# Prediction of Phase Equilibria and Excess Properties for Systems with Sulfones

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*The group contribution method modified UNIFAC (Dortmund) has become very popular because of its broad applications, and reliable predictions for vapor-liquid equilibria, solid-liquid equilibria, liquid-liquid equilibria, activity coefficients at infinite dilution, azeotropic data and excess enthalpies in a wide temperature range. Therefore, the existing parameter matrix for the modified UNIFAC method is continuously extended with the help of the Dortmund Data Bank and by carrying out systematic measurements. The new main group for sulfones, such as that required to describe systems with the selective solvent sulfolane, is introduced, as well as ten new pairs of group interaction parameters for modified UNIFAC.*

## Introduction

For the synthesis, design, and optimization of separation processes, the knowledge of phase equilibrium behavior is necessary. Since experimental data are often not available, the group contribution method can be used for the prediction of the required phase equilibria and excess properties. Recent decades have seen increasing popularity for the group contribution method modified UNIFAC (Dortmund) (Weidlich and Gmehling, 1987; Gmehling et al., 1993, 1998, 2002; Lohmann et al., 2001; Lohmann and Gmehling, 2001; Wittig et al., 2001). As a result, this method has been integrated into most commercial process simulators. The success of the modified UNIFAC (Dortmund) method is mainly caused by the large range of applicability and the reliability of the predicted results.

Besides the prediction of phase equilibria and excess properties, the models can also be used for many other applications of industrial interest, such as for the synthesis and design of thermal separation processes (construction of residue curves, location of separation problems, selection of selective solvents, and so on).

Because of the temperature-dependent group interaction parameters used in modified UNIFAC (Dortmund), the reliable prediction of different thermodynamic mixture properties in a wide temperature range is possible.

The group interaction parameter of modified UNIFAC (Dortmund) are fitted simultaneously to all available, reliable mixture data (vapor-liquid equilibria ($VLE$), activity coefficients at infinite dilution ($\gamma^{\infty}$), excess enthalpies ($h^E$), excess heat capacities ($c_p^E$), liquid-liquid equilibria ($LLE$), solid-liquid equilibria of eutectic systems ($SLE$), and azeotropic data ($AZD$)). For this, $h^E$ and $SLE$ data are used as supporting data at high (up to 413 K) and low ($<273$ K) temperatures, respectively, to ensure the reliability of the temperature-dependence of the activity coefficients (Lohmann and Gmehling, 1999). The required experimental data are mainly taken from the Dortmund Data Bank (DDB). Additionally, a large number of systematic measurements is carried out in our laboratory to extend the necessary database, in particular to get the required supporting data (Gmehling, 1993; Gmehling and Krentscher, 1995; Jakob et al., 1995; Ahlers et al., 1999; Wittig et al., 2001).

Since calculations for systems containing sulfones, such as the industrial important compound sulfolane, were previously not possible, a new main group "sulfones" has been introduced into Modified UNIFAC (Dortmund). This article provides new group interaction parameters for this main group. For example, sulfones are important selective solvents for the separation of aromatics from aliphatics with the help of liquid-liquid extraction or extractive destillation.

## Modified UNIFAC (Dortmund) Model

In the modified UNIFAC (Dortmund) model the activity coefficient is built from a combinatorial and a residual part

$$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R \tag{1}$$

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The combinatorial part considers the form and the size of the molecules. To deal with compounds of very different sizes, an empirical 3/4 term has been introduced into the combinatorial part

$$\ln\gamma_i^C = 1 - V_i' + \ln V_i' - 5q_i\left(1 - \frac{V_i}{F_i} + \ln\frac{V_i}{F_i}\right) \tag{2}$$

