

Predictive Local Composition Models for Solid/Liquid Equilibrium in *n*-Alkane Systems: Wilson Equation for Multicomponent Systems

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The predictive local composition model is applied to multicomponent hydrocarbon systems with long-chain *n*-alkanes as solutes. The results show that it can successfully be extended to high-order systems and accurately predict the solid appearance temperature, also known as cloud point, in solutions of known composition using only binary information. The model can describe the experimentally well-known capacity of heavy alkanes to act as cloud-point depressants and explains it in terms of the nonideality of the solid solutions formed. There are good indications that no significant error is introduced by considering the multiple orthorhombic phases as a single phase. It is shown that for low concentrations in heavy fraction the interaction parameter α_{1s} can be neglected and thus the model becomes purely predictive.

Introduction

The appearance of a solid paraffinic phase, wax, in a hydrocarbon fluid exposed to temperatures below ambient temperature is a common phenomenon occurring in a diversity of situations from petroleum reservoirs to cars on cold mornings. The understanding of this behavior and the capacity to model it are fundamental in dealing with the nuisances that the precipitation of a waxy phase usually produces such as the plugging of reservoirs, pipelines, and fuel filters. Fuel specifications, especially for fuels with application in sensitive environments such as aircrafts and ships, require also the ability to predict the solid appearance temperature in hydrocarbon fluids.

Wax's main components are *n*-alkanes in a proportion that can attain 95% (Pedersen et al., 1989). The wax modeling is thus a problem altogether equivalent to the description of solid/liquid equilibrium in alkane–hydrocarbon systems.

The thermodynamical basis of solid/liquid equilibrium has been established for a long time. An equation relating the thermophysical properties of pure components with the nonideality of the phases in equilibrium and the composition of these phases can be written for each component present in the equilibrium (Prausnitz et al., 1986)

$$\ln \frac{s\gamma^s}{x\gamma^l} = \frac{\Delta h_m}{RT_m} \left(\frac{T_m}{T} - 1 \right) + \frac{\Delta h_t}{RT_t} \left(\frac{T_t}{T} - 1 \right) - \frac{\Delta C_{p,m}}{R} \left(\frac{T_m}{T} - \ln \frac{T_m}{T} - 1 \right) \quad (1)$$

Herefrom, using the data available in the literature for the thermophysical properties (Broadhurst, 1962) and using adequate models for the nonideality of the phases present, a procedure can be developed to calculate the temperature of solid appearance, if the solution composition is known.

Alkane solid phases have a rather complex behavior. The long-chain *n*-alkanes that form the wax phase have at least two different enantiotropic forms and may have up to four (Maroncelli et al., 1982). This number rises even higher for binary systems where the formation of

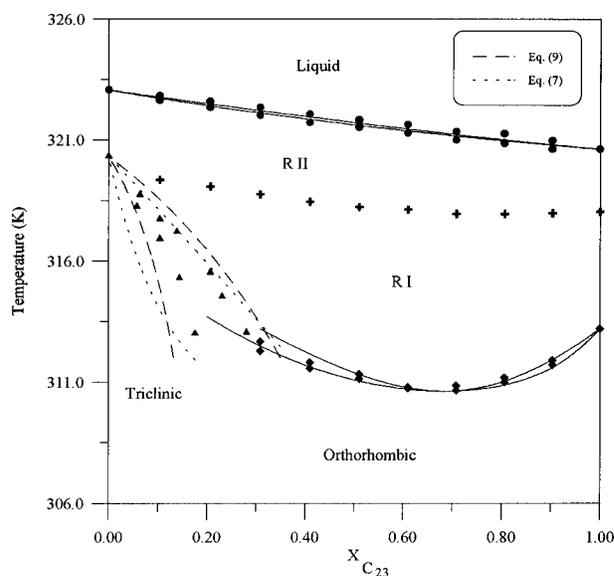


Figure 1. Experimental and calculated phase diagram for *n*-C₂₃H₄₈/*n*-C₂₄H₅₀ (Denicolo et al., 1984).

new crystalline structures that are not present in the pure components occurs. The *n*-C₂₀H₄₂/*n*-C₂₂H₄₆ phase diagram by Luth et al. (1974) showed six different solid phases, and with the development of experimental techniques more solid phases are being identified (Achour, 1994). A phase diagram for the system *n*-C₂₃H₄₈/*n*-C₂₄H₅₀ (Denicolo et al., 1984) is shown in Figure 1. For this system, in addition to the liquid phase, four solid phases are present: two rotator phases, RI and RII, exist at high temperatures, and orthorhombic and triclinic phases are present at lower temperatures. All these phases are of some importance in describing processes of industrial interest. In wax formation only the liquid and the low-temperature solid phases are considered. Because the long-chain alkanes are present in small quantities, the cloud point normally appears below the rotator–orthorhombic phase transition. Under these conditions it is the low-temperature solid phases that are found in equilibrium with the liquid, as is confirmed by X-ray diffraction analyses for the *n*-C₂₂H₄₆/*n*-C₂₀H₄₂/*n*-C₁₂H₂₆ system by Gerson et al. (1993). In binary systems the low-temperature solid phase is, in at least 70% of the composition range, an orthorhombic phase (Achour, 1994). Some results by

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Gerson et al. (1991) indicate that the same is valid in multicomponent systems. In the other cases, when an even n -alkane represents more than 90% of the composition of the solid phase, a triclinic crystal, or for large even n -alkanes a monoclinic crystal, will replace the orthorhombic structure. The main emphasis of this work will be given to the liquid/orthorhombic solid equilibrium, around which revolve the work previously developed with binary systems. The liquid/monoclinic and the liquid/triclinic equilibria will be dealt with in a somewhat more empirical form.

