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Equation-of-State Group Contributions from Infinite-Dilution Activity Coefficients

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This paper investigates the use of infinite-dilution activity coefficients to define the interaction parameters of the Redlich–Kwong equation of state (SRK-EOS), with the Huron–Vidal mixing rules. The group-contributions of a UNIFAC-type model were regressed from experimental infinite-dilution activity coefficients of a number of significant systems, including strongly polar components. Such parameters were then used to predict vapor–liquid equilibria (VLE) over the whole composition range, at pressures up to 6 MPa, with generally good results.

Introduction

The use of cubic equations of state for systems containing highly nonideal components requires a proper definition of the mixing rule for the attractive term a.

The idea of linking the value of a to the excess Gibbs energy (g^E) at infinite pressure was first set forth by Huron and Vidal (1979), and subsequently developed by several authors: among them, Tochigi et al. (1990) presented a UNIFAC-like group contribution approach to predict infinite pressure activity coefficients, with parameters regressed from high pressure equilibrium data.

On the other hand, Michelsen (1990a,b) proposed a method, named the modified Huron–Vidal of the second order (MHV2), where the relationship between a and g^E is developed at zero pressure. The model was made predictive by using the UNIFAC group contributions concept (Dahl and Michelsen, 1990). Finally, MHV2 was extended to take into account supercritical components (Dahl et al, 1991).

More recently, Wong and Sandler (1992a,b) developed a similar but original method based on the excess Helmoltz energy.

In the present paper, the mixing rule proposed by Huron and Vidal is applied at infinite-dilution conditions, where the Michelsen approach cannot be used, and at zero pressure. The model derived accordingly is more concise and simpler than the ones cited above. Furthermore, infinite-dilution activity coefficients were selected as the data source, for the following reasons:

(1) They are particularly representative of conditions found in fractionation towers, where most trays work to separate the last traces of impurities, i.e. at conditions near the infinite dilution.

(2) Interpolation from infinite dilution toward the middle of the composition field generally yields acceptable values for the activity coefficients, regardless of the model applied, while the reverse is not true; as a consequence, determining group contributions from VLE data (which lie in the middle of the concentration range) can lead to unacceptable results when they are applied to conditions of high dilutions.

(3) Infinite-dilution activity coefficients can be measured relatively easily.

The use of infinite-dilution activity coefficients for the calculation of VLE with an equation of state has been treated in a previous work (Alessi et al., 1987).

In the presently proposed approach, infinite-dilution activity coefficients are directly transformed into their corresponding infinite-pressure values thanks to the simplification of the expressions under infinite-dilution and zero pressure conditions. Then, in order to predict such values with a group contributions approach, they are fitted to a UNIFAC-type model, which is simpler than the original UNIFAC model.

The Model: Equation of State

We refer to the Redlich–Kwong EOS as modified by Soave (1972):

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b)} \tag{1}$$

By definition of the dimensionless variables

$$A = \frac{aP}{R^2 T^2}$$

$$B = \frac{bP}{RT} \tag{2}$$

$$\frac{A}{B} = \frac{a}{bRT}$$

$$z = \frac{Pv}{RT}$$

Eq 1 can be written as

$$z^3 - z^2 + zB\left(\frac{A}{B} - 1 - B\right) - \frac{A}{B}B^2 = 0 \tag{3}$$

For pure and subcritical components, A and B are functions of the critical properties and vapor pressure only (Soave, 1986)

$$A = 0.42748\alpha(P^{vap})\frac{P_r}{T_r^2}$$

$$B = 0.08664\frac{P_r}{T_r} \tag{2.1}$$

$$\frac{A}{B} = 4.93396\frac{\alpha(P^{vap})}{T_r}$$

and the corresponding fugacity coefficients can be cal-

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culated by

$$\ln \phi^*_i = z_i - 1 - \ln(z_i - B_i) - \frac{A_i}{B_i}\ln\left(1 + \frac{b_i}{v_i}\right) \quad (4)$$

where the superscript asterisk stands for "pure" and the subscript i denotes each component. For components in mixtures, suitable combination and mixing rules have to be adopted. According to the Huron–Vidal mixing rule

$$B = \sum_i x_i B_i \quad (5)$$

$$\frac{A}{B} = \sum_i x_i \left(\frac{A_i}{B_i} - \frac{\ln \gamma_i^\infty}{\ln 2}\right) \quad (6)$$

where γ_i^∞ is the activity coefficient of component i in the mixture at infinite pressure.

