A LOCAL COMPOSITION MODEL FOR PARAFFINIC SOLID SOLUTIONS

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Abstract—The description of the solid-phase non-ideality remains the main obstacle in modelling the solid–liquid equilibrium of hydrocarbons. A theoretical model, based on the local composition concept, is developed for the orthorhombic phase of n-alkanes and tested against experimental data for binary systems. It is shown that it can adequately predict the experimental phase behaviour of paraffinic mixtures. This work extends the applicability of local composition models to the solid phase. Copyright © 1996 Elsevier Science Ltd.

INTRODUCTION

Solid–liquid equilibrium in alkane systems is a phenomenon of great importance in many industrial fields both directly, as in the study of wax formation in fuels and oils, and indirectly, as a contribution to the understanding of more complex molecules as polymers, fatty acids and other big molecules with big aliphatic chains.

Thermodynamically the solid–liquid equilibrium is well defined. An equation relating the compositions in both phases, x and s, with the non-ideality of these phases, γs and γf, and the pure-component thermophysical properties such as heat capacities, Cp, enthalpies of melting and solid-phase transition, h_m and h_s, and the respective temperatures of phase transition, T_m and T_s, can be written for each component present at equilibrium (Prausnitz et al., 1986):

\[
\ln \frac{s_i}{x_i} = \frac{\Delta h_m}{R T_m} \left( \frac{T_m}{T} - 1 \right) + \frac{\Delta h_s}{R T_s} \left( \frac{T_s}{T} - 1 \right) - \frac{\Delta C_{pm}}{R} \left( \frac{T_m}{T} - \ln \frac{T_m}{T} - 1 \right).
\]

A similar equation can also be written for the solid–solid equilibrium. For paraffins the thermophysical parameters to be used in the equation can be found in the literature (Broadhurst, 1962). The main difficulty in modelling the solid–liquid or the solid–solid equilibrium lies in the description of the non-ideality of the phases.

The characteristic enantiotropy of n-alkanes and the well-known differences in the phase behaviour of pure components related with the parity of the number of carbon atoms in an alkane chain induce complex phase behaviour in paraffinic systems as schematically illustrated in Fig. 1 (Turner, 1971). In this simplified picture representing the equilibrium between an even and odd n-alkane, both with phase transitions in the solid phase, three solid phases (x_e, β_o and β_f) and a liquid phase are present. To describe the solid–liquid (SLE) and solid–solid equilibria (SSE) a thermodynamic description of all the phases in equilibrium, particularly in what concerns the non-ideality of each phase, has to be developed. Similar pictures could be drawn for systems of odd/odd and even/even n-alkanes. In the latter type of systems, up to six different solid phases can be found (Achour et al., 1993).

The liquid phase has been investigated previously. It was found that a Flory free-volume model can provide a good description of the liquid phase of alkane mixtures even if they contain branched or cyclo alkanes (Coutinho et al., 1995a). This is a combinatorial free-volume model, appropriate only for athermal systems, that can be described by

\[
\ln \gamma_{i}^{\text{comb-fv}} = \ln \frac{\phi_i}{x_i} + 1 - \frac{\phi_i}{x_i}
\]

(2)

where

\[
\phi_i = \frac{x_i \left(v_i^{1/3} - v_w^{1/3}\right)^{z_i}}{\sum_j x_j \left(v_j^{1/3} - v_w^{1/3}\right)^{z_j}}
\]

(3)

where v_i are the molar volumes and v_w the van der Waals volumes of component i.

For solutions of n-alkanes in aromatic solvents, the same equation coupled with the UNIFAC residual term also proved to be a good model (Coutinho, 1995). This combination of a combinatorial term with the UNIFAC residual term, without parameter reestimation, was successfully done before with other polymer models like entropic free-volume (Kontogeorgis et al., 1993). With the systems used in this work only the combinatorial free-volume term is used. The high-temperature hexagonal solid phase, also known as rotator phase, was studied elsewhere.

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phase transitions are very weak and they do not significantly modify the solid phase structure. Due to the low non-ideality of the rotator phases, this assumption will not introduce significant uncertainties in the evaluation of the orthorhombic phase behaviour and, thus, it will also be used here.

