

GENERAL RESEARCH

Further Development of Modified UNIFAC (Dortmund):
Revision and Extension 5Antje Jakob, Hans Grensemann,[†] Jürgen Lohmann,[‡] and Jürgen Gmehling*Lehrstuhl für Technische Chemie (Fakultät V), Carl von Ossietzky Universität Oldenburg,
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For the estimation of thermodynamic properties of pure compounds and mixtures, often the group contribution concept is applied. A successful and well-known group contribution model for the prediction of phase equilibria is the group contribution method Modified UNIFAC (Dortmund). Since 1996, a company consortium has supported the further revision and extension of this method. The main objective of this consortium is the systematic revision and extension of the existing parameter matrix and the introduction of new main groups of industrial interest. In this paper, besides parameters for the new main group “formamides”, revised parameters for the already existing groups are given. Furthermore, an empirical expression for the prediction of alkane and cycloalkane solubilities in water is presented, because, as previously described in different articles [Wienke and Gmehling, *Toxicol. Environ. Chem.* **1998**, 65, 57–86; Lohmann et al., *Ind. Eng. Chem. Res.* **2001**, 40, 957–964; Skjold-Jørgensen et al., *Ind. Eng. Process Des. Dev.* **1979**, 18, 714–722], poor solubilities of these compounds in water were accepted, to be able to predict the vapor–liquid equilibrium (VLE) behavior of alcohol–water systems with the desired accuracy. In addition, group interaction parameters of systems are presented, which were fitted to artificial data predicted using the COSMO–RS (Ol) model. This model basically can be used to fill gaps in the parameter matrix of reactive mixtures.

Introduction

Thermodynamic properties of pure fluids and of mixtures can be predicted with the help of group contribution methods. The group contribution concept has a great advantage, in that, although there are thousands of chemical compounds of industrial interest, the number of required functional groups to describe the thermodynamic behavior of these compounds (mixtures) is much smaller.

The group contribution method Modified UNIFAC (Dortmund) is a g^E model, which allows the prediction of liquid-phase activity coefficients γ_i in nonelectrolyte systems,¹ as a function of temperature and composition. The activity coefficient is calculated as the sum of a combinatorial part (C) and a residual part (R):

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (1)$$

The combinatorial part represents the contribution of the excess entropy, which results from the different sizes and shapes of the molecules considered. The residual part represents the contribution of the excess enthalpy, which is caused by energetic interaction between the molecules.²

The temperature-independent combinatorial part is calculated with the help of the van der Waals volume (R_k) and surface

area (Q_k) values of the functional groups. The values can be derived from the quantities that have been tabulated by Bondi.³ In a few cases, for the Modified UNIFAC (Dortmund) model, the van der Waals properties were adjusted in a physical meaningful frame, together with the basic group interaction parameters. In comparison to the original UNIFAC model, in modified UNIFAC, the combinatorial part (V') was changed empirically, to allow for a better description of asymmetric systems.⁴

$$\ln \gamma_i^C = 1 - V'_i + \ln(V'_i) - 5q_i \left[1 - \frac{V_i}{F_i} + \ln\left(\frac{V_i}{F_i}\right) \right] \quad (2)$$

with

$$V'_i = \frac{r_i^{3/4}}{\sum_j x_j r_j^{3/4}} \quad (\text{modified UNIFAC}) \quad (3a)$$

$$V_i = \frac{r_i}{\sum_j x_j r_j} \quad (3b)$$

and

$$F_i = \frac{q_i}{\sum_j x_j q_j} \quad (4)$$

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The relative van der Waals volume (r_i) and surface area (q_i) values of molecule i can be calculated from the known van der Waals properties R_k and Q_k of the structural groups k .

$$r_i = \sum_k v_k^{(i)} R_k \quad q_i = \sum_k v_k^{(i)} Q_k \quad (5)$$

The residual part can be obtained using group activity coefficients of the groups k in the mixture (Γ_k) and for the pure compounds ($\Gamma_k^{(i)}$) (solution of the groups concept):

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

The concentration dependence of the group activity coefficient Γ_k is defined as follows:

$$\ln \Gamma_k = Q_k \left(1 - \ln \left(\sum_m \Theta_m \Psi_{mk} \right) - \sum_m \frac{\Theta_m \Psi_{km}}{\sum_n \Theta_n \Psi_{nm}} \right) \quad (7)$$

with the surface fraction Θ_m :

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

and the molar fraction X_m of group m :

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

The temperature dependence of the group interaction parameter Ψ_{nm} is described by eqs 10a and 10b:

$$\text{original UNIFAC: } \Psi_{nm} = \exp \left(-\frac{a_{nm}}{T} \right) \quad (10a)$$

$$\text{modified UNIFAC: } \Psi_{nm} = \exp \left(-\frac{a_{nm} + b_{nm}T + c_{nm}T^2}{T} \right) \quad (10b)$$

The main differences of Modified UNIFAC, in comparison to original UNIFAC, besides the introduction of the $3/4$ -term in the combinatorial term, is that temperature-dependent parameters are used to permit a reliable description of the real behavior in a wide temperature range. The group interaction parameters a_{nm} (a_{mn}) and b_{nm} (b_{mn}), c_{nm} (c_{mn}) describe the interaction between the groups n and m .

For the design and optimization of thermal separation processes, the use of group contribution methods is helpful, because experimental data are often missing and the measurements of the necessary phase equilibrium and thermophysical data is time-consuming and expensive. Because of the ongoing research, within the scope of the UNIFAC consortium, the accuracy and range of applicability of Modified UNIFAC (Dortmund) is continuously improved.⁵

The accuracy and the range of applicability of the model mainly depend on the quality of the group interaction parameters. The most reliable group interaction parameters are obtained by a simultaneous fit to a large database with experimental data for vapor–liquid equilibria (VLE), activity

coefficients at infinite dilution (γ^∞), excess enthalpies (h^E), liquid–liquid equilibria (LLE), solid–liquid equilibria of eutectic systems (SLE), azeotropic data (AZD), and, in some cases, excess heat capacities (c_p^E).

In the objective function F of the fitting procedure, the deviations for seven different phase equilibria and excess properties are taken into account, using different weighting factors w_i for the various properties.

$$F = w_{\text{VLE}} \sum \Delta \text{VLE} + w_{\text{AZD}} \sum \Delta \text{AZD} + w_{\gamma^\infty} \sum \Delta \gamma^\infty + w_{h^E} \sum \Delta h^E + w_{c_p^E} \sum \Delta c_p^E + w_{\text{LLE}} \sum \Delta \text{LLE} + w_{\text{SLE}} \sum \Delta \text{SLE} \quad (11)$$

The weighting factors are chosen in such a way that a similar contribution of the different type of data is obtained. However, during the fitting procedure, the weighting factors can be changed. At the same time, obviously erroneous data can be excluded.

