

Paraffin crystallization in synthetic mixtures: Predictive local composition models revisited

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Abstract

Aiming at identify the shortcomings of the available models for the description of the solid phase non-ideality, new solid liquid equilibrium data for multicomponent hydrocarbon systems was measured. The Predictive UNIQUAC and Wilson models for the description of the solid phase non-ideality, previously proposed, are here compared against this new data. The weaknesses displayed by these models on the predictive description of the measured phase behavior helps to identify their limitations and this is expected to lead to a new improved model for the solid phase non-ideality. Following this approach a new UNIQUAC based model is proposed that seems to overcome the limitations of the models identified on this work.

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1. Introduction

The development of predictive local composition models for the description of wax formation in hydrocarbon fluids [1–19] lead to a highly successful tool for the description of wax formation in diesels and fuels [7–10,15,16] and dead and live oils [11,13,14,17,19]. Yet the time and experience of various users brought to light some limitations and some behaviors not always well understood. With the acquired experience it is now possible to revisit these models and try to identify and better understand the models' limitations and develop strategies to overcome their problems. For this purpose new data was collected, and modeled to shed new light over the solid phase models, since only on well-defined systems with good quality data can the model deficiencies be pinpointed for future correction. This approach was started in a previous paper recently published for systems with three paraffins in a solvent [20] and is here extended to somewhat

more complex systems of five paraffins in a solvent. The new data were expected to bridge the gap between the very simple systems with one or two paraffins in a solvent [2,3] and complex systems with 10 or more paraffins and complex distributions previously reported by us [3,6,21]. One of the anomalous situations previously identified was that although Predictive modified UNIQUAC was much better than Wilson for complex mixtures [4–6], for simple mixtures Wilson provided better predictions. This odd behavior still holds for the mixtures previously studied [20] and, as will be shown, for the mixtures reported on this paper. Another important limitation relates to the overestimation of the crystallization of light compounds in mixtures. This is particularly clear in this paper for mixture B where octadecane precipitation just below the cloud point is predicted by both models. Although this was expected from Wilson that cannot predict phase split, and thus all the compounds must be present in the solid phase formed, it was unexpected from the modified UNIQUAC.

A new version of the UNIQUAC model for the description of the solid phase non-ideality, where the Z , r and q

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parameters are those of original UNIQUAC is here used and it will be compared against the experimental data measured in this work.

2. Experimental

2.1. Phase equilibria measurements

The experimental measurements carried out in this work followed the methodology previously developed by us to measure solid liquid phase equilibria in hydrocarbon fluids [3]. Two mixtures of five paraffins which concentration is reported in Tables 1 and 2 were prepared using Fluka or Aldrich paraffins with a purity degree >99% without further purification. Ethylbenzene was supplied by Aldrich (purity of 99.8%) and a molecular sieve was used to guarantee the dryness of the solvent.

The method used to characterize the solid liquid phase equilibria consists of separating the precipitate and liquid phases by filtration at controlled temperature and analyzing the phases by gas chromatography. The phase separation is achieved using Autovial syringeless filters from Whatman of 12 mL capacity with filters of 0.45 μm porosity. The paraffin mixtures prepared are distributed by 10 Autovials, which are introduced on a thermostatic bath where the samples are equilibrated at an established temperature for 24 h before separation. When the filtration is completed, the two phases recovered are weighed and analyzed using gas phase chromatography on a Varian 6890 chromatograph equipped with an on-column injector and a 50 mm \times 0.53 mm Chromapack

CP-wax 52 CB capillary column, with a temperature program of 3 K/min from 50 to 320 $^{\circ}\text{C}$.