The chain delta lattice parameter (CDLP) model (Coutinho et al., 1995b) will be used for the description of the rotator phase of n-alkanes. The model was derived using the Bragg-Williams description for a solid solution lattice (Bragg and Williams, 1934) and Vegard’s law. It proved to be adequate for the description of the hexagonal phase in n-alkane solid–liquid equilibrium. The temperature-independent version of this model will be used to deal with the non-ideality of the hexagonal phase in equilibrium with the orthorhombic solid. The CDLP model can be expressed as follows:

\[ g^K = 2317 \left( \frac{l_i - l_s}{l_s^3} \right) x_i x_s \text{kJ/mol} \quad (4) \]

where \( l_i \) and \( l_s \) are the lengths of the long and short alkane molecules in the rotator phase calculated using the following correlation due to Broadhurst (1962):

\[ l_i = 1.270 C_n + 1.98. \quad (5) \]

ENTHALPIC VS ENTROPIC EFFECTS

To gain an understanding of the thermodynamical nature of the orthorhombic phase, it is useful to look at the relation between the energetic and entropic effects and how this relation changes with the phase transitions that lead from the liquid to the orthorhombic solid phase.

The liquid phase

The alkane liquid phases are extremely disordered. The non-ideality arises mainly from entropic effects. The energetic effects are so small that it is common to neglect them and to consider these solutions as athermal. The entropic effects resulting from both size difference and free-volume effects are significant and therefore the excess Gibbs free energy can be represented by the entropic term alone \( (g^F = -TS^E \text{ and } h^F = 0) \).

Rotator phase

With the formation of the solid phase there is a considerable reduction of the disorder that characterizes the liquid. The molecules get confined to fixed positions in the crystalline structure and the chains have little freedom to bend the carbon–carbon bonds, contrary to what happens in the liquid, except for the chain extremities (Denicolo et al., 1984; Maroncelli et al., 1985). The molecules possess also the capacity to rotate around their long axis. Due to their proximity, important intermolecular forces arise between the molecules and these systems present a large value of excess enthalpy (Maroncelli et al., 1985; Wulffinger and Schneider, 1973). The excess Gibbs free energy \( (g^F) \) is, however, relatively small since energetic and
entropic effects approximately counterbalance each other. Thus, in the rotator phase, \( h^e \approx T \Delta f^e \) and therefore \( g^e \approx 0 \) (Coutinho et al., 1995b).

**Orthorhombic phase**

With a further lowering of the temperature, the hexagonal crystalline structure, characteristic of the rotator phase, rearranges itself into an orthorhombic structure with a decrease of the crystalline cell size. Consequently, the degrees of freedom of the chain molecule are further reduced. The characteristic rotation around the long axis present in the rotator phase disappears, and the entropic effects due to molecular vibrations are also reduced (Swallin, 1962). All these factors contribute to lower the system entropy and, accordingly, the value of \( s^e \). On the other hand, due to the closest proximity between the molecules, the energetic effects are now fostered with an increase of the excess enthalpy (Maroncelli et al., 1985; Wurflinger and Schneider, 1973). Following the increase in \( h^e \) and the reduction of \( s^e \), the energetic effects become dominant and thus \( h^e > T \Delta f^e \) with the consequent increase of \( g^e \) and the non-ideality of the system.

It seems clear from this discussion that the transformation of a liquid phase in an orthorhombic solid is followed by a decrease in the entropic and an increase in the energetic effects, with these becoming prevalent in the orthorhombic phase. It is this image of a phase where the molecules are confined to "fixed" positions in a kind of lattice, and with energetic interactions defining their relations that conjures the idea that local composition models would provide a good description of the orthorhombic phase.

**LOCAL COMPOSITION MODELS**

The concept of local composition is the core of local composition models. It was first enounced by Wilson (1964), who formulated the hypothesis according to which concentrations around two unlike molecules would be different and dependent on the energies of interaction between the central and surrounding molecules. Wilson postulated that these local compositions would be related to the overall compositions through a Boltzmann-type expression:

\[
\frac{x_{ij}}{x_{ji}} = \frac{x_j \exp (-\lambda_{ij}/RT)}{x_i \exp (-\lambda_{ji}/RT)}.
\]

The validity of this expression is not restricted to fluid phases but extends to all forms of condensed phases. Some doubts about the validity of eq. (6) have been raised by Flemr (1976) and McDermott and Ashton (1977). They showed that it suffers from some inconsistencies, viz. that it does not obey the conservation equation. A local composition definition that avoids this inconsistency was developed by Panayiotou and Vera (1980). However, Hu et al. (1983) showed that although eq. (6) was not correct from the one-fluid theory point of view, where the equation by Panayiotou and Vera (1980) would be more appropriate, it was correct within the frame of a two-fluid theory where the inconsistencies pointed out by Flemr, and McDermott and Ashton would not apply. Despite the limitations that eq. (6) may hold, it seems to have some theoretical basis and, to a fair extent to be able to describe the fluid behaviour at a molecular level (Hu et al., 1983; Gierycz and Nakashima, 1984).