Each data type provides specific information about the real mixture behavior. Vapor–liquid and azeotropic data are most important. They provide the information about the composition dependence of the activity coefficients. Without VLE data, the group interaction parameters cannot be fitted. Following the Gibbs–Helmholtz equation, excess enthalpies provide the correct information about the temperature dependence of the activity coefficients. At the same time, excess enthalpies at high temperatures are important as supporting data for fitting temperature-dependent parameters. During the last years, the temperature range of several interaction parameters was enlarged, because a large number (~ 700 data sets) of excess enthalpies at high temperature (140 °C) have been measured in our laboratory, using an isothermal flow calorimeter.

Excess heat capacities provide information about the temperature dependence of the excess enthalpies. The activity coefficients at infinite dilution deliver the most-reliable information about the dilute region and also for asymmetric systems, because a great portion of the γ^∞ data were measured especially for the model development using gas–liquid-chromatography (GLC). SLE data of eutectic systems are used as supporting data at low temperatures. LLE data provide valuable information for strong real systems. The description of LLE data is different and more complicated than other phase equilibria calculations, because the binodal construction (composition and temperature dependence) is based only on the activity coefficient, whereas, in the case of VLE or SLE data, the activity coefficient is only a correction term to account for real behavior.

For fitting the Modified UNIFAC (Dortmund) interaction parameters, the pure component and mixture data stored in Dortmund Data Bank (DDB)⁶ are used together with experimental data that have been measured in our laboratory.

During the fitting procedure, the objective function F must be minimized:

$$F(a_{nm}, a_{mn}, b_{nm}, b_{mn}, c_{nm}, c_{mn}) \stackrel{!}{\rightarrow} \min \quad (12)$$

Sometimes, with the basic group interaction parameters, the van der Waals properties R_k and Q_k also are adjusted:

$$F(a_{nm}, a_{mn}, b_{nm}, b_{mn}, c_{nm}, c_{mn}, R_k, Q_k) \stackrel{!}{\rightarrow} \min \quad (13)$$

The number of group interaction parameters (2, 4, or 6) used to describe the experimental data is dependent on the strength of the temperature dependence and the availability of the

Table 1. Thermodynamic Mixture Data Stored in the DDB (February 2006) Used for Fitting the Modified UNIFAC (Dortmund) Group Interaction Parameters

type of thermodynamic mixture data	number of data sets/data points stored in DDB
VLE (normal boiling compounds)	26 100
activity coefficients at infinite dilution, γ^∞	46 700
excess enthalpies, h^E	17 750
excess heat capacities, c_p^E	1 900
LLE	15 700
SLE	16 800
azeotropic data	48 650

different types of data. If only VLE data and activity coefficients at infinite dilution in a limited temperature range are available, constant parameters (a_{nm} , a_{mn}) are fitted, whereas all parameters a_{nm} , a_{mn} , b_{nm} , b_{mn} , c_{nm} , and c_{mn} are fitted, when enthalpies of mixing at different temperatures and/or SLE data are available and the systems show a strong temperature dependence of the real behavior.

To make the procedure fast and simple, a sophisticated software package has been developed for the fitting procedure

with direct access to the pure component data parameters and the mixture data stored in the DDB. Besides the retrieval of the compounds of interest and the experimental data, it allows us to check the quality of the data. At the same time, the results can be judged by various graphical presentations and mean squared deviations of the calculated and experimental data. The fitting procedure has already been described in detail in several papers previously.^{7–13}

The continuous update of DDB guarantees the steady further development of Modified UNIFAC (Dortmund). Table 1 shows the part of the data stored in DDB, which is used for the further development of Modified UNIFAC.

Figure 1 shows the published available group interaction parameters of Modified UNIFAC (Dortmund). During the last nine years, more than 600 new parameters have been fitted and ~100 of the published parameters have been revised. Since last year, a few gaps in the parameter matrix were also filled with the help of artificial data, using the COSMO-RS (OI) model.¹⁴

