



A LOCAL COMPOSITION MODEL FOR PARAFFINIC SOLID SOLUTIONS

JOÃO A. P. COUTINHO, KIM KNUDSEN, SIMON I. ANDERSEN
 and ERLING H. STENBY*

Engineering Research Center, IVC-SEP, Department of Chemical Engineering, Building 229, Technical University of Denmark, DK-2800 Lyngby, Denmark

(Received 22 August 1995; revised manuscript received and accepted 14 November 1995)

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, γ^l and γ^s , and the pure-component thermophysical properties such as heat capacities, C_p , enthalpies of melting and solid-phase transition, h_m and h_i , and the respective temperatures of phase transition, T_m and T_i , can be written for each component present at equilibrium (Prausnitz *et al.*, 1986):

$$\ln \frac{s\gamma^s}{x\gamma^l} = \frac{\Delta h_m}{RT_m} \left(\frac{T_m}{T} - 1 \right) + \frac{\Delta h_i}{RT_i} \left(\frac{T_i}{T} - 1 \right) - \frac{\Delta C_p m}{R} \left(\frac{T_m}{T} - \ln \frac{T_m}{T} - 1 \right). \quad (1)$$

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 sche-

matically 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 (α_h , β_o and β_T) 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

$$\ln \gamma_i^{\text{comb-fv}} = \ln \frac{\phi_i}{x_i} + 1 - \frac{\phi_i}{x_i} \quad (2)$$

where

$$\phi_i = \frac{x_i(v_i^{1/3} - v_{wi}^{1/3})^{3.3}}{\sum_j x_j(v_j^{1/3} - v_{wj}^{1/3})^{3.3}} \quad (3)$$

where v_i are the molar volumes and v_{wi} 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

*Corresponding author.

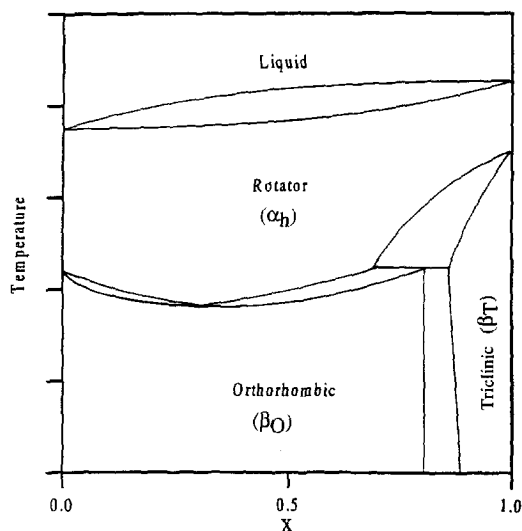


Fig. 1. Schematic phase diagram for a binary system of even/odd *n*-alkanes.

(Coutinho *et al.*, 1995b) and a g^E model known as chain delta lattice parameter (CDLP) model was developed. The CDLP model will be used in the description of the rotator phase in equilibrium with the orthorhombic solid phase.

The orthorhombic solid phase is by far the most important crystalline structure present in alkane SLE or SSE. Because formation is a low temperature phenomenon, occurring typically below the temperature of solid-phase transition (rotator-orthorhombic), the orthorhombic phase is the main, or even the only, phase present in paraffinic deposits (Turner, 1971; Gerson *et al.*, 1991). For this reason, this work will focus on the development of an excess Gibbs free energy model for the orthorhombic phase. Experimental solid–solid equilibrium data in binary *n*-alkane systems will then be used for testing the proposed model.

THE g^E MODEL FOR THE ROTATOR PHASE

The existence of multiple phases making the transition between the orthorhombic solid phase and the liquid phase has been established by Doucet *et al.* (1981) and Ungar (1983). Within the narrow temperature range that separates the orthorhombic and liquid phases, with increasing temperature a quasi-hexagonal phase, where the ratio of lattice parameters $b/a < 3^{1/2}$, undergoes a very weak first-order transition to a true hexagonal phase with $b/a = 3^{1/2}$ (Denicolo *et al.*, 1984). This behaviour has also been identified in several binary systems (Hasnaoui *et al.*, 1988; Achour *et al.*, 1993; Sabour *et al.*, 1995). In the thermodynamic description of these phases it is common to assume that the thermodynamical behaviour of the true hexagonal phase, for which the CDLP model was developed, is not substantially modified by the subsequent phase transitions and that the different phases can be considered identical (Achour, 1994; Sabour, 1994). This is a fair hypothesis because the

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:

$$g^E = 2317 \frac{(l_l - l_s)^3}{l_s^3} x_l x_s \text{ kJ/mol} \quad (4)$$

where l_l 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):

$$l_i = 1.270Cn_i + 1.98. \quad (5)$$

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 ($g^E = -Ts^E$ and $h^E = 0$).