After the filtration only the composition of the liquid phase (L) can be determined accurately directly. The solid phase (S), which is made up of multiple crystals, keeps part of the liquid entrapped in the crystals after the filtration. The filtration residue (SR) corresponds to a mixture of the solid phase (S) and of the trapped liquid (LT). Since in the systems studied the solvent is much lighter than the heavy fraction, the proportion of liquid trapped in the solid phase can be determined from the quantity of solvent measured in the solid residue using the following procedure previously proposed by us [6,7,21]: The presence of solvent in the filtration residue results from the existence of the trapped liquid. As the exact composition of the liquid phase is known from chromatography it is possible to calculate the total amount of entrapped liquid using:

$$w^{\text{LT}} = \frac{w_{\text{solvent}}^{\text{SR}}}{w_{\text{solvent}}^{\text{L}}} \quad (1)$$

in which $w_{\text{solvent}}^{\text{SR}}$ and $w_{\text{solvent}}^{\text{L}}$ correspond to the mass fraction of solvent analyzed in the two parts recovered after filtration. The quantity of solid crystallized (expressed in mass fraction) can thus be corrected by

$$w^{\text{S}} = w^{\text{SR}}(1 - w^{\text{LT}}) \quad (2)$$

The real composition of the solid phase being given by

$$w_i^{\text{S}} = \frac{w_i^{\text{RS}} - w^{\text{LT}} X_i^{\text{L}}}{1 - w^{\text{LT}}} \quad (3)$$

for any compound i in the heavy fraction.

Table 1

Mass fractions for the liquid and solid phases of mixture A

T (K)	W_{EB}	W_{C18liq}	W_{C18sld}	W_{C19liq}	W_{C19sld}	W_{C20liq}	W_{C20sld}	W_{C21liq}	W_{C21sld}	W_{C22liq}	W_{C22sld}
>WAT	0.8060	0.04925		0.04408		0.03869		0.03262		0.02932	
274.9	0.8339	0.04851	0.0609	0.04052	0.1387	0.03213	0.2320	0.02437	0.2821	0.02058	0.2863
273.7	0.8478	0.04735	0.0915	0.03785	0.1708	0.02872	0.2349	0.02107	0.2527	0.01724	0.2500
272.2	0.8604	0.04634	0.0797	0.03564	0.1631	0.02572	0.2338	0.01793	0.2583	0.01397	0.2651
270.8	0.8739	0.04525	0.0917	0.03299	0.1735	0.02229	0.2348	0.01463	0.2495	0.01092	0.2505
269.2	0.8883	0.04349	0.1043	0.02982	0.1847	0.01873	0.2365	0.01147	0.2405	0.00816	0.2340
267.7	0.8924	0.04326	0.1053	0.02905	0.1857	0.01761	0.2366	0.01041	0.2397	0.00726	0.2327
266.2	0.9047	0.04013	0.1246	0.02553	0.1990	0.01490	0.2362	0.00870	0.2270	0.00605	0.2132
264.4	0.9140	0.03773	0.1354	0.02319	0.2004	0.01293	0.2314	0.00724	0.2220	0.00489	0.2108

Table 2

Mass fractions for the liquid and solid phases of mixture B

T (K)	W_{EB}	W_{C18liq}	W_{C18sld}	W_{C24liq}	W_{C24sld}	W_{C25liq}	W_{C25sld}	W_{C26liq}	W_{C26sld}	W_{C27liq}	W_{C27sld}
>WAT	0.8064	0.0297		0.0491		0.0416		0.0395		0.0337	
293.6	0.8410	0.0292	0.0070	0.0430	0.1891	0.0335	0.2371	0.0294	0.2866	0.0238	0.2803
291.1	0.8655	0.0302	0.0021	0.0381	0.2004	0.0273	0.2419	0.0220	0.2839	0.0169	0.2717
288.7	0.8884	0.0305	0.0046	0.0328	0.2062	0.0213	0.2446	0.0158	0.2799	0.0113	0.2636
286.2	0.9051	0.0315	0.0006	0.0279	0.2268	0.0165	0.2524	0.0112	0.2739	0.0077	0.2463
283.7	0.9207	0.0326	0.0035	0.0221	0.2375	0.0119	0.2516	0.0076	0.2670	0.0051	0.2403
281.1	0.9310	0.0336	-0.0032	0.0174	0.2522	0.0089	0.2548	0.0055	0.2626	0.0036	0.2336
279.2	0.9403	0.0315	0.0033	0.0145	0.2605	0.0069	0.2547	0.0041	0.2567	0.0027	0.2248
277.3	0.9462	0.0322	0.0008	0.0116	0.2674	0.0052	0.2554	0.0030	0.2545	0.0019	0.2220
275.3	0.9503	0.0326	-0.0001	0.0096	0.2699	0.0040	0.2551	0.0021	0.2538	0.0013	0.2213

