\Delta H_{m,i}$, $T_{m,i}$, $\Delta C_{p,i}$, $\Delta H_{tr,i}$, and $T_{tr,i}$, are respectively, the molar enthalpy of melting, the melting temperature, the molar heat capacity change (assumed to be independent of operating temperature T) during the melting process, the enthalpy change corresponding to the transition, the transition temperature of the pure component i. R is the universal gas constant and finally x_i, the mole fraction of component i in the liquid phase. The value of $\Delta C_{p,i}$ is lower that enough so the related terms in Eq. (1), are neglected [10]. According to the UNIFAC model modified by Larsen *et al.* [11], activity coefficients γ_i of components in liquid phase are thus calculated using Eqs (2)–(7).

$$\ln(\gamma_i)=\ln(\gamma_i)^{Comb}+\ln(\gamma_i)^{Resid} \qquad (2)$$

$$\ln(\gamma_i^{Comb})=\ln\left(\frac{w_i}{x_i}\right)+1-\frac{w_i}{x_i} \qquad (3)$$

$$w_i=\frac{x_i r_i^{2/3}}{\sum_j x_j r_j^{2/3}} \qquad (4)$$

$$\ln\gamma_i^{Resid}=\sum_k \nu_k^{(i)}\left(\ln\Gamma_k-\ln\Gamma_k^{(i)}\right) \qquad (5)$$

$$\ln\Gamma_k=\frac{z}{2}Q_k\left[1-\ln\left(\sum_m \theta_m \psi_{mk}\right)-\sum_m\frac{\theta_m \Psi_{km}}{\sum_n \theta_n \Psi_{nm}}\right] \qquad (6)$$

$$\Psi_{nm}=\exp\left[-\frac{a_{nm}+b_{nm}(T-T_0)+c_{nm}\left(T\ln\left(\frac{T_0}{T}\right)+T-T_0\right)}{T}\right] \qquad (7)$$

where ω_i, is the surface molecular fraction of molecule i, r_i is the volume parameter of molecule I, $\nu_k^{(i)}$ is the number of group k in molecule i, Γ_k is the group activity coefficient of group k in mixture, $\Gamma_k^{(i)}$ is the group activity coefficient of group k in molecule i, Z is the coordination number, Q_k is the surface area parameter for group k. Surface fractions of groups m and n in the liquid phase are θ_m, θ_n respectively. Ψ_{nm}, a_{nm}, b_{nm}, c_{nm} are UNIFAC group interaction parameters between groups n and m and finally T_0 is the standard temperature.

In the UNIFAC model modified by Gmehling *et al.* [12] activity coefficients of components in liquid phase are calculated using Eqs (2), (5), (8)–(10).

Table 2 SLE of dibenzofuran/naphthalene in solution with *n*-C24

x_1	T/K	x_1	T/K	x_1	T/K
		Dibenzofuran (1) + *n*-C24 (2)			
0.0000	324.10	0.3990	326.43	0.7010	344.04
0.0990	323.65	0.4990	332.21	0.8010	348.94
0.2020	322.35	0.6010	337.75	0.8990	352.84
0.2980	319.34			1.0000	355.10
		Naphthalene (1) + *n*-C24 (2)			
0.0000	324.10	0.4010	317.38	0.6980	336.70
0.1010	323.72	0.4990	324.23	0.8010	344.48
0.2000	321.48	0.5990	330.20	0.8980	348.14
0.2980	318.13			1.0000	353.42

$$\ln(\gamma_{\mathrm{i}}^{\mathrm{Comb}})=\ln\left(\frac{\omega'_{\mathrm{i}}}{x_{\mathrm{i}}}\right)+1-\frac{\omega'_{\mathrm{i}}}{x_{\mathrm{i}}}-5q_{\mathrm{i}}\left(\ln\left(\frac{\omega_{\mathrm{i}}}{\theta_{\mathrm{i}}}\right)-\frac{\omega_{\mathrm{i}}}{\theta_{\mathrm{i}}}+1\right) \quad (8)$$

$$\omega'_{\mathrm{i}}=\frac{x_{\mathrm{i}}r_{\mathrm{i}}^{3/4}}{\sum_{\mathrm{j}}x_{\mathrm{j}}r_{\mathrm{j}}^{3/4}} \quad (9)$$

$$\Psi_{\mathrm{nm}}=\exp\left(-\frac{a_{\mathrm{nm,1}}+a_{\mathrm{nm,2}}T+a_{\mathrm{nm,3}}T^2}{T}\right) \quad (10)$$

where q_{i} and r_{i} are respectively, the surface and the volume parameters of a molecule *i*.