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; Wurfinger and Schneider, 1973). The excess Gibbs free energy (g^E) is, however, relatively small since energetic and

entropic effects approximately counterbalance each other. Thus, in the rotator phase, $h^E \approx Ts^E$ 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 (Swalin, 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; Wurfinger and Schneider, 1973). Following the increase in h^E and the reduction of s^E , the energetic effects become dominant and thus $h^E > Ts^E$ 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 central 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 Boltzman-type expression:

$$\frac{x_{ij}}{x_{jj}} = \frac{x_i \exp(-\lambda_{ij}/RT)}{x_j \exp(-\lambda_{jj}/RT)} \quad (6)$$

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 Nakanishi, 1984).

If the energies of interaction λ_{ij} and λ_{ji} are considered identical, there are three energies of interaction (λ_{ii} , λ_{jj} and $\lambda_{ij} = \lambda_{ji}$) 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 $\Lambda_{ij} = f(\lambda_{ij} - \lambda_{jj})$ and $\Lambda_{ji} = f(\lambda_{ji} - \lambda_{ii})$ 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 λ_{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 (λ_{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 Eckert (1971), the coordination number, Z , was introduced and the like-pair potentials defined as

$$\lambda_{ii} = -\frac{2}{Z}(\Delta h_{\text{vap}} - RT) \quad (7)$$

Based on this concept the local composition models become one-parameter models since only λ_{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 (Bruin 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, λ_{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:

$$\lambda_{ii} = -\frac{2}{Z}(\Delta h_{\text{sublim}} - RT) \quad (8)$$

where Δh_{sublim} 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 λ_{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:

$$\lambda_{ls} = \lambda_{ss} \quad (9)$$

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

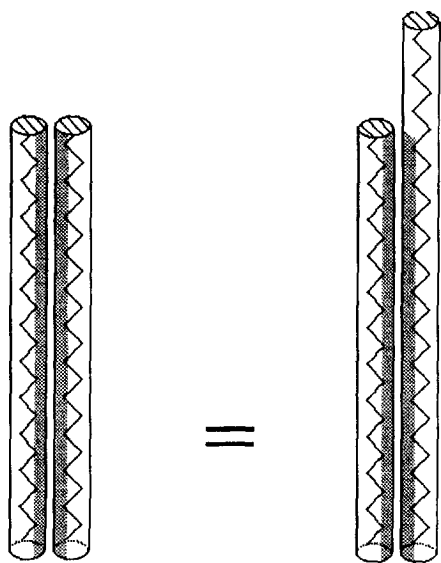


Fig. 2. Axial contact surfaces between two identical and between two non-identical *n*-alkane molecules in the solid phase.

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):

$$\begin{aligned} -(\Delta h_{\text{sublim}} - RT) &= \frac{Z_{\text{axial}}}{2} \lambda_{ii}^{\text{axial}} + \frac{Z_{\text{top/bottom}}}{2} \lambda_{ii}^{\text{top/bottom}} \\ &\approx \frac{Z_{\text{axial}}}{2} \lambda_{ii}. \end{aligned} \quad (10)$$

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 g^E model used is thus

$$\begin{aligned} \frac{g^E}{RT} &= -x_l \ln \left[x_l + x_s \exp \left(-\frac{\lambda_{ls} - \lambda_{ll}}{RT} \right) \right] \\ &\quad - x_s \ln \left[x_s + x_l \exp \left(-\frac{\lambda_{ls} - \lambda_{ss}}{RT} \right) \right] \end{aligned} \quad (11)$$

where the interaction energies, λ_{ll} , λ_{ss} and λ_{ls} , are obtained from the relations presented in eqs (8) and

(9). The second part of this equation vanishes when eq. (9) is used.

RESULTS

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 data base 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, α_{ls} , will have to be introduced in the calculations to take into account the deviations introduced by these uncertainties:

$$\lambda_{ls} = \lambda_{ss}(1 + \alpha_{ls}). \quad (12)$$

The correction factor, α_{ls} , is not a new parameter in the thermodynamics of mixtures. It can be identified

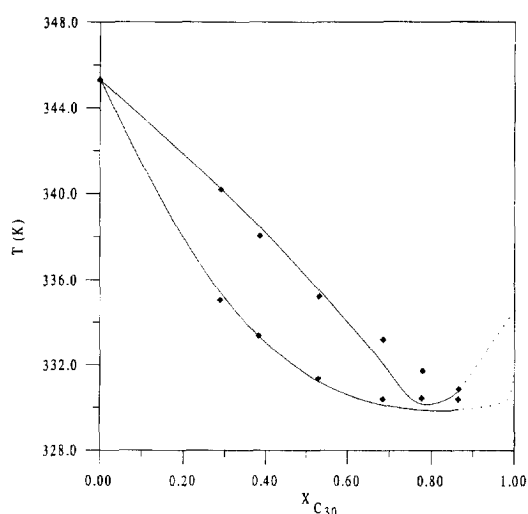


Fig. 4. n -C₃₀H₆₂/ n -C₃₅H₇₂ (Mazec, 1960). Experimental and predicted phase diagrams using $\alpha_{ls} = 0$. In dotted line the metastable region.