In this way, the fugacity coefficient of i in the mixture can be calculated by

$$\ln \phi_i = \frac{B_i}{B}(z - 1) - \ln(z - B) - \left(\frac{A_i}{B_i} - \frac{\ln \gamma_i^\infty}{\ln 2}\right)\ln\left(1 + \frac{b}{v}\right) \quad (7)$$

Since we refer to infinite-dilution conditions, the corresponding limit of eq 7 as $x_i \to 0$ provides

$$\ln \phi_{i(j)} = \frac{b_i}{b_j}(Z_j - 1) - \ln(Z_j - B_j) -$$
$$\left(\frac{A_i}{B_i} - \frac{\ln \gamma_{i(j)}^\infty}{\ln 2}\right)\ln\left(1 + \frac{b_j}{v_j}\right) \quad (7.1)$$

where the properties of the mixture are the corresponding ones of the pure solvent j.

By a combination of eq 7.1 and eq 4 through the general thermodynamic relationship

$$\gamma_{i(j)} = \frac{\phi_{i(j)}}{\phi^*_i} \quad (8)$$

the following expression can be derived:

$$\ln \gamma_{i(j)} = \frac{b_i}{b_j}(Z_j - 1) - (Z_i - 1) - \ln\left(\frac{Z_j - B_j}{Z_i - B_i}\right) -$$
$$\frac{A_i}{B_i}\ln\left(\frac{1 + b_j/v_j}{1 + b_i/v_i}\right) + \frac{\ln \gamma_{i(j)}^\infty}{\ln 2}\ln\left(1 + \frac{b_j}{v_j}\right) \quad (9)$$

which relates the infinite-dilution activity coefficient at infinite pressure $\gamma_{i(j)}^\infty$ to its value $\gamma_{i(j)}$ at pressure P. If eq 9 is written under the limiting condition $P \to 0$, and v and b are used instead of z and B, the following equation is finally obtained:

$$\ln \gamma_{i(j)} = \left(1 - \frac{b_i}{b_j} + \ln\frac{b_i}{b_j}\right) - \ln\left(\frac{v_j/b_j - 1}{v_i/b_i - 1}\right) -$$
$$\frac{A_i}{B_i}\ln\left(\frac{1 + b_j/v_j}{1 + b_i/v_i}\right) + \frac{\ln \gamma_{i(j)}^\infty}{\ln 2}\ln\left(1 + \frac{b_j}{v_j}\right) \quad (9.1)$$

v_i/b_i and v_j/b_j are the solution of eq 1 with $P = 0$:

$$\frac{v}{b} = \frac{1}{2}\left(\frac{A}{B} - 1 \pm \sqrt{\frac{A^2}{B^2} - 6\frac{A}{B} + 1}\right) \quad (10)$$

Since the liquid molar volume is needed, the smallest root is used.

It is noteworthy that the influence of the starting pressure in the calculation of the infinite-dilution activity coefficients at infinite pressure is negligible in the normal

Table 1. Effect of Pressure on the Calculation of Infinite-Pressure and Infinite-Dilution Activity Coefficient of Acetone in Benzene (Experimental Value at Unknown Pressure 1.71)

P (MPa)	$\gamma_{i(j)}^\infty$	% error
0	1.8231	
0.1	1.8229	0.01
1.0	1.8222	0.05
2.5	1.8209	0.12
4.0	1.8196	0.19

Table 2. Experimental and Calculated Values of Activity Coefficients at Low and Infinite Pressures for Alkane–Alkane Systems

solute	solvent	T (K)	$\gamma_{i(j)ex}$	$\gamma_{i(j)ex}^\infty$
pentane	hexadecane	313	0.87	1.00
hexane	hexadecane	313	0.88	1.00
heptane	hexadecane	313	0.90	1.00
octane	hexadecane	313	0.93	1.02
pentane	octadecane	303	0.85	1.06
hexane	octadecane	303	0.87	1.05
heptane	octadecane	303	0.89	1.06
octane	octadecane	303	0.91	1.05

