

# Predictive UNIQUAC: A New Model for the Description of Multiphase Solid–Liquid Equilibria in Complex Hydrocarbon Mixtures

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A predictive version of the UNIQUAC model is proposed for the description of the nonideality of paraffinic solid solutions. With this model, and using only pure component properties, is possible to adequately predict the phase behavior of complex hydrocarbon mixtures. Both liquid and solid phase compositions as well as the fraction of crystals in a partly frozen solution show a good agreement with experimental data from different authors. Unlike previous models, predictive UNIQUAC can deal with the multiple solid phases forming in a paraffinic mixture overcoming one of the main limitations of hydrocarbon SLE modeling.

## Introduction

The deposition of paraffinic waxes from hydrocarbon fluids at low temperatures is one of the still unsolved problems experienced today in petroleum industry. It is always present, from the extraction to the use of refined products, is everywhere, from the North Sea to Brazil, and is a harassing and expensive problem. Enough to say that additives to prevent wax formation in diesels are responsible for half the total costs of the additives used.<sup>1</sup> On the other hand, in processes for the production of lubricants, or of commercial waxes, the precipitation of paraffins is promoted. Be it for prevention of wax formation in reservoirs or pipelines, production of fuels of low pour point, lubricants, or the design of new and better additives, a good understanding of the crystallization behavior of the *n*-alkanes, the main constituents of paraffinic waxes, is required. The development of a thermodynamical model able to describe the solid–liquid equilibrium of hydrocarbon solutions is necessary to deal with all the processes involving paraffin crystallization.

The theoretical basis for the description of solid–liquid equilibria is well-known. Nevertheless, the high nonideality of the *n*-alkane solid solutions remains an obstacle to the development of an adequate phase behavior model. A predictive version of the UNIQUAC model is applied to complex mixtures of up to 15 *n*-alkanes in both aliphatic and aromatic solvents. The results show that the model can adequately describe the experimental phase behavior of these mixtures in what concerns the composition of the liquid phase, the global composition of the solid phase, and the fraction of solids in a partly frozen solution. It allows a solid-phase split to develop and the description of the solid–solid–liquid equilibrium that is known to occur in these mixtures. This model provides, thus, a more sound and accurate description of the phase equilibria than the Wilson model that was, up to now, considered the best model for this kind of systems.<sup>2</sup>

## Solid–Liquid Equilibrium Modeling

The general solid–liquid equilibrium equation is well established.<sup>3</sup> It relates, for each component of the mixture, the composition in both phases with the nonideality of the phases and the pure component thermophysical properties:

$$\left( \ln \frac{sy^s}{xy^l} = \frac{\Delta h_m}{RT_m} \left( \frac{T_m}{T} - 1 \right) + \frac{\Delta h_{tr}}{RT_{tr}} \left( \frac{T_{tr}}{T} - 1 \right) - \frac{\Delta_s^1 C_{p_m}}{R} \left( \ln \frac{T}{T_m} + \frac{T_m}{T} - 1 \right) \right)_i \quad (1)$$

Using the heats and temperature of phase transition available in the literature (correlations for these values based in the data by Broadhurst,<sup>4</sup> used in this work, are presented in the Appendix), the composition and the size of the phases in equilibrium can be calculated as a function of the temperature provided that models for the nonideality of the solid and liquid phases are available.

**Liquid-Phase Nonideality.** In liquid hydrocarbon mixtures, the nonideality arises from both entropic effects, such as size difference and free volume effects, and energetic interactions between unlike molecules as aromatics and aliphatics. The activity coefficient model used for the liquid phase can thus be described as

$$\ln \gamma = \ln \gamma^{\text{res}} + \ln \gamma^{\text{comb-fv}} \quad (2)$$

$\ln \gamma^{\text{res}}$  is given by modified UNIFAC<sup>5,6</sup> and describes the energetic interactions between the molecules. The size difference effects and free volume contributions, given by  $\ln \gamma^{\text{comb-fv}}$ , can be described by the Flory free volume equation:<sup>7</sup>

$$\ln \gamma_i^{\text{comb-fv}} = \ln \frac{\phi_i}{x_i} + 1 - \frac{\phi_i}{x_i} \quad \phi_i = \frac{x_i(V_i^{1/3} - V_{wi}^{1/3})^{3.3}}{\sum_j x_j(V_j^{1/3} - V_{wj}^{1/3})^{3.3}} \quad (3)$$

where  $V_i$  is the molar volume, and  $V_{wi}$  is the van der Waals volume of the component  $i$ .

