

Evaluation of activity coefficient models in prediction of alkane solid–liquid equilibria

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Abstract

In the petroleum industry, the absence of a proper model to describe the liquid phase non-ideality for mixtures of alkanes with large size differences is still one of the main problems in solid–liquid equilibrium calculations. A search is made for a reliable model for the prediction of activity coefficients in these systems. The models investigated were originally developed for the polymer mixtures. The performances of original Flory–Huggins, modified UNIFAC, GCFLORY model, Flory free-volume, Entropic free-volume and some empirical modifications of these last two models are analysed extensively and compared using the deviations between experimental and predicted values of solid appearance temperature as criteria. A comprehensive experimental SLE data base with around 60 binary systems and more than 1000 data points for mixtures of linear, branched and cyclic alkanes is used. An analysis of the errors introduced by the simplifying assumptions more commonly used is also performed. Activity coefficient models that have been used in wax formation predictions, but which are not included in this comparison, are briefly discussed.

It is shown that the original Flory–Huggins activity coefficient model, the regular solution theory and the ideal solution behavior, used in several wax formation models, as well as the modified UNIFAC and original Entropic free-volume models, are not appropriate for the description of the liquid phase in alkane systems. The importance of a free-volume contribution to the phase behavior description of liquid mixtures whose components have significant size differences is evident. The Flory free-volume and a modified version of Entropic free-volume seem to be the simplest and most reliable models.

Keywords: Theory; Methods of calculation; Solid–liquid equilibria; Alkanes

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1. Introduction

Hydrocarbon fluids, like crude oils and fuels, always contain a fair amount of heavy paraffinic or naphthenic molecules along with other kinds of molecules containing long-chain alkyl groups. The cooling of these fluids below the solidification point of the heavy compounds leads to the formation of a solid wax phase. When crude oils are transported across very cold environments, such as those of the Alaskan North Slope and the North Sea, or fuels are used under low temperatures, the precipitation of wax may occur plugging fuel filters or demanding a regular “pigging” of the pipelines to prevent wax build-up inside the pipe. In an attempt to prevent these problems, a number of methods have been published concerning the prediction of wax formation in both crude oils and fuels. A large number of these models are, however, simply empirical correlations relating wax appearance temperatures with properties of the fluid. During the last years, a number of thermodynamically based models have been proposed in the literature. Some of these models use the assumption of ideal liquid phase (Walsh and Mortimer, 1971; Won, 1985; Reddy, 1986). Others use, with different degrees of success, modifications of the regular solution theory (Won, 1986, 1989; Pedersen et al., 1991; Chung, 1992), or the Flory–Huggins model for activity coefficients (Hansen et al., 1988; Chung et al., 1991). Some of these models, which were developed by correlating a set of experimental data, present a bad predictive capacity, and they cannot be successfully applied to oils with compositions different from those used in the model development (Hansen et al., 1988).

This work is the first step towards the development of a thermodynamically based model for the prediction of wax-appearance temperatures in both fuels and crude oils. Believing that the use of an appropriate model for the description of the liquid phase will improve the wax formation prediction, it is the purpose of this work to compare the ability of several types of activity coefficient models in solid–liquid equilibria prediction of hydrocarbon mixtures. Activity coefficient models including the widely known Flory–Huggins (Flory, 1941, 1942; Huggins, 1941, 1942) and modified UNIFAC (Fredenslund et al., 1977; Kikic et al., 1980), and some free-volume models recently presented in the literature are investigated, covering an extensive group of different types of theories. The results of all these models are compared with the results obtained using the assumption of ideal solution for the liquid phase. Furthermore, some activity coefficient models not included in this comparison and also the simplifying assumptions commonly used in wax formation models will be analysed.

2. Thermodynamic framework

Solid–liquid equilibrium (SLE) calculations at low pressure are usually made employing a method described by Prausnitz et al. (1986). It states that at the equilibrium, the fugacities, f , of each component i are identical in all phases present in the system

$$f_i^s = f_i^l \quad (1)$$

or

$$x_i^s \gamma_i^s f_i^{\circ s} = x_i^l \gamma_i^l f_i^{\circ l} \quad (2)$$

where γ_i and f_i° are the activity coefficient and the pure component fugacity of component i at the temperature of the system, respectively.

A thermodynamic cycle is used to obtain the expression for the ratio of pure component fugacities in both phases. Assuming the existence of only one transition point of first order in the solid phase and that (1) the heat capacity of the solid phase before the transition point (solid-II) is similar to the heat capacity of the solid phase after the transition point (solid-I) ($C_{pSII} = C_{pSI}$) and (2) the difference between the heat capacities of the liquid and solid phases is constant and can be properly described by the value at the melting point temperature (ΔC_{pm}), this general expression is obtained:

$$\ln \frac{f^{ol}}{f^{os}} = \frac{\Delta h_m}{RT_m} \left(\frac{T_m}{T} \right) - 1 + \frac{\Delta h_t}{RT_t} \left(\frac{T_t}{T} - 1 \right) - \frac{\Delta C_{pm}}{R} \left(\ln \frac{T}{T_m} + \frac{T_m}{T} - 1 \right) \quad (3)$$

where Δh_m and T_m are the enthalpy and temperature of fusion, respectively, and Δh_t and T_t are the enthalpy and temperature of phase transition in the solid phase, respectively. Further terms similar to the second term are added if more transition points exist. If no transition point exists in the solid phase, then $\Delta h_t = 0$.