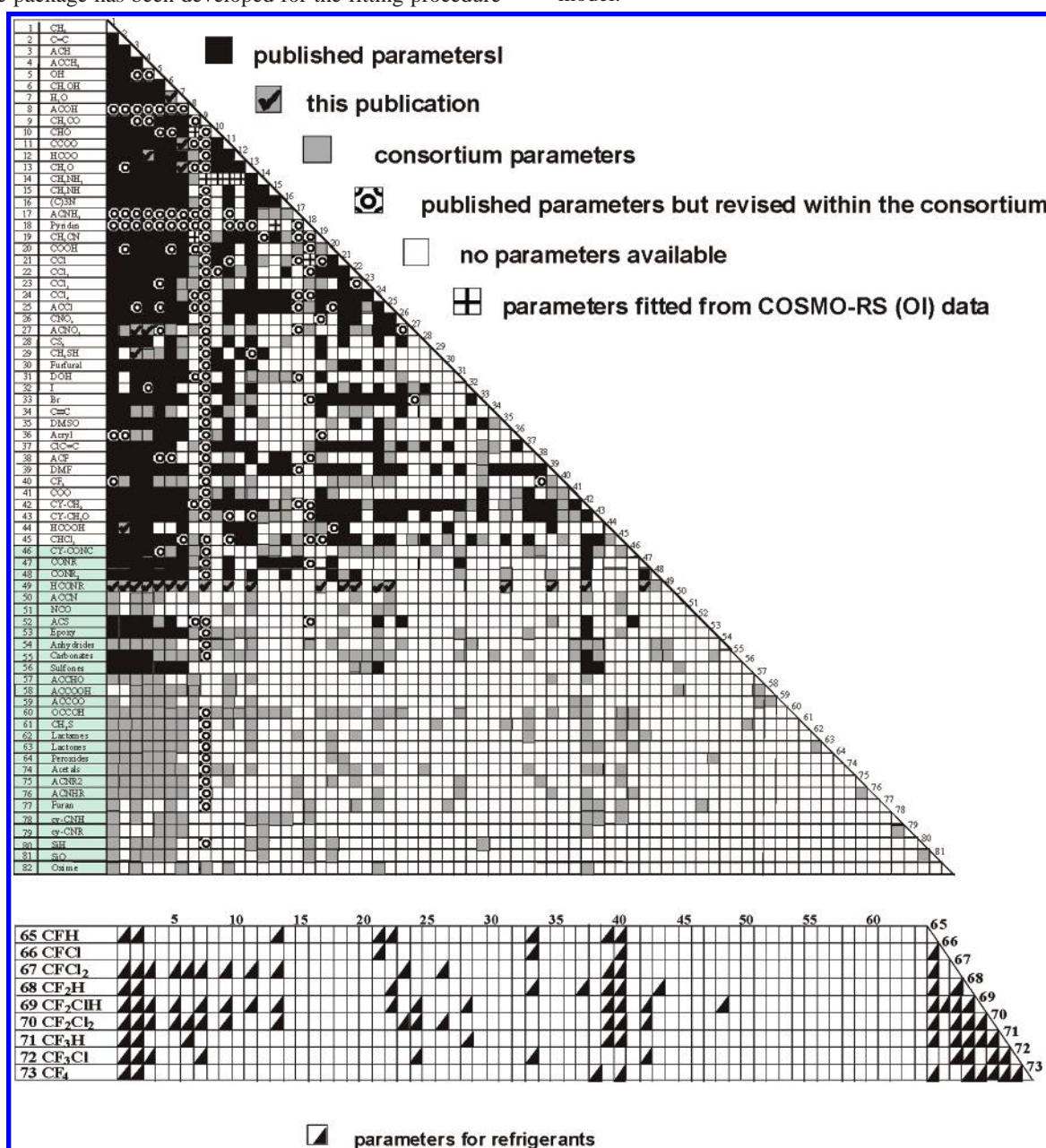


Figure 1. Modified UNIFAC (Dortmund) parameter matrix (September 2005).

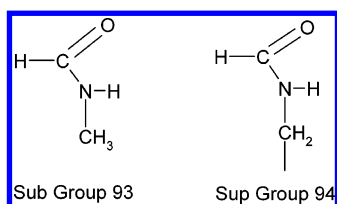
Table 2. Modified UNIFAC (Dortmund) Group Assignments and R_k and Q_k Parameters for the New Main Group 49

main group	R_k	Q_k	subgroup	sample	group assignment
49	2.4617	2.1920	93 HCONHCH ₃	<i>N</i> -methylformamide	1 HCONHCH ₃
"HCONR"	2.4617	1.8420	94 HCONHCH ₂	<i>N</i> -ethylformamide	1 CH ₃ , 1 HCONHCH ₂

Table 3. Modified UNIFAC (Dortmund) Group Interaction Parameters for Main Group 49 "HCONR"

n^a	m	a_{nm} (K)	b_{nm}	c_{nm} (K ⁻¹)	a_{mn} (K)	b_{mn}	c_{mn} (K ⁻¹)
1	49	-923.28	7.8096	-0.881×10^{-2}	183.02	-1.2259	0.583×10^{-3}
2	49	1171.32	3.9213	0.000	90.01	-0.92	0.000
3	49	-103.15	2.6565	-0.282×10^{-2}	45.43	-0.5708	0.281×10^{-3}
4	49	-182.32	3.3673	-0.463×10^{-2}	119.77	-0.6089	0.607×10^{-3}
5	49	-150.96	0.5280	0.000	868.68	-2.201	0.000
6	49	197.40	-0.9860	0.000	-195.13	1.1765	0.000
7	49	-1119.81	7.9591	-0.856×10^{-2}	-128.90	-0.4685	-0.916×10^{-3}
9	49	395.05	-0.9231	0.000	-169.40	0.5128	0.000
11	49	2973.58	-5.4555	0.000	81.64	-1.3111	0.000
13	49	3858.07	-9.2780	0.000	-224.78	-0.4106	0.000
19	49	297.65	-0.6621	0.000	-116.80	0.5475	0.000
21	49	955.83	-1.0001	0.000	-151.04	-0.4588	0.000
22	49	-1017.26	3.0909	0.000	894.51	-2.9316	0.000
24	49	516.97	0.1947	0.186×10^{-2}	-198.68	0.4351	-0.127×10^{-2}
25	49	240.70	0.8653	0.000	4118.74	-15.161	0.000
35	49	-3.4471	0.0000	0.000	-72.17	0.0000	0.000
39	49	-18.38	-0.4503	0.000	-2.2758	0.6011	0.000
42	49	-49.69	3.8663	0.000	159.18	-1.1148	0.000
47	49	-188.91	0.0000	0.000	308.23	0.0000	0.000

^a The assignment of the main group number n (m) to the functional groups can be found in ref 10.

**Figure 2.** Structure of subgroups for the main group 49 "monoalkylated formamides".

Modified UNIFAC (Dortmund) Extension

A main group for monoalkylated formamides (main group number 49) was introduced in modified UNIFAC (Dortmund), because of the special behavior of the different formamides.¹⁵ The most important formamide in the chemical industry is *N*-methylformamide. It is used as an intermediate in the synthesis of the insecticide Formothion,¹⁵ and it is also important as a selective solvent for the separation of aliphatics from aromatics.

Main group 49 was subdivided into two different subgroups, depending on the alkylation of the C atom, as shown in Figure 2.

In Table 2, the van der Waals properties R_k and Q_k for the two subgroups and group assignments for selected formamides are given.

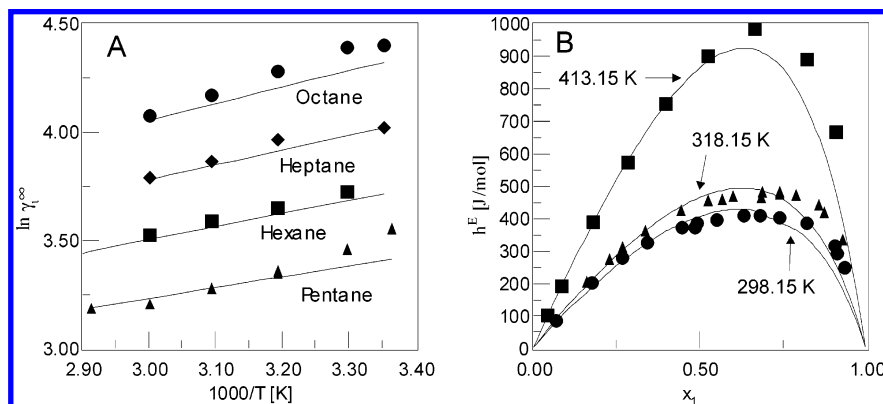
In Table 3, the fitted modified UNIFAC (Dortmund) group interaction parameters for main group 49 "HCONR" (formamides) are listed, along with those of 19 other main groups.