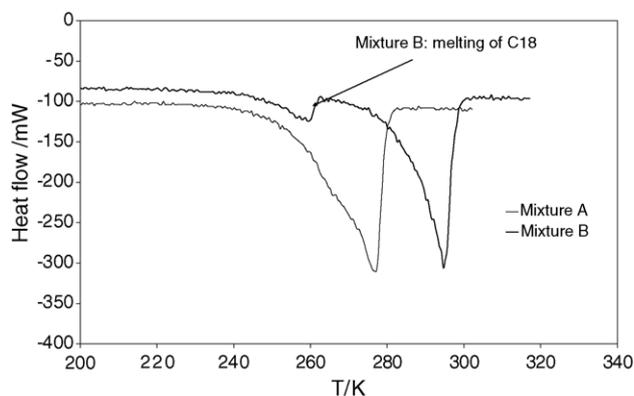


Fig. 1. Thermograms for the two mixtures studied.

2.2. DSC

The calorimetric measurements were performed in a Setaram DSC 141. The sample was cooled to 140 K, kept at that temperature for 15 min to stabilize, and then heated up to 320 K at 3 K/min. A run is shown in Fig. 1 for each mixture studied. They are similar to other DSC measurements for complex mixtures previously reported by us [3,9] except for the crystallization peak of the C18 for mixture B. The assessment of the fraction of paraffins crystallizing with temperature followed the approach previously proposed and detailed elsewhere [3,9].

3. Model

Solid–Liquid equilibrium can be described by an equation relating the composition of component i in the solid and liquid phases with their non-ideality and the thermophysical properties of the pure component [22]:

$$\ln \frac{x_i^s \gamma_i^s}{x_i^l \gamma_i^l} = \frac{\Delta_{\text{fus}} H_i}{RT_{\text{fus},i}} \left(\frac{T_{\text{fus},i}}{T} - 1 \right) + \frac{\Delta_{l2} H_i}{RT_{l2,i}} \left(\frac{T_{l2,i}}{T} - 1 \right) \quad (4)$$

The heats and temperatures of phase transition are obtained from correlations previously proposed [23] based on the values by Broadhurst [24] for the n -alkanes with an odd carbon number chain length. Since the solid phase is orthorhombic [2–6,25–30] the properties for the even numbered chain length paraffins are obtained by interpolating the values for the odd numbered alkanes. From Eq. (4), the composition and the amount of the phases in equilibrium can be calculated if a model for the non-ideality of the phases is available.

3.1. The liquid phase non-ideality

In liquid hydrocarbon mixtures, the non-ideality arises both from entropic effects such as size difference and free volume effects, and energetic interactions between unlike molecules as aromatics and aliphatics. The activity coeffi-

cient model used for the liquid phase is thus:

$$\ln \gamma = \ln \gamma^{\text{res}} + \ln \gamma^{\text{comb-fv}} \quad (5)$$

where $\ln \gamma^{\text{res}}$ is given by modified UNIFAC [31] and describes the energetic interactions between the aromatic and aliphatic molecules. The combinatorial and free volume effects resulting from the size difference between the molecules will be here described by the Flory-free volume model [32]:

$$\ln \gamma_i^{\text{comb-fv}} = \ln \frac{\phi_i}{x_i} + 1 - \frac{\phi_i}{x_i}, \quad \text{with} \quad (6)$$

$$\phi_i = \frac{x_i (V_i^{1/3} - V_{wi}^{1/3})^{3.3}}{\sum_j x_j (V_j^{1/3} - V_{wj}^{1/3})^{3.3}}$$

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

3.2. The solid phase non-ideality – predictive local composition models

The solid phase non-ideality will be described by Wilson [33] and UNIQUAC [34] local composition models.

