ELSEVIER

Fluid Phase Equilibria 158–160 (1999) 447–457

FLUID PHASE EQUILIBRIA

Predictive local composition models: NRTL and UNIQUAC and their application to model solid–liquid equilibrium of *n*-alkanes

João Araújo Pereira Coutinho *

Departamento de Química, Universidade de Aveiro, 3810 Aveiro, Portugal

Received 3 April 1998; accepted 30 September 1998

Abstract

Excess Gibbs energy models based on the local composition concept are applied to the description of the solid–liquid equilibria of paraffins. The energetic parameters used by these models are estimated 'a priori' by relating the interaction energies between pairs of molecules with their enthalpies of sublimation providing a pure predictive model for the description of solid–liquid equilibria of systems with *n*-alkanes. This procedure for parameter estimation is successfully applied to the NRTL and UNIQUAC models. They provide a very good description of the composition of the phases in equilibrium, along with the fraction of crystallised solution. These models make possible to overcome the inability of the Wilson equation to model a phase split in the solid phase. It is shown that the limit for complete miscibility in the solid phase is attained when the difference in chain length between two linear alkanes is of about three carbons. This limit is in a fair agreement with the limits presented by other authors. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Model; Solid–liquid equilibrium; Paraffinic wax

1. Introduction

The precipitation of paraffinic waxes from hydrocarbon solutions at low temperatures is a problem found in the petroleum industry from the extraction to the use of refined products such as fuels and diesels. In spite of the progress achieved in other related fields, e.g., crystallography, the multiple attempts to produce a reliable thermodynamic model for solid–liquid equilibria (SLE) in *n*-alkanes systems have not been successful. The presence of multiple solid phases in equilibrium, some of which are not present in the pure components, make the modelling troublesome.

* UI: Centro de Investigaçáo em Química, Faculdade de Ciências da Universidade de Porto. Tel.: +351-34-25085; fax: +351-34-28600

0378-3812/99/$ - see front matter © 1999 Elsevier Science B.V. All rights reserved.
PII: S0378-3812(99)00085-0

The description of SLE can be done, for each component i present at the equilibrium, by an equation relating the composition in both phases with the non-ideality of the phases and the thermophysical properties of the pure components,

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

Using the pure component thermophysical properties presented in the literature, the composition and the amount of the phases can be calculated as a function of the temperature, provided that models for the non-ideality of the solid and liquid phases are available.

2. The liquid phase g^E model

For a hydrocarbon liquid phase, 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 coefficient model used for the liquid phase can thus be described as:

$$\ln\gamma_i = \ln\gamma_i^{res} + \ln\gamma_i^{comb\text{-}fv} \tag{2}$$

In this work, γ^{res} is given by modified UNIFAC [1] and describes the energetic interactions between the molecules. The size difference effects and free volume contributions, given by ln $\gamma^{comb\text{-}fv}$, can be described by the Flory-free volume equation [2]:

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

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

3. The solid phase g^E model

For the description of the non-ideality of the orthorhombic solid phase of *n*-alkanes, the 'a priori' estimation of the interaction energies used by the local composition models, previously applied to the Wilson equation [2], will be extended here to other local composition models such as NRTL and UNIQUAC.

The pair interaction energies between identical molecules are estimated by relating them to the enthalpy of sublimation of the orthorhombic crystalline phase of the pure component

$$\lambda_{ii} = -\frac{2}{Z}\left(\Delta h_{sblm_i} - RT\right) \tag{4}$$

where Z is the coordination number ($Z = 6$ for the *n*-alkanes in orthorhombic phase [2]) and Δh_{sblm} is the enthalpy of sublimation of the pure *n*-alkane. The unlike pair interaction energy is given by

$$\lambda_{ij} = \lambda_{jj} \tag{5}$$

where j is the smaller *n*-alkane of the pair ij [2].