If the energies of interaction \( \lambda_{ij} \) and \( \lambda_{ji} \) are considered identical, there are three energies of interaction \( \lambda_{ij}, \lambda_{ji} \) and \( \lambda_{ii} \) to be considered in the local composition equations for a binary system. The problem when using these equations for the development of a \( g^e \) model is how to estimate these interaction energies. This is usually overcome by fitting the parameters \( \Lambda_{ij} = f(\lambda_{ij} - \lambda_{ji}) \) and \( \Lambda_{ii} = f(\lambda_{ii} - \Delta \lambda) \) to experimental phase equilibrium and other thermodynamic data. If eq. (6) has a true theoretical meaning, it should be possible to calculate the energies of interaction. This has been attempted before for fluid phases with very interesting results by using molecular mechanics (Homer et al., 1991; McCoubrey et al., 1993; Jonsdottir et al., 1994, 1995). For paraffinic crystalline structures, a method of relating the energies of interaction with known molecular properties of pure fluids is subsequently described. This method will provide a theoretical procedure to calculate the energies of interaction that, together with an excess Gibbs free energy model based on the local composition concept, should provide a predictive and theoretically based model for the description of the orthorhombic solid phase.

**Estimation of \( \lambda_{ii} \)**

Scatchard and Hildebrand (Hildebrand et al., 1970) were the first to relate the energy of interaction between a pair of molecules with the energy of isothermal vaporization between the saturated liquid and the ideal gas state. Later Tassios (1971) adapted this concept to the Wilson equation identifying the energy of interaction between two identical molecules \( \lambda_{ii} \) with the energy of vaporization but using a molar basis instead of a volumetric basis as was done by Scatchard and Hildebrand. By the suggestion of Wong and Eekert (1971), the coordination number, \( Z \), was introduced and the like-pair potentials defined as

\[
\lambda_{ii} = \frac{2}{Z} (\Delta \nu_{ii} \Delta f - RT).
\]

Based on this concept the local composition models become one-parameter models since only \( \lambda_{ij} \) must now be estimated from experimental data. Tassios and co-workers applied successfully this concept to the Wilson equation (Tassios, 1971; Hankinson et al., 1972; Krumins et al., 1980) and it was later applied by several other authors to the development of one-parameter versions of other local composition models like NRTL (Brun and Prausnitz, 1971) and UNIQUAC (Abrams and Prausnitz, 1975). Homer and co-workers (Homer et al., 1991; McCoubrey et al., 1993) applied it in AGAPE, a predictive \( g^e \) model based on the local
composition concept, where the interaction energies, $\lambda_{ij}$, are estimated from molecular potentials. Equation (7) was also used by Homer and Mohammadi (1987) to calculate latent heats of vaporization from dispersion forces for several compounds.

This concept is here extended to the solid phase as follows:

$$\lambda_{it} = -\frac{2}{Z}(\Delta h_{\text{blm}} - RT)$$  \hspace{1cm} (8)

where $\Delta h_{\text{blm}}$ is the isothermal heat of sublimation of the orthorhombic solid phase. If the heat of vaporization reflects the interaction between two molecules in a fluid phase, the enthalpy of isothermal sublimation should provide a measure of the average molecular interactions in a crystal.

**Estimation of $\lambda_{ij}$**

The intermolecular forces acting between two $n$-alkanes result exclusively from London dispersion forces and arise along the contact surface of the molecules. In the solid phase, chain molecules act, to a large extent, as stiff rods. In this case the contact surface would be independent of the length of the long molecule as illustrated in Fig. 2. This means that the interaction energy between a long and a short molecule is the same as the interaction energy between two identical short molecules:

$$\lambda_{ls} = \lambda_{ss}$$  \hspace{1cm} (9)

where $l$ and $s$ represent, respectively, the long and the short $n$-alkane molecules. This hypothesis will be valid if the molecules are not very different in size, otherwise the extremities of the long molecules will bend and further interactions between the molecules will arise, eventually destroying this simplified picture described by Fig. 2 and eq. (9). However, this does not limit the applicability of this model in water concerns paraffinic solid phases, because in these systems two molecules with large size differences will never exist in contact since they would be mutually insoluble (Matheson and Smith, 1985).