Parameters $V_i'$, $V_i$, and $F_i$ are given as

$$V_i' = \frac{r_i^{3/4}}{\sum_j r_j^{3/4} x_j} \tag{3}$$

$$V_i = \frac{r_i}{\sum_j r_j x_j} \tag{4}$$

$$F_i = \frac{q_i}{\sum_j q_j x_j} \tag{5}$$

For the calculation of these parameters, the relative van der Waals values $r_i$ and $q_i$ of the compounds are required. They can be calculated from the relative van der Waals values $R_k$ and $Q_k$ of the subgroups k. These values have not been derived from molecular parameters as in the original UNIFAC method, but fitted together with the basic group interaction parameters to experimental data

$$r_i = \sum_k \nu_k^{(i)} R_k \tag{6}$$

$$q_i = \sum_k \nu_k^{(i)} Q_k, \tag{7}$$

The residual part takes into account the interaction between the molecules and is computed from the different group activity coeffiecients in the mixture, respectively, in the pure substance

$$\ln\gamma_i^R = \sum_k \nu_k^{(i)}\left(\ln\Gamma_k - \ln\Gamma_k^{(i)}\right) \tag{8}$$

The concentration-dependence of the residual part is defined as follows

$$\ln\Gamma_k = Q_k\left[1 - \ln\left(\sum_m \Theta_m\Psi_{mk}\right) - \sum_m \frac{\Theta_m\Psi_{km}}{\sum_n \Theta_n\Psi_{nm}}\right] \tag{9}$$

whereby the group surface area fraction $\Theta_m$ and the group mole fraction $X_m$ are given by the following equations

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \tag{10}$$

$$X_m = \frac{\sum_j \nu_m^{(j)} x_j}{\sum_j \sum_n \nu_n^{(j)} x_j} \tag{11}$$

The parameter $\Psi_{nm}$ contains the temperature-dependent group interaction parameters, which permit a reliable description of the activity coefficient as a function of temperature

$$\Psi_{nm} = \exp\left(-\frac{\left(a_{nm} + b_{nm}T + c_{nm}T^2\right)}{T}\right) \tag{12}$$

## Database Used to Fit Modified UNIFAC (Dortmund) Parameters

Up to seven different types of thermodynamic mixture data (*VLE*, $\gamma^\infty$, $h^E$, $c_p^E$, *LLE*, *SLE* and *AZD*) are used to simultaneously fit the required group interaction parameters. For this, the most actual version of the Dortmund Data Bank (DDB) is used; this means all worldwide published phase equilibrium information and excess properties are taken into account (such as *VLE*: 22,900 data sets, $\gamma^\infty$: 40,800 data points, $h^E$: 16,400 data sets, and so on). Additionally, this databank contains high-pressure vapor-liquid equilibria, gas solubilities, phase equilibrium data for electrolyte systems, excess volumes, adsorption equilibria, and so on. Only a part of these data (approximately 15–20%) have been published in different volumes of the DECHEMA Chemistry Data Series (Gmehling et al., 1977–2001, 1984–1991, 1986–1994; Sørensen et al., 1979–1987) or elsewhere (Gmehling et al., 1994). At the same time, a large number of systematic measurements in particular supporting data have been measured to complete the database.

## Fitting Procedure

Prior to beginning with the fitting procedure, the main group "sulfones" had to be defined. Wu and Sandler (1991) have developed a simple theoretical basis for defining functional groups on the basis of quantum mechanical *ab initio* molecular orbital calculations on single molecules. One of their proposed principles says that each atom in a functional group should have approximately the same charge in all molecules in which the group occurs. Figure 1 shows the molecules cyclohexane and sulfolane, the most important compound for the main group "sulfones". For both molecules, the charge of each atom is calculated with a

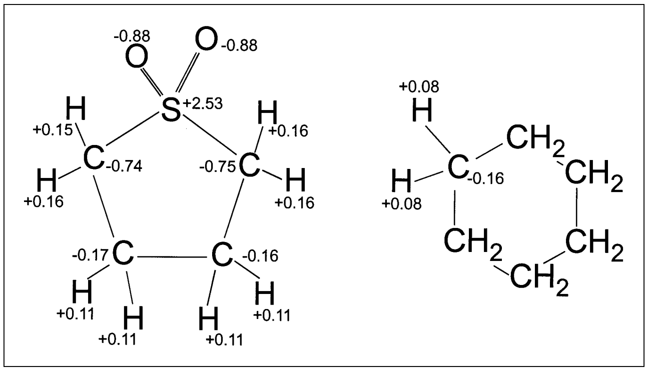

**Figure 1. Charges of the atoms in the molecules sulfolane and cyclohexane.**

**Table 1. Modified UNIFAC (Dortmund) $R_k$ and $Q_k$ -Parameters and Group Assignment for the Main Group 56 "Sulfones"**