The pair interaction energies calculated by this procedure were previously applied to a modified Wilson equation with very good results in the modelling of both simple and complex systems [2–4]. This model suffers, however, from a well known inability to predict phase split and thus to model multiphase equilibria. This is an important deficiency since it is known that in the SLE of paraffins, multiple solid phases may be present. This may actually be one of the explanations for the differences between the experimental and predicted results previously reported [3,4]. In an attempt to overcome this limitation, the method for estimation of pair interaction energies is applied to other local composition models.

Having an 'a priori' method for parameter estimation that provides good results with the Wilson model, two other obvious candidates to apply that method to are the NRTL and UNIQUAC models. Unfortunately, the extension to these new models is not straightforward. NRTL has an extra parameter, α, to be estimated, and since UNIQUAC was derived for fluid phases its application to the solid phase required some modifications to be made.

3.1. NRTL model

The NRTL g^{E} model was derived by Renon and Prausnitz [5],

$$\frac{g^{\mathrm{E}}}{RT} = \sum_{i=1}^{n} x_i \sum_{j=1}^{n} \frac{x_j \exp\left(-\alpha \dfrac{\lambda_{ij}-\lambda_{ii}}{RT}\right)}{\sum_{k=1}^{n} x_k \exp\left(-\alpha \dfrac{\lambda_{ki}-\lambda_{ii}}{RT}\right)} \frac{(\lambda_{ij}-\lambda_{ii})}{RT} \tag{6}$$

The parameter α is a measure of the non-randomness of the mixture. In their original work, Renon and Prausnitz used the quasi-chemical theory of Guggenheim to show that $\alpha = 2/Z$, Z being the co-ordination. Actually, in the original article appears $\alpha = 1/Z$, but to avoid counting twice the same interaction the correct value should be $\alpha = 2/Z$ as can easily be shown. This provides an estimation for the parameter α making the NRTL model purely predictive. It must be noted that the value of $\alpha = 0.33$ is within the range of values commonly founded for α in VLE and LLE correlation.

3.2. UNIQUAC model

The application of the method for estimation of interaction energies to UNIQUAC is less straightforward. Since it was developed to work with a fluid phase, some adaptations have to be performed to use it with solid phases.

The UNIQUAC model was originally developed by Abrams and Prausnitz [6] as a generalisation of Guggenheim's quasi-chemical theory through the introduction of local area fractions as the primary concentration variable, and the use of Staverman's combinatorial entropy as boundary condition for athermal mixtures. It can be written as

$$\frac{g^{\mathrm{E}}}{RT} = \sum_{i=1}^{n} x_i \ln\left(\frac{\Phi_i}{x_i}\right) + \frac{Z}{2}\sum_{i=1}^{n} q_i x_i \ln\frac{\theta_i}{\Phi_i} - \sum_{i=1}^{n} x_i q_i \ln\left[\sum_{j=1}^{n} \theta_j \exp\left(-\frac{Z}{2}\frac{\lambda_{ij}-\lambda_{ii}}{q_i RT}\right)\right] \tag{7}$$

with

$$\Phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \text{ and } \theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \tag{8}$$

The same equation could also be derived within the frame of a two-fluids theory. In both derivations, the local compositions dependency on the energy parameters is not the same as the original presented by Wilson and it is hard to justify why the coordination number should be contained in the Boltzmann factor [7]. If the original Wilson dependence is used, an alternative form for this equation is obtained where the last term appears multiplied by $Z/2$. This version of UNIQUAC is known to be more correct from a theoretical point of view [1], and was shown to be more adequate to describe simulation results than the original [7]. Authors using 'a priori' methods for the estimation of the interaction parameters [8,9] have found that the best version of UNIQUAC to describe experimental VLE data is an equation similar to that previously described but with $Z/2 = 1$ in the last term. No explanation for this has been presented but, in this work, a similar conclusion about the superiority of this modification for SLE predictions was achieved. The UNIQUAC equation used can thus be written as:

$$\frac{g^{\mathrm{E}}}{RT} = \sum_{i=1}^{n} x_i \ln\left(\frac{\Phi_i}{x_i}\right) + \frac{Z}{2}\sum_{i=1}^{n} q_i x_i \ln\frac{\theta_i}{\Phi_i} - \sum_{i=1}^{n} x_i q_i \ln\left[\sum_{j=1}^{n} \theta_j \exp\left(-\frac{\lambda_{ij}-\lambda_{ii}}{q_i RT}\right)\right] \tag{7b}$$

