

GENERAL RESEARCH

Analysis of the UNIFAC-Type Group-Contribution Models at the Highly Dilute Region. 1. Limitations of the Combinatorial and Residual Expressions

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An analysis of the behavior of UNIFAC-type group-contribution models at the infinite-dilution region is presented. It is shown that the modified UNIFAC and Entropic-FV combinatorial expressions account satisfactorily for the combinatorial effects, but not the Flory–Huggins and original UNIFAC ones. It is also shown that available residual terms fail to account sufficiently for the residual effects, performing actually better when combined with the aforementioned poorer Flory–Huggins and original UNIFAC combinatorial expressions. The ensuing implications of these limitations of the residual terms on the accuracy of infinite-dilution activity coefficient correlation are then demonstrated.

Introduction

Knowledge of activity coefficients at the dilute region is very important in chemical and environmental engineering. Since in many cases experimental data are not available, predictive empirical models are used. The most representative predictive models are the ones belonging to the UNIFAC class. In UNIFAC (Fredenslund et al., 1975), like in all the group-contribution models based on the local composition concept, the activity coefficient of a component in a mixture is built up by two terms according to the following equation:

$$\ln \gamma_i = \ln \gamma_i^{\text{comb}} + \ln \gamma_i^{\text{res}} \quad (1)$$

The combinatorial term of the original UNIFAC model is only a function of the mole fraction of the components in the mixture and their van der Waals (vdW) volume (r_i) and area (q_i) parameters as shown in eqs 2–5. The

$$\ln \gamma_i^{\text{comb}} = \ln F_i + 1 - F_i - 5q_i \left(\ln \frac{\Phi_i}{\Theta_i} + 1 - \frac{\Phi_i}{\Theta_i} \right) \quad (2)$$

$$F_i = \frac{r_i^k}{\sum_j x_j r_j^k}, \quad k = 1 \quad (3)$$

$$\Phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \quad (4)$$

$$\Theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \quad (5)$$

first three terms in eq 2 are, in fact, the Flory–Huggins (F–H) expression, and the last one is the Staverman–Guggenheim correction term.

The residual part of UNIFAC is obtained by using the relations

$$\ln \gamma_i^{\text{res}} = \sum_k v_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(i)}) \quad (6)$$

$$\ln \Gamma_k = Q_k \left[1 - \ln \left(\sum_m \theta_m \Psi_{mk} \right) - \sum_m \frac{\theta_m \Psi_{km}}{\sum_n \theta_n \Psi_{nm}} \right] \quad (7)$$

whereby the group area fraction θ_m is given by the equation

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \quad (8)$$

and the group mole fraction X_m by

$$X_m = \frac{\sum_j v_m^{(j)} x_j}{\sum_j \sum_n v_n^{(j)} x_j} \quad (9)$$

Finally, in the original UNIFAC model the group interaction parameter Ψ_{mn} is given by

$$\Psi_{mn} = \exp(-a_{mn}/T) \quad (10)$$

Application of eq 2 to alkane mixtures, which are considered to be athermal, leads to substantial overestimation of the mixture nonideality. Thus, Donohue and Prausnitz (1975) introduced some additional parameters using the Flory–Huggins expression, while Kikic et al. (1980) and Weidlich and Gmehling (1987) introduced different exponents in eq 3 for the F–H term in order to obtain better results for such mixtures.

From a different point of view Oishi and Prausnitz (1979) introduced an extra term in eq 1, which takes

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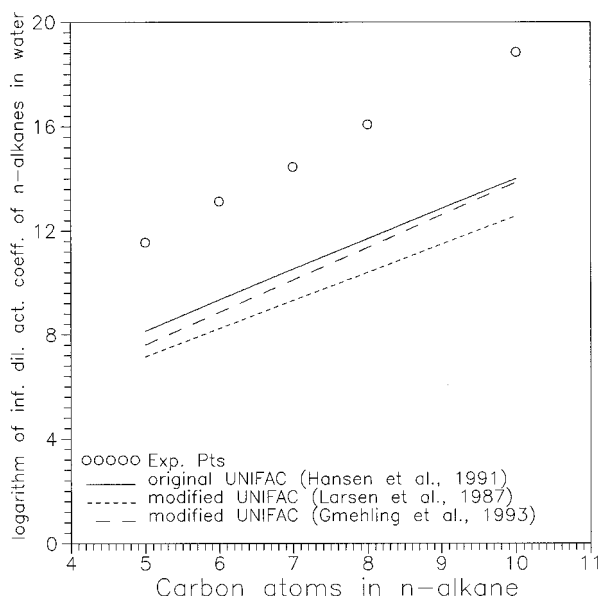


Figure 1. Experimental and predicted, from different UNIFAC-type models, infinite-dilution activity coefficients of *n*-alkanes in water at 298 K. Experimental data from McAuliffe (1966, 1969).

into account differences in the free volume of the molecules for treating mixtures containing polymeric compounds. Finally, modified residual expressions for UNIFAC have also been used in order to treat special effects in some kind of mixtures, like association. An example is the "effective" UNIFAC model of Nagata and Koyabu (1981).