Eqs. (2) and (3) do not take into account the effect of pressure on the properties of solid and sub-cooled liquid. Unless the pressure is very large, this effect is not important.

Several models describing wax formation are based on this equation. They differ mainly in the further simplifying assumptions, the methods used to calculate the Δh_m , Δh_t , T_m , T_t , and ΔC_{pm} , and the model for the activity coefficients of the phases present.

A brief review of the models describing solubility in hydrocarbon mixtures and wax formation shows that their major difference lies in the description of the non-ideality of the liquid phase.

3. Investigated models

The activity coefficient, in most of the activity coefficient models, can be expressed as the product of two contributions: a combinatorial part, accounting for the differences in size and shape between the molecules, and a residual part, a result of the energetic interactions between the components.

$$\gamma_i = \gamma_i^{\text{comb}} \gamma_i^{\text{res}} \quad (4a)$$

An additional contribution owing to free-volume (fv) is needed for mixtures with components differing significantly in size.

$$\gamma_i = \gamma_i^{\text{comb}} \gamma_i^{\text{fv}} \gamma_i^{\text{res}} \quad (4b)$$

Hydrocarbon mixtures are a particular case of mixtures where one or more of these contributions can be ignored. They are known to behave almost athermally, meaning that the activity coefficient is almost temperature independent. In these cases, the residual contribution may be assumed to be small and the deviations from ideality in the liquid phase are considered to arise from the shape and free-volume differences between the components. Moreover, if the compounds do not present large size differences, the free-volume contribution can also be ignored. Models using the three contributions for the activity coefficient, as well as models that, employing these assumptions, use only one or two contributions are investigated in this work, covering all types of activity coefficient models.

GCFLORY (Chen, 1990; Bogdanic and Fredenslund, 1993) is the model studied that uses all the three types of contributions. It was initially developed as an equation of state but has been used as an activity coefficient model with interaction parameters estimated at zero pressure. Entropic free-volume (Elbro et al., 1990) and Flory free-volume (Flory, 1970) use only a combinatorial-free-volume term without a residual contribution. Modified UNIFAC is a model without a free-volume contribution but uses combinatorial and residual contributions. The residual term has, however, a zero value for mixtures of alkanes and, like the original Flory–Huggins, only a combinatorial contribution is used in the calculation of the activity coefficient.

The combinatorial term for all these models can be expressed in the following general form

$$\ln \gamma_i^{\text{comb}} = \ln \frac{\phi_i}{x_i} + 1 - \frac{\phi_i}{x_i} \quad (5)$$

where ϕ_i is the composition fraction of component i defined by

$$\phi_i = \frac{x_i S_i}{\sum_j x_j S_j} \quad (6)$$

The models investigated correspond to the different definitions of the parameter S_i presented in Table 1.

For the Entropic-free-volume model, p is defined as

$$p = 1 - \frac{V_{\text{wsmall}}}{V_{\text{wlarge}}} \quad (7)$$

Table 1

Description of the parameter S_i and average percentage deviations for the models investigated in this work

Model	S_i	Model abbreviation	%AAD
Original Flory–Huggins	V_i	FH	1.048
Modified UNIFAC	$r_i^{2/3}$	modUNIFAC	0.452
GCFLORY model	r_i	GCFLORY	0.350
Flory-free-volume	$(V_i^{1/3} - V_{wi}^{1/3})^{3c}$		
	with $c = 1.1$	F-FV1.1	0.330
	with $c = 1.2$	F-FV1.2	0.380
	with $c = 1.5$	F-FV1.5	0.695
Entropic-free-volume	$(V_i - V_{wi})^\Lambda$		
	with $\Lambda = 1$	E-FV	0.683
	with $\Lambda = 2/3$	E-FV2/3	0.338
	with $\Lambda = 3/4$	E-FV3/4	0.356
	with $\Lambda = p$	E-FV p	0.366
Ideal solution		Ideal	0.628

where V_{wsmall} is the van der Waals volume of the short-chain alkane of a binary mixture, and V_{wlarge} the volume of the long-chain alkane (Kontogeorgis et al., 1994).

The van der Waals volumes are calculated using the group volume increments presented by Bondi (1968). Whenever possible, molar volumes of alkanes were estimated from the DIPPR correlation (Daubert and Danner, 1989), for the other compounds they were estimated by the GCVOL model (Elbro et al., 1991).