Another important 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 in such a way as to be proportional to the van der Waals volume and area of a methylene group. This is correct for a fluid phase where the unit of interaction of two molecules can easily be assumed to be the methylene group. It should not be the case, however, for a chain molecule in a crystal lattice where the interaction takes place as a whole along the contact area between two molecules. The r and q parameters should then be redefined to incorporate the actual contact unit for the solid phase. Two attempts in this direction have been made. In the first case, an approach similar to that presented by Abrams and Prausnitz [6], described in Appendix A, was used to estimate the volume and area of a cylinder of 25 methylene units considered to be a representative interaction unit for the *n*-alkanes used in this work. This yielded a standard segment volume of 58.39 $\mathrm{cm}^3/\mathrm{mol}$ and a standard segment area of $11.56 * 10^9$ $\mathrm{cm}^2/\mathrm{mol}$ that provides the new values for r and q:

$$r_i = \frac{V_{\mathrm{w}i}}{58.39} \text{ and } q_i = \frac{A_{\mathrm{w}i}}{11.56 * 10^9} \tag{9}$$

used to define UNIQUAC-25.

Alternatively, a simpler, yet more empirical approach, was used defining the new interaction unit as having 10 of the 'original' methylene units and thus the new r and q values are obtained simply by dividing the original r and q values by the respective values for 10 methylene units:

$$r_i = \frac{r_{\mathrm{iorg}}}{6.744} \text{ and } q_i = \frac{q_{\mathrm{iorg}}}{5.40} \tag{10}$$

The UNIQUAC version so defined will be labelled UNIQUAC-10.

4. Results

The proposed solid phase g^E models were first used to investigate the limits of complete miscibility in the solid phase found at small chain length differences between two *n*-alkanes. These were then compared to correlations of experimental results by other authors [10,11] to evaluate the quality of the phase split predicted by the models. The criterion for phase stability, $\partial^2 G/\partial x^2 \geq 0$, was applied to the proposed models with the interaction energies estimated as described. For each *n*-alkane, the interaction energies leading to a phase split were estimated and related to the chain length of the heavier *n*-alkane that would still be completely soluble with it at 10 K below the temperature of transition between the orthorhombic and rotator phases. The results are shown in Fig. 1 together with the published correlations. The solubility limits of NRTL and both UNIQUAC versions are very similar and compare well with the other correlations. For the lower *n*-alkanes, the solubility limit predicted by the proposed g^E models is similar to the results of Matheson and Smith [10] and with the increase in chain length they become comparable to the values of Dorset [11]. These results indicate that the phase split predicted by the g^E models is physically meaningful and closely follows the trend of the experimental values.

The proposed models were then used to predict the SLE behaviour of several ternary and quaternary systems measured by Coutinho and Ruffier-Meray [3] and Pauly et al. [4]. For these systems, and according with the results of Fig. 1, the models would predict complete solid phase miscibility. However, the effect of temperature could lead to a phase split at lower temperatures as could be expected for, e.g., the system ethylbenzene/*n*-C19/*n*-C21 where two solid phases are predicted for temperatures below 255 K. To be able to calculate multiphase equilibria a multiphase flash algorithm was required. Due to its simplicity, the algorithm of resolution of the Rachford–Rice equations applied to multiphase systems as proposed by Leivobici and Neoschil [12] was used in the calculations. Since no phase stability analyses was performed, a number of phases was set by excess and decreased until all the solutions became physically meaningful (no phases exist with a negative phase fraction or larger than unity).