The Wilson equation used in this work can be written as

$$\frac{g^E}{RT} = - \sum_{i=1}^m x_i \ln \left[\sum_{j=1}^m x_j \exp \left(- \frac{\lambda_{ij} - \lambda_{ii}}{RT} \right) \right] \quad (7)$$

and the UNIQUAC model as

$$\frac{g^E}{RT} = \sum_{i=1}^n x_i \ln \left(\frac{\Phi_i}{x_i} \right) + \frac{Z}{2} \sum_{i=1}^n q_i x_i \ln \frac{\theta_i}{\Phi_i} - \sum_{i=1}^n x_i q_i \ln \left[\sum_{j=1}^n \theta_j \exp \left(- \frac{\lambda_{ij} - \lambda_{ii}}{q_i RT} \right) \right] \quad (8)$$

with

$$\Phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \quad \text{and} \quad \theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \quad (9)$$

Two version of the UNIQUAC model will be used here. One where the structural parameters used, $r_{i\text{org}}$ and $q_{i\text{org}}$, are obtained directly from the UNIFAC parameter table [31], named UNIQUAC, and another with the definition for the structural parameters r and q previously proposed [4,5,23], subsequently named modified UNIQUAC:

$$r_i = \frac{r_{i\text{org}}}{6.744} = 0.1C_{ni} + 0.0672 \quad (10)$$

$$q_i = \frac{q_{i\text{org}}}{5.40} = 0.1C_{ni} + 0.1141 \quad (11)$$

The predictive local composition concept [2,4,5,23] allows the estimation of the interaction energies, λ_{ij} , used by these models without fitting to experimental data. The pair interaction energies between two identical molecules are estimated

from the heat of sublimation of an orthorhombic crystal of the pure component:

$$\lambda_{ii} = -\frac{2}{Z}(\Delta_{\text{sub}}H_i - RT) \quad (12)$$

where Z is the coordination number, a value of the coordination number of 6 will be used for the Wilson [2,23] and modified UNIQUAC [4,5,23] and 10 for UNIQUAC [31,34]. The heats of sublimation are calculated at the melting temperature of the pure component. The heat of vaporisation, $\Delta_{\text{vap}}H$, is assessed using a correlation by Morgan and Kobayashi [35] and the heats of phase transition are obtained from the correlations mentioned above [23].

The pair interaction energy between two non-identical molecules is given by

$$\lambda_{ij} = \lambda_{ji} = \lambda_{jj} \quad (13)$$

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

The Solid–liquid equilibrium model is thus a purely predictive model that uses in the calculation of the phase behavior only pure component properties. The three models here described will be used to predict the phase equilibrium data measured for the two mixtures studied on this work. Two of these models, Wilson and modified UNIQUAC, have previously been used for prediction of wax formation in hydrocarbon fluids [1–20], and are being evaluated on this work to identify their limitations. The third model, UNIQUAC, will here be used for the first time for describing the solid phase non-ideality and is under investigation to attempt overcoming the shortcomings of the previous models.

4. Discussion of results

Experimental data for the composition of the liquid and solid phases for mixtures A and B for a series of partially frozen mixtures at temperatures below the cloud point are reported in Tables 1 and 2. The concentration of the octadecane (C18) in the liquid phase of mixture B slightly increases while for the solid phase it shows a zero concentration within the experimental uncertainty (negative values may appear since the solid phase is obtained indirectly from Eqs. (1) to (3); experimental uncertainty associated to the composition values produces a fluctuation of the solid phase composition around its true value of zero leading, in some cases, to apparently negative concentrations). These data support the idea, also conveyed by the thermogram presented in Fig. 1, that, unlike for mixture A where the octadecane always precipitates from solution below the cloud or wax appearance point (WAT), the octadecane in mixture B only starts precipitating at temperatures well below the WAT. The difference in size between C18 and the heavier n -alkanes does not allow it to co-precipitate with these. The performance of the models studied on this work in the prediction of the evolution of the composition of the liquid and solid phases with temperature is presented in Figs. 2–5. To avoid jamming the fig-

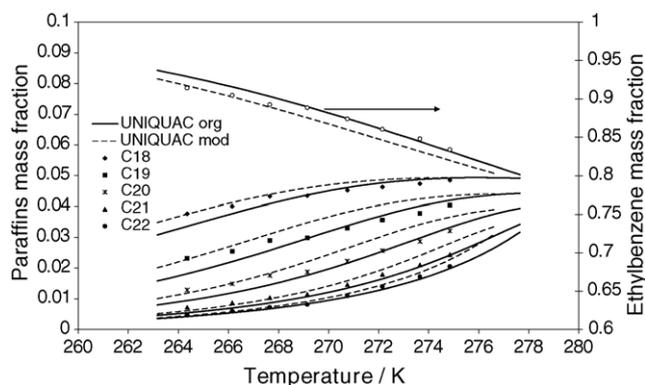


Fig. 2. Liquid phase compositions for mixture A.