For Flory-FV and Entropic-FV models, Eq. (5) represents the combinatorial-free-volume term. The GCFLORY model presents, besides the combinatorial term, a free-volume and a residual (attractive) term. A complete description of the model can be found in Chen et al. (1990) and Bogdanic and Fredenslund (1993).

Empirical variations of the Entropic free-volume (Elbro et al., 1990; Kontogeorgis et al., 1993) and Flory free-volume models (Flory, 1970; Oishi and Prausnitz, 1978) are used to compare the efficiency of different exponents in the definition of free volume. For the Entropic free-volume model, the exponents are chosen by analogy with the modifications of UNIFAC (Kikic et al., 1980; Weidlich and Gmehling, 1987) and for the Flory free-volume model, they are chosen to cover a range of possible c values, since c is known to have values larger than 1, i.e. the value for argon-like molecules (Beret and Prausnitz, 1975). The importance of a system-dependent exponent in the combinatorial-free-volume expressions has been emphasized by several authors (Lichtenthaler et al., 1973, 1974; Donohue and Prausnitz, 1975). An example of this type of model has been recently proposed by Kontogeorgis et al. (1994) and its ability to describe the liquid phase behavior is investigated below. The ideal liquid solution behavior that has been used in some wax formation models (Walsh and Mortimer, 1971; Won, 1985; Reddy, 1986) is also considered here, and compared with the other models.

4. Data base

The ability of the models presented in the previous sections to describe the liquid phase is evaluated through their use in SLE predictions by means of Eq. (3). This is an effective process for evaluating activity coefficient models in solutions of alkanes with large size differences because the experimental values of activity coefficients for these systems are obtained from SLE data (Kniaz, 1991a). Instead of an evaluation of the models against activity coefficient values that would correspond to an indirect comparison with experimental data, it is more reliable to compare the models directly with the data available from SLE measurements. An example of SLE predictions is shown in Fig. 1 where experimental data for the system $n\text{-C}_{32}/n\text{-C}_7$ (Madsen and Boistelle, 1976) is compared with the values predicted by some of the investigated models (ideal solution assumption, Flory-FV1.1, Flory-Huggins and GCFLORY). It is assumed, in the calculation procedure, that the solid phase formed is a pure compound. This is a fair hypothesis as it is known that in simple systems a solute whose carbon number differs from all other components by more than two would precipitate as a pure crystal upon cooling (Prausnitz et al., 1986; Won, 1989). It is known, however, that for oils, the behavior can be somewhat more complex and co-precipitation of both paraffins of similar size (wax appearance), and of paraffins and asphaltenes even with large size differences, may occur (Bosselet et al., 1983; Irani et al., 1985). Only systems where the molecule sizes were different enough to prevent co-precipitation were used.

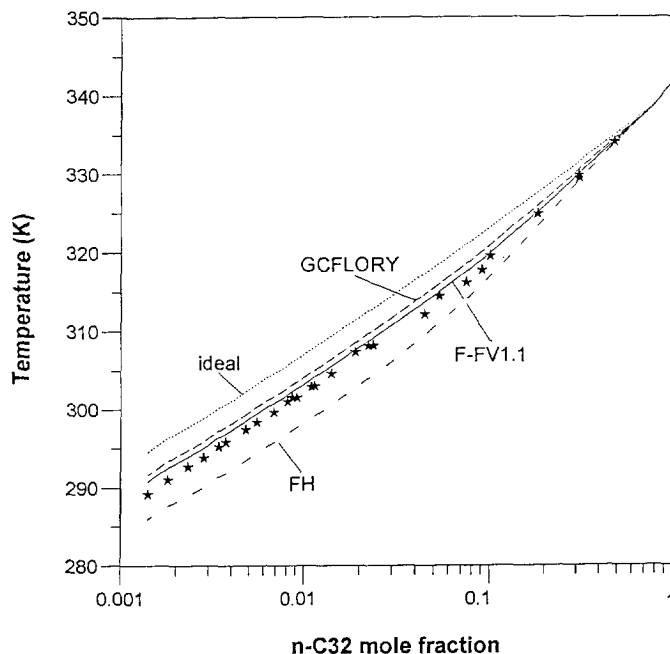


Fig. 1. Experimental SLE data (*) for the system $n\text{-C}_{32}/n\text{-C}_7$ (Madsen and Boistelle, 1976) compared with the predictions obtained using GCFLORY model, Flory-FV1.1, Flory-Huggins, and ideal solution.