Some of the modelling results are presented in Figs. 2–4. The solid phase composition presented is the global composition taking into account the composition of all phases present. The results show

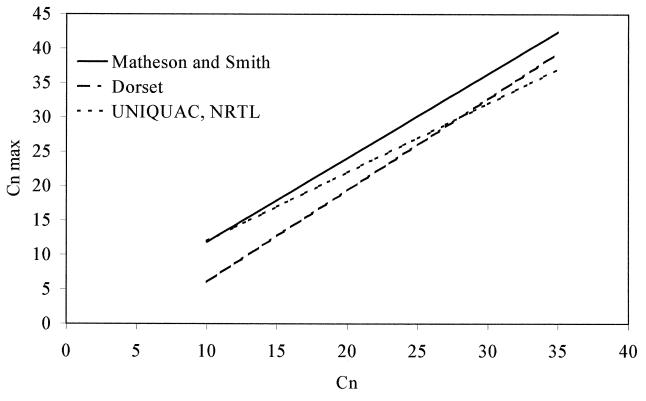

Fig. 1. Comparison between the complete miscibility limits predicted by the proposed models and correlations by Matheson and Smith [10] and Dorset [11].

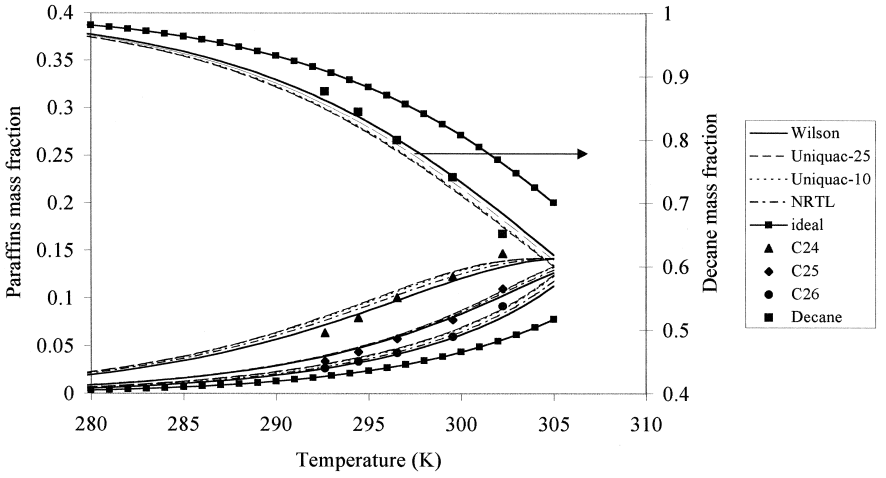

Fig. 2. Liquid phase: comparison between experimental data [15] and the model predictions for the system *n*-C10/*n*-C24/*n*-C25/*n*-C26. Ideal solid phase results are presented for decane and hexacosane.

that all the models are generally equivalent. In all cases, the predictions are within the experimental uncertainty (not presented). The proposed models seem to be equivalent to the Wilson model (that was shown to be the best model for hydrocarbons SLE available [4]) in the absence of a solid–solid phase split. The advantages of these new models appear in the modelling of multicomponent mixtures where the phase split phenomenon is important [13,14]. Comparison with model results assuming ideal solid phase is presented in Figs. 2 and 4. As expected, the description of the equilibria is poor. A comparison with other models is not presented here since it can be found elsewhere [4].