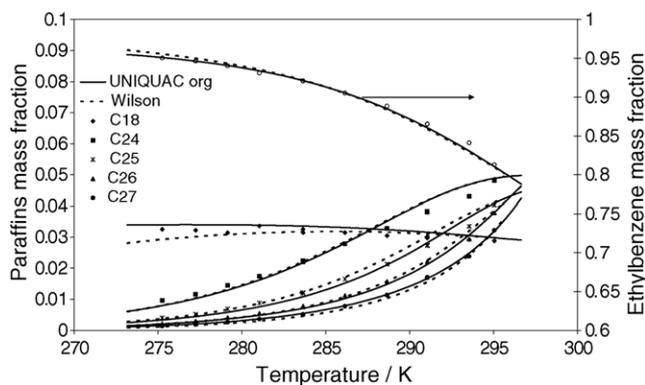


Fig. 3. Liquid phase compositions for mixture B.

ures with results data for mixture A is used to compare the two UNIQUAC versions studied, and UNIQUAC is evaluated against Wilson on the data for mixture B. Although it was previously shown [4–6,10] that modified UNIQUAC is better than Wilson for complex mixtures, these six compounds mixtures do not seem to be complex enough for the advantages of the modified UNIQUAC to emerge. In fact, as is manifest in all the results obtained for these mixtures, modified UNIQUAC predictions provide only a fair description of the experimental data measured. The description of the data is much superior when using Wilson as shown in previous

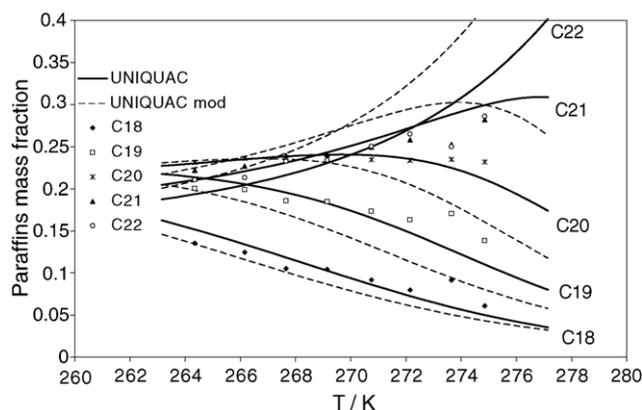


Fig. 4. Solid phase compositions for mixture A.

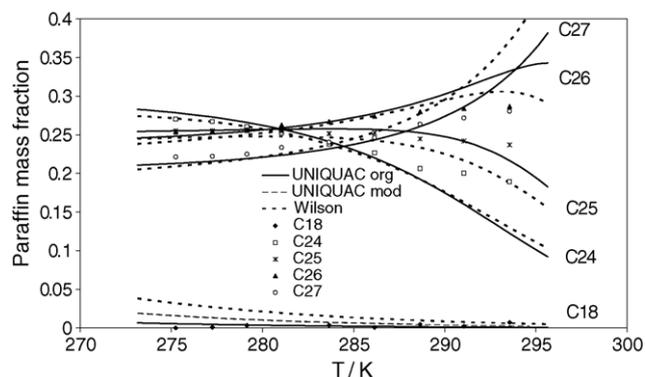


Fig. 5. Solid phase compositions for mixture B.