Table 3. Table and Dimensions of Groups

	main groups	subgroups	Q_k
1	CH2	CH3–	0.848
		–CH2–	0.540
		>CH–	0.228
		>C<	0.000
2	ACH	ACH	0.400
		AC–	0.120
		ACCH3	0.968
		ACCH2–	0.660
		ACCH<	0.348
3	COH	–CH2OH	1.124
		–CHOH–	0.812
		>COH–	0.584
4	CO	>CO	1.600

range of pressure (as an example, see Table 1, where eq 9 was applied); therefore, eqs 9.1 and 10 can be profitably used to convert infinite-dilution data to the corresponding ones at infinite pressure. Since in the infinite-dilution activity coefficient data base considered by us (Tiegs et al., 1986) the experimental pressures are not reported, our procedure is correct provided the values remain moderate.

The Model: Modified UNIFAC

It is known that the original UNIFAC (Fredenslund et al., 1977) is calibrated on VLE data and performs rather poorly for infinite-dilution activity coefficient calculations; subsequent extensions of UNIFAC (Gmehling et al., 1982; Hansen et al., 1991) perform similarly. A significant improvement can be achieved by means of the modified UNIFAC by Weidlich and Gmehling (1987), which was explicitly adapted also to infinite-dilution activity coefficients.

In view of modifying the UNIFAC model in a form suitable to reproduce activity coefficients at infinite pressure, a simplified formulation is proposed, where the model is reduced to its residual part only.

With respect to this fact, preliminary calculations showed that a combination term was not required and was even detrimental. As an example, the case of alkane–alkane systems is considered in Table 2: here, according to the proposed model, the activity coefficients at infinite pressure should always be 1, while the experimental values at low pressure are significantly different from unity. As it can be noted from the last column of Table 2, the values calculated by eq 9.1 at infinite pressure are very close to 1.
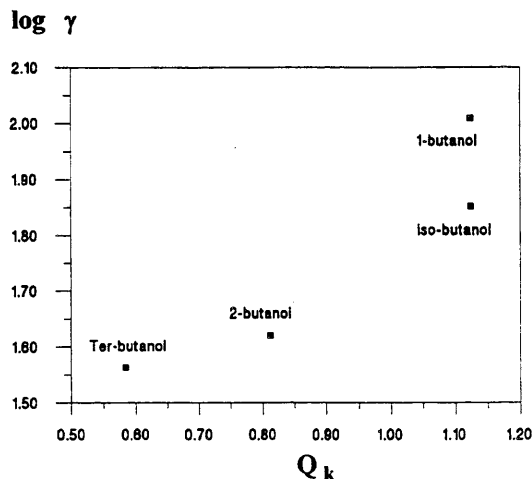
log γ

Figure 1. Experimental activity coefficients at infinite dilution for some butanols in squalane as a function of the dimension of CH_nOH group according to Bondi.

The activity coefficient model is then expressed by the following equations:

$$\ln \gamma_i = \ln \gamma_i^R \tag{11}$$

$$\ln \gamma_i^R = \sum_k \nu_{k,i}(\ln \Gamma_k - \ln \Gamma_{k,i}) \tag{12}$$

$$\ln \Gamma_i = Q_k\left[1 - \ln(\sum_m \Theta_m\psi_{m,k}) - \sum_m \frac{\Theta_m\psi_{k,m}}{\sum_n \Theta_n\psi_{n,m}} \right] \tag{13}$$

with

$$\Theta_m = \frac{X_mQ_m}{\sum_n X_nQ_n}$$

$$X_m = \frac{\sum_j \nu_m^j x_j}{\sum_j \sum_n \nu_n^j x_j} \tag{14}$$

$$\psi_{n,m} = \exp\left(-\frac{a_{n,m} + b_{n,m}/T}{T}\right) \tag{15}$$

Neglecting the combination part, only group surface areas, Q_k are used for the calculation of activity coefficients.