Unfortunately, measurements of the composition of the individual solid phases, when a solid–solid phase split occurs, have not yet been possible. It is thus not possible to compare the model results for

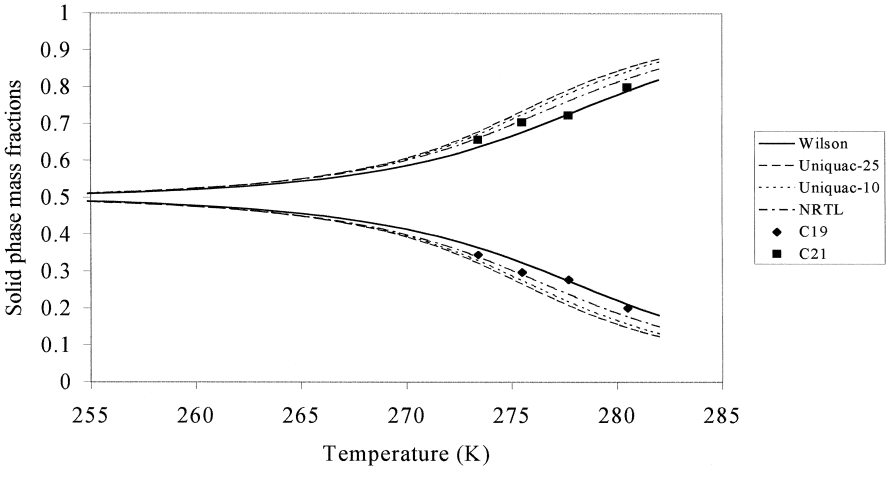

Fig. 3. Solid phase: comparison between experimental data [3] and the model predictions for the system ethylbenzene/*n*-C19/*n*-C21.

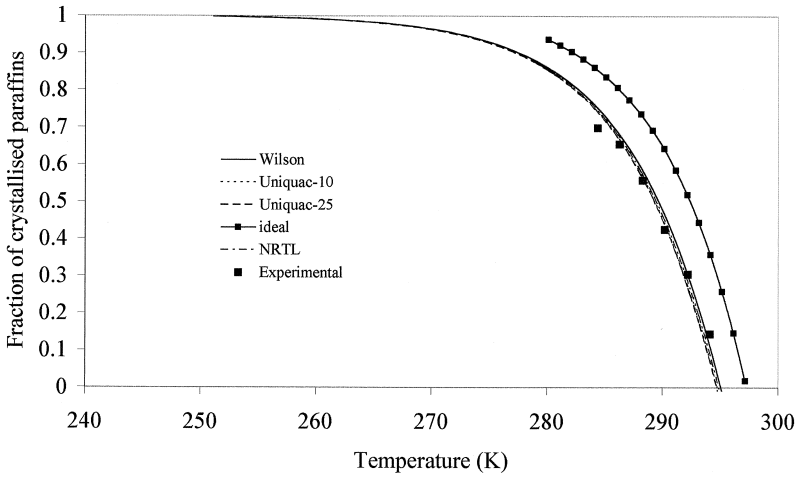

Fig. 4. Fraction of crystallised paraffins: comparison between experimental data [3] and the model predictions for the system ethylbenzene / *n*-C23 / *n*-C24.

the composition of the two solid phases in equilibrium with experimental data. This can only be done for the global composition of the solid phase(s). It is nevertheless interesting to observe the predicted evolution of the solid phase compositions with the temperature for a system where a solid–solid phase split is present and this is shown in Figs. 5 and 6 for the system decane / eicosane / tetracosane. For this system the UNIQUAC-25 model predicts that at 284 K, a new solid phase that is almost pure eicosane starts to precipitate (the NRTL results are similar). The inflexion point in the curve for the fraction of crystallised paraffins that appears then is very interesting. This inflexion is found in