| Main Group | Subgroup | No. | $R_k$ | $Q_k$ | Sample | Group Assignment |
|---|---|---|---|---|---|---|
| 56 Sulfones | $CH_2SuCH_2$ | 110 | 2.6870 | 2.1200 | Sulfolane | 1 $CH_2SuCH_2$, 2 cy-$CH_2$ |
| | $CH_2SuCH$ | 111 | 2.4600 | 1.8080 | 2,4-Dimethylsulfolane | 1 $CH_2SuCH$, 2 $CH_3$, 1 cy-$CH_2$, 1 cy-CH |

**Table 2. New Modified UNIFAC (Dortmund) Interaction Parameters**

| $n$ | $m$ | $a_{nm}$/K | $b_{nm}$ | $c_{nm}/K^{-1}$ | $a_{mn}$/K | $b_{mn}$ | $c_{mn}/K^{-1}$ |
|---|---|---|---|---|---|---|---|
| 1 | 56 | 1,058.31 | −1.1856 | 0.0000 | 438.76 | −1.2256 | 0.0000 |
| 2 | 56 | 775.56 | 0.0000 | 0.0000 | −65.66 | 0.0000 | 0.0000 |
| 3 | 56 | −522.32 | 3.8856 | $-0.4212\times10^{-2}$ | 562.72 | −2.4316 | $0.2420\times10^{-2}$ |
| 4 | 56 | −307.42 | 4.1819 | $-0.7723\times10^{-2}$ | 1,661.26 | −8.6970 | $0.1424\times10^{-1}$ |
| 5 | 56 | 34.94 | 1.0075 | $-0.2547\times10^{-2}$ | 942.22 | −2.3183 | $0.1188\times10^{-2}$ |
| 6 | 56 | 166.42 | 0.9940 | $-0.3346\times10^{-2}$ | 1,683.48 | −8.0031 | $0.1159\times10^{-1}$ |
| 7 | 56 | −302.93 | 0.5975 | 0.0000 | 652.86 | −1.8013 | 0.0000 |
| 24 | 56 | 120.59 | 1.2816 | 0.0000 | 261.15 | −0.8815 | 0.0000 |
| 42 | 56 | −581.16 | 4.1194 | 0.0000 | 660.47 | −2.0132 | 0.0000 |
| 43 | 56 | 19.22 | 0.4413 | 0.0000 | 117.21 | −0.3946 | 0.0000 |

semi-empirical method (AM1). It can be seen that the charge of both carbon atoms related to the sulfur atom differ from the other carbon atoms in sulfolane. Furthermore, the charge of the carbon atoms in cyclohexane is in good agreement with the carbon atoms not in close vicinity to the sulfur atom in sulfolane. Considering the above mentioned principle, it is reasonable to include the neighboring methylene groups into the new sulfones subgroup ($CH_2$-$SO_2$-$CH_2$).

The different binary mixture data sets (*VLE*, $\gamma^\infty$, $h^E$, $c_p^E$, *LLE*, *SLE* and *AZD*) are then searched from the mixture databank. The *VLE* data are checked for thermodynamic consistency using the Van Ness point test (Van Ness et al., 1973) and Redlich-Kister area test (Redlich and Kister, 1948), while the other mixture data have to be evaluated using plausibility tests. Finally, the different mixture data are reduced with the help of programs in order to ensure a good distribution of the systems regarding compounds and temperature. The data files generated are then used to fit the group interaction parameters and $R_k$- and $Q_k$-values.