In a recent work Voutsas and Tassios (1996) have shown that the existing UNIFAC-type models perform poorly when applied in the prediction of infinite-dilution activity coefficients in polar mixtures, especially in water-containing ones. A typical example is shown in Figure 1 where predicted infinite-dilution activity coefficients of *n*-alkanes in water are compared with the experimental ones. Order of magnitude differences between predicted and experimental γ^∞ values are observed.

In this paper we analyze the performance of the combinatorial and residual terms of the UNIFAC model. Both nonpolar and polar systems are considered including asymmetric ones, where the effect of the combinatorial contribution to the activity coefficients is more pronounced. The investigation is carried out in the infinite-dilution region where the maximum degree of nonideality is encountered and, also, where most data for asymmetric systems are available.

Methodology and Models

Let us consider the case of binary mixtures where an alkane (1) is at infinite-dilution condition in a solvent (2) and vice versa. If we consider the solvent to be a single-group one, then the expressions for the infinite-dilution activity coefficients are given by

$$\ln \gamma_1^\infty = \ln \gamma_1^{\infty, \text{comb}} + q_1(1 - \ln \Psi_{21} - \Psi_{12}) \quad (11)$$

$$\ln \gamma_2^\infty = \ln \gamma_2^{\infty, \text{comb}} + q_2(1 - \ln \Psi_{12} - \Psi_{21}) \quad (12)$$

where Ψ_{12} and Ψ_{21} are the interaction parameters between the CH_2 group of the alkane and the solvent and q_1 and q_2 are the area parameters of the alkane and of the solvent, respectively.

If a particular model represents exactly the experimental data, $\ln \gamma_i^{\infty, \text{exp}}$ can be replaced by $\ln \gamma_i^{\infty, \text{exp}}$ and eqs 11 and 12 respectively can be written, after rearrangement, as

$$\ln \gamma_1^{\infty, \text{exp}} - \ln \gamma_1^{\infty, \text{comb}} = q_1(1 - \ln \Psi_{21} - \Psi_{12}) \quad (13)$$

$$\ln \gamma_2^{\infty, \text{exp}} - \ln \gamma_2^{\infty, \text{comb}} = q_2(1 - \ln \Psi_{12} - \Psi_{21}) \quad (14)$$

The left-hand side of eq 13, which is in effect the residual infinite-dilution activity coefficient, must then be a linear function to the vdW area parameter of the alkane (q_1) passing through the origin, for constant temperature data. The slope of this line is determined by the two interaction parameters. Similarly, in eq 14 the right-hand side is constant at constant temperature since both the term in parentheses and q_2 are constant. So, the left-hand side of this equation if plotted versus q_1 must give a straight line parallel to the q axis.

To check the validity of the above requirements for the different combinatorial expressions, the following general form was used for them:

$$\ln \gamma_i^{\infty, \text{comb}} = \ln \frac{r_i^k}{r_j^k} + 1 - \frac{r_i^k}{r_j^k} + \ln \gamma_i^{\infty, \text{SG}} \quad (15)$$

where i and j are the solute and solvent, respectively, and $\ln \gamma_i^{\infty, \text{SG}}$ is the Staverman–Guggenheim term.

In this study the following specific forms are considered: (i) the original UNIFAC one, where $k = 1$; (ii) the Flory–Huggins (F–H) one using segments, where $k = 1$ and the Staverman–Guggenheim term has been disregarded; (iii) the modified UNIFAC expression of Larsen et al. (1987), where $k = 2/3$ (modified-2/3) and the Staverman–Guggenheim term has been disregarded; (iv) the modified UNIFAC expression of Weidlich and Gmehling (1987) and Gmehling et al. (1993), where $k = 3/4$ (modified-3/4).

We have also included in the evaluation the Entropic-FV expression (Elbro et al., 1990), which in addition to the combinatorial contributions also takes into account effects coming from differences in the free volume of the components of a mixture. The purpose for this is to investigate if inclusion of a free-volume contribution leads to improved results over the usual combinatorial expressions. In this model, r of eq 15 with $k = 1$ is replaced by the free volume (V_f) of the components, defined as $V_f = V - V_w$, where V is the molar volume of the component at a specific temperature and V_w is its van der Waals volume. Also, the Staverman–Guggenheim correction term is not included in this expression.