In the case of a binary mixture at infinite dilution of component 1 in component 2, eq 12 can be simplified into the following:

$$\ln \gamma_1^R = \sum_k \nu_{k,1}(\ln \Gamma_{k,2} - \ln \Gamma_{k,1}) \tag{12.1}$$

It is noteworthy that the temperature dependence of interaction parameters as given by eq 15 is a simple way to account for polar effects: in fact, calculations showed that the original term (a_{nm}/T) from UNIFAC was adequate for hydrocarbon mixtures but a_{nm} varied with temperature in the presence of polar compounds. For those systems a b_{mn}/T^2 term was added, which should represent a "polar" contribution, with a stronger dependence on temperature, as dictated by the theory.

A complete table including all functional groups of practical interest is beyond the scope of this work; as a first approach, only four main groups and 13 subgroups
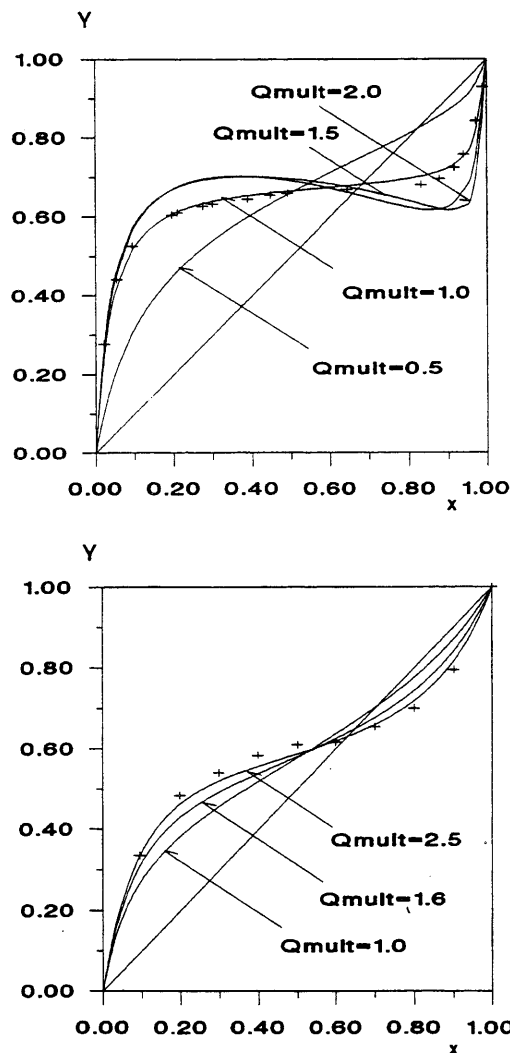

Figure 2. VLE prediction for the systems hexane–ethanol at 323 K (a, top) and acetone–hexane at 1 bar (b, bottom) as a function of the Q_k multiplier. For the first system a common multiplier is applied to all groups; for the second one, the reported multiplier is applied to the >CO group only (all other multipliers are set to 1).

Table 4. Best-Fit Interaction Parameters a_{nm}

	CH2	ACH	COH	CO
CH2	0	–6.0	282.2	–51.9
ACH	–6.0	0	9.3	163.0
COH	784.7	758.1	0	90.4
CO	–51.9	163.0	–479.5	0

have been considered, as reported in Table 3. However they are sufficient to show the potential of the proposed method.

As far as the definition of groups is concerned, some changes are made with respect to UNIFAC, summarized below:

(1) The aromatic group includes both aromatic C atoms and those adjacent to aromatic rings.

(2) The ketone group is kept separated from the adjacent aliphatic groups since the UNIFAC asymmetric division appears arbitrary.