Typical results for the new main group are shown in Figures 3 and 4. In Figure 3, experimental activity coefficients at infinite dilution for four alkanes and excess enthalpy data for benzene at three different temperatures are shown, together with the calculated data using Modified UNIFAC (Dortmund) for binary systems that contain *N*-methylformamide.

In Figure 4, besides the experimental and predicted SLE data, experimental and predicted isobaric VLE for water/*N*-methylformamide systems at different pressures also are shown. All calculations shows satisfactory agreement with the experimental data.

Modified UNIFAC (Revision)

With the enlargement of the database, sometimes it is observed that the already existing group interaction parameters

**Figure 3.** Phase equilibria for systems that contain *N*-methylformamide: (A) activity coefficients at infinite dilution of different *n*-alkanes in *N*-methylformamide (Experimental values taken from refs 16–18; the solid line represents the calculation with Modified UNIFAC (Dortmund)) and (B) enthalpies of mixing at different temperatures for benzene (1) and *N*-methylformamide (2) (experimental values taken from refs 19 and 23; the solid line represents the calculation with Modified UNIFAC (Dortmund)).

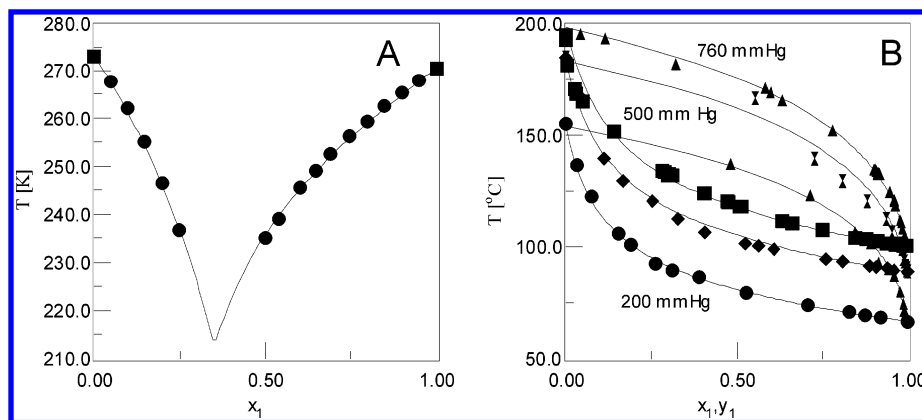


Figure 4. Phase equilibria for systems that contain *N*-methylformamide–water: (A) solid–liquid equilibrium (SLE) of *N*-methylformamide (1) with water (2) (experimental values taken from ref 20; the solid line represents the calculation with Modified UNIFAC (Dortmund)) and (B) vapor–liquid equilibria (VLE) data at different pressures for water (1) and *N*-methylformamide (2) (experimental values taken from refs 21 and 22; the solid line represents the calculation with Modified UNIFAC (Dortmund)).

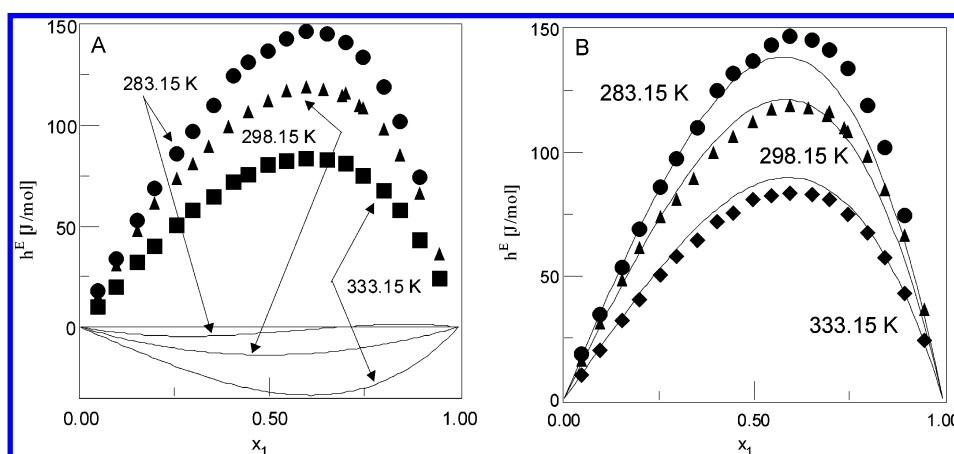


Figure 5. Experimental and predicted enthalpies of mixing for the benzene (1)/*n*-butylmercaptane (2) system: (A) with already published interaction parameters (main groups 3 and 29) and (B) with revised Modified UNIFAC (Dortmund) parameters. Experimental data taken from ref 24. Solid line represents the calculation with Modified UNIFAC (Dortmund).

Table 4. Revised Group Interaction Parameters for Modified UNIFAC (Dortmund)

n^a	m^a	a_{nm} (K)	b_{nm}	c_{nm} (K $^{-1}$)	a_{mn} (K)	b_{mn}	c_{mn} (K $^{-1}$)
3	27	936.34	−4.4141	0.000	1866.23	−9.2814	0.000
3	29	77.08	−0.3094	0.000	−2.1662	0.1196	0.000
4	12	136.98	0.0000	0.000	377.26	0.0000	0.000
4	27	391.04	0.1964	0.000	1931.39	−5.1507	0.000
7	11	−433.29	3.0862	$−0.2012 \times 10^{-2}$	311.97	−1.3412	0.1074×10^{-2}
7	13	177.66	−3.7291	0.1076×10^{-1}	433.21	−0.6053	$−0.9140 \times 10^{-3}$

^a The assignment of the main group number n (m) to the functional groups can be found in ref 10.

can be improved, because the temperature or pressure covered by the new data is out of the range where the parameters have been fitted previously. A great proportion of the parameters were fitted between 1985 and 1993. During this time, no SLE data and only a few h^E data at high temperatures were available for fitting the group interaction parameters. That is the main reason sometimes the prediction at high temperatures (>140 °C) as well as low temperatures leads to poor results. Therefore, some of the already existing group interaction parameters, e.g. for systems with aromatics, substituted aromatics and water were revised using the new available data at low and high temperature. With the revised group interaction parameters for Modified UNIFAC listed in Table 4, in most cases, improved results are obtained for the different properties. For all revised main group combinations, the relative deviations obtained with the published and revised parameters are listed in Table 5a–f. In a few cases, a larger deviation for one of the properties must be accepted.