works concerning simple systems [2,3,21]. It seems that the advantages of modified UNIQUAC only become evident for systems where multiple solid phases are present [4,25–27]. The UNIQUAC model is here applied for the first time to the prediction of wax formation in hydrocarbon systems. A comparison of its predictions against those produced by the modified UNIQUAC as shown in Figs. 2, 4 and 6 reveals its superiority concerning the description of these systems. In all cases and for both phases the predictions provided by the UNIQUAC model are very good. If for the liquid phase of both mixtures its results are only slightly superior to those provided by the Wilson equation, as shown in Fig. 3 for mixture B, for the solid phase its predictions are consistently and noticeably superior to those obtained using Wilson. This is particularly striking on the concentration of C18 in mixture B in Fig. 5 where this version of the model seems to be able to describe the non-precipitation of the octadecane. Wilson, not being able to predict a phase split, overestimates the presence of octadecane in the solid and similar results are presented by modified UNIQUAC. This is also clear in Fig. 7 where again UNIQUAC provides a superior description of the amount of octadecane crystallized. One of the major problems with the Wilson and modified UNIQUAC solid phase models previously proposed is that they tend to overestimate the concentration of the light alkanes present in the solid phase because they underestimate the non-ideality of light alkanes in the

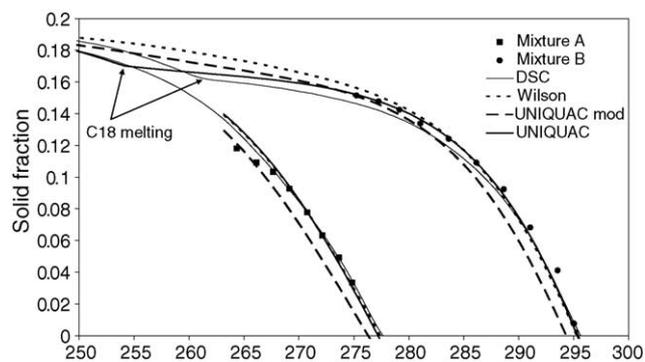


Fig. 6. Experimental fraction of crystallized material for mixtures A and B and predictions using the models studied.

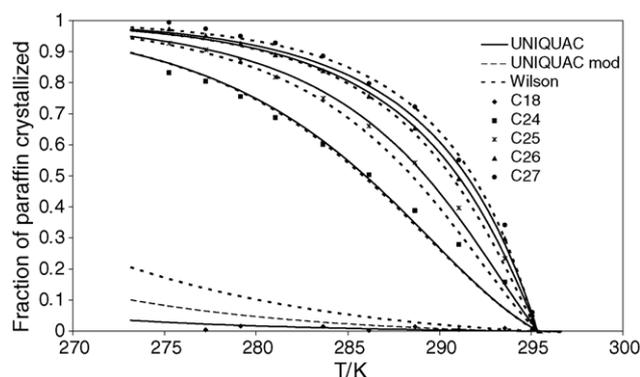


Fig. 7. Fraction of crystallized paraffins for mixture B.

solid solution. This version of the model seems to minimize this problem.

Equally revealing are the results concerning the fraction of crystallized solution presented in Fig. 6 where the three models are compared against the experimental fraction of solid material obtained by both phase equilibrium measurements and DSC for both mixtures. Here the modified UNIQUAC displays a tendency to underestimate both the cloud points and the total solid content while Wilson provides a much superior description of the experimental behavior. The version of UNIQUAC here proposed provides a description of the data that is essentially equivalent to Wilson within the temperature range studied with phase equilibrium data. The superiority of this UNIQUAC model becomes clear for mixture B at lower temperatures where it more closely reproduces the DSC curve and, although with a 10 K difference, is able to describe the phase transition of octadecane. The actual difference between the model and the true melting point of the octadecane may be much lower than this value. The low mobility of the molecules in the solid phase and the heating rate used on the DSC may delay the melting of the octadecane leading to a measured melting point above the true equilibrium value.

Values for the crystallized fraction of each paraffin are reported in Tables 3 and 4. Comparisons between the experimental data and predictions obtained using the models studied on this work are presented in Figs. 7 and 8. The behavior displayed is similar to what was discussed above. The UNIQUAC version here employed is much superior to the

Table 3

Mass percent for the total solid content and for each paraffin crystallized in mixture A

T (K)	Solid	C18	C24	C25	C26	C27
274.9	3.34	4.13	10.51	20.03	28.89	32.63
273.7	4.92	9.14	19.07	29.89	38.13	41.98
272.2	6.32	10.23	23.37	38.17	50.02	57.14
270.8	7.77	14.47	30.58	47.13	59.41	66.39
269.2	9.26	19.62	38.81	56.62	68.31	73.95
267.7	10.33	22.08	43.52	63.19	75.91	82.02
266.2	10.91	27.59	49.22	66.57	75.89	79.32
264.4	11.81	32.49	53.71	70.65	80.40	84.95