**THE COORDINATION NUMBER**

Equation (8) requires the use of a coordination number for the estimation of the energies of interaction between identical molecules. As discussed before, it is in the contact surface between two molecules that interaction energies arise. In an alkane crystal there are two types of contact surfaces between molecules: axial contact surfaces that appear along the long axis of the molecules between a central and surrounding molecules and top/bottom contact surfaces between the extremities of a molecule and the extremities of the molecules that are on the layers immediately above and below the layer to which the molecule belongs. Clearly these two types of contacts are very different. If the energy of interaction is proportional to the contact area of two molecules, the axial interactions are much more important than the interactions between the extremities of the molecules. For this reason only the axial interactions will be taken into consideration and a value of $Z_{\text{axial}} = 6$, characteristic of axial interactions in an $n$-alkane orthorhombic structure, is used. This assumption is summarized in eq. (10):

$$-(\Delta h_{\text{blm}} - RT) = \frac{Z_{\text{axial}}}{2} \lambda_{\text{axial}} + \frac{Z_{\text{top/bottom}}}{2} \lambda_{\text{top/bottom}}$$

$$\approx \frac{Z_{\text{axial}}}{2} \lambda_{it}.$$  \hspace{1cm} (10)

**THE WILSON EQUATION**

At this stage any local composition model could be chosen, but the Wilson equation was preferred due to its theoretical basis. Its first appearance was made in a rather empirical manner (Wilson, 1964) by simply replacing overall volume fractions by local volume fractions in the Flory–Huggins equation. Later several authors have shown that under certain assumptions, theoretically based derivations of the Wilson equation or versions of it could be obtained (Renon and Prausnitz, 1969; Maurer and Prausnitz, 1978).

In the present work a version of the Wilson equation presented in eq. (11) will be used. It was derived by Hiranuma (1974) using the lattice theory and, thus, there should not be any limitations in the applicability of this equation to a crystalline phase. The $f^w$ model used is thus

$$\frac{g^w}{RT} = -x_i \ln \left[ \frac{x_i + x_s \exp \left( -\frac{\lambda_{ls} - \lambda_{lt}}{RT} \right)}{x_l + x_s \exp \left( -\frac{\lambda_{ls} - \lambda_{lt}}{RT} \right)} \right]$$

$$-x_s \ln \left[ \frac{x_s + x_l \exp \left( -\frac{\lambda_{ls} - \lambda_{lt}}{RT} \right)}{x_l + x_s \exp \left( -\frac{\lambda_{ls} - \lambda_{lt}}{RT} \right)} \right]$$  \hspace{1cm} (11)

where the interaction energies, $\lambda_{it}$, $\lambda_{ss}$ and $\lambda_{ls}$, are obtained from the relations presented in eqs (8) and

![Fig. 2. Axial contact surfaces between two identical and between two non-identical $n$-alkane molecules in the solid phase.](image-url)
The proposed model for the orthorhombic phase of \( n \)-alkanes is now tested in the description of the equilibrium between the orthorhombic and the hexagonal phases in binary systems of \( n \)-alkanes. The heat of sublimation used in eq. (8) is calculated using the corresponding states principle model for heats of vaporization of long-chain hydrocarbons by Morgan and Kobayashi (1994) and the experimental values for heats of melting and solid-phase transition are obtained from Broadhurst (1962). It is assumed that the difference in heat capacities of the solid phases could be neglected. The thermophysical properties for the metastable solid-phase transitions between the hexagonal and the orthorhombic phases for even \( n \)-alkanes were obtained from interpolation of the experimental values for odd \( n \)-alkanes (Cautinho, 1995). In even/even systems the multiple orthorhombic solid phases were considered to be identical and the previously described procedure applied to the estimation of their thermophysical properties. The database used in this study is presented in the Appendix.