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**Solid-Phase Nonideality.** The paraffins crystallize from solution in an orthorhombic solid phase. Its nonideality was successfully described before with the predictive local composition concept applied to the Wilson equation.<sup>8,9</sup>

The predictive local composition concept allows the "a priori" estimation of the interaction energies used by the local composition models. The pair interaction energies between identical molecules are estimated by relating them to the heat of sublimation from the orthorhombic crystalline phase of the pure component

$$\lambda_{ii} = -\frac{Z}{2}(\Delta h_{\text{sblm}_i} - RT) \quad (4)$$

where  $Z$  is the coordination number (6 for the  $n$ -alkanes orthorhombic crystal). The unlike pair interaction energy is given by<sup>8</sup>

$$\lambda_{ij} = \lambda_{ji} \quad (5)$$

where  $j$  is the  $n$ -alkane with the shorter chain of the pair  $ij$ .

The pair interaction energies calculated by this procedure were previously applied to the Wilson equation<sup>10</sup> in the phase behavior predictions of both simple and complex systems.<sup>2,11</sup> Despite the good results obtained when compared with other models available for these kind of systems, this equation suffers from a well-known inability to predict phase split and thus to model multiphase equilibria. This constitutes an important limitation because it is known that in the SLE of paraffins, multiple solid phases tend to develop.<sup>11</sup> This may actually be one of the explanations for the differences between the experimental and predicted results previously reported for complex mixtures.<sup>2,11</sup> In an attempt to overcome the limitations of Wilson model the method for estimation of pair interaction energies is applied to UNIQUAC.

### Predictive UNIQUAC

The application of the method for estimation of interaction energies to UNIQUAC is not straightforward. Since this model was developed for fluid phases, some adaptations have to be performed to use it with solid phases.

The UNIQUAC model was originally developed by Abrams and Prausnitz.<sup>12</sup> In this work a slightly modified version of UNIQUAC was used:

$$\frac{g^E}{RT} = \sum_{i=1}^n x_i \ln \left( \frac{\Phi_i}{x_i} \right) + \frac{Z}{2} \sum_{i=1}^n q_i x_i \ln \frac{\theta_i}{\Phi_i} - \sum_{i=1}^n x_i q_i \ln \left[ \sum_{j=1}^n \theta_j \exp \left( -\frac{\lambda_{ij} - \lambda_{ii}}{q_i RT} \right) \right] \quad (6)$$

with

$$\Phi_i = \frac{x_i r_i}{\sum_{j=1}^n x_j r_j} \quad \theta_i = \frac{x_i q_i}{\sum_{j=1}^n x_j q_j} \quad (7)$$

There is no good explanation for making  $Z = 2$  in the residual term, but authors using molecular mechan-

ics<sup>13,14</sup> or "ab initio"<sup>15</sup> calculations for estimating the interaction parameters used the same value.

Another issue to be addressed in applying the UNIQUAC model to the solid phase is the evaluation of the structural parameters  $r$  and  $q$ . They were originally defined to be proportional to the van der Waals volume and area of a methylene group.<sup>12</sup> This is reasonable for a fluid phase; however, for a solid phase, the structural parameters should be different. The need to modify the values of the structural parameters appeared before for other systems. Anderson and Prausnitz<sup>16</sup> did it for alcohols to reflect the extent to which the interaction were dominated by the OH group. Donohue and Prausnitz<sup>17</sup> showed that for large molecules the lower the flexibility of the molecule the larger the interaction unit must be. Since in a crystal the flexibility of a molecule is very small, the structural parameters,  $r$  and  $q$ , had to be reestimated.

A simple, yet very empirical, approach was used to define the new interaction unit. Since the  $n$ -alkanes of interest range between C15 and C30, the interaction unit was assumed to be proportional to half the size of the paraffin molecule.<sup>18</sup> An interaction unit with 10 of the "original" methylene units was chosen, and the new  $r$  and  $q$  values are obtained simply by dividing the original  $r$  and  $q$  values by the  $r$  and  $q$  for the 10 methylene units:

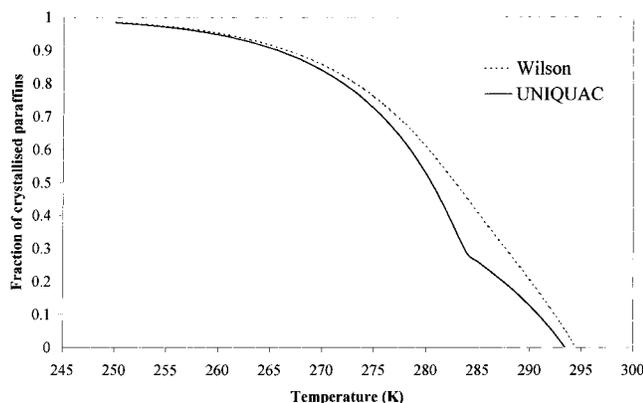
$$r_i = \frac{r_{\text{iorg}}}{6.744} \quad \text{and} \quad q_i = \frac{q_{\text{iorg}}}{5.40} \quad (8)$$

Correlations for the values of  $r_i$  and  $q_i$  are presented in the Appendix.

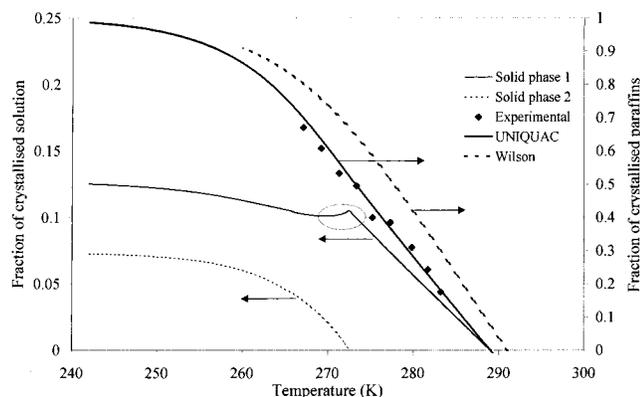
No attempt was done to optimize this value that was found to be satisfactory for the purposes of the work. It is possible that the use of another interaction unit would lead to better results. It is also reasonable to think that solid phases with different composition would optimally require different interaction units, but this would unnecessarily complicate a model that is intended to be simple. Moreover it is difficult to achieve a theoretically sound definition for the values of the structural parameters. Using multiple definitions for them in the same model would introduce a large degree of empiricism and uncertainty in a model wanted to be predictive.

### Results

With the use of the UNIQUAC model it was expected to obtain a phase split in the solid phase and thus to have equilibria with at least three phases (SSLE). To deal with equilibria with three or more phases a multiphase flash algorithm was required. Due to its simplicity, the algorithm of resolution of the Rachford-Rice equations applied to multiphase systems proposed by Leivobici and Neoschil<sup>19</sup> was used in the calculations. It is a very stable algorithm because of its continuity across phase boundaries leading to nonphysical phase amounts for the unstable phases. This is a very useful feature because it allows the use of the algorithm without a phase stability analysis setting a number of phases by excess and decreasing it until all the solutions become physically meaningful; i.e., no phases exist with a negative size or larger than unity. For all the systems considered in this work the higher number of phases found in equilibrium was three, two solid and one liquid phase. It is expected that in more complex mixtures more solid phases will appear.



**Figure 1.** Calculated fraction of crystallized paraffins, using both UNIQUAC and Wilson models, for a mixture of *n*-decane/*n*-eicosane/*n*-tetracontane. UNIQUAC shows an inflection point due to the appearance of a second solid phase.



**Figure 2.** Experimental and predicted fraction of crystallized paraffins for mixture A. The lower lines showing the fraction of crystallized solution in each solid phase present a maximum for solid phase 1 at the appearance of the second solid phase.

The main advantage of the UNIQUAC model over Wilson lies in its capability to predict solid-phase split. It was shown before that the solubility limits due to size differences predicted by the model agree well with the correlations based on experimental data presented by other authors.<sup>18</sup> It also allows the modeling of the eutectic type phase diagrams that are known to appear in the paraffins SLE when their size differences are too large for the development of solid-phase solubility.

The solid-phase split predicted by the model helps not only to improve the modeling results but also to understand some peculiar features of the experimental data further supporting the idea that they are caused by the deposition of a new solid phase. In Figure 1 is shown how the appearance of a second solid phase induces an inflection point in the UNIQUAC calculated curve of the fraction of crystallized paraffins in a partly frozen solution for a ternary mixture of *n*-decane/*n*-eicosane/*n*-tetracontane (composition 80%/14%/6% w/w). No inflection point is present in the Wilson curve where a single solid phase is calculated. This inflection point is identical to what was experimentally found by DSC measurements in mixtures A and B.<sup>11</sup> While too light too be seen, the second derivative of the predicted  $\alpha$  curve for mixtures A and B also indicates the presence of this inflection point due to the crystallization of a second solid phase. It is interesting to notice, as shown in Figure 2 for mixture A, that, according to the model, with the appearance of the second solid phase the crystallization takes place mostly in this second phase