An extensive and reliable data base of around 60 binary systems with more than 1000 experimental data points was used. The compounds range between C_{12} and C_{36} for the solute and between C_3 and C_{12} for the solvent, but were in most cases within the range of C_5 to C_7 . The experimental data used was mainly obtained from Seyer (1938), Ralston et al. (1944), Hoerr and Harwood (1951), Madsen and Boistelle (1976, 1979), Ott and Goates (1983), Domanska et al. (1987a,b), Domanska and Kniaz (1990a,b) and Kniaz (1991a,b). The pure component thermal properties Δh_m , Δh_t , ΔC_{pm} , T_m and T_t were obtained from the DIPPR data base (Daubert and Danner, 1989) and Parks et al. (1930), Douslim and Huffman (1946), Schaerer et al. (1955), Finke et al. (1954), Messerly et al. (1967) and Kniaz (1991a).

The models were evaluated using the average percentage deviations of the predictions defined here as:

$$\%AAD = \frac{1}{N_{\text{systems}}} \sum \frac{1}{n_{\text{points}}} \sum |T_{\text{exp}} - T_{\text{cal}}/T_{\text{exp}}| \quad (8)$$

where N is the number of systems and n the number of experimental data points in each system.

5. Discussion of results

The main feature of the results is the importance of the free-volume contribution on SLE predictions in systems whose components are significantly different in size. The models without

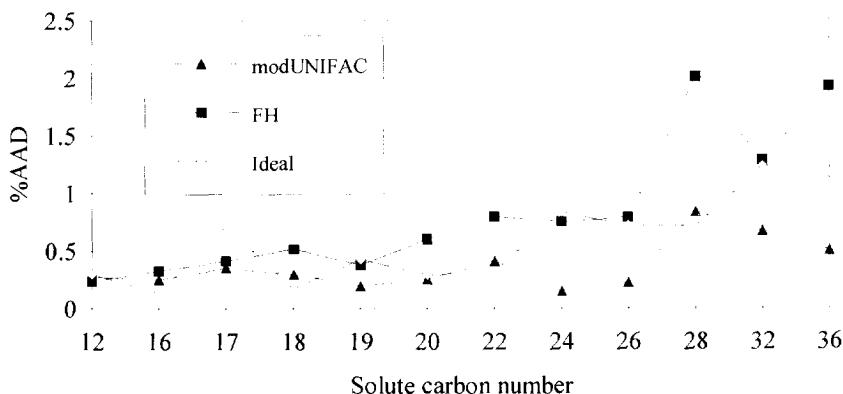


Fig. 2. Average deviations as a function of the solute carbon number for models with only a combinatorial term.

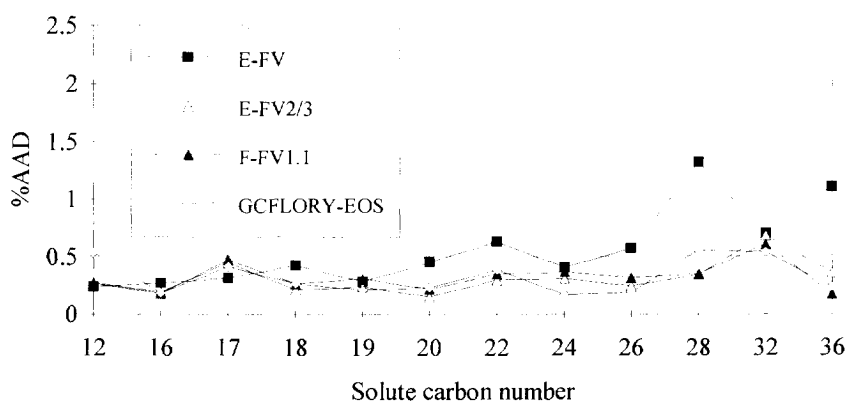


Fig. 3. Average deviations as a function of the solute carbon number for models with a free-volume contribution.

a free-volume term present an increase of the deviations with the size of the solute molecules as shown in Fig. 2. Nevertheless these models provide reasonable results for systems containing molecules smaller than C_{20} . Modified UNIFAC seems to be, in accordance with previous results (Larsen et al., 1987; Kontogeorgis et al., 1994), a model with the ability to predict with a fair accuracy the behavior of mixtures of alkanes with size differences that are not too large. Models with a free-volume contribution, on the contrary, are largely independent of the size of the molecules in solution, as can be seen in Fig. 3. The Entropic free-volume model presents an atypical behavior with clearly increasing deviations with increasing molecular size of the solute.

From the results presented in Table 1 and Fig. 4, it is clear that, with the exception of the original Entropic-FV, the models using a free-volume term achieve better predictions than the models using only a combinatorial term in the activity coefficient expressions. The better results are obtained for empirical variations of Entropic-FV and Flory-FV. The GCFLORY model also produces similar results. The use of these models generally reduces the deviations to almost half compared with the ideal solution assumption.