Liquid-Phase g^E Model

A hydrocarbon liquid phase is extremely disordered, with long and short molecules coexisting in solution. If only saturated hydrocarbons are present, no, or only small energetic, interactions arise between the molecules and the system can to a fair extent be considered athermal. The nonideality arises thus mainly from entropic effects such as size difference and free-volume effects. The Flory free-volume equation can effectively deal with such kinds of interactions (Coutinho et al., 1995a) and will be used to describe the liquid phase:

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

with

$$\phi_i = \frac{x_i(V_i^{1/3} - V_{wi}^{1/3})^{3.3}}{\sum_j x_j(V_j^{1/3} - V_{wj}^{1/3})^{3.3}} \quad (2b)$$

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

It is not uncommon that unsaturated hydrocarbons, such as aromatic compounds, may also be present in a natural hydrocarbon solution. In this case it is not possible to neglect the energetic interactions that arise between the aromatic and saturated hydrocarbons. To take these effects into consideration, a residual contribution is added to the Flory free-volume equation. Following what was done in previous works (Kontogeorgis et al., 1993), the UNIFAC residual term was added to the combinatorial free-volume term without parameter reestimation. While this procedure is not entirely correct, it was found that the resulting model could describe binary systems of long alkanes in aromatic solvents with the same accuracy provided by Flory free volume for saturated systems (Coutinho, 1995). The model used for the liquid phase can thus be described as:

$$\ln \gamma = \ln \gamma^{\text{res}} + \ln \gamma^{\text{comb-fv}} \quad (3)$$

where $\ln \gamma^{\text{comb-fv}}$ is described by eqs 2a and 2b and $\ln \gamma^{\text{res}}$ is given by UNIFAC (Fredenslund et al., 1977; Hansen et al., 1991). The importance of the residual contribution is stated by the results presented in Figure 2.

Solid-Phase g^E Models

As previously discussed multiple solid phases can coexist. In the low-temperature solid phase, monoclinic, triclinic, and orthorhombic solid phases may be present. In the even/even binary systems, moreover, several orthorhombic solid phases are encountered (Luth et al.,

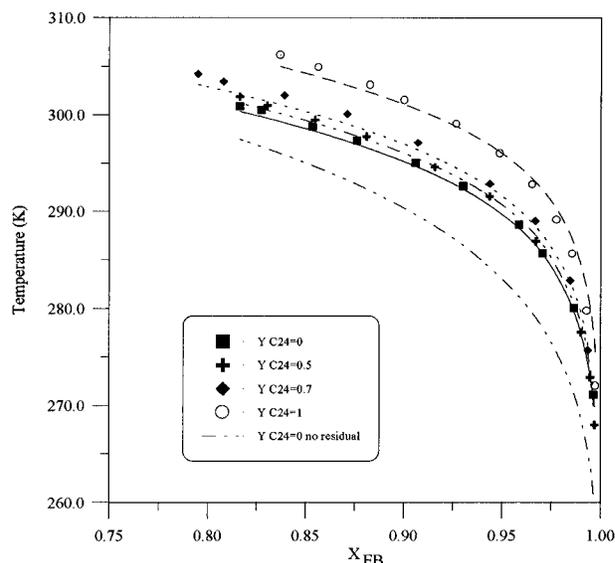


Figure 2. Temperature vs solvent composition for the system $n\text{-C}_{23}\text{H}_{48}/n\text{-C}_{24}\text{H}_{50}/\text{EB}$. Experimental data by Ghogomu et al. (1989).

1974; Achour, 1994). In eq 1 the thermophysical properties, such as heats and temperatures of phase transition, of each component are required to perform solid/liquid equilibrium calculations, but only the properties of the phase transitions present in the pure components are known. It will be assumed that the metastable rotator-orthorhombic phase transition for even n -alkanes can be obtained by interpolation of the known values for the neighboring odd homologues given by Broadhurst (1962). The correlations used for this purpose are presented in the Appendix.

No simple way seems to exist to estimate the thermophysical properties of the multiple orthorhombic solid phases present in even/even binary systems, and so it will be here presumed that the multiple orthorhombic solid phases may be treated as a single phase with pure-component thermophysical properties obtained by interpolation of the properties of the neighboring odd n -alkanes.

Compositional analyses show that only the heavy components are present in the solid phase. When, due to size differences, no coprecipitation occurs, the solid phase is a pure solid formed by only one of the heavier molecules present in the solution (Brownawell and Hollyday, 1962; Holder and Winkler, 1965). Analyses of waxes obtained from diesel fuels show also the absence of light components in the solid phase (Gerson et al., 1991; Burger et al., 1981; Lewtas et al., 1991).

Predictive Local Composition Model for the Orthorhombic Phase. For the description of the nonideality of orthorhombic solid phases, a predictive version of the Wilson equation developed by Coutinho et al. (1995c) is used. The model is basically a version of the Wilson equation where local mole fractions instead of local volumetric fractions are employed as shown in eq 4. The pair interaction energies, λ_{ls} , λ_{ll} , and

$$\frac{g^E}{RT} = -x_l \ln \left(x_l + x_s \exp \left(-\frac{\lambda_{ls} - \lambda_{ll}}{RT} \right) \right) - x_s \ln \left(x_s + x_l \exp \left(-\frac{\lambda_{ls} - \lambda_{ss}}{RT} \right) \right) \quad (4)$$

λ_{ss} , are obtained from physical considerations relating the molecular interactions with macroscopical properties. The procedure for calculation of interaction ener-

gies is summarized in eqs 5a and 5b. where α_{is} is a

$$\lambda_{ii} = -\frac{2}{Z}(\Delta h_{\text{sblm},i} - RT) \quad (5a)$$

$$\lambda_{is} = \lambda_{ss}(1 + \alpha_{is}) \quad (5b)$$

correction factor that takes into account deviations to the predicted behavior. The values of α_{is} used are obtained from correlation of experimental phase behavior for binary systems or in the absence of experimental data from the correlation:

$$\alpha_{is} = -73.98 \frac{(l_i - l_s)^2}{l_s^3} + 0.01501 \quad (6)$$

presented by Coutinho et al. (1995c), where l_i is the length of the crystal cell in angstroms as given by Broadhurst (1962). This version of the Wilson equation, like the original version, requires only binary pair interaction energies when applied to multicomponent systems.