Data Base

The data base used for the evaluation of the different combinatorial expressions consists of the following binary mixtures: (i) alkane/alkane; (ii) alkanes in water; (iii) alkane/*N,N*-dimethylformamide (DMF); (iv) alkanes in ethanol; (v) alkanes in butanone; (vi) alkanes in phenol; (vii) alkanes in furfural.

The selection of the data base when working with infinite-dilution activity coefficients is a very difficult task since no consistency test can be applied to them. Many of the data used in this work are from the compilation of Pierotti et al. (1959), which were obtained by extrapolation of vapor–liquid equilibrium data close to the infinite-dilution region and, consequently, they include a degree of uncertainty, which, however, has

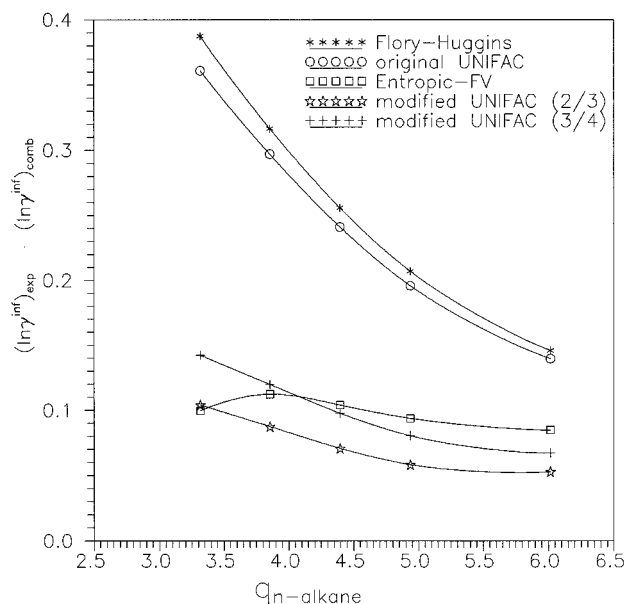


Figure 2. Variations of $\ln \gamma_1^{\infty, \text{exp}} - \ln \gamma_1^{\infty, \text{comb}}$ values for n -alkane (1)/ n -eicosane (2) mixtures, obtained from different combinatorial expressions, with q of n -alkane. Experimental data from Parcher et al. (1975) at $T = 353$ K.

been taken into account in reaching our conclusions. Also, the experimental γ^∞ values of alkanes in water have been obtained from mutual solubility data of McAuliffe (1966, 1969), which are extensively used in the literature. In all cases the data were checked through plots versus carbon number.

The required values for the estimation of the combinatorial activity coefficient van der Waals volume and area parameters have been taken from the DIPPR compilation (Daubert and Danner, 1989). The molar volumes of the solvents and normal alkanes, having less than 20 carbon atoms, have been calculated using the DIPPR data correlations. For the long-chain alkanes (number of carbon atoms greater than 20) the GCVOL model (Elbro et al., 1991) has been used.

Results

For the nearly athermal alkane/alkane mixtures the residual contribution to the activity coefficient is considered equal to zero in all UNIFAC and the Entropic-FV (FV) models and, consequently, the right-hand side of eqs 13 and 14 must be equal to zero. To test the performance of the various combinatorial expressions to this requirement, we present in Figures 2 and 3 plots of $\ln \gamma_1^{\infty, \text{exp}} - \ln \gamma_1^{\infty, \text{comb}}$ values for n -alkanes (1) in n -eicosane (2) and n -alkanes (1) in n -hexatriacontane (2), respectively, versus q of n -alkane. The reverse is shown in Figures 4 and 5, where $(\ln \gamma_2^{\infty, \text{exp}} - \ln \gamma_2^{\infty, \text{comb}})$ values for large n -alkanes (1)/ n -pentane (2) and large n -alkanes (1)/ n -hexane (2) mixtures, respectively, are plotted versus q of the large n -alkane. The two modified UNIFAC and the FV expressions come closer to meeting the requirements coming from eqs 13 and 14, even though they demonstrate a slight system asymmetry dependence, especially for the case of $\ln \gamma_1^{\infty, \text{exp}} - \ln \gamma_1^{\infty, \text{comb}}$ values, while the F-H and original UNIFAC ones predict much smaller values for $\gamma^{\infty, \text{comb}}$, especially for the higher asymmetries.