The values of activity coefficients calculated using these two versions of modified UNIFAC model are compared with those obtained using DSC, by calculating the average standard deviation ratios (%) defined in relation (11):

$$\sigma_{\mathrm{i}}=\left[\frac{1}{n}\sum_{\mathrm{j}}\left(\frac{\gamma_{\mathrm{i,exp}}^{\mathrm{j}}-\gamma_{\mathrm{i,cal}}^{\mathrm{j}}}{\gamma_{\mathrm{i,exp}}^{\mathrm{j}}}\right)^2\right]^{1/2}\cdot 100 \quad i=1,2 \quad (11)$$

where σ_{i} is the average standard deviation (%), *n* is the number of experimental points. Subscripts *exp* and *cal* stand respectively for experimental and calculated values. The average standard deviations obtained for studied systems are presented in Table 3. The energetic interaction parameters are those of Gmehling *et al.* and *Larsen et al.*

Considering the average standard deviations obtained in the case of mixtures rich in aromatic and for the both versions, we note that the variations are significant in the case of the polar molecule like dibenzofuran (Figs 4 and 5). This result can be explained by the presence of the group ACO, which was substituted by group HCO in fitting calculations. UNIFAC model was selected as a frequently used model to represent thermodynamic properties of mixtures containing large size molecules and the combinatorial term thoroughly studied. Numerous authors devoted much time either following modifications initially proposed by Kikic [10] or trying several new solutions. Combinatorial term is essential for modelling thermodynamic data. The previous studies dealt exclusively with systems composed by one long chain molecule and one small molecule.

Table 3 Mean % dev. (dibenzofuran/naphthalene+*n*-C24)

Larsen and Rasmussen modified UNIFAC			
Using original parameters		a_{12} fitted and a_{21} original parameter	
σ_1/%	σ_2/%	σ_1/%	σ_2/%
16.6661	–	5.8726	8.7578
Weidlich and Gmehling modified UNIFAC			
Using original parameters		a_{12} fitted and a_{21} original parameter	
σ_1/%	σ_2/%	σ_1/%	σ_2/%
33.4358	–	12.0018	9.8323

In our case, calculations were performed with the two versions of the UNIFAC model proposed by Larsen *et al.* and Gmehling *et al.* [11, 12] using their established parameters. The obtained deviations showed that the application of this statistical model with original interaction parameters cannot reproduce a good behavior for the studied systems. That can be explained by one of limits of this predictive model established first from molecules of low size. At this stage of difficulty, it is advisable to carry out an adjustment of the interaction parameters by seeking the minimum of an objective function linking the difference between measurements and the computed values

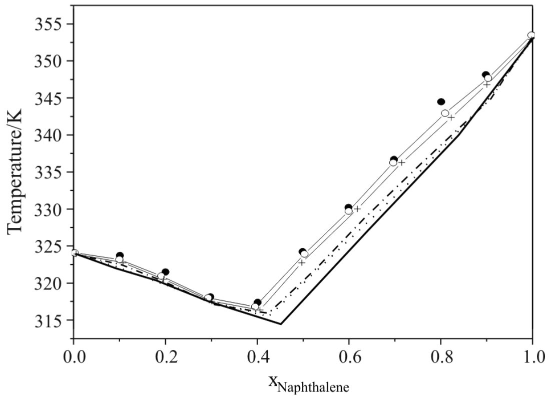

Fig. 4 Solid-liquid phase diagram of naphthalene (1) in solution with *n*-C24 (2); ···· – Gmehling original parameters, –·–· – Larsen original parameters, –+– – a_{12} readjusted (Gmehling), –°–°– – a_{12} readjusted (Larsen), ■ – Points experimental values, solid line: ideal model