Monoclinic and Triclinic Phases. Given their less importance, the monoclinic and triclinic phases have, contrary to the orthorhombic phase, not been the object of a thorough experimental or theoretical study. Little data are available for binary systems, and several authors even fail to acknowledge the presence of a nonorthorhombic solid phase (Mazee, 1960; Basson and Reynhardt, 1991). These phases are normally associated with large temperature variations within a narrow composition range, and consequently thermal effects are of importance in their description. A model like the Wilson equation, that possesses a very deficient temperature dependence as shown by Coutinho et al. (1995c), will not be able to correctly describe their phase behavior. A more adequate model will be used for even/odd systems.

Using a solid solution lattice approach and assuming negligible entropic effects, it is possible to derive a g^E model such as

$$g^E = \Omega x_i x_j \quad (7)$$

with Ω being a binary parameter characteristic of the system i/j . To introduce in this model the entropic effects, a relation between excess entropies and enthalpies in the solid phase will be used.

Using statistical thermodynamics, Tanaka (1995) showed that the relation between excess entropies and enthalpies previously derived for the liquid phases (Tanaka et al., 1990) is also valid for solids.

$$\frac{h^E}{s^E} = \alpha \frac{T_{mi} T_{mj}}{T_{mi} + T_{mj}} = \alpha \phi \quad (8)$$

This relation was first applied with success to alloys, and later Oonk and co-workers (van der Kemp et al., 1993) showed its validity for a range of organic systems. Coutinho et al. (1995b) extended the applicability of eq 8 to the rotator phase of n -alkanes. In the absence of excess enthalpy data for the monoclinic and triclinic phases in binary n -alkane systems, it is not possible to confirm the validity of this relation but it seems a fair hypothesis to assume that the relation presented in eq 8 is valid also for the nonorthorhombic n -alkane solid phases and to introduce it in eq 7, obtaining a temperature-dependent excess Gibbs free energy model for the monoclinic and triclinic n -alkane phases.

$$g^E = \Omega \left(1 - \frac{T}{\alpha \phi}\right) x_i x_j \quad (9)$$

This model has two parameters for each binary, Ω and α , that can be obtained by correlation of phase behavior data.

Results and Discussion

Data for multicomponent solid/liquid equilibria of n -alkanes in model systems with defined composition are rather scarce and only available for systems with a maximum of two heavy components in solution. Still many of these data are not usable because the results are presented just in a qualitative form (Gerson et al., 1993) or are not equilibrium data (Roberts et al., 1994). Others use undefined solvents (Holder and Winkler, 1965) or cloud-point measurement procedures of poor accuracy (Brownawell and Hollyday, 1962). Only the data by Ghogomu et al. (1989) seem to fulfill the requirements of accuracy and composition definition to be used in the evaluation of the capacity of the predictive local composition model to deal with high-order systems. These authors present data for both n -C₂₂H₄₆/ n -C₂₄H₅₀/ethylbenzene (EB) and n -C₂₃H₄₈/ n -C₂₄H₅₀/ethylbenzene measured by thermal analysis. These sets of data are thoroughly compared with the phase behavior predicted by the proposed model. The model predictions are also compared against the data by Brownawell and Hollyday (1962) and Holder and Winkler (1965). Due to the poor accuracy of the data of the former and the unsatisfactory definition of the composition of the latter, the deviations between the experimental and calculated data are unsurprisingly larger than those for the previous systems, but still a reasonable description of the experimental data is possible and interesting conclusions can be drawn from them. Data for the system n -C₂₄H₅₀/ n -C₂₈H₅₈/ n -C₇H₁₆ were measured in our laboratory during the development of a new experimental technique for cloud-point measurements (Bach et al., 1995). The amount of data is not very large and regrettably not sufficiently accurate yet. Some of the data are here used to be compared with the model predictions in a study of the influence of the value of α_{is} in the calculations.

The data by Ghogomu et al. (1989) for the two ternary systems were modeled by using eq 1, and the procedure for estimation of pure-component thermophysical properties, and the g^E models described before: the liquid phase is described by the Flory free-volume UNIFAC model, the orthorhombic phase by the predictive Wilson model, and the nonorthorhombic phases, whenever their description was possible, by means of eqs 7 or 9.

The calculated phase diagram for the binary n -C₂₃H₄₈/ n -C₂₄H₅₀ is shown in Figure 1 and compared with the experimental data by Denicolo et al. (1984). A good description of the phase behavior is obtained for the liquid/rotator and rotator/orthorhombic equilibria. The rotator/triclinic equilibrium, described both by means of eq 7 and eq 9, shows a somewhat larger deviation. The description of the low-temperature equilibrium between the triclinic and orthorhombic solids was not attempted. For the calculation with ternary systems the description of the triclinic phase by means of eq 7 was preferred, in spite of the globally worse performance, due to the good description of the upper boundary of the two-phase region. The model parameters used in the calculations of the phase behavior of this and the following systems are presented in Table 1.