We turn now to systems involving n -alkanes in a single polar solvent where a plot of $\ln \gamma_1^{\infty, \text{exp}} - \ln \gamma_1^{\infty, \text{comb}}$ values vs q of n -alkane should yield a straight

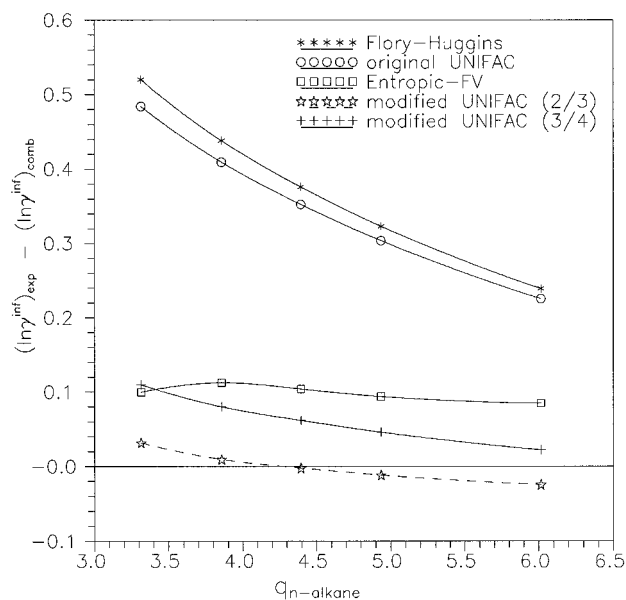


Figure 3. Variations of $\ln \gamma_1^{\infty, \text{exp}} - \ln \gamma_1^{\infty, \text{comb}}$ values for n -alkane (1)/ n -hexatriacontane (2) mixtures, obtained from different combinatorial expressions, with q of n -alkane. Experimental data from Parcher et al. (1975) at $T = 373$ K.

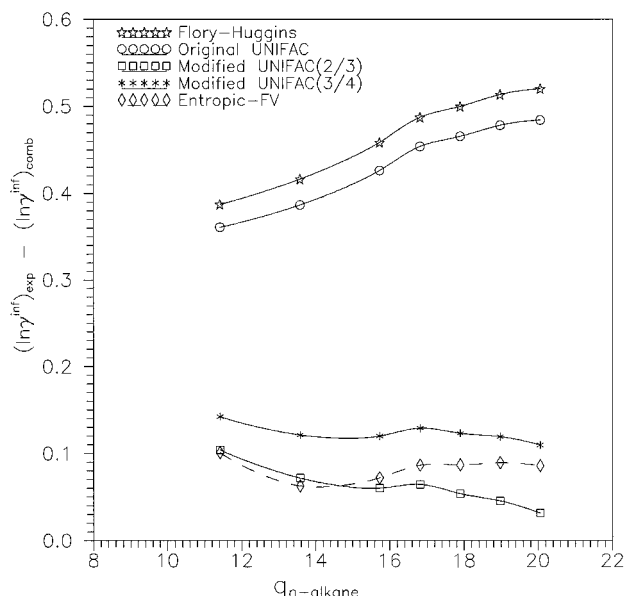


Figure 4. Variations of $\ln \gamma_2^{\infty, \text{exp}} - \ln \gamma_2^{\infty, \text{comb}}$ values for large n -alkane (1)/ n -pentane (2) mixtures, obtained from different combinatorial expressions, with q of the large n -alkane. Experimental data from Parcher et al. (1975) at $T = 373$ K.

line passing through the origin. Intercept values for six different solvents are presented in Table 1 and typical plots in Figures 6 and 7. In Table 1 intercepts obtained from the models using the fitted r and q values for water and ethanol (Hansen et al., 1991) are also presented. The physical and fitted r and q values of solvents used in this study are presented in Table 2. It must be noted that phenol, butanone, and ethanol have been treated as monogroup molecules so that eqs 13 and 14 are directly applicable to the mixtures of these compounds with alkanes. The results of Table 1—and the typical ones shown graphically in Figures 6 and 7—indicate that, while no expression yields a line that passes through the origin, it is now the F-H and original UNIFAC ones that give the smallest intercepts. Notice that use of the fitted r and q parameters of Hansen et al. for water and ethanol gives worse results. Further-

Table 3. $\ln \gamma_2^{\infty, \text{exp}} - \ln \gamma_2^{\infty, \text{comb}}$ Values for Alkane (1)/DMF (2) Mixtures Obtained from Different Models Using Physical r and q Values for DMF

alkane	original UNIFAC	Flory–Huggins	modified UNIFAC(2/3)	modified UNIFAC(3/4)	Entropic-FV
<i>n</i> -heptane	2.95	2.96	2.90	2.90	3.11
<i>n</i> -octane	2.82	2.83	2.75	2.75	2.97
<i>n</i> -nonane	2.82	2.84	2.72	2.73	2.96
<i>n</i> -decane	2.78	2.81	2.67	2.67	2.92
% Dev ^a	5.6	5.3	8.2	7.9	6.1

^a % Dev is the percent deviation between the greatest and the lowest estimated value.