**Table 1.** Composition (Mass %) of the Paraffin Solutions

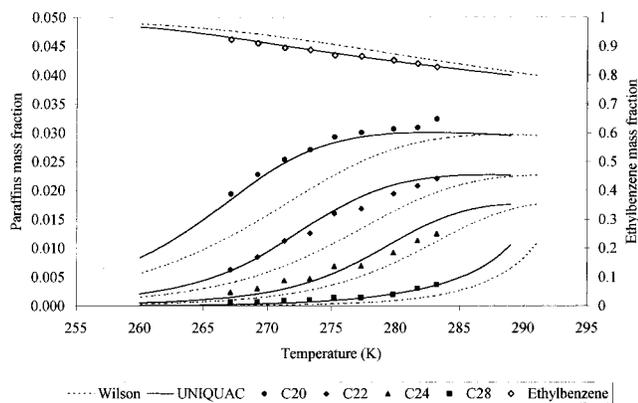
	mixture A <sup>a</sup>	mixture B <sup>a</sup>	mixture C <sup>b</sup>	mixture E <sup>b</sup>	mixture F <sup>b</sup>
ethylbenzene	79.95	76.75			
fluorene		3.998			
<i>n</i> -C10			64.73	64.72	65.02
<i>n</i> -C18				4.84	3.55
<i>n</i> -C19	3.340	3.207		4.33	3.55
<i>n</i> -C20	2.954	2.836	10.30	3.87	3.56
<i>n</i> -C21	2.565	2.463	7.40	3.48	3.55
<i>n</i> -C22	2.266	2.176	5.29	3.13	3.53
<i>n</i> -C23	2.000	1.918	3.79	2.81	3.51
<i>n</i> -C24	1.760	1.690	2.70	2.51	3.48
<i>n</i> -C25	1.541	1.480	1.93	2.24	3.45
<i>n</i> -C26	1.364	1.310	1.37	2.01	3.41
<i>n</i> -C27	1.198	1.152	0.97	1.79	3.39
<i>n</i> -C28	1.062	1.020	0.69	1.62	
<i>n</i> -C29			0.49	1.41	
<i>n</i> -C30			0.35	1.25	

<sup>a</sup> Coutinho and Ruffier-Meray (1997).<sup>11</sup> <sup>b</sup> Pauly et al. (1998).<sup>2</sup>

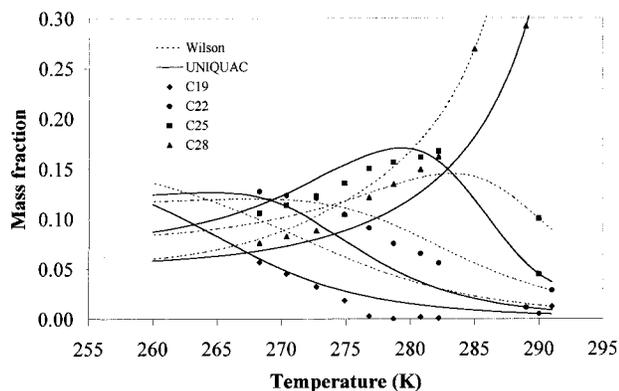
with the heavier solid-phase growing much slower. This curious behavior is the responsible for the inflection point at the appearance of a second solid phase. This result seems to indicate that the inflection points presented by Pedersen et al.<sup>20</sup> in NMR results for North Sea oils may be due to the crystallization of multiple solid phases and not just to the scatter of experimental data. Also worth noticing is the maximum presented by solid-phase 1. With the appearance of the second solid phase a part of the lighter compounds of the first solid phase "moves" from the old to the new solid phase. This is explained by the lower value of the excess free energy that some of the components have in this new phase. While no experimental data for SSLE exist to support it, this seems to be a physically meaningful behavior since something similar is known to occur for VLE when a new phase appears.