(3) For alcohols the original –OH group is replaced by $-CH_nOH$, on the basis of the concept that an alkyl group adjacent to a hydroxyl cannot be treated as a "normal" alkyl group and to take into account the fact that isomeric alcohols with the same number of carbon atoms behave differently: for example, in Figure 1 the infinite-dilution activity coefficients of n-, iso-, sec-, and tert-butanol in the same solvent at the same temperature show marked
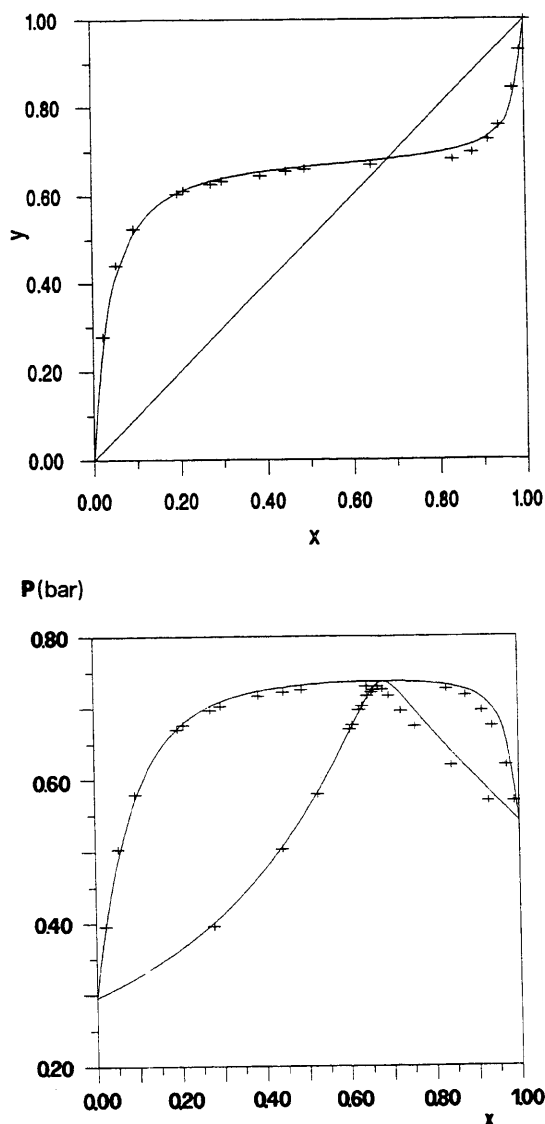
Figure 3. Hexane(1)–ethanol(2) at $T = 323$ K: x–y (a, top) and P–x (b, bottom) diagrams.

Table 5. Best-Fit Interaction Parameters b_{nm}

	CH2	ACH	COH	CO
CH2	0	12420	317350	175000
ACH	12420	0	268750	20040
COH	–138590	–145820	0	–39620
CO	175000	20040	243630	0

Table 6. Relative RMS Errors (%) in the Reproduction of the Database

	CH2	ACH	COH	CO
CH2	X	10.5	10.4	13.4
ACH		X	5.4	10.6
COH			X	5.9
CO				X

differences: according to original UNIFAC assumptions, all four groups would be represented by the same Q_k.

(4) Q_k values are the original ones given by Bondi (1968) for all subgroups except >CO, whose value was increased for better results in VLE calculations. For the systems containing ketones, it is not possible to reproduce experimental data unless original Q_k values are multiplied by a factor greater than 1: therefore, a value of 2.5 has been chosen for the >CO group.

It is noteworthy that the value of the multiplier applied to Q_k strongly affects the calculation of VLE, as shown in
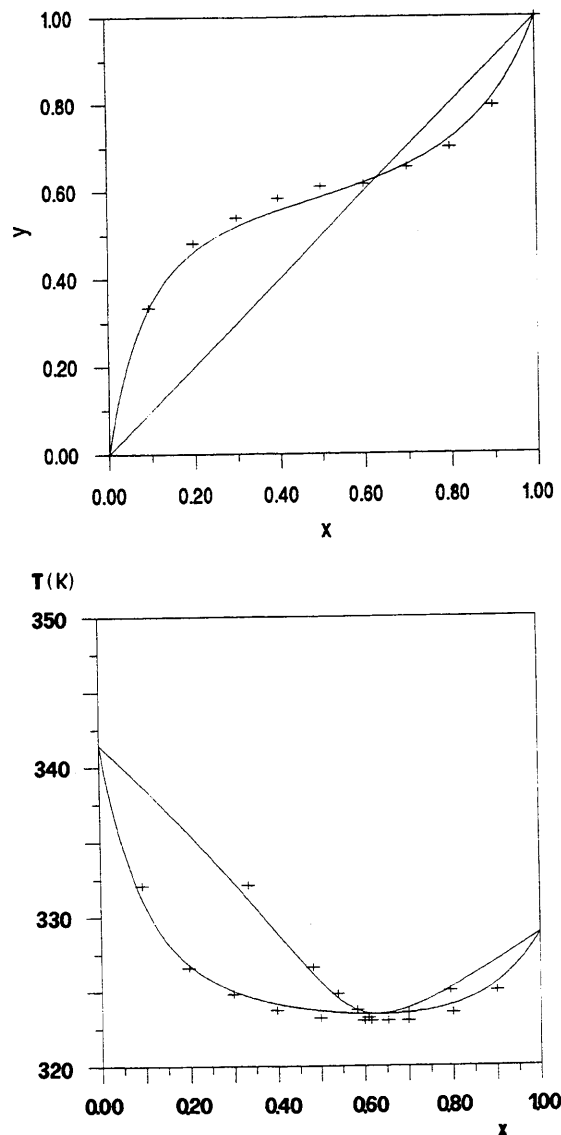