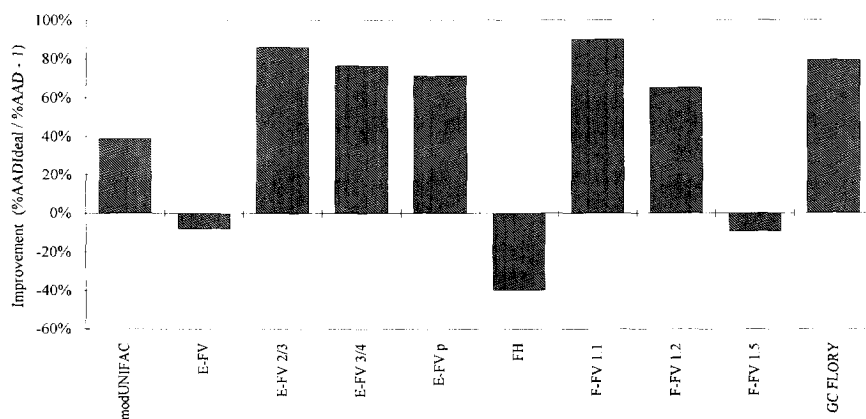


Fig. 4. Improvement achieved by the models investigated over the ideal solution assumption.

The ideal solution assumption was expected to be the poorest model. To evaluate the improvements obtained by the investigated models over this extreme behavior, the ratio of the deviations presented by this model to the other models were calculated and presented in Fig. 4. Surprisingly, some models such as the original Flory–Huggins and Entropic free-volume present larger deviations than the ideal solution assumption. It is known that the original Flory–Huggins is not a good activity coefficient model (Kniaz, 1991b; Haulait-Pirson et al., 1987) and that, even with the introduction of the parameter χ (Flory, 1953), it can hardly be used as a predictive model. Hence poor results were expected from its use. It is evident from the work of Hansen et al. (1988) that the modified Flory–Huggins activity coefficient model is not able to predict the wax appearance temperature of any oil that has not been used in the correlation of the parameter χ . More unexpected is the behavior of the Entropic free-volume model, considering that it has been successfully applied to the prediction of phase equilibria in polymer solutions (Elbro et al., 1990; Kontogeorgis et al., 1993).

The strong influence of the exponent used in the definition of free volume upon the results of a model is also surprising. Large differences are presented by both the Flory-FV models when the parameter c varies between 1.1 and 1.5, and between the original Entropic-FV and its modifications as is apparent from Fig. 4. The variable exponent p used with the Entropic-FV model, where p is defined by Eq. (7), does not seem to yield improved accuracy relative to a constant exponent. For Flory-FV model, the best value of c was found to be 1.1. Owing to its nature, c is expected to vary with the molecular size and shape (Orwoll and Flory, 1967), but because a constant value of $c = 1.1$ is often used in the literature (Flory, 1970; Beret and Prausnitz, 1975; Oishi and Prausnitz, 1978; Kontogeorgis et al., 1994) and the predictions using this model are expected to be within the experimental error no further optimization of the value c was attempted.

The GCFLORY model is a theoretical model of some complexity. It uses an attractive term as well as the combinatorial and free-volume terms. This model gives good predictions of SLE but no improvement is achieved compared with the empirical modifications of the Entropic-FV and the Flory-FV models. This can be interpreted in two ways. First, it is known (Hildebrand, 1947; Kikic et al., 1980; Elbro et al., 1990; Kniaz, 1991a) that the models based on Eq. (5) tend

to overestimate the degree of non-ideality of a solution, predicting values which are too low for the activity coefficients. The empirical exponent in the definition of the free volume acts on the activity coefficient estimation by forcing the values to increase, thus emulating the behavior of a residual contribution. Alternatively, the variations with temperature shown by the activity coefficients of alkane mixtures (Kniaz, 1991a) are small enough and can be taken into account by the combinatorial-free-volume term alone and consequently no improvement is obtained from the use of a residual contribution on the GCFLORY model.

Other activity coefficient models or modifications of investigated models have been used in wax formation predictions. They were not included in this comparison either because they do not apply to simple mixtures or they are not able to describe alkane systems. They have, however, been studied and their deviations in predictions of SLE is hereafter investigated.

The regular solution theory (RST) (Hildebrand et al., 1970) is a model that, with some modifications, has been frequently used in wax formation predictions (Won, 1986; Pedersen et al., 1991; Chung, 1992). In the original form, it cannot predict negative deviations from the ideal solution assumption, while activity coefficients for alkane mixtures reported in the literature always show negative deviations. The RST is an enthalpic model which takes into account only the excess enthalpy of the mixture and neglects the excess entropy. However the alkane mixtures are better described as athermal solutions ($h^c = 0$) with their non-ideality arising from entropic effects. For this reason, the RST cannot be a good activity coefficient model for alkane systems and the results obtained, employing its SLE calculations, will be worse than those of ideal solution assumption.