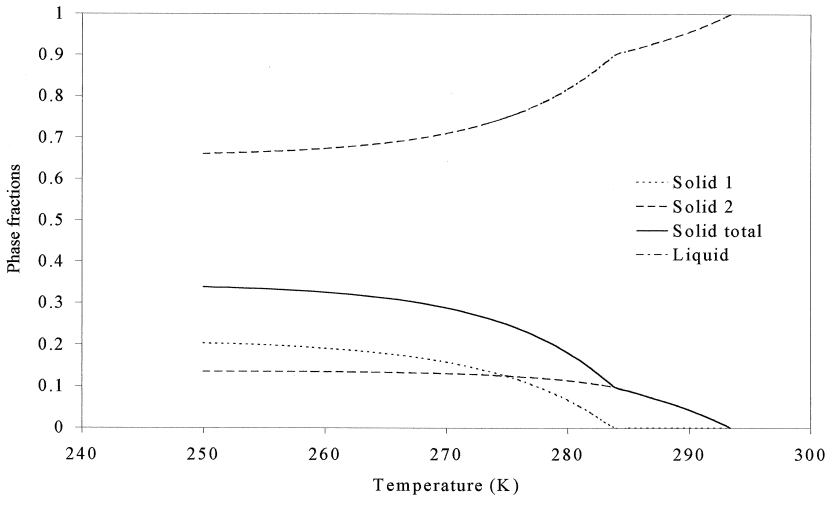

Fig. 5. Change of the fractions of the solid and liquid phases with temperature, predicted for the system *n*-C10 / *n*-C20 / *n*-C24 using UNIQUAC-25.

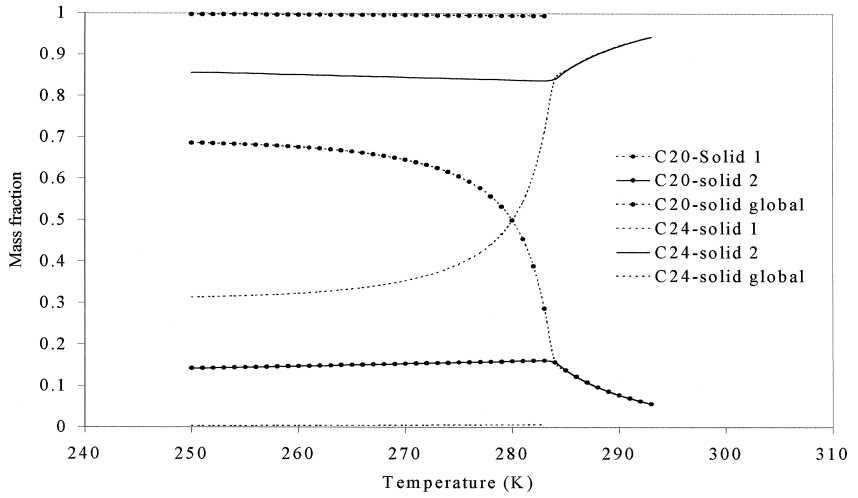

Fig. 6. Change of the solid phases composition with temperature for the system *n*-C10/*n*-C20/*n*-C24 using UNIQUAC-25.

experimental data for multicomponent systems [3,14] and the model seems to confirm the idea that it was due to the presence of a second solid phase.

5. Conclusions

Two new solid phase g^E models have been proposed. They are versions of well known local composition models such as NRTL and UNIQUAC. The 'a priori' method of estimation of interaction energies was extended to these new models with good results. It was shown that both NRTL and the UNIQUAC versions proposed in these work provide as good predictions for the composition of the phases in equilibrium and the amount of the phases as the Wilson model that seems to be the best available model for the description of the non-ideality of the solid phase. These new models allow the calculation of multiphase equilibria overcoming one of the main limitations of the Wilson equation. It was shown that the limits of solubility predicted by these models are in agreement with those presented by other authors.

6. List of symbols

Cp	heat capacity
g	Gibbs energy
h	enthalpy
q	UNIQUAC structural parameter
r	UNIQUAC structural parameter
R	universal gas constant
T	temperature

V	molar volume
V_w	van der Waals volume
x	molar fraction
Z	coordination number

Greek letters

α	NRTL parameter
γ	activity coefficient
λ	pair interaction energy

Subscripts

i	component i
j	component j
m	melting
sblm	sublimation
tr	solid phase transition

Superscripts

E	excess property
l	liquid
s	solid

Appendix A

For the UNIQUAC model, the standard segment used to define the structural parameters had to be redefined. This was done in two ways.