Table 4

Mass percent for total solid content and for each paraffin crystallized in mixture B

T (K)	Solid	C18	C24	C25	C26	C27
295.1	0.76	0.63	3.02	4.30	5.45	6.01
293.6	4.11	0.96	15.83	23.40	29.84	34.21
291.1	6.79	0.49	27.87	39.65	49.09	55.08
288.7	9.23	1.44	38.79	54.23	65.45	72.27
286.2	10.90	0.22	50.38	66.09	75.66	79.75
283.7	12.43	1.47	60.05	74.98	83.94	88.57
281.1	13.38	-1.44	68.75	81.86	89.01	92.80
279.2	14.24	1.58	75.58	87.13	92.63	95.06
277.3	14.77	0.40	80.46	90.60	95.22	97.37
275.3	15.14	-0.06	83.27	92.78	97.34	99.49

modified version and provides a much lower error than Wilson on the overestimation of the crystallization of the lower alkanes of the mixtures.

This study allows for the identification of a number of poorly known shortcomings concerning the modified UNIQUAC and Wilson models previously proposed. Although the Wilson model performs better for simple systems, where a single solid phase is present, and the modified UNIQUAC consistently provides much superior predictions for complex mixtures, both show a number of limitations concerning the overestimation of the precipitation of the lighter alkanes of the mixture. A new UNIQUAC model here proposed seems to overcome some of these limitations. It can accurately describe the phase equilibria for the mixtures studied on this work with results that are even superior to the Wilson models while retaining the ability to predict the existence of multiple solid phases. It also seems particularly effective in minimizing the overestimation of the crystallization of the lighter alkanes of the mixtures. However a more detailed study of its capabilities on a broad range of systems, as was previously reported for the two other models, is required for a complete evaluation of the model. Studies of other systems on the verge of the appearance of multiple solid phases will be carried in the near future to deepen the understanding on the limitations and advantages of the different solid phase models available leading to an enhanced solid phase model applicable to real systems of fuels and crudes.

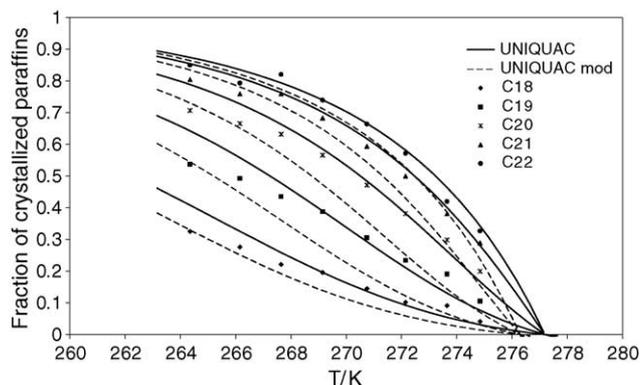


Fig. 8. Fraction of crystallized paraffins for mixture A.