For fitting the remaining reliable data, the following objective function $F$ is used

$$F(a_{nm},a_{mn},b_{nm},b_{mn},c_{nm},c_{mn},R_k,Q_k) \overset{!}{=} \text{Minimum} \quad (13)$$

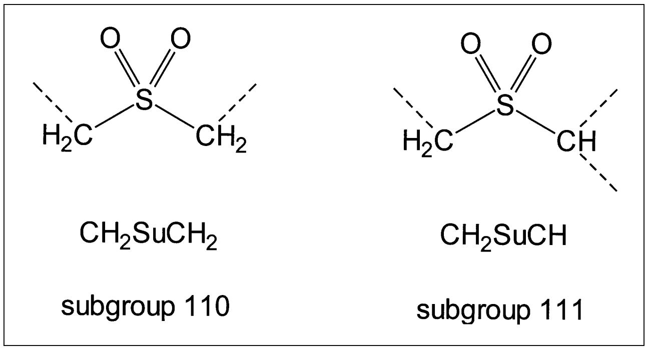

**Figure 2. Structure of the subgroups $CH_2SuCH_2$ (110) and $CH_2SuCH$ (111).**

The van der Waals values $R_k$ and $Q_k$ are fitted only, when the basic parameters for a new main group are fitted (such as, cyclic alkanes - sulfones).

In the objective function $F$ the deviations between experimental and calculated data of the different phase equilibria and excess properties are summed up.

$$F = \sum \Delta VLE + \sum \Delta\gamma^\infty + \sum \Delta h^E + \sum \Delta c_p^E + \sum \Delta LLE + \sum \Delta SLE + \sum \Delta AZD \quad (14)$$

For *VLE* data, it is necessary to distinguish between the different data types

$$[x,y,P,T] \;\; \Delta VLE = \frac{1}{n_w \cdot n_k} \sum_{k=1}^{n_w} \sum_{i=1}^{n_k} \left( w_{VLE} \frac{\gamma_{ik} - \gamma_{ik,\text{calc}}}{\gamma_{ik}} \right)^2 \quad (15)$$

$$[x,P,T] \;\; \Delta VLE = \frac{1}{n_w} \sum_{k=1}^{n_w} \left( w_{VLE} \frac{P_k - P_{k,\text{calc}}}{P_k} \right)^2 \quad (16)$$

$$[x,y,T] \;\; \Delta VLE = \frac{1}{n_w \cdot n_k} \sum_{k=1}^{n_w} \sum_{i=1}^{n_k} \left( w_{VLE} \frac{K_{ik} - K_{ik,\text{calc}}}{K_{ik}} \right)^2 \quad (17)$$

whereby the following equations are used to calculate vapor-liquid equilibria

$$P_{\text{calc}} = \sum x_i \gamma_i \frac{f_i^0}{\varphi_i^V} \quad (18)$$

$$K_{i,\text{calc}} = \frac{y_i}{x_i} = \frac{\gamma_i f_i^0}{\varphi_i^V P_{\text{calc}}} \quad (19)$$

The real phase behavior of the vapor phase was taken into account by using the Soave-Redlich-Kwong equation of state ($k_{12} = 0.0$).

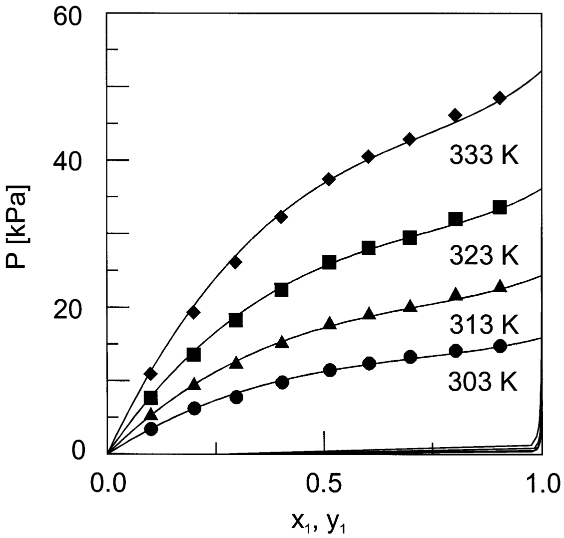

**Figure 3. Experimental and calculated $P$-$x$ data for the system Benzene (1)+Sulfolane (2).**

(●) At 303.15 K, (▲) at 313.15 K, (■) at 323.15 K, (◆) at 333.15 K (Karvo, 1980); (——) modified UNIFAC (Dortmund).