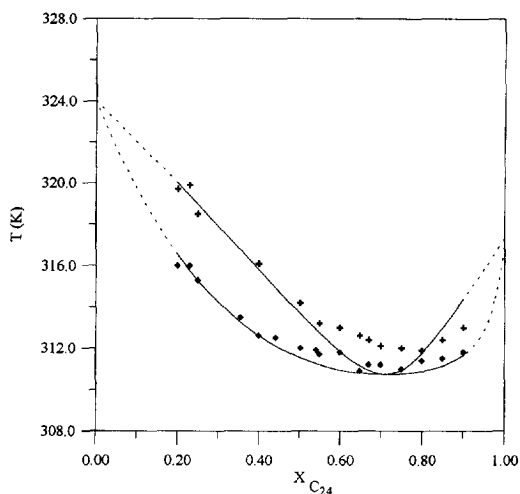


Fig. 3. n -C₂₄H₅₀/ n -C₂₆H₅₄ (Achour, 1994). Experimental and predicted phase diagrams using $\alpha_{ls} = 0$. In dotted line the metastable regions.

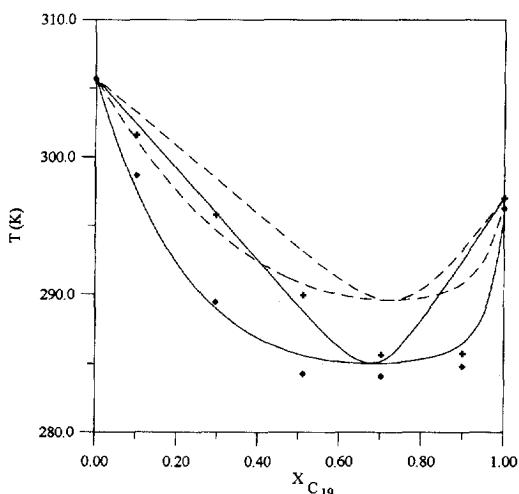


Fig. 5. n -C₁₉H₄₀/ n -C₂₁H₄₄ (Maroncelli *et al.*, 1985). Experimental and calculated phase diagrams. Dashed line $\alpha_{ls} = 0$ and solid line $\alpha_{ls} = -0.0118$.

with the parameter l_{ij} used in the regular solution theory (Prausnitz *et al.*, 1986).

The α_{is} correlation

The correction factors, α_{is} , 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 ± 0.02 , which means that the variations to the value of λ_{is} predicted by the model are inferior to 2% and hence a good indication of the validity of eq. (9). The α_{is} 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

$$\alpha_{is} = -73.98 \frac{(l_i - l_s)^2}{l_s^3} + 0.01501 \quad (13)$$

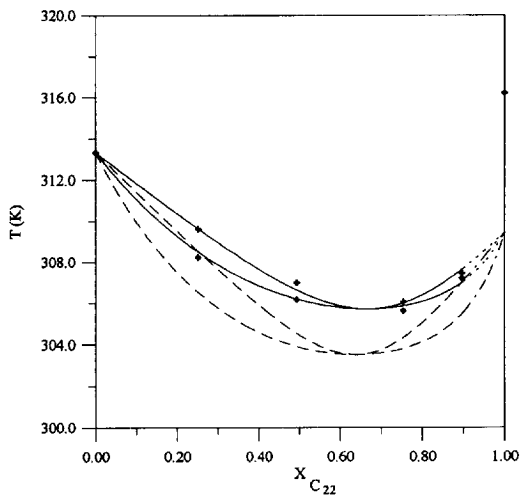


Fig. 6. $n\text{-C}_{22}\text{H}_{46}/n\text{-C}_{23}\text{H}_{48}$ (Mazee, 1960). Experimental and calculated phase diagrams. Dashed line $\alpha_{is} = 0$ and solid line $\alpha_{is} = 0.0105$.