Table 4. Infinite-Dilution Activity Coefficient Correlation Results for Alkane (1)/Water (2) Mixtures at 298 K Using the Physical r and q Values for Water^a

system	$\ln \gamma_1^{\infty, \text{exp}}$	$\Delta \gamma_1$ %				
		original UNIFAC	Flory–Huggins	modified UNIFAC(2/3)	modified UNIFAC(3/4)	Entropic-FV
<i>n</i> -pentane/H ₂ O	11.551	23.6 (44.0)	12.1 (16.6)	52.8 (52.7)	55.9 (67.0)	80.7 (90.3)
<i>n</i> -hexane/H ₂ O	13.128	22.7 (38.7)	14.6 (17.8)	47.9 (47.8)	50.6 (60.7)	70.8 (82.3)
<i>n</i> -heptane/H ₂ O	14.450	1.3 (15.1)	−4.5 (−2.3)	26.0 (25.7)	28.7 (39.6)	49.6 (65.1)
<i>n</i> -octane/H ₂ O	16.077	8.6 (14.8)	7.4 (7.8)	22.3 (22.0)	24.1 (31.7)	43.8 (58.1)
<i>n</i> -decane/H ₂ O	18.839	−23.5 (−35.7)	−14.5 (−18.0)	−40.8 (−41.0)	−41.5 (−43.7)	−42.4 (−37.0)
% AAD		15.9 (29.7)	10.6 (12.5)	38.0 (37.8)	40.2 (48.5)	57.5 (66.5)

^a In parentheses there are included the results obtained using the fitted r and q values for water. Experimental data are from McAuliffe (1966, 1969).

Table 5. Infinite-Dilution Activity Coefficient Correlation Results for Alkane (1)/DMF (2) Mixtures at 333 K Using Physical r and q Values for DMF^a

system	$\ln \gamma_1^{\infty, \text{exp}}$	$\Delta \gamma_1$ %				
		original UNIFAC	Flory–Huggins	modified UNIFAC(2/3)	modified UNIFAC(3/4)	Entropic-FV
<i>n</i> -hexane/DMF	2.497	14.1	12.6	21.5	21.2	20.6
<i>n</i> -octane/DMF	2.907	4.0	3.4	7.8	7.5	6.8
<i>n</i> -nonane/DMF	3.086	−1.9	−1.8	−1.8	−1.8	−2.1
<i>n</i> -decane/DMF	3.254	−8.4	−7.5	−13.3	−13.0	−12.3
% AAD		7.1	6.4	11.1	10.9	10.4

^a Experimental data are from Hradetzky et al. (1990).

Table 6. Infinite-Dilution Activity Coefficient Correlation Results for Alkane (1)/Ethanol (2) Mixtures at 323 K^a

alkane	$\ln \gamma_1^{\infty, \text{exp}}$	$\Delta \gamma_1$ %				
		original UNIFAC	Flory–Huggins	modified UNIFAC(2/3)	modified UNIFAC(3/4)	Entropic-FV
<i>n</i> -butane	1.931	15.8 (33.5)	7.8 (21.1)	43.1 (46.1)	43.6 (51.6)	40.9 (42.7)
<i>n</i> -pentane	2.092	7.7 (25.7)	−1.0 (12.4)	39.5 (42.4)	39.7 (47.7)	34.1 (34.4)
<i>n</i> -decane	3.005	3.5 (14.3)	−1.8 (5.2)	33.4 (35.5)	32.9 (38.7)	21.6 (19.0)
<i>n</i> -hexadecane	3.828	0.4 (0.5)	1.2 (−0.2)	7.3 (10.3)	7.0 (11.4)	2.7 (1.1)
<i>n</i> -eicosane	4.248	−6.9 (−15.5)	−1.4 (−8.8)	−31.2 (−26.0)	−30.5 (−26.8)	−19.6 (−19.7)
% AAD		6.9 (17.9)	2.6 (9.5)	30.9 (32.1)	30.7 (35.2)	23.8 (23.9)

^a In parentheses there are included the results obtained using the fitted r and q values for ethanol. Experimental data are from Pierotti et al. (1959).