For the ternary system the average deviations of the predictions are presented in Table 2. The average

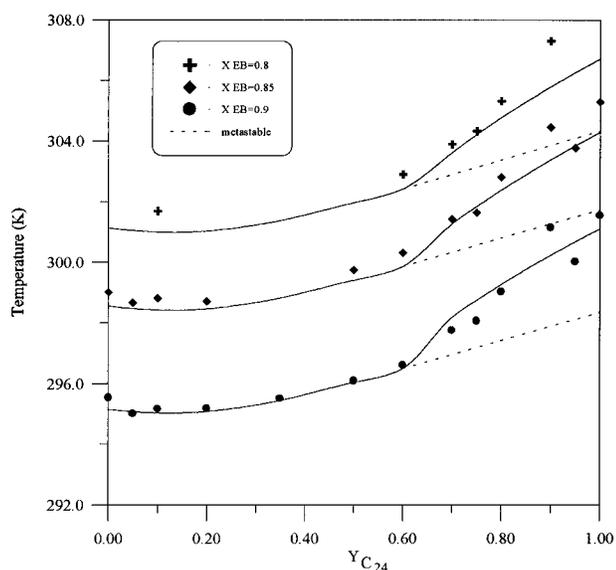
Table 1. Binary and Interaction Parameters Used in the Description of the Solid Phases

system	solid phase	parameter
C23/C24	orthorhombic	$\alpha_{1S} = 0.0093$
	triclinic (eq 7)	$\Omega = 3900 \text{ J/mol}$
	triclinic (eq 9)	$\alpha = 2.055, \Omega = 86\,000 \text{ J/mol}$
C22/C24	orthorhombic	$\alpha_{1S} = -0.006$
C22/C20	orthorhombic	$\alpha_{1S} = -0.023$
C24/C20	orthorhombic	$\alpha_{1S} = -0.078$
C24/C28	orthorhombic	$\alpha_{1S} = -0.023$
C28/C20	orthorhombic	

Table 2. Deviations between the Predicted and Experimental Phase Diagrams for the System C₂₃/C₂₄/EB

Y_{C24}	$\Delta \bar{T}$ (K)	Y_{C24}	$\Delta \bar{T}$ (K)
0.0000	0.47	0.7001	0.72
0.0000	6.14 ^a	0.7500	0.79
0.0497	0.52	0.7998	1.64
0.1002	0.70	0.8999	2.69
0.2000	0.50	0.9500	1.80
0.3498	0.63	1.0000	2.68
0.5001	0.68	1.0000	1.16 ^b
0.6001	0.63	$\Delta \bar{T}_{\text{orth}}$	0.63

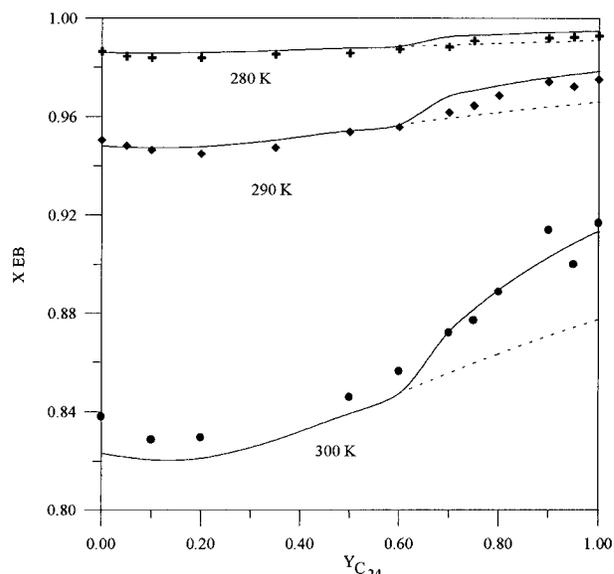
^a Calculated with $\gamma^{\text{res}} = 1$. ^b Triclinic.

**Figure 3.** Temperature vs solute composition for the system $n\text{-C}_{23}\text{H}_{48}/n\text{-C}_{24}\text{H}_{50}/\text{EB}$. Experimental data by Ghogomu et al. (1989).

temperature deviation for the entire orthorhombic region is about 0.6 K, which is expected to be within the experimental accuracy of the data. Three projections of the ternary diagram are presented in Figures 2–4. Figure 2 shows some calculated temperature vs composition curves at a constant composition in basis without solvent, as defined in eq 10, against the measured data. The results presented in Table 2 show

$$Y_i = x_i / \sum_{j \neq \text{solvent}} x_j \quad (10)$$

that the predictions are very good up to the peritectic point situated around $Y_{C24} = 0.75$. The calculation for $Y_{C24} = 0$ is performed with and without residual contribution. The average error for the results with $\gamma^{\text{res}} = 1$ is about 15 times larger as shown in Table 2, asserting the importance of a residual contribution for nonathermal solutions. For $Y_{C24} = 1$ the equilibrium with the triclinic phase is presented. The data used in Figures 3 and 4 are interpolated from the measured data. In Figure 3 three curves at a constant composition

**Figure 4.** Isotherms for the ternary diagram $n\text{-C}_{23}\text{H}_{48}/n\text{-C}_{24}\text{H}_{50}/\text{EB}$ (Ghogomu et al., 1989).**Table 3. Deviations between the Predicted and Experimental Phase Diagrams for the System C₂₂/C₂₄/EB**

Y_{C24}	$\Delta \bar{T}$ (K)	Y_{C24}	$\Delta \bar{T}$ (K)
0.0000	3.92	0.3998	0.78
0.0000	0.91 ^a	0.5290	0.87
0.0504	0.80	0.5755	0.90
0.0900	0.40	0.5999	0.84
0.0999	0.48	0.6750	0.44
0.1151	0.43	0.7350	0.55
0.1303	0.50	0.7999	1.26
0.1499	0.51	0.9000	2.00
0.2030	1.13	1.0000	2.68
0.3003	0.69	1.0000	1.16 ^a
0.3497	0.81	$\Delta \bar{T}_{\text{orth}}$	0.68

^a Triclinic.

of the solvent are presented, while Figure 4 displays some isotherms for this system. A good predictive description of the ternary phase diagram is obtained by use of only binary information. For this system α_{1S} was obtained from binary experimental data, but, as will be discussed later, the use of the correlation for α_{1S} would lead to similar results and not significantly larger deviations would be obtained by considering $\alpha_{1S} = 0$.