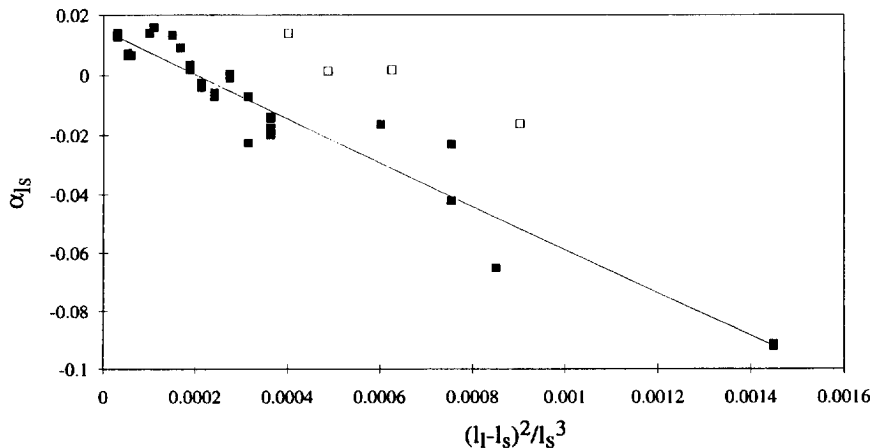


Fig. 7. Correlation of the correction factors α_{is} .

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 $\text{C}_{30}\text{--C}_{40}$ 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 λ_{is} 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 α_{is} 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 $\lambda_{is} > \lambda_{ss}$. The values of α_{is} would thus be not negative but positive and described by a curve crossing the x axis for $l_i = l_s$. This is not the behaviour found in Fig. 7 where the estimated values for α_{is} are presented against a size difference parameter. The main contribution to α_{is} 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 α_{is} 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

Table 1. Comparison of correlations for enthalpy of vaporization of alkanes at $T = 340$ K

Model	$n\text{-C}_{30}\text{H}_{62}$ h_{vap} (kJ/mol)	$n\text{-C}_{35}\text{H}_{72}$ h_{vap} (kJ/mol)
Morgan and Kobayashi (1994)	143.5	167.7
Basarova and Svoboda (1995)	124.9	141.9

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^E -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 α_{1s} , 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^E 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 $n\text{-C}_{19}\text{H}_{40}/n\text{-C}_{21}\text{H}_{44}$. 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 α_{1s} 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 α_{1s} is negligible in the calculations. This can be appreciated in Fig. 9, where experimental data for the system $n\text{-C}_{24}\text{H}_{50}/n\text{-C}_{28}\text{H}_{58}/n\text{-C}_7\text{H}_{16}$ with a ratio of heavy alkanes of $\text{C}_{24}\text{H}_{50}:\text{C}_{28}\text{H}_{58} = 1$, measured in our laboratory (Bach *et al.*, 1995), are compared with the results obtained using three different values for α_{1s} : the solid line is calculated using α_{1s} 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

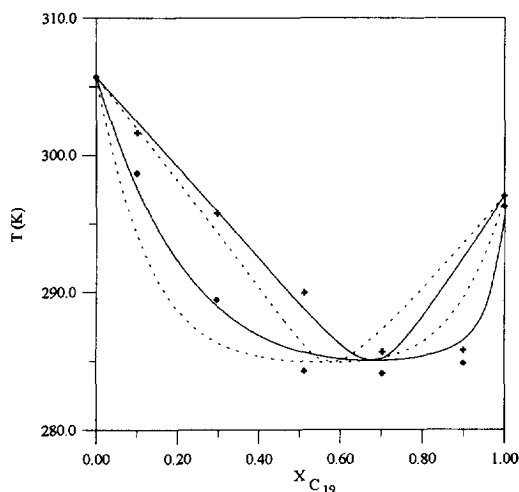


Fig. 8. $n\text{-C}_{19}\text{H}_{40}/n\text{-C}_{21}\text{H}_{44}$ (Maroncelli *et al.*, 1985). Comparison between calculated phase diagrams using Margules second-order equation (dotted line $A = 4000$ J/mol) and predictive Wilson (solid line $\alpha_{1s} = -0.0118$).

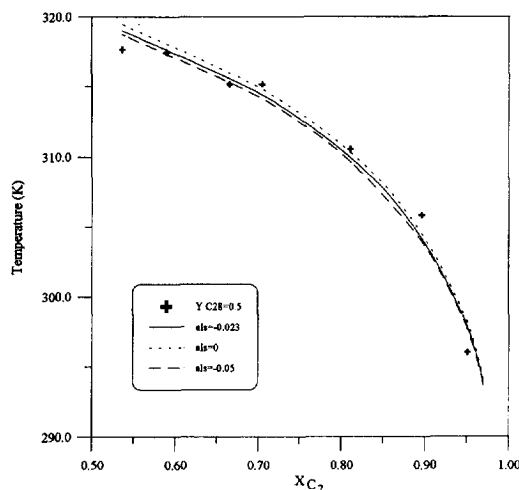


Fig. 9. Study of the influence of α_{1s} in the phase behaviour predictions for high solvent concentration.