Only recently data for multicomponent hydrocarbon mixtures with defined compositions become available. A couple of years ago when predictive Wilson was proposed for modeling the solid paraffin phase only ternary data existed.<sup>9</sup> Today it is possible to collect a few sets of data for multicomponent systems in both aromatic and aliphatic solvents.<sup>2,11</sup> The phase behavior predictions by UNIQUAC and Wilson models are compared against experimental data for five mixtures which composition are presented in Table 1. The mixtures have between 10 and 13 paraffins in both aromatic (ethylbenzene) and aliphatic (*n*-decane) solvents. One of the mixtures (mixture B) besides the paraffins has also a heavy aromatic compound in solution (fluorene). The amount of paraffins in solution ranges from 20% to 35% (mass) covering the range of a great deal of waxy fluids. The paraffins distribution in solution covers also a wide number of possible real systems. Nevertheless some important experimental information is still missing. Mixtures with a continuous distribution of paraffins between the solvent and the solutes would allow one to evaluate the range of crystallizing paraffins, and data for the composition of the multiple solid phases in equilibrium are not available. Yet the results reported below indicate that the model should be able to deal with real mixtures with a good degree of accuracy.

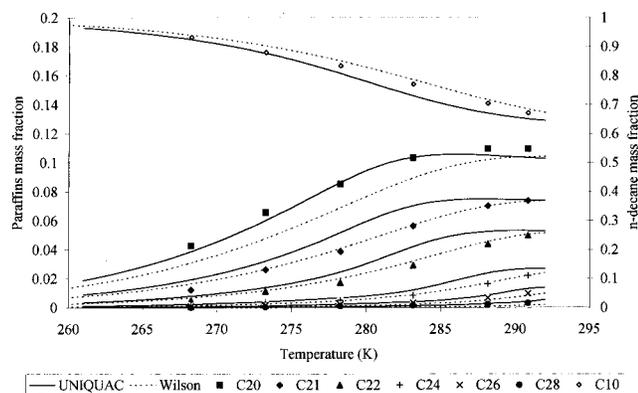
Results of the predictions obtained using UNIQUAC and Wilson models are compared with experimental data in Figures 2–7. To make the figures readable and given their similarity, only selected results for some of the compounds are presented for each mixture. The



**Figure 3.** Experimental and predicted results for the liquid-phase composition of mixture A.



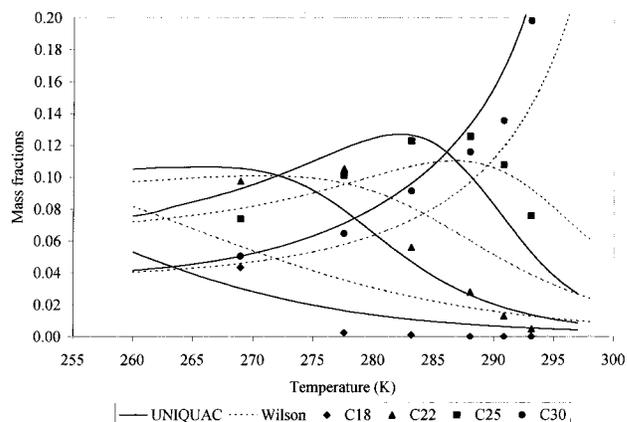
**Figure 4.** Experimental and predicted results for the global solid-phase composition of mixture B.



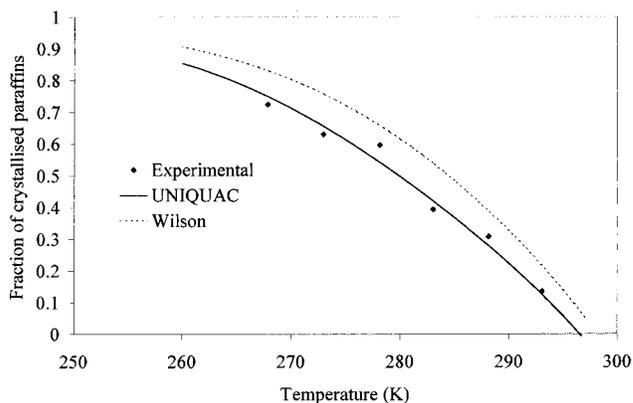
**Figure 5.** Experimental and predicted results for the liquid-phase composition of mixture C.

solid-phase compositions are the composition of the global solid phase since no data for the composition of the individual solid phases were available. Both liquid phase and global solid-phase compositions as well as the fraction of crystallized paraffins in a partly frozen solution are shown.