The deviations of the predictions for the system $n\text{-C}_{22}\text{H}_{46}/n\text{-C}_{24}\text{H}_{50}/\text{EB}$ are presented in Table 3. An average deviation inferior to 0.7 K within the whole orthorhombic region is obtained. This result is particularly interesting because the calculation procedure presumes the existence of a single orthorhombic solid phase instead of the multiple orthorhombic phases known experimentally to exist (Luth et al., 1974; Achour, 1994). It is apparent from the results that this simplification does not significantly affect the predictions. The metastable regions at the extremes of composition can be easily recognized by the large deviations. This identification of the metastable region is confirmed by the X-ray diffraction results by Gerson et al. (1993). The attempts to describe the nonorthorhombic regions were not successful for even/even systems. The nonideality of these regions seems to have a large dependence on the temperature and to be dominated by the entropy of the phases. Figures 5–7 show the ternary diagram projections equivalent to those presented to the previous system: curves at a constant value of Y_{C24} for the heaviest component in Figure 5, isothermal cuts in the ternary diagram in

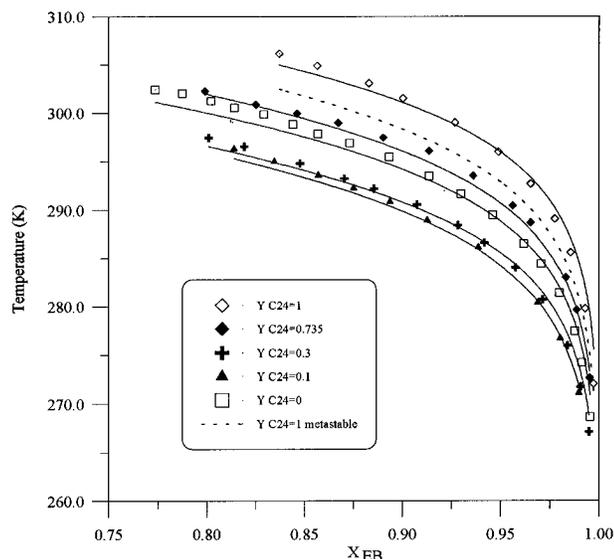


Figure 5. Temperature vs solvent composition for the system $n\text{-C}_{22}\text{H}_{46}/n\text{-C}_{24}\text{H}_{50}/\text{EB}$. Experimental data by Ghogomu et al. (1989).

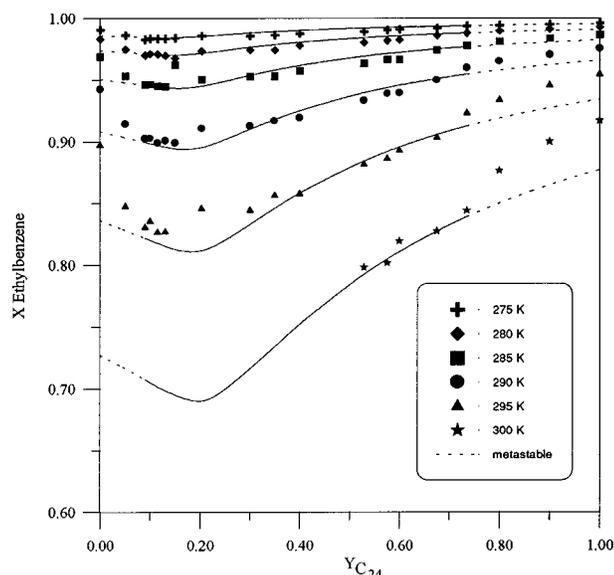


Figure 6. Isotherms for the ternary diagram $n\text{-C}_{22}\text{H}_{46}/n\text{-C}_{24}\text{H}_{50}/\text{EB}$ (Ghogomu et al., 1989).

Figure 6, and curves of isocomposition for the solvent in Figure 7. In Figure 5, for $Y_{C_{24}} = 0$ and $Y_{C_{24}} = 1$ the equilibria with the triclinic phase are presented. The ternary diagram is well described.

The low deviations for these systems provide a validation of the model for multicomponent systems since the predictions are within the accuracy of the experimental data. They also indicate that the procedure used to obtain the metastable thermophysical properties by interpolation of the actual values for homologue neighbors is correct. The accurate description of the ternary diagrams in the solvent-rich region shows that the model can successfully be extended to temperatures well removed from those of the binaries to which it was previously applied.

Brownawell and Hollyday (1962) provided one of the first studies of wax formation in fuels using ternary model systems. Unfortunately, in their measurements they have used a standardized ASTM cloud-point test that is not very accurate because the solution is not cooled uniformly and also the cooling rate is irregular (Holder and Winkler, 1965). ASTM cloud-point tests

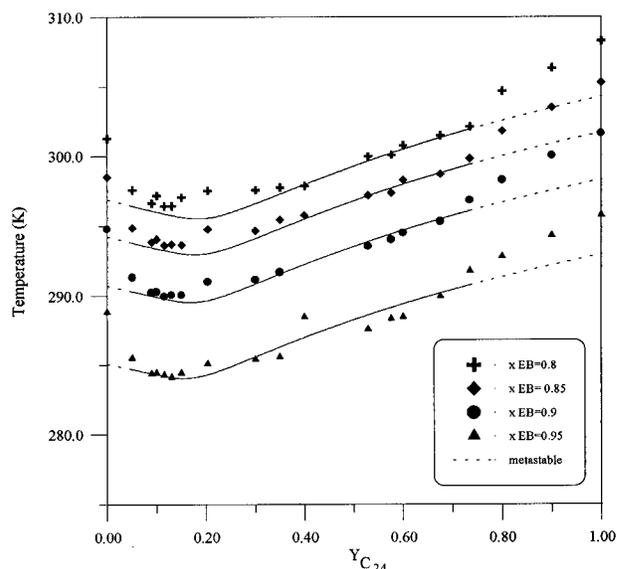


Figure 7. Temperature vs solute composition for the system $n\text{-C}_{22}\text{H}_{46}/n\text{-C}_{24}\text{H}_{50}/\text{EB}$. Experimental data by Ghogomu et al. (1989).