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

a crystalline phase that can be used in a local composition model conferring to it 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 α_s 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 α_s can be neglected. The results obtained in this work extend the applicability of local composition models to the solid phase.

Acknowledgements—The authors would like to thank G. Kontogeorgis for the encouragement and fruitful discussions, and P. Rasmussen for the “harsh” criticism that greatly helped to improve this work. J. A. P. C. wishes also to acknowledge the Junta Nacional de Investigação Científica e Tecnológica (Portugal) for financial support.

NOTATION

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

Greek letters

α	correction factor in eq. (10)
γ	activity coefficient
Δ	variation
λ	pair interaction energy

Subscripts

<i>i</i>	component <i>i</i>
<i>j</i>	component <i>j</i>
<i>l</i>	long molecule
<i>m</i>	melting point
<i>s</i>	short molecule
sb _{lm}	sublimation
<i>t</i>	transition point
vap	vaporization

Superscripts

<i>E</i>	excess property
<i>l</i>	liquid phase
<i>s</i>	solid phase

REFERENCES

- Abrams, D. S. and Prausnitz, J. M., 1975, Statistical thermodynamics of liquid mixtures: a new expression for the excess Gibbs energy of partly or completely miscible systems. *A.I.Ch.E. J.* **21**, 116–128.
- Achour, Z., 1994, Thermodynamic and structural study of the *n*-tetracosane: *n*-hexacosane system. Ph.D. thesis, Institut National Polytechnique de Lorraine, Nancy, France (in French).
- Achour, Z., Bourdet, J. B., Bouroubka, M. and Dirand, M., 1993, Binary systems of even-numbered *n*-alkanes ($C_{2p}H_{4p+2}$ – $C_{2p+2}H_{4p+6}$, $10 \leq p \leq 12$). *J. Chim. Phys.* **90**, 325–332.
- Bach, A., Frederiksen, R. A. and Lei, F., 1995, Solubility of *n*-tetracosane and *n*-octacosane mixtures in *n*-heptane. IVC-SEP Internal Report, Institut for Kemiteknik, DTU, Lyngby, Denmark (in Danish).
- Basarova, P. and Svoboda, V., 1995, Prediction of the enthalpy of vaporization by the group contribution method. *Fluid Phase Equilibria* **105**, 27–47.
- Bragg, W. L. and Williams, E. J., 1934, The effect of thermal agitation on atomic arrangement in alloys. *Proc. R. Soc. A* **145**, 699–730.
- Broadhurst, M. G., 1962, An analysis of the solid phase behavior of the normal paraffins. *J. Res. Natl Bur. Stand.* **66A**, 241–249.
- Bruin, S. and Prausnitz, J. M., 1971, One-parameter equation for excess Gibbs energy of strongly nonideal liquid mixtures. *Ind. Engng Chem. Process Des. Dev.* **10**, 562–572.
- Coutinho, J. A. P., 1995, Phase equilibria in petroleum fluids: multiphase regions and wax formation. Ph.D. thesis, Institut for Kemiteknik, DTU, Lyngby, Denmark.
- Coutinho, J. A. P., Andersen, S. I. and Stenby, E. H., 1995a, Evaluation of activity coefficient models in prediction of alkane solid–liquid equilibria. *Fluid Phase Equilibria* **103**, 23–29.
- Coutinho, J. A. P., Andersen, S. I. and Stenby, E. H., 1995b, Solid–liquid equilibrium of *n*-alkanes using a modified delta lattice parameter model. Presented at 7th FPPECPD, Snowmass, CO, 18–23 June.
- Coutinho, J. A. P. and Stenby, E. H., Submitted, Predictive local composition models for solid–liquid and solid–solid equilibrium in *n*-alkanes: Wilson equation for multicomponent systems. *Ind. Engng Chem. Res.*
- Denicolo, I., Craievich, A. F. and Doucet, J., 1984, X-ray diffraction and calorimetric phase study of a binary paraffin: C₂₃H₄₈–C₂₄H₅₀. *J. chem. Phys.* **80**, 6200–6203.
- Doucet, J., Denicolo, I. and Craievich, A. F., 1981, X-ray study of the “rotation” phase of the odd-numbered paraffins C₁₇H₃₆, C₁₉H₄₀ and C₂₁H₄₄. *J. chem. Phys.* **75**, 1523–1529.
- Flemr, V., 1976, A note on excess Gibbs energy equations based on local composition concept. *Coll. Czech. Chem. Commun.* **41**, 3347–3349.
- Gerson, A. R., Roberts, K. J. and Sherwood, J. N., 1991, X-ray diffraction studies of single and mixed *n*-alkanes in the homologous series C₁₈H₃₈ to C₂₈H₅₈, In *Particle Design Via Crystallization* (Edited by Ramanarayanan, R., Kern, W., Larson, M. and Sikdar, S.), *A.I.Ch.E. Symp. Ser.* **284**, 138–142.
- Gierycz, P. and Nakanishi, K., 1984, Local composition in binary mixtures of Lennard–Jones fluids with differing sizes of components. *Fluid Phase Equilibria* **16**, 255–273.
- Hankinson, R. W., Langfitt, B. D. and Tassios, D., 1972, A single parameter equation for the prediction of multicomponent vapor–liquid data from binary isobaric data. *Can. J. Chem. Engng* **50**, 511–514.
- Hasnaoui, N., Dellacherie, J., Schuffeucker, L., Dirand, M. and Balesdent, D., 1988, Mise en évidence, par diffraction de rayons-X, a 20°C de trois phases intermédiaires orthorhombiques dans le système de deux *n*-alkanes: docosane-tetracosane. *J. Chim. Phys.* **85**, 153–160.