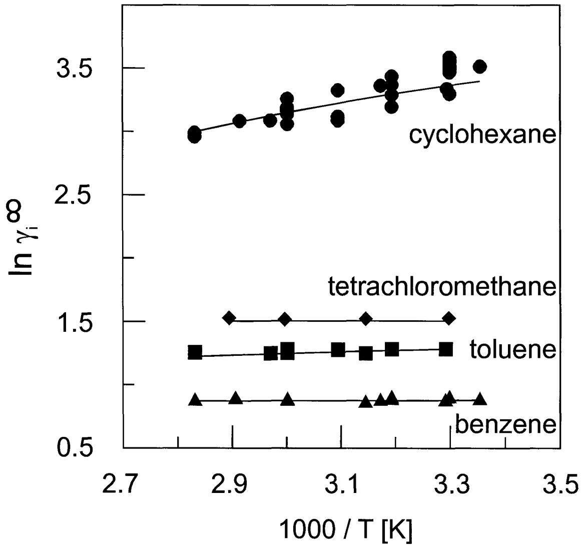

**Figure 5. Activity coefficients at infinite dilution.**

Cyclohexane (●), tetrachloromethane (◆), toluene (■) and benzene (▲) in sulfolane (Abramovic et al., 1974; Deal and Derr, 1964; Elsner, 1985; Gaile et al., 1974; Hongqin, 1995; Moellmann and Gmehling, 1997; Rawat et al., 1976; Van Aken and Broersen, 1977; Marusina et al., 1994; Wufeng et al., 1984; Bai et al., 1990; Hradetzky et al., 1978; Letcher and Moollan, 1995; Popescu et al., 1967; Sarius et al., 1978); (——) modified UNIFAC (Dortmund).

For fitting the parameters, the Simplex-Nelder-Mead method (Nelder and Mead, 1965) is first used to obtain good initial values for the Marquardt method (Marquardt, 1963). Both methods are integrated in a special program. By varying the weighting factors $w$ in the objective function for the different thermodynamic properties, the results can be influenced in the desired direction. The fitting procedure was always started with temperature-independent group interaction parameters $(a_{nm}/a_{mn})$. If enough temperature-dependent mixture data such as $h^E$, $VLE(T)$, $\gamma^\infty(T)$ were available, linear temperature-dependent parameters $(a_{nm}/a_{mn}, b_{nm}/b_{mn})$ were fitted. In case of a strong temperature-dependence ($h^E(T)$, besides $VLE(T)$, $\gamma^\infty(T)$) quadratic temperature-dependent parameters $(a_{nm}/a_{mn}, b_{nm}/b_{mn}, c_{nm}/c_{mn})$ were used. The fitting results are tested graphically and numerically (deviation from the experimental data). If the results are satisfactory, the group interaction parameters are entered in the

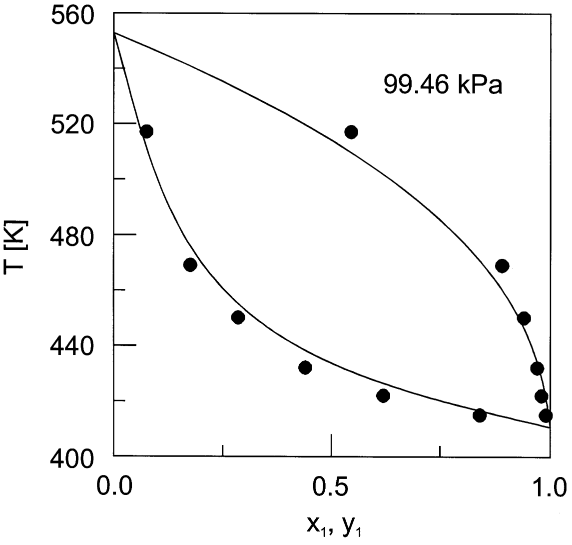

**Figure 4. Experimental and calculated $T$-$x$ data for the system $p$-Xylene (1)+2,4-Dimethylsulfolane (2).**

(●) At 99.46 kPa (Chu et al., 1954); (——) modified UNIFAC (Dortmund).