Figure 4. Acetone(1)–hexane(2) at $P = 1$ bar: x–y (a, top) and T–x (b, bottom) diagrams.

Figure 2: note that for each value of the multiplier a different set of interaction parameters has been fitted and used.
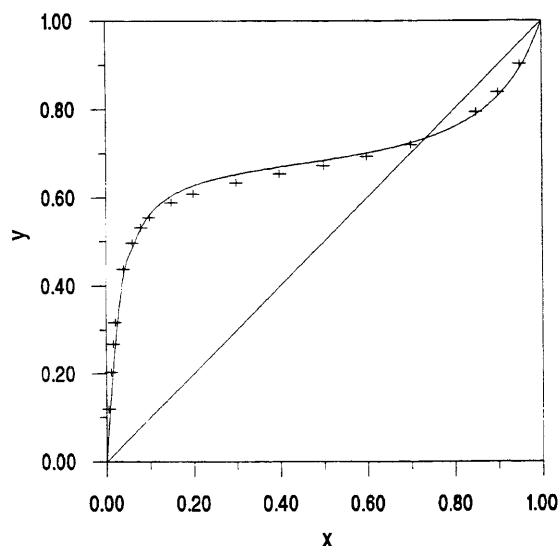
(5) Symmetric binary parameters $a_{mn} = a_{nm}$ and $b_{nm} = b_{mn}$ can be assumed in systems not containing associated compounds, with negligible loss of accuracy, as confirmed by calculations. As a result, a single a_{mn} parameter was sufficient for the alkane–aromatic pair and two parameters were sufficient a_{nm} and b_{nm} for pairs with the ketones. Only with alkanols were four separate parameters needed.

Parameter Determination

Each data point for $\ln \gamma_{i(j)}$ was converted into its value at infinite pressure by means of eqs 9.1 and 10; all of these values were reproduced by using the modified model for UNIFAC (eq 11–15), and best-fit parameters were obtained by minimizing the objective function

$$ OF = \frac{1}{n_p} \sqrt{ \sum_{m=1}^{np} (\ln \gamma^{\infty}_{i(j)cal} - \ln \gamma^{\infty}_{i(j)ex})^2 } \qquad (16) $$

Data regressions were carried out sequentially, starting with the more ideal systems, i.e. those containing hydrocarbons pairs.
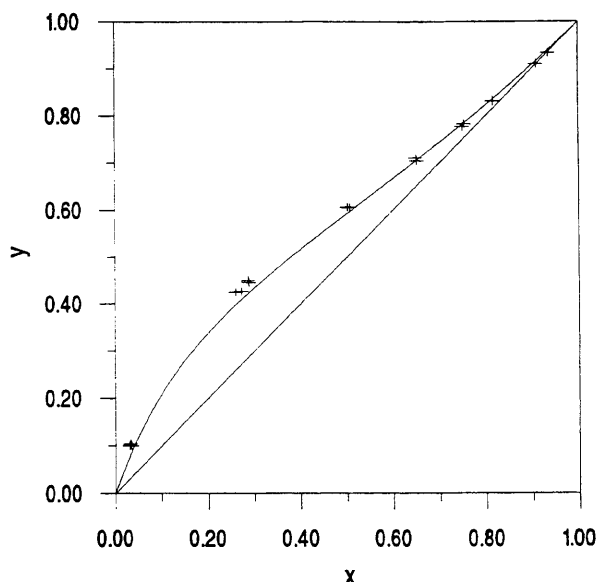
Figure 5. Hexane(1)–benzene(2) at P = 0.267 bar.