Using the proposed model good predictions are obtained for many of the studied systems. Illustrative examples are presented in Figs 3 and 4 where the dotted lines correspond to the metastable region. They provide a strong support to the validity of the theoretical model used in the calculations. For certain systems the model presents some deviation to the experimental behaviour, either by overprediction of the temperatures of phase transition, as in Fig. 5, or underpredicting them, as in Fig. 6 where the dashed lines represent the predictions by the proposed model. Despite the deviations in temperature, especially around the minimum that occurs for compositions between 0.6 and 0.8 in the short alkane, it is clear that the shape of these very asymmetric phase diagrams as well as the composition at which the minimum occurs are correctly predicted. The deviations are mainly related to uncertainties in the enthalpies of sublimation, especially because of the poor knowledge of the heats of vaporization of heavy alkanes as discussed below. In the absence of more reliable data for heats of vaporization, an empirical correction factor, \( \alpha_{ts} \), will have to be introduced in the calculations to take into account the deviations introduced by these uncertainties:

\[
\lambda_{ts} = \lambda_{ts}(1 + \alpha_{ts}).
\]

The correction factor, \( \alpha_{ts} \), is not a new parameter in the thermodynamics of mixtures. It can be identified
with the parameter $l_{ij}$ used in the regular solution theory (Prausnitz et al., 1986).

The $x_{ls}$ correlation

The correction factors, $x_{ls}$, were estimated for all the systems in the studied data base. It was found that generally only a very small correction is required. For most of the systems studied its value is within the range $\pm 0.02$, which means that the variations to the value of $\lambda_{ls}$ predicted by the model are inferior to 2% and hence a good indication of the validity of eq. (9). The $x_{ls}$ values were plotted against the size dependency function used in the CDLP model. (There is no particular reason to use this and not another relation to correlate these values.) The generality of data falls closely to a straight line described by

$$x_{ls} = -73.98 \left( \frac{(l_1 - l_3)}{l_1^2} \right) + 0.01501$$

(13)

![Diagram](image)

Fig. 6. $n$-C$_{23}$H$_{46}$/$n$-C$_{23}$H$_{48}$ (Mazee, 1960). Experimental and calculated phase diagrams. Dashed line $x_{ls} = 0$ and solid line $x_{ls} = 0.0105$.

as shown in Fig. 7. A few sets of data, represented by white squares in Fig. 7, do not fall into this line requiring a smaller correction parameter than that predicted by the correlation. All these data sets have one or more components in the C$_{30}$–C$_{40}$ range. Even though some of these data sets are not very reliable, the quality of experimental data alone cannot explain the deviations. This behaviour may be related to non-equilibrium phenomena as described by Snyder et al. (1992, 1994). Nevertheless, even these few systems of large molecules do not part from the behaviour predicted by the proposed model and they also use a correction to $\lambda_{ls}$ inferior to 2%.

Deviations to the behaviour described by eq. (9) could be expected to arise due to increased size differences between the molecules. This would force the large molecule to bend and new interactions to arise, increasing the pair interaction energies. This is not expected to happen since a paraffinic solid solution can only exist if the molecules have similar sizes (Matheson and Smith, 1985), granting thus the validity of eq. (9) for these systems. The values of the parameter $x_{ls}$ also give good indications that they do not result from deviations to the behaviour proposed in eq. (9) resulting from size differences. If new interactions would develop due to the size difference between the molecules then $\lambda_{ls} > \lambda_{ss}$. The values of $x_{ls}$ would thus be not negative but positive and described by a curve crossing the $x$ axis for $l_1 = l_3$. This is not the behaviour found in Fig. 7 where the estimated values for $x_{ls}$ are presented against a size difference parameter. The main contribution to $x_{ls}$ comes from the correlation for the heats of vaporization. These are the most important contribution to enthalpies of sublimation but the correlations available have an accuracy of only 2% (Morgan and Kobayashi, 1994) that is of the same order of magnitude as the $x_{ls}$ values. The comparison of enthalpy of vaporization values presented by two different correlations in Table 1 also shows how large is the uncertainty associated with the heats of vaporization. The reason why the errors in

![Diagram](image)

Fig. 7. Correlation of the correction factors $x_{ls}$. 
the heat of sublimation do not have a larger effect in the calculations as would be expected from the magnitude of the uncertainty shown in Table 1 is that the $g^b$-model presented in eq. (11) uses the differences in the pair interaction energies and not their actual values and these differences are much less sensitive to these uncertainties than their actual values.

Using the correlation for $x_n$, a good description of the systems for which the pure prediction was not satisfactory is now achieved. The results are presented in Figs 5 and 6 as solid lines.

These results are obtained with none or only a small correction factor. If any other one-parameter $g^b$ model is used as for instance Margules, a large parameter would be required to fit the minimum in temperature and the asymmetry of the diagram would be very poorly described as shown in Fig. 8, where Margules and the proposed model are compared in the description of the phase diagram for the system $n$-$C_{19}H_{40}$/$n$-$C_{21}H_{44}$. The model based on the Wilson equation will naturally have all the limitations known to hold for this equation, viz. the inability to predict the phase split in the solid phase. The procedure to estimate the energies of interaction is, however, universal and can be applied together with any other local composition model like NRTL or UNIQUAC if the solid-phase split proves to be important.