Table 4. Analyses of the Accuracy of Binary Experimental Data by Brownawell and Hollyday (1962)

system	W_{C7}	T_{exp}	T_{clc}
C20/C7	0.9193	274.95 ^a	274.75
C20/C7	0.95	277.31	269.66
C20/C7	0.98	268.73	260.99
C20/C7	0.99	267.48	256.21
C22/C7	0.95	278.98	277.48
C22/C7	0.98	265.74	269.91
C22/C7	0.99	258.61	264.53
C24/C7	0.98	270.93	275.99
C24/C7	0.9793	275.55 ^a	276.24

^a Data by Domanska et al. (1987).

also show a bad reproducibility, typically around 2 K (Lando and Oakley, 1969; Reddy, 1986). The data presented are thus expected to be rather poor. This is especially visible in the points for binary systems at the extremes of the phase diagrams, where large differences are found in comparison with the predicted results (known to be accurate within 1 K (Coutinho et al., 1995)), and experimental data by other authors as shown in Table 4. The predictions can in any case provide a fair representation of the results both in terms of their qualitative features and in what concerns the cloud points. The results are presented in Figures 8 and 9. The W are mass fractions in basis without solvent defined in a way similar to eq 10. The predictions seem to be within the experimental uncertainty of the data. Figure 8 shows the effect of the total amount of heavy material in the cloud point for three cases in which 1, 2, or 5% weight of heavy material was used. The open symbols are the calculated values for the binaries as presented in Table 4. The influence of the size of the second heavy compound is shown in Figure 9. It is interesting to notice that for $W_{\text{heaviest}} > 0.5$ the cloud points are dominated by the heaviest compound, the influence of the second heavy compound being very small.

The last systems studied are by Holder and Winkler (1965). They found ASTM tests very inaccurate, rejected them, and developed another measurement technique that seems to be more appropriate for the measurement of cloud points. Unfortunately, no information about the solvent used is provided besides that it is a "dewaxed gas oil that gave no ASTM cloud point

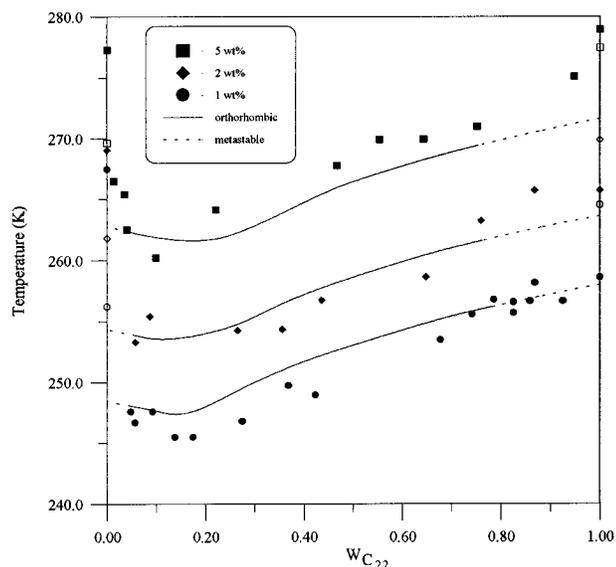


Figure 8. Temperature vs solute composition for the system $n\text{-C}_{22}\text{H}_{46}/n\text{-C}_{20}\text{H}_{42}/n\text{-C}_7\text{H}_{16}$ for three concentrations of heavy fraction (Brownawell and Hollyday, 1962).

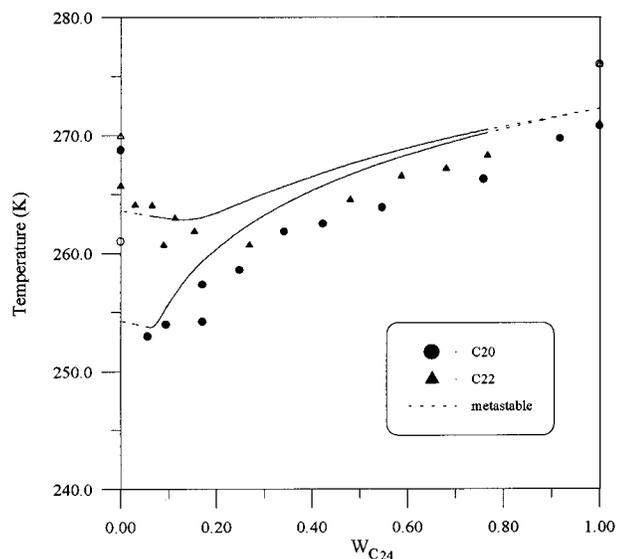


Figure 9. Temperature vs solute composition for the systems $n\text{-C}_{22}\text{H}_{46}/n\text{-C}_{24}\text{H}_{50}/n\text{-C}_7\text{H}_{16}$ and $n\text{-C}_{20}\text{H}_{42}/n\text{-C}_{24}\text{H}_{50}/n\text{-C}_7\text{H}_{16}$ for a total concentration of heavy fraction of 2 wt % (Brownawell and Hollyday, 1962).

at -70°F . 2,4-Dipropylheptane (C13) was used for calculation purposes as solvent. It is expected to provide a fair representation of the dewaxed gas oil and has an estimated melting point around -70°F (Constantinou and Gani, 1994). They measured data for three systems in which $n\text{-C}_{20}$ is used as the first heavy component and the second alkane changes among $n\text{-C}_{22}$, $n\text{-C}_{24}$, and $n\text{-C}_{28}$. For each system, cloud points for three total concentrations of heavy material, 2, 4, and 8% weight, are presented. A comparison between experimental and calculated data is outlined in Figures 10–12. Once again the predictions seem to be in very good agreement with the experimental data, with the exception of two curves for the $\text{C}_{20}/\text{C}_{24}$ system. These data sets, attending to the error presented by the binaries, shown as open symbols in Figure 11, are of much lower accuracy than the rest of the data by the same authors, and thus the deviations would be a result of poor quality of the data and not of a model failure.