Modified versions of RST that have been applied in wax formation models (Won, 1986; Pedersen et al., 1991) are used to calculate the activity coefficients in both phases. The solid phase activity coefficient is calculated with a modified solubility parameter. Again, the deviations predicted are always positive and very large. No experimental evidence exists to support the assumption of a non-ideal solid with such a large positive deviation to ideality. Apparently the use of activity coefficients for the solid phase enables the ratio of activity coefficients to behave as a pseudo activity coefficient for the liquid phase predicting negative deviations to the ideality if the solid phase is considered ideal. These pseudo activity coefficients are generally over-predicted with differences larger than 100% compared with experimental values for similar systems. The errors introduced by this model in the solid appearance temperature (SAT) predictions of binary systems range between 5 K for the model of Pedersen et al. (1991) and more than 10 K for Won's model.

Another model by Won (1989) couples the RST with the Flory–Huggins activity coefficient model. The over-prediction by the Flory–Huggins model is compensated by RST and a model for activity coefficients, with a lower degree of over-prediction, is obtained. Comparisons with experimental values show that the deviations of the activity coefficients are between 20 and 30%, producing errors on SAT of 2 K in average. Similar deviations in the activity coefficients are obtained using the Flory–Huggins model with an enthalpic contribution (Hansen et al., 1988). The δ parameter is correlated as a function of the molecular size differences expressed as a number of carbon atoms. All these models are far less accurate than the best models investigated in this work. The errors indicated in this analysis refer to the low concentration region ($x_{\text{heavy}} < 0.01$) because this is the region of concentration of heavy molecules in a waxy fluid. They show that the use of a good model for activity coefficient estimations can considerably improve the SAT predictions.

The influence of the activity coefficient on the SAT predictions at low concentrations of heavy alkane is shown in Fig. 1 where the results obtained using the ideal solution assumption are compared with experimental data. Even this extreme case can be a fair activity coefficient model for molar fractions of the heavy component above 0.5 but, for low concentrations, the error can be as large as 5 K in this example. Similar conclusions can be drawn from the Flory–Huggins predictions and this applies also to the activity coefficient models based on RST.

An analysis of the error introduced in the SAT predictions, caused by the error in the activity coefficient, shows that while the estimation of activity coefficients may still be improved, this improvement would not enhance the SAT predictions significantly. Between them, the best models investigated present deviations in the activity coefficients inferior to 10%. In a comparison with activity coefficients at infinite dilution for alkane systems, Kontogeorgis et al. (1994) reported average errors of 10% for the same models. The error in the infinite dilution activity coefficient is the largest possible error. It therefore assumes that the error in the activity coefficients cannot be larger than this value. Such a deviation causes a fluctuation in SAT around 0.5 K which is within the experimental uncertainty for wax appearance temperatures (WAT).

6. Models shortcomings

As mentioned previously, hydrocarbon systems are approximately athermal and thus the activity coefficient presents a very slight temperature dependence. With the exception of modified UNIFAC, which presents no temperature dependence, and regular solution theory, which shows the right dependence on the temperature, all the models investigated present a temperature dependence that is opposite to the experimental.

Experimental activity coefficient data (Won, 1989) show a decreasing value of the activity coefficient with increasing temperature, denoting an augmentation of the non-ideality of the system. Both theoretical considerations and experimental data (Tancrede et al., 1977; Barbe and Patterson, 1980; Kniaz, 1991a) reveal a positive value for the excess enthalpy, indicating that this trend is correct for both the activity coefficient of large-chain solutes in short-chain solvents and of short-chain solvents in large-chain solutes as can be understood from Eq. (9)

$$\left(\frac{\partial \ln \gamma_i}{\partial T}\right)_p = -\frac{h_i^E}{RT^2} \quad (9)$$

As can be seen in Fig. 5, the models predict either an increasing value of the activity coefficient with increasing temperature or a U-shape variation when GCVOL is used instead of DIPPR for the evaluation of the molar volume. These variations are very slight, as expected for hydrocarbon systems, and thus their influence in the predictive capacities of the models can be ignored.

Another type of problem, besides the temperature dependence, occurs in the GCFLORY model. Despite the fair predictions obtained by using this model, the activity coefficients predicted present a physically wrong trend for temperatures above 300 K, as shown in Fig. 6. With increasing temperatures, the model predicts a minimum in the values of the activity coefficient as a function of the composition and, above 300 K, positive deviations to ideality. This behavior disappears at low temperatures for the systems investigated and this is the reason