Figure 7. Acetone(1)–ethanol(2) at T = 313 K.

Figure 6. Ethanol(1)–toluene(2) at T = 318 K.

Figure 8. Acetone(1)–benzene(2) at T = 318 K.

Data were taken from an extensive compilation from DECHEMA (Tiegs et al., 1986). However not all available data could be used, since the application of the proposed method requires that both solute and solvent can be divided according to the table of groups (Table 3); moreover, the critical properties (P_c, T_c, and ω) and the vapor pressure must be known. It was decided to use only data of compounds with well known critical constants and vapour pressure in order to ensure the best reliability.
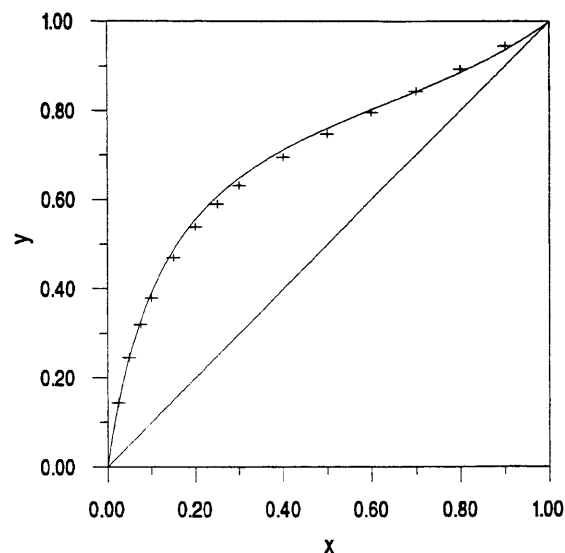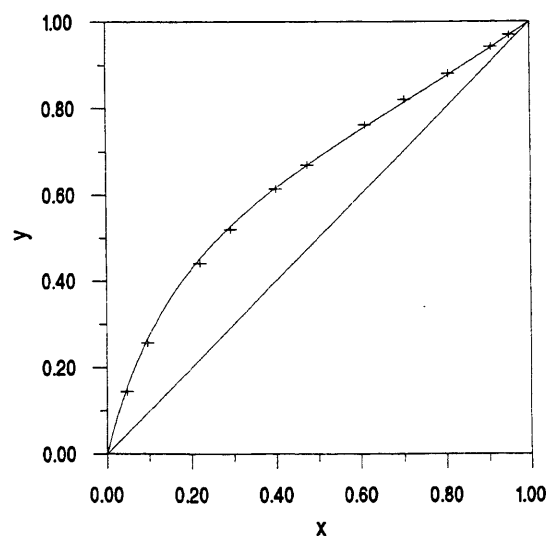
Tables 4 and 5 present the values of best fitting parameters a_{nm} and b_{nm} for all pairs, and Table 6 presents the corresponding results in terms of percent relative quadratic deviation (rms) on the experimental infinite-dilution activity coefficients of the data base.

In summary, the experimental activity coefficients considered were correlated with an overall rms error of 10.7%, of the same order of magnitude as the uncertainty of experimental data.

Prediction of Vapor–Liquid Equilibria

The method presently proposed is useful in the prediction of VLE for multicomponent mixtures.

The equilibrium ratios for all components are evaluated by

$$K_i = \frac{\phi_i^L}{\phi_i^v} \tag{17}$$

where ϕ_i^L and ϕ_i^v are expressed by eq 7, which has to be applied twice, for the liquid and vapor phases, respectively, at the pertinent compositions.

The calculation proceeds as follows: evaluate parameters A_i, B_i for pure components from eq 2.1; for each phase calculate the activity coefficients of all components at infinite pressure with eqs 11–15, calculate A/B from eq 6 and B from eq 5, solve eq 3 for the pertinent root z_L or z_V, and calculate ϕ_i^L or ϕ_i^V from eq 7; evaluate the equilibrium ratios from eq 17.