Table 7. Infinite-Dilution Activity Coefficient Correlation Results for Alkane (1)/2-Butanone (2) Mixtures at 298 K^a

alkane	$\ln \gamma_1^{\infty, \text{exp}}$	$\Delta \gamma_1$ %				
		original UNIFAC	Flory–Huggins	modified UNIFAC(2/3)	modified UNIFAC(3/4)	Entropic-FV
<i>n</i> -pentane	1.297	7.3	3.9	27.3	26.4	18.1
<i>n</i> -heptane	1.470	−5.6	−9.3	19.6	18.1	8.0
<i>n</i> -decane	1.798	−6.9	−9.4	16.6	14.9	4.1
<i>n</i> -uncosane	2.681	4.2	8.6	−15.8	−15.0	−8.1
% AAD		6.0	7.8	19.8	18.6	9.6

^a Experimental data are from Pierotti et al. (1959).

consider the quality of the obtained correlation of the experimental data with the different models. This is demonstrated for *n*-alkanes in several solvents in Tables 4–9, where the percent error in γ^∞ ($\Delta \gamma_i^\infty$) and the percent average absolute deviation in the γ^∞ 's (% AAD) are presented:

$$\Delta \gamma_i \% = \left(\frac{\gamma_i^{\infty, \text{exp}} - \gamma_i^{\infty, \text{calc}}}{\gamma_i^{\infty, \text{exp}}} \right) \times 100 \quad (16)$$

$$\% \text{ AAD} = \frac{1}{\text{NDP}} \sum_{i=1}^{\text{NDP}} \left| \frac{\gamma_i^{\infty, \text{exp}} - \gamma_i^{\infty, \text{calc}}}{\gamma_i^{\infty, \text{exp}}} \right| \times 100 \quad (17)$$

NDP is the total number of experimental data points. The temperature-independent interaction parameters of the models in eq 10 were calculated by minimizing the % AAD in the calculation of γ^∞ .

Substantial differences in the quality of the obtained correlations are observed as dictated by the intercepts presented in Table 1. Best results are provided by the

Table 8. Infinite-Dilution Activity Coefficient Correlation Results for Alkane (1)/Phenol (2) Mixtures at 298 K^a

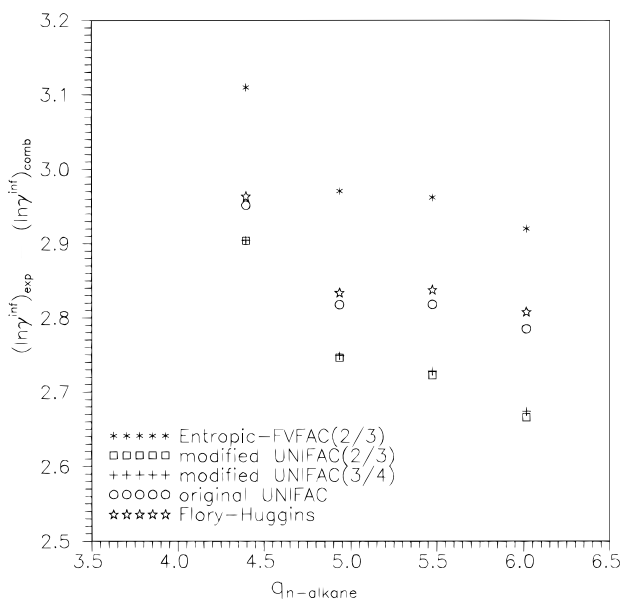
alkane	$\ln \gamma_1^{\infty, \text{exp}}$	$\Delta \gamma_1$ %				
		original UNIFAC	Flory–Huggins	modified UNIFAC(2/3)	modified UNIFAC(3/4)	Entropic-FV
<i>n</i> -pentane	2.708	56.4	60.7	73.2	67.9	64.7
<i>n</i> -heptane	2.996	47.0	51.4	69.4	63.5	58.2
<i>n</i> -decane	3.434	37.2	41.2	64.5	58.3	50.3
<i>n</i> -hexadecane	4.197	19.2	22.2	50.1	43.6	33.0
<i>n</i> -eicosane	4.654	7.0	9.1	35.2	29.0	20.1
<i>n</i> -triacontane	5.704	−26.0	−27.5	−34.8	−34.6	−32.4
% AAD		32.1	35.4	54.5	49.5	43.1

^a Experimental data are from Pierotti et al. (1959).**Table 9. Infinite-Dilution Activity Coefficient Correlation Results for Alkane (1)/Furfural (2) Mixtures at 298 K^a**

alkane	$\ln \gamma_1^{\infty, \text{exp}}$	$\Delta \gamma_1$ %				
		original UNIFAC	Flory–Huggins	modified UNIFAC(2/3)	modified UNIFAC(3/4)	Entropic-FV
<i>n</i> -butane	2.640	46.3	50.5	66.6	61.0	58.5
<i>n</i> -hexane ^b	3.296	45.9	49.1	69.4	64.3	60.0
<i>n</i> -heptane	3.555	43.9	46.8	69.0	63.9	58.8
<i>n</i> -hexadecane	5.348	14.0	15.9	49.7	43.7	32.4
<i>n</i> -triacontane	7.901	−18.9	−19.4	−22.3	−22.8	−22.4
% AAD		33.8	36.3	55.4	51.1	46.5