The influence of $x_n$ in the calculations

The application of the proposed model to multi-component systems is straightforward as shown in a recent work (Coutinho and Stenby, submitted). The results indicate that for molar concentrations of heavy fraction inferior to 10% the influence of $x_n$ is negligible in the calculations. This can be appreciated in Fig. 9, where experimental data for the system $n$-$C_{24}H_{50}$/$n$-$C_{28}H_{56}$/$n$-$C_{31}H_{64}$ with a ratio of heavy alkanes of $C_{24}H_{50}$ : $C_{28}H_{56}$ = 1, measured in our laboratory (Bach et al., 1995), are compared with the results obtained using three different values for $x_n$; the solid line is calculated using $x_n$ fitted from binary experimental data; the other two lines correspond to values of the interaction parameter of 0 and $-0.05$.

All these results indicate that a predictive and theoretical model based on the local composition concept can be applied to the description of the orthorhombic phase in paraffinic systems. They provide a strong indication for the theoretical validity of the Wilson equation showing that the energy parameters in a local composition model are not just empirical adjustable parameters but that they actually have physical meaning that under certain conditions can be related to macroscopical properties of the pure fluids.

CONCLUSIONS

In this work a model for the non-ideality of paraffinic solid solutions is developed. The model is simultaneously theoretically based and predictive. A procedure is presented for an a priori estimation of interaction energies between paraffin molecules in

<table>
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<tr>
<th>Model</th>
<th>$n$-$C_{19}H_{40}$ $h_{nap}$ (kJ/mol)</th>
<th>$n$-$C_{21}H_{44}$ $h_{nap}$ (kJ/mol)</th>
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<td>Morgan and Kobayashi (1994)</td>
<td>143.5</td>
<td>167.7</td>
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<tr>
<td>Basarova and Svoboda (1995)</td>
<td>124.9</td>
<td>141.9</td>
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Fig. 8. $n$-$C_{19}H_{40}$/$n$-$C_{21}H_{44}$ (Maroncelli et al., 1985). Comparison between calculated phase diagrams using Margules second-order equation (dotted line $A = 4000$ J/mol) and predictive Wilson (solid line $x_n = -0.0118$).

Fig. 9. Study of the influence of $x_n$ in the phase behaviour predictions for high solvent concentration.
a crystalline phase that can be used in a local composition model conforming to a predictive character. Using the equation of Wilson, this model was applied to the description of the orthorhombic solid phase of n-alkanes. Good predictions are obtained for the solid–solid phase diagrams of systems of odd/odd, odd/even and even/even n-alkanes considering identical the multiple orthorhombic solid phases.

Deviations to the proposed model have been identified to be due to difficulties in the estimation of the isothermal enthalpy of sublimation and a correction factor $\alpha_0$ was introduced to take them into account. Typically, corrections inferior to 2% of the predicted value for the energy of interaction are required. A correlation for this parameter is presented. It is also shown that for multicomponent systems, for low concentrations in heavy components, the parameter $\alpha_0$ can be neglected. The results obtained in this work extend the applicability of local composition models to the solid phase.

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NOTATION

- $a$: crystalline lattice parameter
- $b$: crystalline lattice parameter
- $C_p$: heat capacity
- $g$: Gibbs free energy
- $h$: enthalpy
- $l$: molecular chain length, Å
- $R$: universal gas constant
- $s$: entropy
- $s_p$: solid-phase molar fraction
- $T$: temperature
- $x$: liquid-phase molar fraction
- $Z$: coordination number

Greek letters

- $\alpha$: correction factor in eq. (10)
- $\gamma$: activity coefficient
- $\Delta$: variation
- $\lambda$: pair interaction energy

Subscripts

- $i$: component $i$
- $j$: component $j$
- $l$: long molecule
- $m$: melting point
- $s$: short molecule
- subl: sublimation
- $t$: transition point
- vap: vaporization

Superscripts

- $E$: excess property
- $l$: liquid phase
- $s$: solid phase

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**APPENDIX**

In the following table, the data base used in the study of the adequacy of the proposed model to the description of the orthorhombic phase is presented.

<table>
<thead>
<tr>
<th>System</th>
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<td>C18H36 – C22H44</td>
<td>Mazee (1960)</td>
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<td>Wurtflinger and Schneider (1973)</td>
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