The results for mixture B shown in Figure 3 indicate that the presence of heavy compounds that do not coprecipitate with the paraffins, as is the case of the fluorene present in this mixture, do not influence the modeling results. While not presented because fluorene does not precipitate within the temperature range studied, the model can easily accommodate an extra solid phase for it or for other heavy compounds present in the mixture that do not cocrystallize with the paraf-



**Figure 6.** Experimental and predicted results for the global solid-phase composition of mixture D.

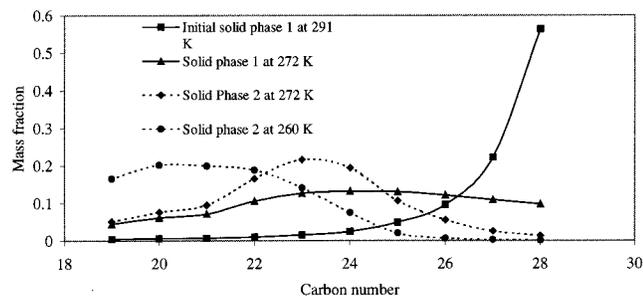


**Figure 7.** Experimental and predicted results for the fraction of crystallized paraffins for mixture E.

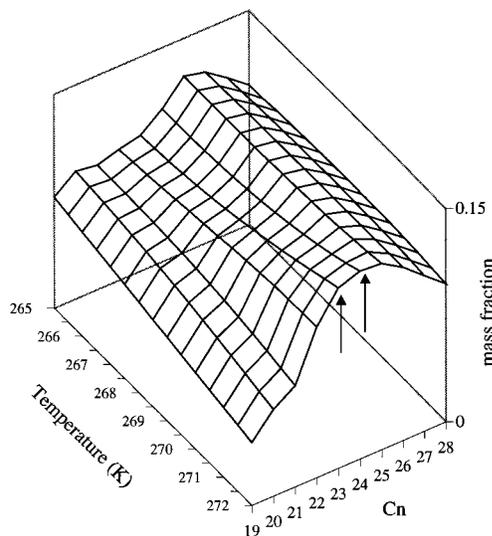
ins; however, the local composition parameter estimation procedure presented in eqs 4 and 5 cannot be used for their description.

The results clearly demonstrate the superiority of the UNIQUAC over the Wilson model. While in some cases the latter can perform better for the composition of some intermediate compounds or in a narrow temperature range, such as for mixture C presented in Figure 5, the global behavior of UNIQUAC model is much superior and quite impressive if you think that these are purely predictive results where only pure component information is used. There is no good explanation for the fact that mixture C behaves so differently than mixtures A or B since the paraffin distribution for these three mixtures is identical.

Globally the UNIQUAC model can provide an accurate description of the composition of the phases in equilibrium and the fraction of solids precipitated in both aromatic and aliphatic solvents. More comparisons with experimental data are, however, required to provide an insight on the model limitations. For the moment the most important problem found is related with the solid-phase compositions. The experimental evidence is not very strong, but it seems to indicate that the light compounds start to precipitate only with the appearance of a second solid phase. This is clear in Figures 4 and 6. Nevertheless the model predicts a crystallization of the light compounds with the first solid phase, although in small quantities, leading in all cases to an overestimation of the composition of the light compounds in the solid phase. Simultaneously, while difficult to evaluate due to the lack of data, the tem-



**Figure 8.** UNIQUAC-10 predictions for the evolution of the composition of the solid phases with temperature for mixture A.



**Figure 9.** Model predictions for the evolution of composition of solid-phase 1 with temperature after the appearance of a second solid phase showing the decrease in composition of C23 and C24 with temperature for mixture A.

**Table 2. Group Values for the Estimation of the *n*-Alkane Structural Parameters<sup>6</sup>**

group	$r_i$	$q_i$
CH <sub>3</sub>	0.9011	0.848
CH <sub>2</sub>	0.6744	0.540

perature of appearance of the second solid phase seems to be somehow underestimated.

In some practical applications it may be important to achieve an very precise description of the experimental data available. This can be done within the framework of the proposed model. A binary interaction parameter can be introduced into eq 5 giving an extra flexibility to the model at the price of the loss of its predictive character.<sup>8</sup> This interaction parameter can be shown to be essentially identical to the binary interaction parameter used with the regular solution theory.

The evolution of the composition of the solid phases with temperature is shown in Figure 8 for mixture A. The first crystal is, as expected, very rich in the heavy paraffins, and as solid deposition progresses, an enrichment in light components occur. When the second solid phase makes its appearance it is rich in middle components, part of which, as discussed previously "migrated" from the first solid phase. Then, gradually, the phase becomes richer in light components as they start to crystallize with the decreasing temperature. This migration of compounds from the heavy to the lower phase is well described by Figure 9, where it is shown

the composition evolution of solid phase 1 with the temperature with the appearance of the second solid phase. Unlike the heavy compounds, for which the composition is very much constant, for *n*-tricosane and *n*-tetracosane, that are the compounds for which the second phase is richer, the composition clearly decreases with the development of the second solid phase.