References

- [1] J.A.P. Coutinho, K. Knudsen, S.I. Andersen, E.H. Stenby, *Chem. Eng. Sci.* 51 (1996) 3273–3282.
- [2] J.A.P. Coutinho, E.H. Stenby, *Ind. Eng. Chem. Res.* 35 (1996) 918–925.
- [3] J.A.P. Coutinho, V. Ruffier-Meray, *Ind. Eng. Chem. Res.* 36 (1997) 4977–4983.
- [4] J.A.P. Coutinho, *Ind. Eng. Chem. Res.* 37 (1998) 4870–4875.
- [5] J.A.P. Coutinho, *Fluid Phase Equilib.* 158–160 (1999) 447–457.
- [6] C. Dauphin, J.L. Daridon, J.A.P. Coutinho, P. Baylère, M. Potin-Gautier, *Fluid Phase Equilib.* 161 (1999) 135–151.
- [7] J.A.P. Coutinho, C. Dauphin, J.L. Daridon, *Fuel* 79 (2000) 607–616.
- [8] J.A.P. Coutinho, *Energy Fuels* 14 (2000) 625–631.
- [9] A.J.N. Queimada, C. Dauphin, I.M. Marrucho, J.A.P. Coutinho, *Thermochim. Acta* 372 (2001) 93–101.
- [10] F.I.C. Mirante, J.A.P. Coutinho, *Fluid Phase Equilib.* 180 (2001) 247–255.
- [11] J. Pauly, J.L. Daridon, J.A.P. Coutinho, F. Montel, *Energy Fuels* 15 (2001) 730–735.
- [12] J. Pauly, J.L. Daridon, J.A.P. Coutinho, *Fluid Phase Equilib.* 187–188 (2001) 71–82.
- [13] J.A.P. Coutinho, J.L. Daridon, *Energy Fuels* 15 (2001) 1454–1460.
- [14] J.A.P. Coutinho, J. Pauly, J.L. Daridon, *Brazilian J. Chem. Eng.* 18 (2001) 411–422.
- [15] J.A.P. Coutinho, F. Mirante, J.C. Ribeiro, J.M. Sansot, J.L. Daridon, *Fuel* 81 (2002) 963–967.
- [16] J. Pauly, J.L. Daridon, J.M. Sansot, J.A.P. Coutinho, *Fuel* 82 (2003) 595–601.
- [17] J.M. Sansot, J. Pauly, J.A.P. Coutinho, J.L. Daridon, *AIChE J.*, in press.
- [18] J. Pauly, J.L. Daridon, J.A.P. Coutinho, *Fuel* 84 (2005) 453–459.
- [19] J.A.P. Coutinho, B. Edmonds, T. Moorwood, R. Szczepanski, X. Zhang, *SPE* 78324 (2001).
- [20] J. Pauly, J.L. Daridon, J.A.P. Coutinho, *Fluid Phase Equilib.* 224 (2004) 237–244.
- [21] J. Pauly, C. Dauphin, J.L. Daridon, *Fluid Phase Equilib.* 149 (1998) 191–207.
- [22] J.M. Prausnitz, R.N. Lichtenthaler, E.G. Azevedo, *Molecular Thermodynamics of Fluid-phase Equilibria*, 3rd ed., Prentice-Hall, Englewood Cliffs, NJ, 1999.
- [23] J.A.P. Coutinho, J. Pauly, J.L. Daridon, in: R. Gani, G.M. Kontogeorgis (Eds.), *Computer Aided Property Estimation for Process/Product Design*, Elsevier, Amsterdam, 2004, pp. 229–250.
- [24] M.G. Broadhurst, *J. Res. Nat. Bur. Stand.* 66A (1962) 241–249.
- [25] M. Dirand, V. Chevallier, E. Provost, M. Bouroukba, D. Petitjean, *Fuel* 77 (1998) 1253–1260.
- [26] V. Chevallier, E. Provost, J.B. Bourdet, M. Bouroukba, D. Petitjean, M. Dirand, *Polymer* 40 (1999) 2121–2128.
- [27] V. Chevallier, D. Petitjean, M. Bouroukba, M. Dirand, *Polymer* 40 (1999) 2129–2137.
- [28] S.R. Craig, G.P. Hastie, K.J. Roberts, A.R. Gerson, J.N. Sherwood, R.D. Tack, *J. Mater. Chem.* 8 (1998) 859–869.
- [29] A.R. Gerson, K.J. Roberts, J.N. Sherwood, *Am. Inst. Chem. Eng. Symp. Ser.* 284 (1991) 138–142.
- [30] J.A.P. Coutinho, J.A. Lopes da Silva, A. Ferreira, M.R. Soares, J.L. Daridon, *Petr. Sci. Tech.* 21 (2003) 381–391.
- [31] B.L. Larsen, P. Rasmussen, Aa. Fredenslund, *Ind. Eng. Chem. Res.* 26 (1987) 2274.
- [32] J.A.P. Coutinho, S.I. Andersen, E.H. Stenby, *Fluid Phase Equilib.* 103 (1995) 23–29.
- [33] G.M. Wilson, *J. Am. Chem. Soc.* 86 (1964) 127–130.
- [34] D.S. Abrams, J.M. Prausnitz, *AIChE J.* 21 (1975) 116–128.
- [35] D.L. Morgan, R. Kobayashi, *Fluid Phase Equilib.* 94 (1994) 51.