A.1. UNIQUAC-25

To obtain the new structural parameters, the Abrams and Prausnitz approach [6] was used. As they did, it must be emphasised that the choice of a standard segment of interaction is arbitrary. Here, it is defined as a cylinder containing 25 methylene units such that for a polymethylene of infinite length is satisfied the identity

$$\frac{Z}{2}(r-q)=r-1 \tag{A.1}$$

and also $r/q=2/3$. As usual r_i and q_i are defined as

$$r_i=\frac{V_{wi}}{V_{ws}} \tag{A.2}$$

$$q_i=\frac{A_{wi}}{A_{ws}} \tag{A.3}$$

and the van de Waals volume and area of an n-mer of polymethylene are n times the volume and area of a methylene group as given by Bondi

$$V_{wi} = 10.23\, n\, \mathrm{cm}^3/\mathrm{mol} \tag{A.4}$$

$$A_{wi} = 1.35 * 10^9\, n\, \mathrm{cm}^2/\mathrm{mol} \tag{A.5}$$

The volume and area of the standard segment in terms of its radius, R, and length, L, are given by:

$$V = \pi R^2 L \tag{A.6}$$

$$A = 2\pi R(L + R) \approx 2\pi RL \tag{A.7}$$

Considering that the angles between carbon atoms in the polymethylene chain are of 112° geometric considerations shows that

$$L = D(1 + 24 * \sin 56) \tag{A.8}$$

$$R = \frac{D}{2}(1 + \cos 56) \tag{A.9}$$

replacing Eqs. (A.2), (A.3), (A.4), (A.5), (A.6), (A.7), (A.8) and (A.9) in (A.1), as n tends to infinity fixes the value of $D = 1.344 * 10^{-8}$ cm/molecule, and gives a standard segment volume of 58.39 cm^3/mol and a standard segment area of $15.56 * 10^9$ cm^2/mol.

A.2. UNIQUAC-10

The r and q values used in the original UNIQUAC can be estimated by a group contribution method [1]. Assuming a $(CH_2)_{10}$ chain as interaction unit, the structural parameters obtained by group contribution are divided by the r and q values for 10 CH_2 units, thus the values of 6.744 [10 * 0.6744] and 5.40 [10 * 0.54] of Eq. (10). For an n-alkane with n carbon atoms, the r and q values are correlated by:

$$r_n = 0.1 * C_n + 0.0672 \tag{A.1′}$$

$$q_n = 0.1 * C_n + 0.1141 \tag{A.2′}$$

References

[1] B.L. Larsen, P. Rasmussen, Aa. Fredenslund, Ind. Eng. Chem. Res. 26 (1987) 2274–2286.
[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. Pauly, C. Dauphin, J.L. Daridon, Fluid Phase Equilibria 149 (1998) 173–189.
[5] H. Renon, J.M. Prausnitz, AIChE J. 14 (1968) 135.
[6] D.S. Abrams, J.M. Prausnitz, AIChE J. 21 (1975) 116–128.
[7] J. Fischer, Fluid Phase Equilibria 10 (1983) 1–7.
[8] S.O. Jónsdóttir, K. Rasmussen, Aa. Fredenslund, Fluid Phase Equilibria 100 (1994) 121–138.
[9] A.K. Sum, S.I. Sandler, 1998, submitted to Fluid Phase Equilibria.

[10] R.R. Matheson, P. Smith, Polymer 26 (1985) 288–292.
[11] D.L. Dorset, Macromolecules 23 (1990) 623–633.
[12] C.F. Leibovici, J. Neoschil, Fluid Phase Equilibria 112 (1995) 217–221.
[13] J.A.P. Coutinho, Ind. Eng. Chem. Res. 37 (1998) 4870–4875.
[14] C. Dauphin, J.L. Daridon, J.A.P. Coutinho, P. Baylere, M. Potin-Gautier, 1999, submitted to Fluid Phase Equilibria, in press.
[15] J. Pauly, C. Dauphin, J.L. Daridon, 1998, submitted to J. Chim. Phys.