## Conclusions

A predictive version of the UNIQUAC equation is proposed to model the solid phase nonideality of paraffinic mixtures. The results presented show that this model performs better than Wilson, adequately predicting the phase behavior for complex hydrocarbon mixtures in both aliphatic and aromatic solvents. It also overcomes one of the main limitations of the Wilson model since it can deal with multiphase equilibria that are known to arise in complex hydrocarbon mixtures. The mixtures used cover a wide range of paraffin distributions and composition. Nevertheless the model needs a more extensive testing against experimental data to find its limitations and shortcomings. There is a result particularly worth noticing concerning the inflection points in the deposit curves. The model indicates that they are related to the appearance of a new solid phase.

The results obtained in this work indicate that the proposed model is probably the best model available for this kind of mixtures. It is not limited to these synthetic mixtures but should be able to describe the wax formation in real fluids such as diesels and fuels or to be used in the modeling of deparaffination processes for lubricant production.

## Appendix

**Structural Parameters.** The  $r$  and  $q$  values used in the original UNIQUAC can be estimated by a group contribution method.<sup>6</sup> The group values for *n*-alkanes are presented in Table 2. Since a (CH<sub>2</sub>)<sub>10</sub> chain is used as interaction unit, the structural parameters obtained from the original values are divided by the  $r$  and  $q$  values for 10 CH<sub>2</sub> units, thus the values of 6.744 and 5.40 of eq 8. For an *n*-alkane with  $n$  carbon atoms

$$r_n = 0.1C_n + 0.0672 \quad (\text{A.1})$$

$$q_n = 0.1C_n + 0.1141 \quad (\text{A.2})$$

**Thermophysical Properties.** The solid phases for both odd and even *n*-alkanes are postulated to be orthorhombic phases that undergo a solid–solid transition to a rotator phase before melting.<sup>8,9</sup> The temperatures of phase transition used are obtained from a correlation of the values of Broadhurst<sup>4</sup> proposed by Lindeloff:<sup>21</sup>

$$T_m [\text{K}] = 0.0091x^3 - 0.7636x^2 + 23.775x + 66.968 \quad (\text{A.3})$$

$$T_{tr} [\text{K}] = 0.0041x^3 - 0.4483x^2 + 17.876x + 89.288 \quad (\text{A.4})$$

The heats of sublimation are considered to be temperature independent and calculated at the temperature of melting of the normal alkane. They are obtained by adding the heats of vaporization, melting, and solid–solid transition. The heats of melting and solid-phase

transition used are the correlations proposed by Lindeloff<sup>21</sup> from the Broadhurst<sup>4</sup> values:

$$\Delta h_{\text{sblm}} = h_{\text{vap}} + h_{\text{m}} + h_{\text{tr}} \quad (\text{A.5})$$

$$\Delta h_{\text{m}} [\text{kJ/mol}] = 0.0034x^3 - 0.2318x^2 + 7.3261x - 34.532 \quad (\text{A.6})$$

$$\Delta h_{\text{tr}} [\text{kJ/mol}] = -0.005x^3 + 0.3475x^2 - 6.1759x + 39.77 \quad (\text{A.7})$$

The heats of vaporization are estimated using the Morgan and Kobayashi model.<sup>22</sup>

## Nomenclature

$g$  = Gibbs free energy  
 $h$  = enthalpy  
 $q$  = UNIQUAC structural parameter  
 $r$  = UNIQUAC structural parameter  
 $R$  = universal gas constant  
 $s$  = solid-phase molar fraction  
 $T$  = temperature  
 $V$  = molar volume  
 $V_w$  = van der Waals volume  
 $x$  = liquid-phase molar fraction  
 $Z$  = coordination number

### Greek Letters

$\alpha$  = fraction of crystallized material  
 $\gamma$  = activity coefficient  
 $\lambda$  = pair interaction energy

### Subscripts

$i$  = component  $i$   
 $j$  = component  $j$   
 $m$  = melting  
 $\text{sblm}$  = sublimation  
 $\text{tr}$  = solid-phase transition

### Superscripts

$E$  = excess property  
 $l$  = liquid  
 $s$  = solid

## Literature Cited

- (1) Pipenger, G. Making "premium" diesel fuel. *Hydrocarbon Process.* **1997**, *2*, 63.
- (2) Pauly, J.; Dauphin, C.; Daridon, J. L. Liquid-Solid equilibria in a decane + multi-paraffins system. *Fluid Phase Equilib.* **1998**, *149*, 173.
- (3) Prausnitz, J. M.; Lichtenthaler, R. N.; Azevedo, E. G. *Molecular Thermodynamics of Fluid-Phase Equilibria*; 2nd ed.; Prentice Hall: Englewood Cliffs, NJ, 1986.
- (4) Broadhurst, M. G. An analysis of the solid phase behaviour of the normal paraffins. *J. Res. Nat. Bur. Stand.* **1962**, *66A*, 241.