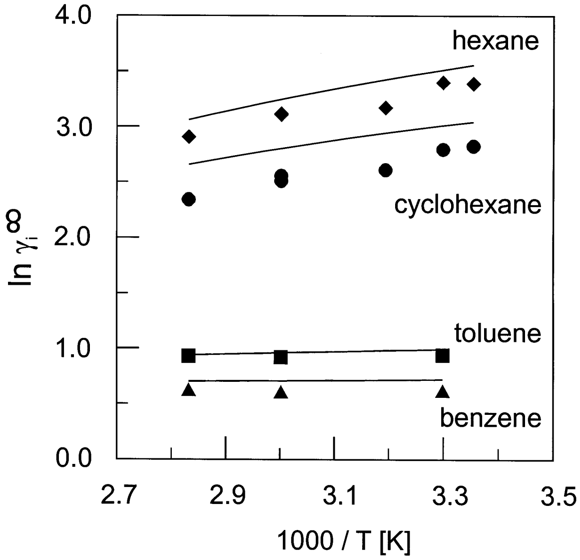

**Figure 6. Activity coefficients at infinite dilution.**

Hexane (◆), cyclohexane (●), toluene (■) and benzene (▲) in 3-methylsulfolane (Rawat et al., 1976; Van Aken and Broersen, 1977); (——) modified UNIFAC (Dortmund).

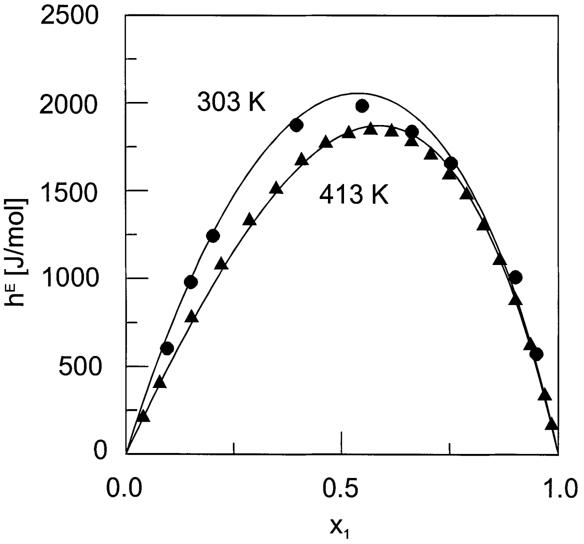

**Figure 7. Experimental and calculated $h^E$ data for the system Ethanol (1)+Sulfolane (2).**

At 303.15 K (●) (Tommila et al., 1969); 413.15 K (▲) (Gmehling, unpublished data); (——) modified UNIFAC (Dortmund).

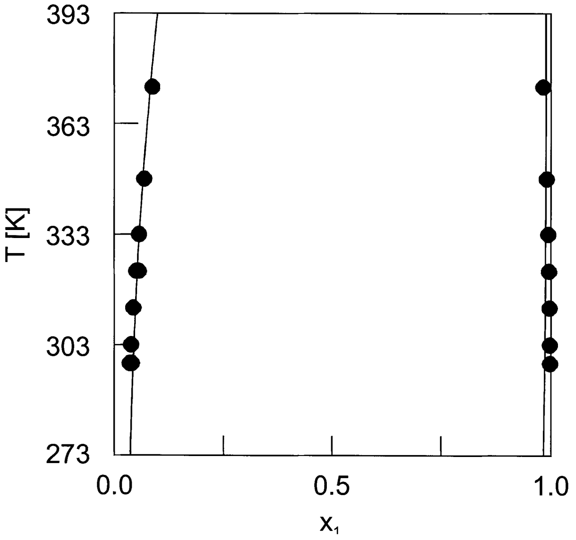

**Figure 9. Experimental and calculated *LLE* data.**

The system cyclohexane (1)+sulfolane (2) (Cassell et al., 1989; De Fre and Verhoeye, 1976a,b; Nissema and Karvo, 1979); (——) modified UNIFAC (Dortmund).

parameter matrix. If poor results are obtained, the database is checked again. Thus, data sets which do not agree with main part of the experimental data are excluded from the fitting procedure.

## Results

The new group interaction parameters for Modified UNIFAC (Dortmund) and the van der Waals properties $R_k$ and $Q_k$ together with the group assignment of the new main group "sulfones" are given in Tables 1 and 2. Additionally, the structure of the subgroups $CH_2SuCH_2$ (110) and $CH_2SuCH$ (111) are shown in Figure 2.