In Figures 5–7, typical results calculated with the revised and the already published parameters are shown. Figure 5 shows a comparison of experimental and predicted enthalpies of mixing for the benzene–*N*-butylmercaptane system in the temperature range of 283.15–333.15 K, using published and the revised Modified UNIFAC (Dortmund) group interaction parameters. As can be seen, in contrast to the old parameters, now, with the revised parameters, the correct endothermal excess enthalpies for these systems are obtained.

Similar improvements with the revised group interaction parameters are obtained for vapor–liquid equilibrium and azeotropic data, as shown in Figures 6 and 7. In Figure 6, isothermal experimental VLE data for the dimethyl ether–water system in the temperature of 323.15–375.15 K are shown, together with the predicted data using the already available interaction parameters and the revised group interaction parameters.

Figure 7 shows the experimental and predicted azeotropic data at different temperatures for the methyl acetate–water

Table 5. Main Group Pairs

	data sets ^a	deviation using published parameters	deviation using revised parameters
(a) Main Group Pair 3/27 (ACH/ACNO ₂)			
$\Delta y_{\text{abs}}/\Delta y_{\text{rel}}\%$	3/3	0.0772/31.81	0.0627/26.99
$\Delta T_{\text{abs}}/\Delta T_{\text{rel}}\%$	3/3	11.20/2.69	8.16/1.97
$\Delta P_{\text{abs}}/\Delta P_{\text{rel}}\%$	3/3	4.52/3.91	3.22/3.50
h_{rel}^E	8	24.85	15.16
$\gamma_{\text{rel}}^\infty$	27	39.35	25.70
(b) Main Group Pair 3/29 (ACH/CH ₃ SH)			
$\Delta y_{\text{abs}}/\Delta y_{\text{rel}}\%$	4/3	0.0084/2.46	0.0082/2.46
$\Delta P_{\text{abs}}/\Delta P_{\text{rel}}\%$	4/3	9.80/1.39	10.81/1.50
h_{rel}^E	3	83.12	3.63
$\gamma_{\text{rel}}^\infty$	1	0.07	1.80
(c) Main Group Pair 4/12 (ACCH ₂ /HCOO)			
$\Delta y_{\text{abs}}/\Delta y_{\text{rel}}\%$	3/1	0.0053/2.05	0.0049/1.86
$\Delta T_{\text{abs}}/\Delta T_{\text{rel}}\%$	3/1	0.18/0.05	0.16/0.04
$\Delta P_{\text{abs}}/\Delta P_{\text{rel}}\%$	3/1	2.63/0.89	2.32/0.73
h_{rel}^E	2	49.06	10.89
$\gamma_{\text{rel}}^\infty$	1	5.09	5.40
(d) Main Group Pair 4/27 (ACCH ₂ /ACNO ₂)			
$\Delta y_{\text{abs}}/\Delta y_{\text{rel}}\%$	1/1	0.0018/2.33	0.0079/6.20
$\Delta P_{\text{abs}}/\Delta P_{\text{rel}}\%$	1/1	2.29/1.02	12.05/5.76
h_{rel}^E	11	12.69	7.79
$\gamma_{\text{rel}}^\infty$	30	185.02	29.72
(e) Main Group Pair 7/11 (H ₂ O/CCOO)			
$\Delta y_{\text{abs}}/\Delta y_{\text{rel}}\%$	55/51	0.0538/25.27	0.0572/24.82
$\Delta T_{\text{abs}}/\Delta T_{\text{rel}}\%$	55/51	3.35/0.89	3.65/0.97
$\Delta P_{\text{abs}}/\Delta P_{\text{rel}}\%$	55/51	21.88/4.19	17.25/4.13
h_{rel}^E	36	8.12	10.62
$\gamma_{\text{rel}}^\infty$	5	21.19	18.65
(f) Main Group Pair 7/13 (H ₂ O/CH ₂ O)			
$\Delta y_{\text{abs}}/\Delta y_{\text{rel}}\%$	17/17	0.1562/67.08	0.0701/30.07
$\Delta T_{\text{abs}}/\Delta T_{\text{rel}}\%$	17/17	8.32/2.47	4.88/1.38
$\Delta P_{\text{abs}}/\Delta P_{\text{rel}}\%$	17/17	117.48/26.77	77.19/33.75
h_{rel}^E	25	66.81	37.35
$\gamma_{\text{rel}}^\infty$	38	41.86	108.85

*All data from DDB.⁹ The second number indicates the amount of inconsistent data.

system, using published parameters (dotted line) and revised group interaction parameters (solid line) for the main groups 7 and 11.

Hydrocarbon Solubilities. The solubility of organic compounds in water is of interest in several areas. For example, in environmental technology, water solubilities and octanol–water partition coefficients K_{ow} are of great importance. Original and modified UNIFAC have been developed to be able to predict VLE. The difficulties in the proper description of alkane solubilities in water and the VLE behavior of alcohol–water systems become clear, when one examines the activity coefficients for water–alkane and water–alcohol systems. Although, for the description of the hydrocarbon solubility in water, an activity coefficient of $\sim 10\,000$ to several hundred thousand is required, the replacement of one hydrogen by an alcohol group reduces the activity coefficient to values of ~ 100 .

To obtain a reliable description of alkane–water solubilities, the alkane–water parameters should be fitted solely to the LLE data of alkane–water systems. However, at the same time, these group interaction parameters are required, in addition to the alkane–alcohol and water–alcohol group interaction parameters to predict the azeotropic behavior and the miscibility gaps of alcohol–water systems. To be able to predict the correct VLE behavior and the occurrence of a miscibility gap of alcohol–water systems, the group interaction parameters between alkanes and water have been fitted simultaneously to alcohol/water and alcohol/alkane data. From this observation, it follows that larger