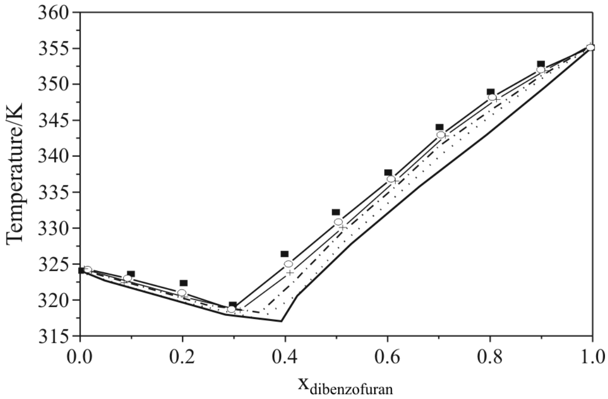

Fig. 5 Solid-liquid phase diagram of dibenzofuran (1) in solution with *n*-C24 (2); ···· – Gmehling original parameters, –·–· – Larsen original parameters, –+– – a_{12} readjusted (Gmehling), –°–°– – a_{12} readjusted (Larsen), ■ – Points experimental values, solid line: ideal model

of the activity coefficients. In our case, the objective function translates clearly the summation of the average standard deviations; it is defined by the relations (12) and (13):

$$F_{0_1} = \left[\frac{1}{n}\sum_{\mathrm{j}}\left(\frac{\gamma^{\mathrm{j}}_{1,\mathrm{exp}} - \gamma^{\mathrm{j}}_{1,\mathrm{cal}}}{\gamma^{1}_{1,\mathrm{exp}}}\right)^2\right] \quad (j=1, 2\ldots, n) \quad (12)$$

$$F_{0_2} = \left[\frac{1}{n}\sum_{\mathrm{j}}\left(\frac{\gamma^{\mathrm{j}}_{2,\mathrm{exp}} - \gamma^{\mathrm{j}}_{2,\mathrm{cal}}}{\gamma^{1}_{2,\mathrm{exp}}}\right)^2\right] \quad (j=1, 2\ldots, n) \quad (13)$$

F_{0_1} and F_{0_2} indicate respectively, the objective functions representing the part rich in aromatic and that rich in aliphatic. The minimization of the total objective function is carried out by means of the simplex procedure. The parametric fitting is carried out on only one parameter of the a_{nm} type. This last is estimated for each pair of groups *n* and *m*; the estimation depends thus on the considered groups. In our case, three types of groups are considered: an aliphatic group, an aromatic group and an ether group [13]. For the latter, we considered two 'types of pairs' of groups (aliphatic-aromatic) and (aliphatic-ether). Dibenzofuran contains oxygen atom in 'ether position' inside the aromatic structure. The energetic interactions parameters obtained after fitting calculations are presented in Table 4 (parameters established by Gmehling *et al.* are 114.20 and 16.07 and those established by Larsen *et al.* are 62.88 and –1.447).

Discussion

As shown by Figs 4 and 5, the systems are strongly non-ideal. Estimations given by Larsen's version are reliable with experimental data. The model modified by Gmehling gave important differences with experimental data and the variations obtained in our case are more significant. Figures 6 and 7 illustrate the evolution of the activity coefficients in liquid phase with positive deviations from the ideal solubility curves.

Parameter a_{ij} was fitted using experimental data of the two considered systems. As it can be seen from Table 3, satisfactory representation of SLE of the investigated systems is obtained. As expected, the fit improved the representation of the dibenzofuran or naphthalene activity coefficients and did not change that of *n*-tetracosane.

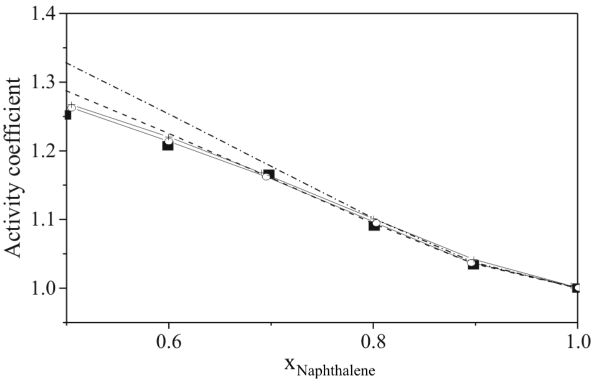

Fig. 6 Evolution of activity coefficients of naphthalene (1) in solution with *n*-C24 (2); ···· – Gmehling original parameters, –·–· – Larsen original parameters, –+– – a_{12} readjusted (Gmehling), –°–°– – a_{12} readjusted (Larsen), ■ – Points experimental values