- Hildebrand, J. H., Prausnitz, J. M. and Scott, R. L., 1970, *Regular and Related Solutions*. Van Nostrand Reinhold, NY.
- Hiranuma, M., 1974, A new expression similar to the three-parameter Wilson equation. *Ind. Engng Chem. Fundam.* **13**, 219–222.
- Homer, J., Jenkins, J. D., Porter, K. E. and Kakhu, A. I., 1991, Prediction of vapour–liquid equilibrium data for binary mixtures from molecular parameters using a generalized London potential. *J. Chem. Soc. Faraday Trans.* **87**, 57–62.
- Homer, J. and Mohammadi, M. S., 1987, Polyatomic London dispersion forces. *J. Chem. Soc. Faraday Trans.* **2** **83**, 1957–1974.
- Hu, Y., Azevedo, E. G. and Prausnitz, J. M., 1983, The molecular basis for local compositions in liquid mixture models. *Fluid Phase Equilibria* **13**, 351–360.
- Jonsdottir, S. O., Klein, R. A. and Rasmussen, K., Submitted, UNIQUAC interaction parameters for alkane/amine systems determined by molecular mechanics. *Fluid Phase Equilibria*.
- Jonsdottir, S. O., Rasmussen, K. and Fredenslund, Aa., 1994, UNIQUAC parameters determined by molecular mechanics. *Fluid Phase Equilibria* **100**, 121–138.
- Kontogeorgis, G. M., Fredenslund, Aa. and Tassios, D., 1993, Simple activity coefficient model for the prediction of solvent activities in polymer solutions. *Ind. Engng Chem. Res.* **32**, 362–372.
- Krumins, A. E., Rastogi, A. K., Rusak, M. E. and Tassios, D., 1980, Prediction of binary vapor–liquid equilibrium from one-parameter equations. *Can. J. Chem. Engng* **58**, 663–669.
- McCoubrey, J., Homer, J., Jenkins, J. D. and Kakhu, A. I., 1993, Uses and limitations of rigid lattice models for rationalising excess thermodynamic functions of binary liquid mixtures at low pressures. *J. Chem. Soc. Faraday Trans.* **89**, 3767–3772.
- McDermott, C. and Ashton, N., 1977, Note on the definition of local composition. *Fluid Phase Equilibria* **1**, 33–35.
- Maroncelli, M., Strauss, H. L. and Snyder, R. G., 1985, Structure of the *n*-alkane binary solid *n*-C₁₉H₄₀/*n*-C₂₁H₄₄ by infrared spectroscopy and calorimetry. *J. phys. Chem.* **89**, 5260–5267.
- Matheson, R. R. and Smith, P., 1985, A simple thermodynamical analysis of solid-solution formation in binary systems of homologous extended-chain alkanes. *Polymer* **26**, 288–292.
- Maurer, G. and Prausnitz, J. M., 1978, On the derivation and extension of the UNIQUAC equation. *Fluid Phase Equilibria* **2**, 91–99.
- Mazee, W. M., 1960, Paraffins, composition and phase behavior of the most important components: the *n*-alkanes. *Erdoel Kohle* **13**, 88–93.
- Morgan, D. L. and Kobayashi, R., 1994, Extension of Pitzer CSP models for vapor pressures and heats of vaporization to long-chain hydrocarbons. *Fluid Phase Equilibria* **94**, 51–87.
- Panayiotou, C. and Vera, J. H., 1980, The quasi-chemical approach for non-randomness in liquid mixtures. Expressions for local surfaces and local compositions with an application to polymer solutions. *Fluid Phase Equilibria* **5**, 55–80.
- Prausnitz, J. M., Lichtenthaler, R. N. and Azevedo, E. G., 1986, *Molecular Thermodynamics of Fluid-phase Equilibria*, 2nd Edition. Prentice-Hall, Englewood Cliffs, NJ.
- Renon, H. and Prausnitz, J. M., 1969, Derivation of the three-parameter Wilson equation for the excess Gibbs energy of liquid mixtures. *A.I.Ch.E. J.* **15**, 785.
- Sabour, A., 1994, Experimental and thermodynamic study of binary systems of even–odd *n*-alkanes (*n*-C₂₃:*n*-C₂₄ and *n*-C₂₃:*n*-C₂₂). Modelling and calculation of phase diagram. Ph.D. thesis, Institut National Polytechnique de Lorraine, Nancy, France (in French).
- Sabour, A., Bourdet, J. B., Bouroubka, M. and Dirand, M., 1995, Modifications to the binary phase diagram of the alkane mixtures *n*-C₂₃–*n*-C₂₄. *Thermochim. Acta* **249**, 269–283.
- Snyder, R. G., Goh, M. C., Srivatsavoy, V. J. P., Strauss, H. L. and Dorset, D. L., 1992, Measurement of the growth kinetics of microdomains in binary *n*-alkane solid solutions by infrared spectroscopy. *J. phys. Chem.* **96**, 10,008–10,019.
- Snyder, R. G., Srivatsavoy, V. J. P., Cates, D. A., Strauss, H. L. and Dorset, D. L., 1994, Hydrogen/deuterium effects on microphase separation in unstable crystalline mixtures of binary *n*-alkanes. *J. Phys. Chem.* **98**, 674–684.
- Swallin, R. A., 1962, *Thermodynamics of Solids*. Wiley, NY.
- Tassios, D., 1971, A single parameter equation for isothermal vapor–liquid equilibrium correlations. *A.I.Ch.E. J.* **17**, 1367–1371.
- Turner, W. R., 1971, Normal alkanes. *Ind. Engng Chem. Prod. Res. Dev.* **10**, 238–260.
- Ungar, G., 1983, Structure of rotator phases in *n*-alkanes. *J. phys. Chem.* **87**, 689–695.
- Wilson, G. M., 1964, Vapor–liquid equilibrium. XI. A new expression for the excess free energy of mixing. *J. Am. Chem. Soc.* **86**, 127–130.
- Wong, K. F. and Eckert, C. A., 1971, Dilute solution behavior of two cyclic anhydrides. *Ind. Engng Chem. Fundam.* **10**, 20–23.
- Wurfinger, A. and Schneider, G. M., 1973, Differential thermal analysis under high pressures II: investigation of the rotational transition of several *n*-alkanes. *Ber. Bunsenges. Phys. Chem.* **77**, 121–128.