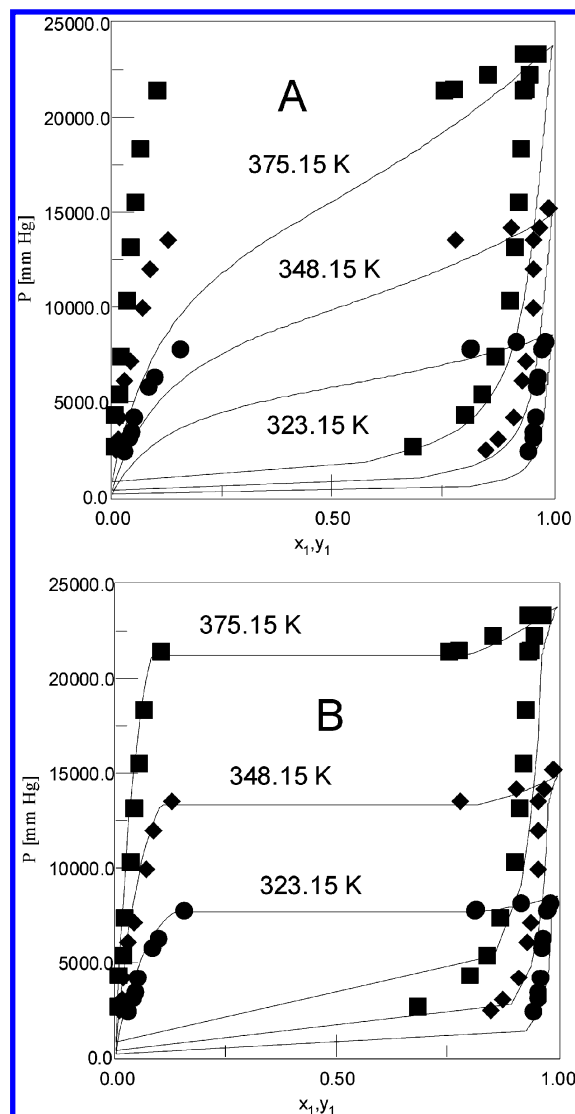


Figure 6. Experimental and predicted VLE data for the dimethyl ether (1)–water (2) system: (A) published Modified UNIFAC (Dortmund) group interaction parameters and (B) revised Modified UNIFAC (Dortmund) group interaction parameters (main group 7 and 13). Experimental data taken from ref 25. Solid line represents the calculation with Modified UNIFAC (Dortmund).

deviations for the solubilities of alkanes or naphthenes in water were accepted.

This means that the solubilities (activity coefficients) of alkanes or naphthenes in water, which are calculated using modified UNIFAC (Dortmund) parameters, are larger (smaller) than the experimental values.

Because of the large miscibility gap, the solubilities of the hydrocarbons in water at 298.15 K can be calculated by Modified UNIFAC, using the following equation derived from the iso-activity criterion:

$$\log c_i^{\text{w,s}} = \log \left(\frac{55.56}{\gamma_{\text{org} \rightarrow \text{aq}}^\infty} \right) \quad (14)$$

The experimental and predicted solubilities calculated with eq 14 are shown in Figure 8. The figure shows that, as mentioned previously, the experimental values are much lower than those predicted by modified UNIFAC.

The reason is that the predicted activity coefficients at infinite dilution, γ^∞ (e.g., at 298.15 K using modified UNIFAC), are too small to describe the low solubilities. For the *n*-hexane–

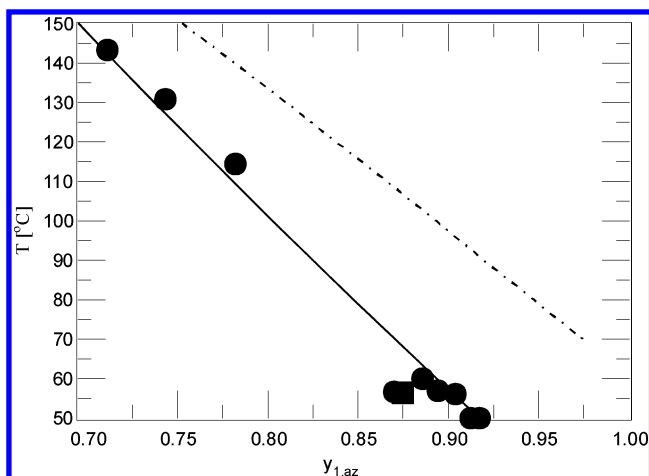


Figure 7. Experimental^{26–32} and predicted azeotropic data for the methyl acetate (1)–water (2) system: (– · – · –) published parameters and (–) revised parameters.

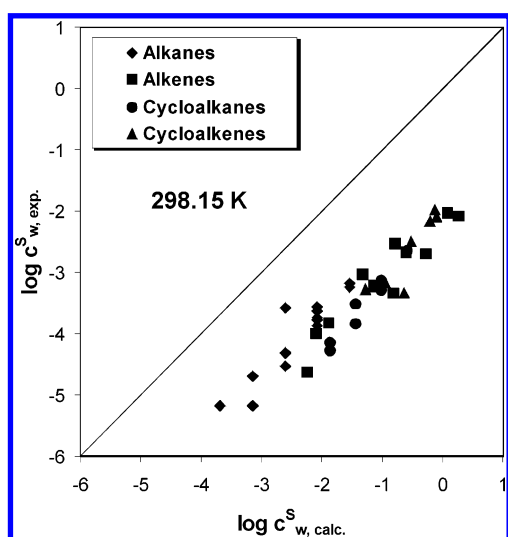


Figure 8. Comparison between experimental and calculated water solubilities of different hydrocarbons at 298.15 K calculated using eq 14.

water system, this is shown in Figure 9. The activity coefficient at infinite dilution for hexane in water at 298.15 K, calculated with published parameters of Modified UNIFAC (Dortmund) (denoted as the solid line), is ~6600. With interaction parameters fitted only to the hexane–water systems (dotted line), the activity coefficient is greater by a factor of 24. It can be observed that much a higher activity coefficient at infinite dilution is required to describe the solubility of *n*-hexane in water.

Banerjee³³ suggested an empirical relation to improve the calculated solubilities of alkanes, alkenes, and cycloalkanes in water. Through a simple regression analysis, we derived the following relation to obtain reliable solubilities of alkanes or naphthenes in water in the temperature range of 273.15–373.15 K. For the regression, 40 different compounds with 5–10 C atoms and more than 150 experimental hydrocarbon solubilities in water were used to fit the parameters of eq 15.

$$\log c_i^{w,s} = 1.104 \log \left(\frac{55.56}{\gamma_{\text{org} \rightarrow \text{aq}, 298.15 \text{ K}}^{\infty}} \right) + 0.0042T - 2.817 \quad (15)$$

For the calculation of the hydrocarbon solubilities using eq 15, only the activity coefficient at infinite dilution of the hydrocarbon in water at 298.15 K is required.