^a Experimental data are from Pierotti et al. (1959). ^b The datum is from Tiegs et al. (1986).**Table 10. Infinite-Dilution Activity Coefficient Correlation Results for Alkane (1)/DMF (2) Mixtures at 333 K^a**

system	$\ln \gamma_2^{\infty, \text{exp}}$	$\Delta \gamma_2$ %				
		original UNIFAC	Flory–Huggins	modified UNIFAC(2/3)	modified UNIFAC(3/4)	Entropic-FV
<i>n</i> -heptane/DMF	2.851	10.8	10.2	14.4	14.0	13.7
<i>n</i> -octane/DMF	2.667	−2.0	−2.2	−0.2	−0.4	−0.7
<i>n</i> -nonane/DMF	2.617	−1.9	−1.8	−2.6	−2.6	−2.6
<i>n</i> -decane/DMF	2.533	−5.4	−4.9	−8.6	−8.3	−7.8
% AAD		5.0	4.8	6.4	6.3	6.2

^a Experimental data are from Hradetzky et al. (1990).**Figure 8.** Variations of $\ln \gamma_2^{\infty, \text{exp}} - \ln \gamma_2^{\infty, \text{comb}}$ values for *n*-alkane (1)/DMF (2) mixtures, obtained from different combinatorial expressions, with q of *n*-alkane. Experimental data from Hradetzky et al. (1990) at 333 K.

models that better satisfy the requirement of eq 13 and thus give the smallest intercepts, i.e., the F–H and original UNIFAC ones especially for the alkane/water and alkane/ethanol mixtures.

In Table 10 infinite-dilution activity coefficient correlation results of DMF in *n*-alkanes are tabulated. For these mixtures the necessary group-interaction param-

eter values were obtained by simultaneous regression of both sets of γ^∞ data. As expected from Figure 8 all models give similar results, with the largest error for the case of the smallest solvent (*n*-heptane) that deviates the most from the horizontal line.

Discussion

Let us first summarize our observations on the obtained results:

1. For athermal systems the two modified UNIFAC combinatorial expressions and the FV one give good results, while the F–H and the original UNIFAC expressions give poor ones.

2. The opposite is the case with polar systems, where the last two expressions provide the better results.

3. The problem is very pronounced in the case of hydrogen-bonded solvents (water, ethanol, phenol) and when large solute/solvent size asymmetries are involved as in the case of alkanes in phenol and furfural (up to *n*-triacontane). Furthermore, in the latter two cases the superiority of the original UNIFAC and F–H expressions tends to disappear.

To find an explanation for these results, we start from the expression for the excess Gibbs free energy G^E , which at constant pressure and temperature is given by

$$G^E = H^E - TS^E - PV^E \quad (18)$$

Consequently, the appropriate expression for γ should account for all three contributions to G^E , enthalpic, entropic, and excess volume of mixing. In eq 1 the combinatorial term accounts for the entropic effects which arise from differences in the size and, in some

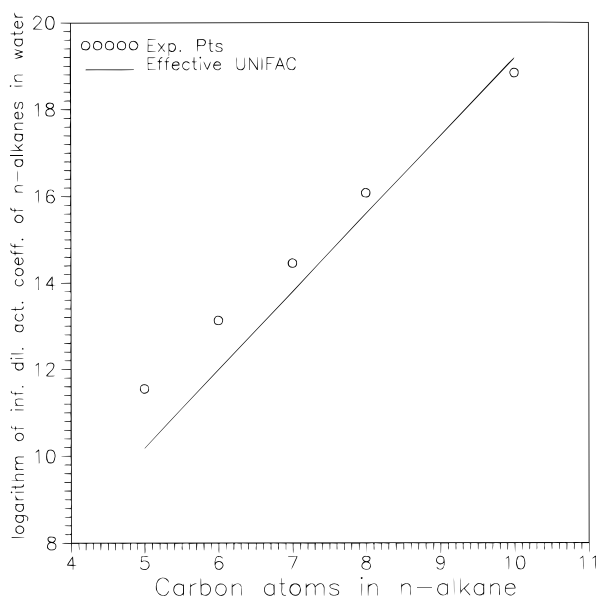


Figure 9. Infinite-dilution activity coefficient correlation results for *n*-alkanes in water obtained with the "effective" UNIFAC model.

cases, the shape of the molecules, while the residual term is supposed to describe all remaining effects. This, of course, represents an extremely demanding requirement for the residual term considering, especially, the complexity of the systems in this study.