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 A1. Data base for the phase diagrams of solid/solid equilibrium of *n*-alkanes

System	References
C ₁₉ H ₄₀ –C ₂₁ H ₄₄	Mazee (1960) Wurfinger and Schneider (1973) Pechhold <i>et al.</i> (1966) Maroncelli <i>et al.</i> (1985)
C ₁₉ H ₄₀ –C ₂₃ H ₄₈	Pechhold <i>et al.</i> (1966)
C ₂₀ H ₄₂ –C ₂₂ H ₄₆	Luth <i>et al.</i> (1974) Kieras <i>et al.</i> (1964)
C ₂₁ H ₄₄ –C ₂₃ H ₄₈	Mazee (1949) Bensor and Bloor (1977)
C ₂₂ H ₄₆ –C ₂₃ H ₄₈	Sabour (1994) Mazee (1960)
C ₂₂ H ₄₆ –C ₂₄ H ₅₀	Achour <i>et al.</i> (1992) Mazee (1960)
C ₂₃ H ₄₈ –C ₂₄ H ₅₀	Denicolo <i>et al.</i> (1984) Sabour (1994)
C ₂₃ H ₄₈ –C ₂₅ H ₅₂	Kieras <i>et al.</i> (1964) Retief <i>et al.</i> (1985)
C ₂₃ H ₄₈ –C ₂₇ H ₅₆	Kieras <i>et al.</i> (1964)
C ₂₄ H ₅₀ –C ₂₆ H ₅₄	Achour (1994) Mazee (1960)
C ₂₄ H ₅₀ –C ₂₈ H ₅₈	Basson and Reynhardt (1991) Asbach and Kilian (1970) Asbach <i>et al.</i> (1982) Hohne and Blankenhorn (1994) Hohne and Blankenhorn (1994)
C ₂₄ H ₅₀ –C ₃₀ H ₆₂	Kieras <i>et al.</i> (1964)
C ₂₅ H ₅₂ –C ₂₇ H ₅₆	Piper <i>et al.</i> (1931)
C ₂₆ H ₅₄ –C ₂₈ H ₅₈	Nakafuku and Sugiuchi (1993)
C ₂₆ H ₅₄ –C ₃₀ H ₆₂	Asbach <i>et al.</i> (1982)
C ₂₆ H ₅₄ –C ₃₂ H ₆₆	Hohne and Blankenhorn (1994)
C ₂₈ H ₅₈ –C ₂₉ H ₆₀	Piper <i>et al.</i> (1931)
C ₂₈ H ₅₈ –C ₃₂ H ₆₆	Asbach <i>et al.</i> (1982)