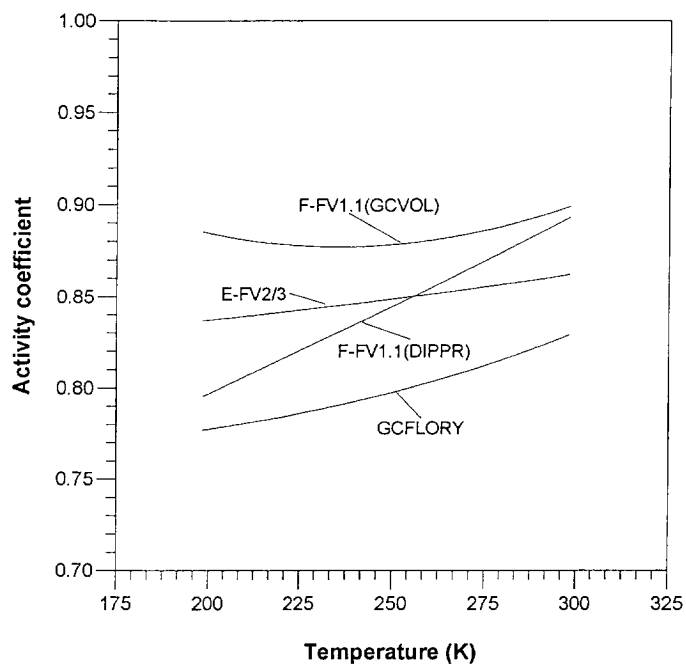


Fig. 5. Temperature dependence of the activity coefficients predicted by three of the investigated models for the system $n\text{-C}_{20}/n\text{-C}_6$ ($X_{C_{20}} = 0.1$).

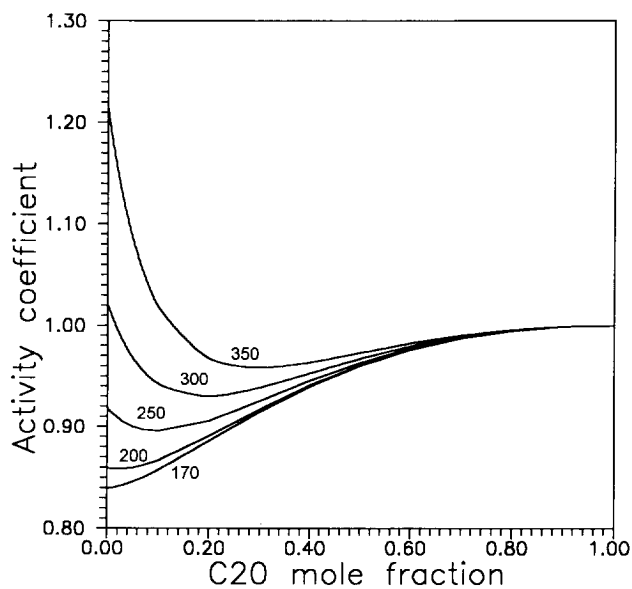


Fig. 6. Activity coefficients as function of composition and temperature (K) for the system $n\text{-C}_{20}/3\text{-methyl pentane}$ using GCFLORY model.

for the good performance of the model in the comparison. For heavy solutes this behavior will appear only at very high temperatures. This is a big deficiency of the model and since the temperature range of interest for wax formation is around 300 K and the molecular size of solutes ranges between C_{20} and C_{30} , the GCFLORY model should not be used for wax formation predictions.

7. Analyses of simplifying assumptions

When Eq. (3) is used in wax formation models, some simplifying assumptions are usually made. The most common simplifications are to consider the ΔC_p term equal to zero and the use of an enthalpy of phase transition representing both the fusion and the phase transition enthalpy:

$$\Delta H = \Delta h_m + \Delta h_t \quad (10a)$$

and

$$T_t = T_m \quad (10b)$$

to express the assumption that no phase transitions exist in the solid phase. These two simplifying assumptions are analysed here, using the three best models, to evaluate the error that they introduce in the calculations.

The first simplification was analysed for the three best models previously investigated, comparing the deviations presented by employing the assumption of the ΔC_p being zero with the original deviations. Only systems with an accurately known $\Delta C_{p,m}$ were used in the comparison. The average deviations are reported in Table 2. A slight decrease in the deviations of two of the models is found. This result is somewhat unexpected but not surprising and can be explained as follows. It must be considered that the temperature function in the last term of Eq. (3) is always positive but close to zero and the value of $\Delta C_{p,m}$ is, usually, also low and positive. Under these circumstances the value of this term is very small compared with the other terms. Moreover an underestimation of the value of ΔC_p by considering it as zero will contribute to an overestimation of the solid appearance temperature as can be easily recognized from Eq. (3). The opposite phenomenon occurs in the estimation of the activity coefficient. The activity coefficient is overestimated and this contributes to an underestimation of the temperature values. As is known, and was previously discussed, activity coefficient models based on Eq. (5) generally over-predict the activity coefficient for alkane mixtures. In this way, by means of a cancellation

Table 2
Analysis of the simplifying assumption $\Delta C_p = 0$ using the three best models investigated

Model	%AAD using $\Delta C_p = \Delta C_{p,m}$	%AAD using $\Delta C_p = 0$	%change
E-FV2/3	0.261	0.271	+3.8
F-FV1.1	0.294	0.270	-8.2
GCFLORY	0.327	0.323	-1.2

Table 3

Analysis of the assumption of no phase transition taking place in the solid phase

Model	%AAD using one transition point in the solid phase	%AAD using no phase transition in the solid phase	%change
E-FV2/3	0.405	0.535	32.1
F-FV1.1	0.382	0.431	12.8
GCFLORY	0.402	0.429	6.7

of errors, this simplification produces a slight improvement on the predictions of solid–liquid equilibria. For activity coefficient models that underestimate the activity coefficient, the simplification will have the effect of reinforcing the error in the prediction of solid appearance temperatures. The value of this term is however always very low and consequently this simplification will never introduce a large error in the calculations. Using a model system with average properties to represent a solution of a heavy alkane in a light one, it was found that this simplification, even for a component with a ΔC_p of 100 J mol^{-1} , would introduce an error of less than 0.5 K.