The calculated water solubilities of cyclohexane, *n*-hexane, *n*-octane, and *n*-dodecane in water obtained with this equation

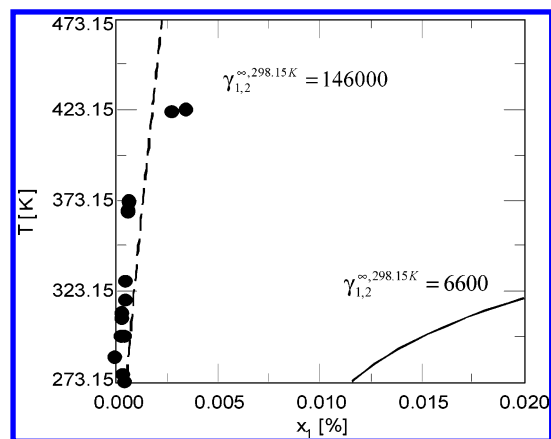


Figure 9. Comparison of calculated activity coefficient at infinite dilution and the needed value for the description of liquid–liquid equilibrium (LLE) data for the hexane (1)/water (2) system:³⁴ (–) calculated with Modified UNIFAC (Dortmund) and (– · –) calculated with parameters refitted only to LLE data.

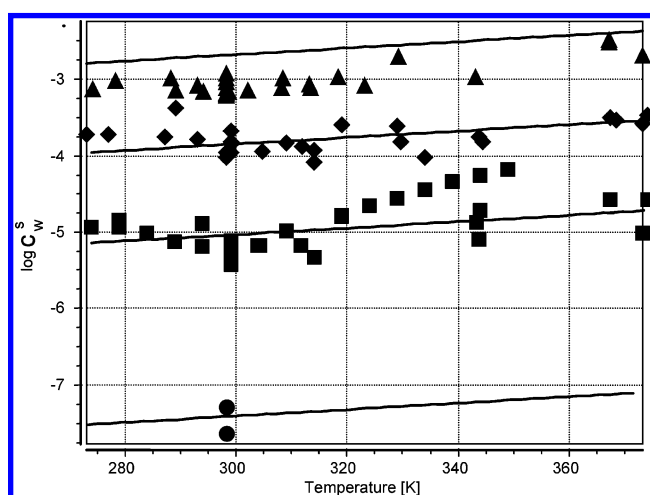


Figure 10. Experimental and calculated solubilities using eq 15 of (▲) cyclohexane, (◆) hexane, (■) octane, and (●) dodecane in water in the temperature range of 273.15–375.15 K.

Table 6. Average Absolute Deviations of $\log c_i^{w,s}$ for Different Alkanes Derived from eqs 14 and 15, Calculated with Modified UNIFAC (Dortmund)

	data points	$\Delta \log c_i^{w,s}$	
		eq 14	eq 15
cyclohexane	32	1.96	0.34
<i>n</i> -hexane	27	1.69	0.12
<i>n</i> -octane	32	1.76	0.23
<i>n</i> -dodecane	2	2.17	0.17

are shown in Figure 10 together with the experimental data. In Table 6, the average absolute deviations of $\log c_i^{w,s}$ are given.

Filling Gaps Using COSMO-RS (OI). Despite the reliability and simple applicability of group contribution methods, there are some well-known disadvantages. The fragmentation of the molecules cause that group contribution models cannot distinguish among isomers, and proximity effects also are disregarded. For multifunctional components (e.g., pharmaceuticals), the results of UNIFAC and Modified UNIFAC (Dortmund) are sometimes poor, because the interaction parameters are basically fitted to simple representatives of the main groups. However, the main drawback is that at least a minimum of experimental data is required for fitting the group interaction parameters. For reactive systems such as isocyanates with alcohols, experimental phase equilibrium cannot be measured but quantum chemical

Table 7. Modified UNIFAC (Dortmund) Interaction Parameters Fitted to “Artificial” Data Calculated with COSMO-RS (OI)

n^a	m^a	a_{nm} (K)	b_{nm}	c_{nm} (K ⁻¹)	a_{mn} (K)	b_{mn}	c_{mn} (K ⁻¹)
8	10	42.69	0.0000	0.000	-375.24	0.0000	0.000
8	19	71.73	0.1207	0.000	-290.90	0.5037	0.000
9	14	-176.67	1.0645	0.000	589.37	-2.145	0.000
10	14	174.34	0.0000	0.000	97.69	0.0000	0.000
11	14	471.44	0.0000	0.000	-218.87	0.0000	0.000
12	14	166.74	0.0000	0.000	71.88	0.0000	0.000
15	18	-1147.4	0.0000	0.000	-326.24	0.0000	0.000
18	21	-192.74	-0.2474	-0.2000×10^{-3}	-5849.00	10.940	0.4000×10^{-2}

^a The assignment of the main group number n (m) to the functional groups can be found in ref 10.

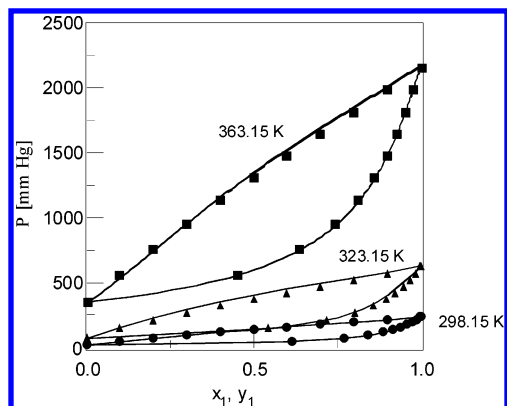


Figure 11. “Artificial” and calculated VLE Data for the *N,N*-diethylamine (1)–pyridine (2) system predicted by COSMO-RS (OI). Data points (●, ■, ▲) represent data calculated with COSMO-RS (OI), whereas the solid line represents the Modified UNIFAC (Dortmund) results.

methods, e.g., the Conductor-like Screening Model for Real Solvents (COSMO-RS) developed 1995 by Klamt,^{35–37} allows the result of quantum chemical calculations for a single molecule to be used to calculate the chemical potential (activity coefficients) of any species in a mixture. This means “artificial data” obtained from quantum chemical methods can theoretically be used to fill gaps in the Modified UNIFAC matrix.

For the prediction of the required activity coefficients (phase equilibrium data), a program package based on the various publications of the COSMO-RS model was developed,³⁸ which is directly linked with the calculation programs of the Dortmund Data Bank. This program package includes the COSMO-RS (OI) model and allows the prediction of “artificial” phase equilibrium data for selected binary systems. These “artificial data” can then be used as pseudoexperimental data to fill gaps in the Modified UNIFAC (Dortmund) matrix.