Table A1. (Continued)

System	References
C ₂₉ H ₆₀ -C ₃₁ H ₆₄	Piper <i>et al.</i> (1931)
C ₃₀ H ₆₂ -C ₃₂ H ₆₄	Asbach <i>et al.</i> (1982)
C ₃₀ H ₆₂ -C ₃₄ H ₇₀	Dorset (1990)
C ₃₀ H ₆₂ -C ₃₅ H ₇₂	Mazee (1960)
C ₃₀ H ₆₂ -C ₃₆ H ₇₄	Dorset (1986)
C ₃₃ H ₆₈ -C ₃₅ H ₇₂	Kieras <i>et al.</i> (1964)

BIBLIOGRAPHY

- Achour, Z., 1994, Ph.D. thesis, Institut National Polytechnique Lorraine, Nancy, France.
- Achour, Z., Barbillon, P., Bouroubka, M. and Dirand, M., 1992, *Thermochim. Acta* **204**, 187.
- Asbach, G. I. and Kilian, H. G., 1970, *Ber. Bunsen Gesellschaft* **74**, 814-823.
- Asbach, G. I., Kilian, H. G. and Stracke, Fr., 1982, *Colloid Polym. Sci.* **260**, 151-163.
- Basson, I. and Reynhardt, E. C., 1991, *J. chem. Phys.* **95**, 1215-1222.
- Batalin, O. Yu. and Zakharov, M. Yu., 1990, *Russian J. Phys. Chem.* **64**, 444.
- Bonsor, D. H. and Bloor, D., 1977, *J. Mater. Sci.* **12**, 1559-1564.
- Denicolo, I., Craievich, A. F. and Doucet, J., 1984, *J. chem. Phys.* **80**, 6200-6203.
- Dorset, D. L., 1986, *Macromolecules* **19**, 2965-2973.
- Dorset, D. L., 1990, *Macromolecules* **23**, 623-633.
- Hohne, G. W. H. and Blankenhorn, K., 1994, *Thermochim. Acta* **238**, 351-370.
- Kieras, J. A., Turner, W. R. and Melpolder, F. W., 1964, *Am. Chem. Soc. Div. Petrol. Chem. Prepr.* **9**, 257-263.
- Luth, H., Nyburg, S. C., Robinson, P. M. and Scott, H. G., 1974, *Mol. Cryst. Liq. Cryst.* **27**, 337-357.
- Maroncelli, M., Strauss, H. L. and Snyder, R. G. J., 1985, *Phys. Chem.* **89**, 5260-5267.
- Mazee, W., 1949, *J. Inst. Petroleum* **35**, 97-102.
- Mazee, W., 1960, *Erdol und Kohle* **13**, 88-93.
- Nakafuku, C. and Sugiyuchi, T., 1993, *Polymer* **34**, 4945-4952.
- Pechhold, W., Dollhopf, W. and Engel, A., 1966, *Acustica*, **17**, 61-72.
- Piper, S. H., Chibnall, A. C., Hopkins, S. J., Pollard, A., Smith, J. A. B. and Williams, E. F., 1931, *Biochem. J.* **25**, 2072-2094.
- Retief, J. J., Engel, D. W. and Boonstra, E. G., 1985, *J. Appl. Cryst.* **18**, 156-158.
- Sabour, A., 1994, Ph.D. thesis, Institut National Polytechnique de Lorraine, Nancy, France.
- Wurflinger, A. and Schneider, G. M., 1973, *Ber. Bunsenges Phys. Chem.* **73**, 121-128.