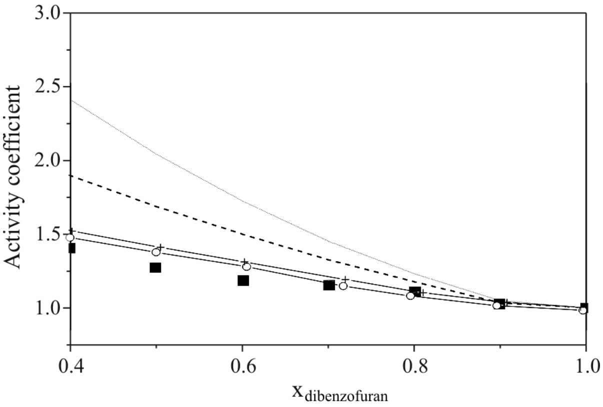

Fig. 7 Evolution of activity coefficients of dibenzofuran (1) in solution with *n*-C24 (2); ···· – Gmehling original parameters, –·–· – Larsen original parameters, –+– – a_{12} readjusted (Gmehling), –°–°– – a_{12} readjusted (Larsen), ■ – Points experimental values

The modified UNIFAC model allowed appreciably the restitution of solubilities for the two considered systems in presence of polar or non polar compound in solution with the normal alkane. The adjustment of interaction parameters in the case of the version established by Weidlich and Gmehling, allowed a clear improvement of the obtained results; the variations decrease from 33 to 12% (Table 3). In our case, UNIFAC modified by Larsen *et al.* with original parameters, gave better results than those obtained using

Table 4 Interaction parameters obtained with fitting a_{12} (dibenzofuran/naphthalene + *n*-C24)

	A(al, ar)	*A*(ar, al)	*A*(al, ether)	*A*(ether, al)
Gmehling *et al.*	68.16	–	173.37	–
Larsen *et al.*	41.27	–	156.15	–

al: CH_3, ar: ACH, ether: ACO instead of HCO

Gmehling modified model. It is worthy to note that the adjustment of the energetic interaction parameters by considering the studied systems, made it possible to correct the shift between the values of calculated solubilities.

Experimental results of SLE of these binaries were used to estimate the influence of the heteroatom on polyaromatic hydrocarbon interactions with the normal alkane. It could be suggested that the introduction of an oxygen atom in ‘ether position’ inside the aromatic structure like dibenzofuran, does not modify significantly the activity coefficients.

Conclusions

Thermodynamic properties of polyaromatics with long chain *n*-alkanes are crucial for understanding phase transformations in heavy reservoir fluids. Phase equilibria of binary mixtures formed by a polyaromatic or a hetero-polyaromatic compound in a long chain normal alkane, were investigated. These systems showed an eutectic behavior. The experimental liquid-solid phase transformation temperatures were compared with predictions obtained from eutectic equilibrium model.

The important conclusion to be drawn from the present study is that activity coefficients of components in the systems containing a long chain *n*-alkane cannot be estimated using the UNIFAC method with energetic interaction parameters determined using experimental data for small molecules. Therefore, it was possible to obtain an interesting representation of these non ideal systems by a readjustment of one of the UNIFAC interaction parameters. Taking account of the original interaction parameters induced a shift between the theoretical values and the experimental results, this shift is decreased by adjusting one of the interaction parameters. In the case of the model UNIFAC modified by Weidlich and Gmehling, the adjustment of the parameters allowed a substantial improvement of the results compared to those calculated using original interaction parameters. However, the version of UNIFAC model suggested by Larsen *et al.*, used with the original parameters, gave better results than that of Gmehling modified model, particularly for the mixtures rich in aromatic.

To improve the effectiveness of the UNIFAC method with present systems, the comparison with existing and currently used versions was necessary. It is interesting to note that the combinatorial part is different with the two models studied; the difference of results between these two versions is due to this phenomenon. Probably both combinatorial models are not adequate in this case, consequently we improved representation modifying one of the interaction parameters.

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