Minima in the Cloud-Point Temperatures. One of the particular features of these results is the mini-

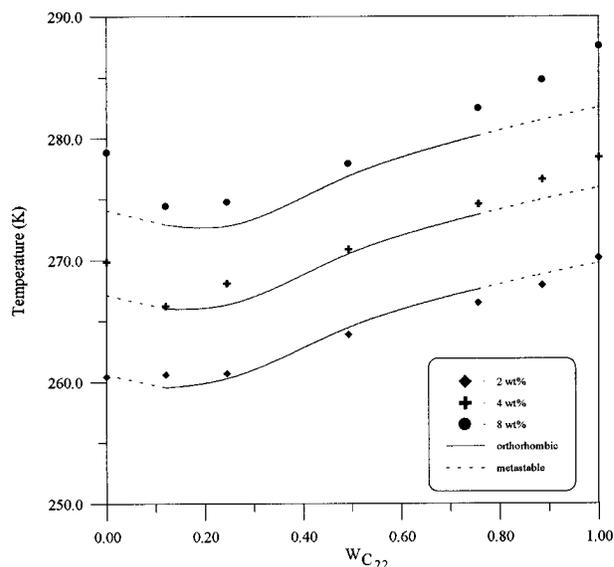


Figure 10. Temperature vs solute composition for $n\text{-C}_{22}\text{H}_{46}/n\text{-C}_{20}\text{H}_{42}/\text{C}_{13}$ at three different concentrations of heavy fraction (Holder and Winkler, 1965).

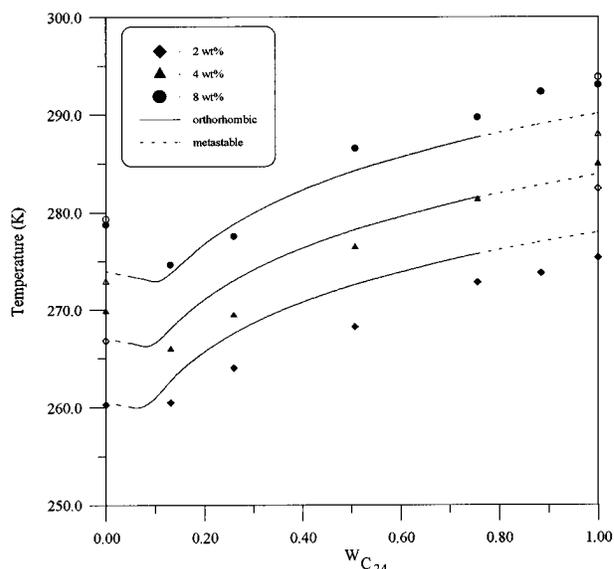


Figure 11. Temperature vs solute composition for $n\text{-C}_{24}\text{H}_{50}/n\text{-C}_{20}\text{H}_{42}/\text{C}_{13}$ at three different concentrations of heavy fraction (Holder and Winkler, 1965).

mum present in the diagrams of Figures 6 and 7. A similar behavior can be observed in Figures 8–11 but not in Figure 12. It is also present in Figure 3, but the minima are extremely shallow for a system with reduced nonideality. These minima are still more pronounced if the nonorthorhombic regions at the extremes of the phase diagram are taken into account. This is a well-known phenomenon and has been experimentally described for the last 30 years without a proper explanation (Brownawell and Hollyday, 1962; Holder and Winkler, 1965; Ghogomu et al., 1989; Gerson et al., 1993). The model can accurately describe this peculiar phase behavior and explain it in terms of the nonideality of the solid solutions. The increased solubility of a heavy n -alkane in the presence of another heavy n -alkane is due to the strong nonideality of the solutions formed by them. Physically, this phenomenon can be viewed as the difficulty of crystal formation in the presence of impurities, or in another way as the lower melting point presented by a mixed crystal compared with the pure crystal and the lower stability of the orthorhombic structure relative to the nonorthorhombic

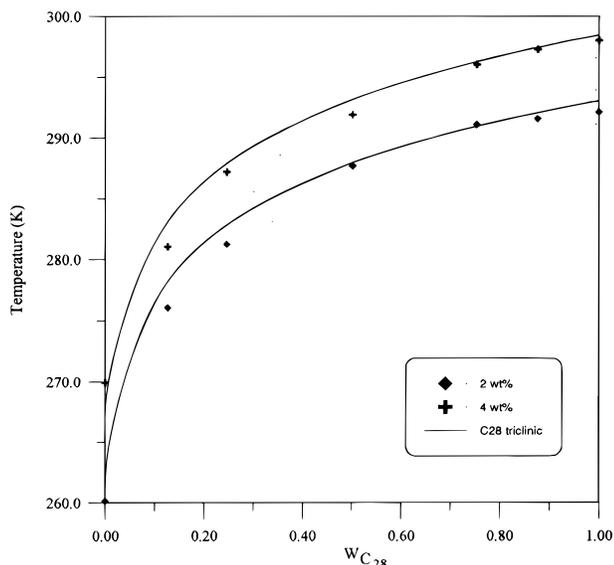


Figure 12. Temperature vs solute composition for $n\text{-C}_{28}\text{H}_{58}/n\text{-C}_{20}\text{H}_{42}/\text{C13}$ at two different concentrations of heavy fraction (Holder and Winkler, 1965).