The good results of the two modified UNIFAC models and the Entropic-FV one with the athermal systems indicate that they do provide a successful description of the combinatorial effects. Their failure, on the other hand, with polar systems indicates that the UNIFAC residual expression fails to successfully account for the aforementioned residual effects. This observation is further supported by the good performance of the F-H and original UNIFAC expressions with polar systems, while they give poor results for the athermal ones: the underestimated combinatorial effects compensate the overestimated residual ones. This compensation, however, becomes less effective when large solute/solvent asymmetries are involved, as suggested by the alkanes in phenol and furfural results.

It is apparent from eqs 11 and 12 that no improvement can be realized by adjusting the interaction parameters in the residual term of UNIFAC. This limitation of the residual term should not be surprising, however, considering the aforementioned expectations from it. It is worth mentioning here the "effective" UNIFAC (Nagata and Koyabu, 1981), which was developed with emphasis to associated compounds and has a different type of residual term (presented briefly in Appendix). A test similar to that provided by eqs 13 and 14 for UNIFAC is not possible here because of the form of its residual term. Correlation results, however, shown in Figure 9 for the infinite-dilution activity coefficients of alkanes in water demonstrate the limitations of this residual term as well.

Conclusions

A combination of experimental and UNIFAC obtained γ^∞ values through eqs 13 and 14 is used for the systematic analysis of different UNIFAC-type models. It is demonstrated that the modified UNIFAC (2/3, 3/4) and the Entropic-FV combinatorial terms perform successfully with athermal mixtures, providing, thus, a

satisfactory description of combinatorial effects. The same models, however, perform poorly for polar mixtures when combined with the UNIFAC residual term. Here it is the original UNIFAC and Flory-Huggins combinatorial terms, which fail badly for athermal mixtures, that provide better—but not satisfactory—results. The problem is more pronounced when large solute/solvent size asymmetries are involved. It is apparent, therefore, that a new residual expression is needed for a successful group-contribution model.

Possible modifications of UNIFAC, at the expense, however, of its general group-contribution character, are discussed in part 2 of this series and are successfully applied to the water/hydrocarbon mixtures.

List of Symbols

% AAD = average absolute percent deviation

a_{mn} = UNIFAC group interaction parameter between groups *m* and *n*

$a_{mn}^{(0)}$ = empirical coefficient

$a_{mn}^{(1)}$ = empirical coefficient

$a_{mn}^{(2)}$ = empirical coefficient

G^E = excess Gibbs free energy

H^E = excess enthalpy

NDP = number of data points

P = pressure

q = relative van der Waals area

Q = relative van der Waals area of subgroup

r = relative van der Waals volume

S^E = excess entropy

T = temperature

V^E = excess volume

x = mole fraction

X = group mole fraction in the liquid phase

Greek Symbols

γ = activity coefficient

Γ = group activity coefficient

$\Gamma^{(i)}$ = group activity coefficient in the pure substance

Θ = surface area fraction

$\nu^{(i)}$ = number of structural groups in a molecule

Φ = segment fraction

Ψ = UNIFAC group interaction parameter

Subscripts

i = component *i*

j = component *j*

n, *m*, *k* = groups in a molecule

Superscripts

comb = combinatorial

res = residual

∞ = infinite dilution

Appendix. The "Effective" UNIFAC Model

The effective UNIFAC model (Nagata and Koyabu, 1981) uses the combinatorial expression of the original UNIFAC model and for the residual activity coefficient the following one:

$$\ln \gamma_i^{\text{res}} = \sum_k \nu_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(i)}) - \left(\ln \frac{\Theta_i}{x_i} + 1 - \frac{\Theta_i}{x_i} \right) \quad (\text{A-1})$$

The term in the last parentheses is actually a Flory-Huggins type term, where Θ_i is given by eq 5. The group residual activity coefficient (Γ_k) is calculated from the equation

$$\ln \Gamma_k = 1 - \ln \left(\sum_m X_m \Psi_{mk} \right) - \sum_m \left(\frac{X_m \Psi_{km}}{\sum_n X_n \Psi_{nm}} \right) \quad (\text{A-2})$$

where the mole fraction of group m in the mixture is given by

$$X_m = \frac{\sum_j v_m^{(j)} x_j}{\sum_j \sum_n v_n^{(j)} x_j} \quad (\text{A-3})$$

Finally, the group interaction parameter Ψ_{mn} is given by

$$\Psi_{mn} = \left(\frac{Q_m}{Q_n} \right) \left[\exp \left(- \frac{a_{mn}}{T} \right) \right] \quad (\text{A-4})$$

As evident eq A-1 cannot be reduced, at the infinite-dilution condition, to a function like the right-hand side of eq 13 or the one of eq 14, and as a result the requirements coming from these equations are not valid for the effective UNIFAC model.

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