(5) Fredenslund, Aa.; Gmehling, J.; Rasmussen, P. *Vapor-liquid Equilibria Using UNIFAC. A Group-Contribution Method*; Elsevier Scientific: Amsterdam, 1977.

(6) Larsen, B. L.; Rasmussen, P.; Fredenslund, Aa. A modified UNIFAC group-contribution model for prediction of phase equilibria and heats of mixing. *Ind. Eng. Chem. Res.* **1987**, *26*, 2274.

(7) Coutinho, J. A. P.; Andersen, S. I.; Stenby, E. H. Evaluation of activity coefficient models in prediction of alkane solid-liquid equilibria. *Fluid Phase Equilib.* **1995**, *103*, 23.

(8) Coutinho, J. A. P.; Knudsen, K.; Andersen, S. I.; Stenby, E. H. A local composition model for paraffinic solid solutions. *Chem. Eng. Sci.* **1996**, *51*, 3273.

(9) Coutinho, J. A. P.; Stenby, E. H. Predictive local composition models for solid-liquid and solid-solid equilibrium in  $n$ -alkanes: Wilson equation for multicomponent systems. *Ind. Eng. Chem. Res.* **1996**, *35*, 918.

(10) Wilson, G. M. Vapor-Liquid equilibrium. XI. A new expression for the excess free energy of mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127.

(11) Coutinho, J. A. P.; Ruffier-Meray, V. Experimental measurements and thermodynamical modelling of paraffinic wax formation in undercooled solutions. *Ind. Eng. Chem. Res.* **1997**, *36*, 4977.

(12) Abrams, D. S.; Prausnitz, J. M. Statistical thermodynamics of liquid mixtures: A new expression for the excess Gibbs energy of partly or completely miscible systems. *AIChE J.* **1975**, *21*, 116.

(13) Jónsdóttir, S. O.; Rasmussen, K.; Fredenslund, Aa. UNIQUAC parameters determined by molecular mechanics. *Fluid Phase Equilib.* **1994**, *100*, 121.

(14) Jonsdottir, S. O.; Klein, R. A. UNIQUAC interaction parameters for molecules with -OH groups on adjacent carbon atoms in aqueous solution determined by molecular mechanics-glycols, glycerol, and glucose. *Fluid Phase Equilib.* **1997**, *132*, 117.

(15) Sum, A. K.; Sandler, S. I. Application of Ab Initio methods to phase equilibria predictions using activity coefficient models. *Fluid Phase Equilib.*, in press.

(16) Anderson, T. F.; Prausnitz, J. M. *Ind. Eng. Chem. Process Des. Dev.* **1978**, *17*, 561.

(17) Donohue, M. D.; Prausnitz, J. M. Combinatorial entropy of mixing molecules that differ in size and shape. A simple approximation for binary and multicomponent mixtures. *Can. J. Chem.* **1975**, *53*, 1586.

(18) Coutinho, J. A. P. Predictive local composition models: NRTL and UNIQUAC and their application to model solid-liquid equilibrium of  $n$ -alkanes. *Fluid Phase Equilib.*, in press.

(19) Leibovici, C. F.; Neoschil, J., A solution of Rachford-Rice equations for multiphase systems. *Fluid Phase Equilib.* **1995**, *112*, 217.

(20) Pedersen, W. B.; Hansen, A. B.; Larsen, E.; Nielsen, A. B.; Ronningsen, H. P. Wax precipitation from North-Sea crude oils: 2. Solid-Phase content as function of temperature determined by pulsed NMR. *Energy Fuels* **1991**, *5*, 908.

(21) Lindeloff, N. Formation of Solid Phases in Hydrocarbon Mixtures. M.Sc. Dissertation, Technical University of Denmark, Lyngby, 1996.

(22) Morgan, D. L.; Kobayashi, R. Extension of Pitzer CSP models for vapor pressures and heats of vaporisation to long chain hydrocarbons. *Fluid Phase Equilib.* **1994**, *94*, 51.

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