Results

The group contribution method developed, based on information at infinite-dilution only, was applied to calculate vapor–liquid equilibria of binary systems over the whole concentration range; a number of systems were investigated, representative of all pairs of groups considered.

Some examples are reported in the diagrams of Figures 3–8: here, all the system types are shown. As it can be seen, the results obtained are generally good with a satisfactory reproduction of the azeotropic points. Also,
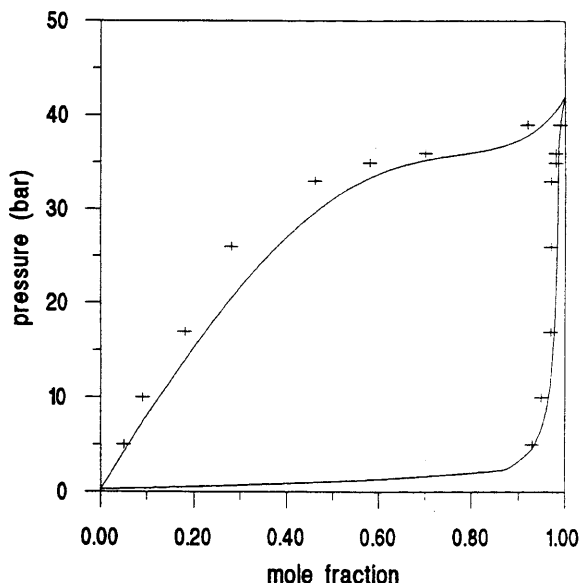
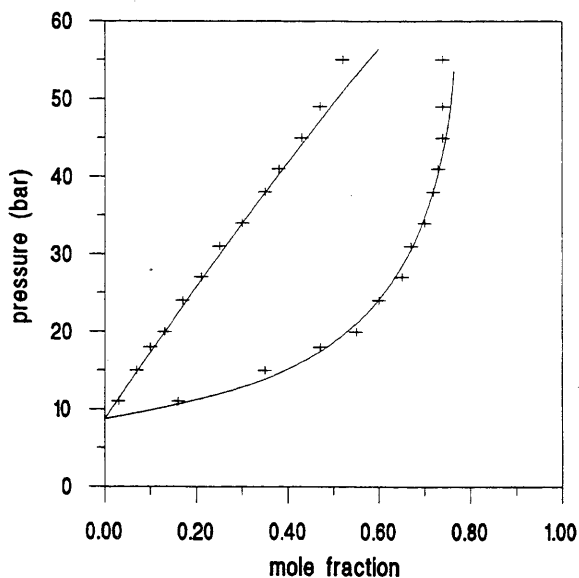**Figure 9.** Ethane(1)–acetone(2) at T = 298 K.

Figure 10. Propane(1)–benzene(2) at T = 444 K.

predictions of dew and bubble temperatures and pressures are generally acceptable (cf., Figures 3b and 4b).

The new method shows a significant improvement with respect to UNIFAC (1977 version) and is slightly better than the modified UNIFAC (1987).

Finally, the method was applied to systems at high pressure and/or containing supercritical components. Although only few cases were considered, the results are of good accuracy, as can be seen in Figures 9 and 10.

Conclusions

An original method is proposed, to predict vapor–liquid equilibria of systems containing polar and/or nonpolar substances. The method is based on a cubic equation of state and the Huron–Vidal mixing rules.

Infinite-pressure activity coefficients were predicted by the use of group contributions, determined by regression of experimental infinite-dilution activity coefficient data.

The method was applied to predict vapor–liquid equilibria of binary systems formed by alkanes, aromatic hydrocarbons, alcohols, and ketones, as representative of the various types of substances (polar, nonpolar, associated). The results were good over the whole concentration range, thus proving that infinite-dilution activity coefficients are reliable data on which to base a group-contribution method.

Unlike activity coefficient-based methods, the proposed one can be applied to systems containing supercritical components and/or systems at high pressure. A few applications to such systems gave satisfactory results.

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