The slight increase in the deviations with Entropic-FV is due to the underestimation of the activity coefficient in some cases.

The possibility of making the simplification described by Eqs. (10a) and (10b) was also investigated using three different models for the activity coefficient. Only systems with compounds having solid phase transition points were used. For *n*-hexatriacontane, just one transition point was considered. The results are reported in Table 3.

As expected, there is a general increase in the deviations but it is very interesting to notice that the models are affected differently by the simplification. Only a small increase of 6.7% in the deviations is presented by the GCFLORY model and a somewhat large deviation (13%) by the Flory-FV, indicating that the simplification can be used with these two models. However, the modification of the Entropic-FV model used has an increase of more than 30% in the deviations, making the possibility of using the simplification with this model doubtful. The results indicate that the simplification is not universal and that it may be used with some models but with others the increase in the error may be too large. A reasoning similar to that developed for the previous analysis can also be made.

The use of Eqs. (10a) and (10b) is equivalent to the use of a larger value for the enthalpy of phase transition or, in other words, a larger value for the solid phase transition point temperature. The effect of this simplification is an overestimation of the solid appearance temperature as occurred in the previous simplification. The simplification would be expected to reduce the deviations as before; however there is a general increase on the deviations. This is due to the large effect of this simplification over the predictions. It not only compensates for the error of underestimation of the temperature as a result of the overestimation of the activity coefficients but also contributes to a further overestimation of the temperature. If this is the effect of this simplification on models that overestimate the activity coefficient, it can hardly be expected that it can be used with models that underestimate the activity coefficient because the errors would be added, resulting in a large increase in total deviations as is found to happen with the Entropic-FV model.

The results suggest that there is still an under-prediction of the activity coefficients by the models but that this effect contributes to a reduction of the error introduced by the simplifications investigated.

It shall be taken into account that the data used in this comparison included the entire composition range. The heavy paraffins in waxy crude oils have concentrations lower than 0.05 in molar fraction. The deviations are usually larger for these low concentration regions and the deviations presented herein are much larger in the region of interest for wax formation studies.

The models investigated here are activity coefficient models and consequently their use is restricted to pressures around atmospheric pressure. For high pressures, as can be found in a reservoir, a different approach has to be used, employing an equation of state instead of an activity coefficient model to describe the fluid phases.

8. Conclusions

A thorough comparison of activity coefficient models has been performed based on their ability to predict solid–liquid equilibria in mixtures of hydrocarbons with large size differences. It is clear from this comparison that the free volume strongly influences the description of the mixtures of compounds with large size differences. The large size differences found in the mixtures where wax formation takes place require a treatment different from that used with mixtures of small molecules with similar size. With the exception of the Flory–Huggins model used by Hansen et al. (1988), the activity coefficient models that have been employed in wax formation predictions perform very poorly or are even physically unreasonable. The Flory-FV model with a value of c of 1.1 or the Entropic-FV model with a modified free-volume definition ($p = 2/3$) seem to be the activity coefficient models with the best performance. Despite the good results presented in this comparison, the GCFLORY model does not seem to be a reliable model to be used with alkane systems within the temperature range of interest for wax formation predictions.

The predictions using the recommended models have an accuracy superior to the experimental data itself thus, it seems that no further improvement to SLE calculations can be obtained from the use of a more accurate activity coefficient model.

Two of the most common simplifications used in solubility and wax formation models were also analysed. It was found that their effect on the predictions is dependent on the activity coefficient model employed, and that their action can be either to cancel or to increase the deviations of the predictions. The assumption of $\Delta C_p = 0$ has little effect and can usually be employed. However, care should be taken when assuming that no phase transition takes place in the solid phase since for certain models it can greatly increase the deviations of the predictions.

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List of symbols

C_p	heat capacity
f	fugacity
h	enthalpy
n	number of points
N	number of systems
r	van der Waals molecular volume
R	universal gas constant
T	temperature
V	molar volume

Greek letters

δ	solubility parameter
Δ	variation
γ	activity coefficient
χ	Flory–Huggins residual contribution

Subscripts

cal	calculated
exp	experimental
i	component i
m	melting point
s	solid phase
t	transition point

Superscripts

comb	combinatorial
fv	free volume
l	liquid phase
o	pure component
res	residual
s	solid phase

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