crystalline structures. The importance of solid solution formation in the appearance of minima is perceived from the comparison between the results for systems where the solid solution is present, as $n\text{-C}_{22}/n\text{-C}_{24}/\text{EB}$ in Figure 7, and those for systems where there is no formation of solid solutions due to large size differences between the heavy compounds, as for instance $n\text{-C}_{20}/n\text{-C}_{28}/\text{C13}$ in Figure 12. The latter system does not show the presence of a minimum in the temperature composition diagram, as does the former. Moreover, for systems of weak nonideality in the solid phase, as for $n\text{-C}_{23}/n\text{-C}_{24}/\text{EB}$, the minima are present but are not very pronounced. The minima are particularly deep for even/even systems where the minimum caused by the nonideality of the orthorhombic phase is further extended by the peritectic formed with the nonorthorhombic phases.

Influence of α_{1s} . The experimental data for the system $n\text{-C}_{24}\text{H}_{50}/n\text{-C}_{28}\text{H}_{58}/n\text{-C}_7\text{H}_{16}$ at $Y_{\text{C}24} = 0.5$, measured in our laboratory, are used to study the effect of the interaction parameter α_{1s} in the calculated results. In Figure 13 the experimental data are compared with the results obtained using three different values for α_{1s} : the solid line is calculated using α_{1s} obtained from binary experimental data; the two other lines correspond to values of the interaction parameter of 0 and -0.05 . It is clear from the figure that as the content in the heavy components decreases the effect of α_{1s} becomes less and less important. For molar compositions of the heavy fraction inferior to 10%, a value typical of waxy fluids, it is reasonable to assume that the interaction parameter has no effect on the calculated results. The value of α_{1s} can thus be neglected for low concentrations of heavy fraction conferring a pure predictive character to the solid phase model. Within this region the phase behavior of a multicomponent system can be calculated using only pure-component information for the solid phase.

Conclusions

The predictive local composition model based on the Wilson equation was applied to ternary systems formed by two heavy alkanes in a solution of a lower molecular weight compound. The results obtained confirm the applicability of the model to multicomponent systems,

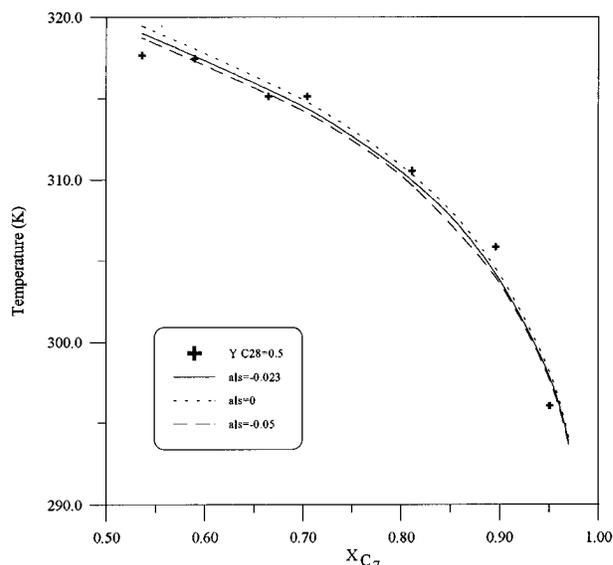


Figure 13. Study of the influence of α_{1s} in the phase behavior predictions for high solvent concentration.

showing that the model is successful in predicting the phase behavior for the studied systems within the uncertainty of the experimental data available. They also show that the model is able to cover large temperature ranges and accurately describe the solvent-rich region, well removed from the binaries of heavy alkanes for which it had been tested. The increased solubility of a n -alkane in the presence of another n -alkane of similar size is explained, and it can be described correctly by the model. The results for $\text{C}22/\text{C}24/\text{EB}$ indicate that no significant error is introduced by considering the multiple orthorhombic phases as a single phase. The calculated phase behavior is insensitive to the values of the interaction parameters α_{1s} when the molar composition of the heavy fraction is inferior to 10%. In this situation a value of $\alpha_{1s} = 0$ can be used without significant losses in accuracy, becoming the purely predictive model.

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Nomenclature

C_p = heat capacity
 g = Gibbs free energy
 h = enthalpy
 l = molecular chain length (\AA)
 s = solid-phase molar fraction
 R = universal gas constant
 T = temperature
 V = molar volume
 V_w = van der Waals volume
 W = mass fraction in basis without solvent
 x = liquid-phase molar fraction
 Y = molar fraction in basis without solvent
 Z = coordination number

Greek Letters

α = correction factor defined in eq 5b
 α = parameter in eq 8
 Δ = variation
 γ = activity coefficient
 λ = pair interaction energy

Subscripts

clc = calculated
 exp = experimental
 i = component i
 j = component j
 l = long molecule
 m = melting point
 orth = orthorhombic
 s = short molecule
 sbm = sublimation
 t = transition point
 vap = vaporization

Superscripts

E = excess property
 l = liquid phase
 s = solid phase
 - = average

Appendix

The correlations for the estimation of the metastable rotator-orthorhombic phase transitions for even *n*-alkanes were obtained using the data by Broadhurst (1962) for the same transition of odd *n*-alkanes. They can be expressed by the following equations:

$$T_{tr} = 94.2068 + 17.13945N_c - 0.4195133N_c^2 + 3.776898 \times 10^{-3}N_c^3 \quad (\text{A.1})$$

$$h_{tr} = 9.480751 - 1.47185N_c + 8.283144 \times 10^{-2}N_c^2 - 1.18138 \times 10^{-3}N_c^3 \quad (\text{A.2})$$

where T_{tr} is given in K and h_{tr} in kcal/mol.

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