Although it was developed for reactive systems, such as isocyanates with alcohols, etc., it was first tested for normal systems to compare the results that are obtained with subsequent measured experimental data. In Table 7, interaction parameters for eight group combinations are given, for which no experimental data were stored in the DDB. The parameters were fitted to “artificial vapor–liquid equilibrium data” that was predicted using COSMO-RS (OI).

Figure 11 shows the “artificial data” for the *N,N*-diethylamine–pyridine system predicted with COSMO-RS (OI), together with the results of the fitted group interaction parameters between the main groups 15 and 18 at three different temperatures.

In Figure 12, a comparison between the artificial data, the calculated data using modified UNIFAC (Dortmund) (represented by the solid line), and experimental data measured afterward is shown for the same *N,N*-diethylamine–pyridine system. Not surprisingly, the artificial and calculated values are in good agreement. However, in this case, also no great deviations are observed between the experimental and artificial data using COSMO-RS (OI) method.

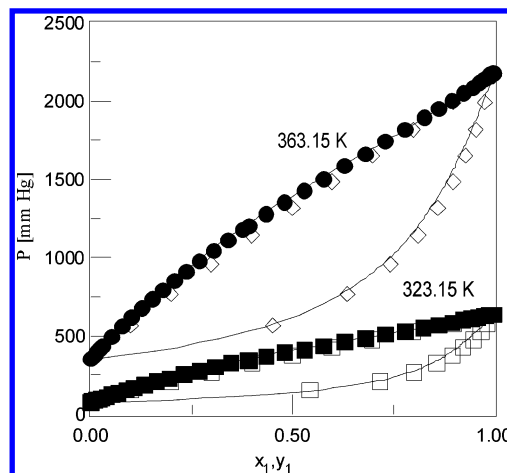


Figure 12. Artificial VLE data (denoted by open symbols (◇, □)), experimental VLE data²³ (denoted by solid symbols (●, ■)), and calculated VLE data (represented by the solid line) for the *N,N*-diethylamine (1)–pyridine (2) system at 323.15 and 363.15 K.

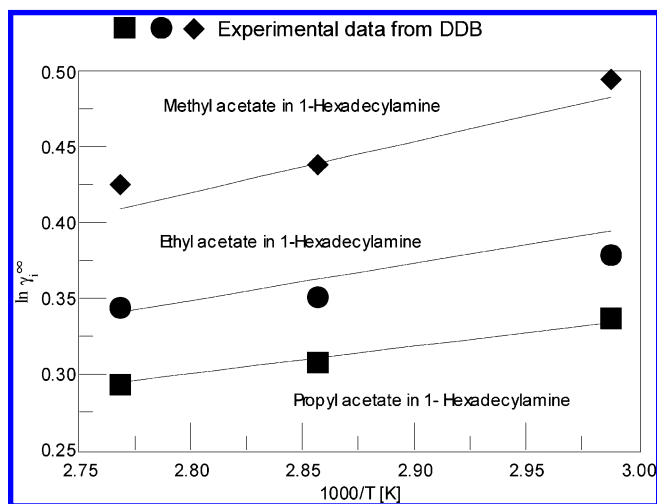


Figure 13. Activity coefficients at infinite dilution for different esters in 1-hexadecylamine.³⁹

In Figure 13, the calculated and experimental activity coefficients at infinite dilution for different esters in 1-hexadecylamine (Modified UNIFAC (Dortmund) main groups 11 and 14) are shown. The parameters for this calculation were also derived from “artificial” VLE data using COSMO-RS (OI). However, in this case, experimental activity coefficients at infinite dilution were also available from the DDB. Again, it can be seen that the COSMO-RS (OI) method can provide reasonable results and encourage using the model to fill gaps at least when measurements are impossible.

However, of course, there is the disadvantage of this procedure, in that sometimes the quality of the artificial data derived using the quantum chemical approach is poor, which, of course, would directly influence the accuracy of the results

of modified UNIFAC. An idea about the quality of the results of the quantum chemical approach can be gained from the paper of Grensemann and Gmehling.¹⁴

Outlook

The research work on the revision and extension of the Modified UNIFAC (Dortmund) and the measurements of the required experimental data will be continued with the support of the members of the UNIFAC Consortium. The main focus of the consortium is to examine and revise the existing group interaction parameters, to fill gaps in the matrixes of UNIFAC and the Modified UNIFAC (Dortmund), as well as PSRK, and to extend the range of applicability by adding new main groups.

Furthermore, the combination of modified UNIFAC (Dortmund) with a generalized volume-translated cubic equation of state is planned. This combination allows the extension of the group contribution concept to systems with supercritical compounds. The combination of the volume-translated Peng–Robinson equation of state VTPR with modified UNIFAC leads to a universal group contribution equation of state, which is able to predict phase equilibrium data and excess enthalpies over a wide temperature and pressure range also for asymmetric systems.

At the same time, VTPR provides good results for other properties (liquid densities, heats of vaporization, heat capacities, etc). Furthermore, the effects of strong electrolytes on phase equilibrium behavior (VLE, gas solubilities) can directly be taken into account⁴⁰ using the electrolyte model (LIFAC).⁴¹

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Notation

a_{nm} = interaction parameter of mod. UNIFAC
 b_{nm} = interaction parameter of mod. UNIFAC
 c_{nm} = interaction parameter of mod. UNIFAC
 $c_i^{w,s}$ = solubility of hydrocarbon i in water [mol/m³] (s: saturation)
 C = combinatorial part of the activity coefficient
 F_i = surface area fraction of compound i in the mixture
 q_i = relative van der Waals surface area of compound i
 Q_k = relative van der Waals surface area of subgroup k
 r_i = relative van der Waals volume of compound i
 R = residual part of the activity coefficient
 T = absolute temperature [K]
 V_i = volume/mole fraction of compound i in the mixture
 V'_i = modified volume/mole fraction of compound i in the mixture
 X_m = mole fraction of subgroup m
 x_j = mole fraction of component j
 w_i = weighting factor
 \ln = natural logarithm (base e)
 \log = logarithm (base 10)

Greek Letters

γ_i = activity coefficient of compound i
 γ_i^∞ = activity coefficient of compound i at infinite dilution
 Γ_k = group activity coefficient of subgroup k

Θ_k = surface area fraction of subgroup k

$\Psi_{n,m}$ = temperature term of the UNIFAC/Mod. UNIFAC equation

$\nu_k^{(i)}$ = number of subgroups k in component i

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