Figures 3–9 show the calculated results of modified UNIFAC (Dortmund) for various types of experimental mixture data (*VLE*, $\gamma^\infty$, $h^E$, *SLE* and *LLE*) for systems consisting of sulfolane, 3-methylsulfolane and 2,4-dimethylsulfolane using the new group interaction parameters for the new main group "sulfones". For all systems, a very good agreement between the experimental and calculated data is obtained. The especially good description of the $h^E$ and *SLE* data used as supporting data at high, respectively, low temperature for the parameter fitting leads to a reliable description of the temperature-dependence of the activity coefficients. Further-

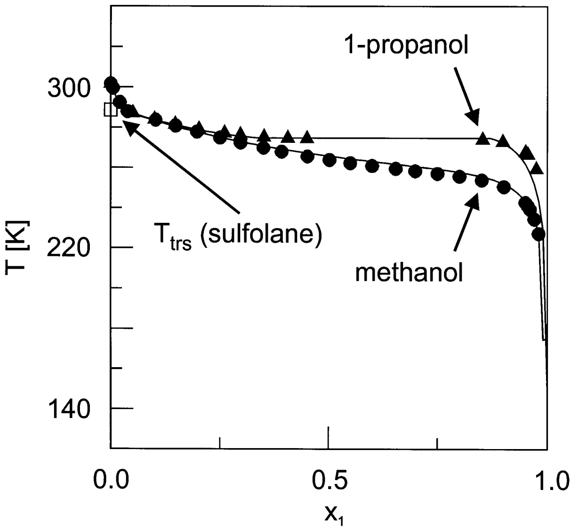

**Figure 8. Experimental and calculated *SLE* data.**

The system 1-propanol (▲) and methanol (●) (1)+sulfolane (2) (Ahlers et al., 1999); (——) modified UNIFAC (Dortmund).

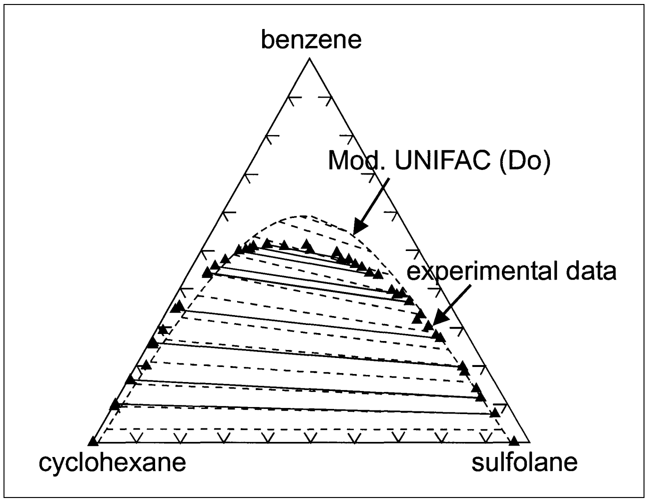

**Figure 10. Experimental and predicted ternary *LLE* data.**

The system cyclohexane (1)+benzene (2)+sulfolane (3) at 298.15 K (De Fre and Verhoeye, 1976a,b); (– – –) modified UNIFAC (Dortmund).

more, a reliable presentation of the real behavior of phase equilibria in the dilute region is achieved with the new group interaction parameters. Also, the *LLE* data of the strong real system Cyclohexane + Sulfolane are calculated accurately in the given temperature range.

Figure 10 shows the experimental ternary *LLE* data for the system Cyclohexane + Benzene + Sulfolane at 298.15 K. The predicted results of modified UNIFAC (Dortmund) demonstrate that new group interaction parameters are suitable for the prediction of ternary *LLE* data necessary for liquid-liquid extraction of aromatics from aliphatics with the help of sulfolane.

## Conclusion

The examples show that the new modified UNIFAC (Dortmund) parameters for the main group "sulfones" allow a reliable prediction of phase equilibria and excess enthalpies. Therefore, and because of the large range of applicability, it is a suitable model for a variety of applications of

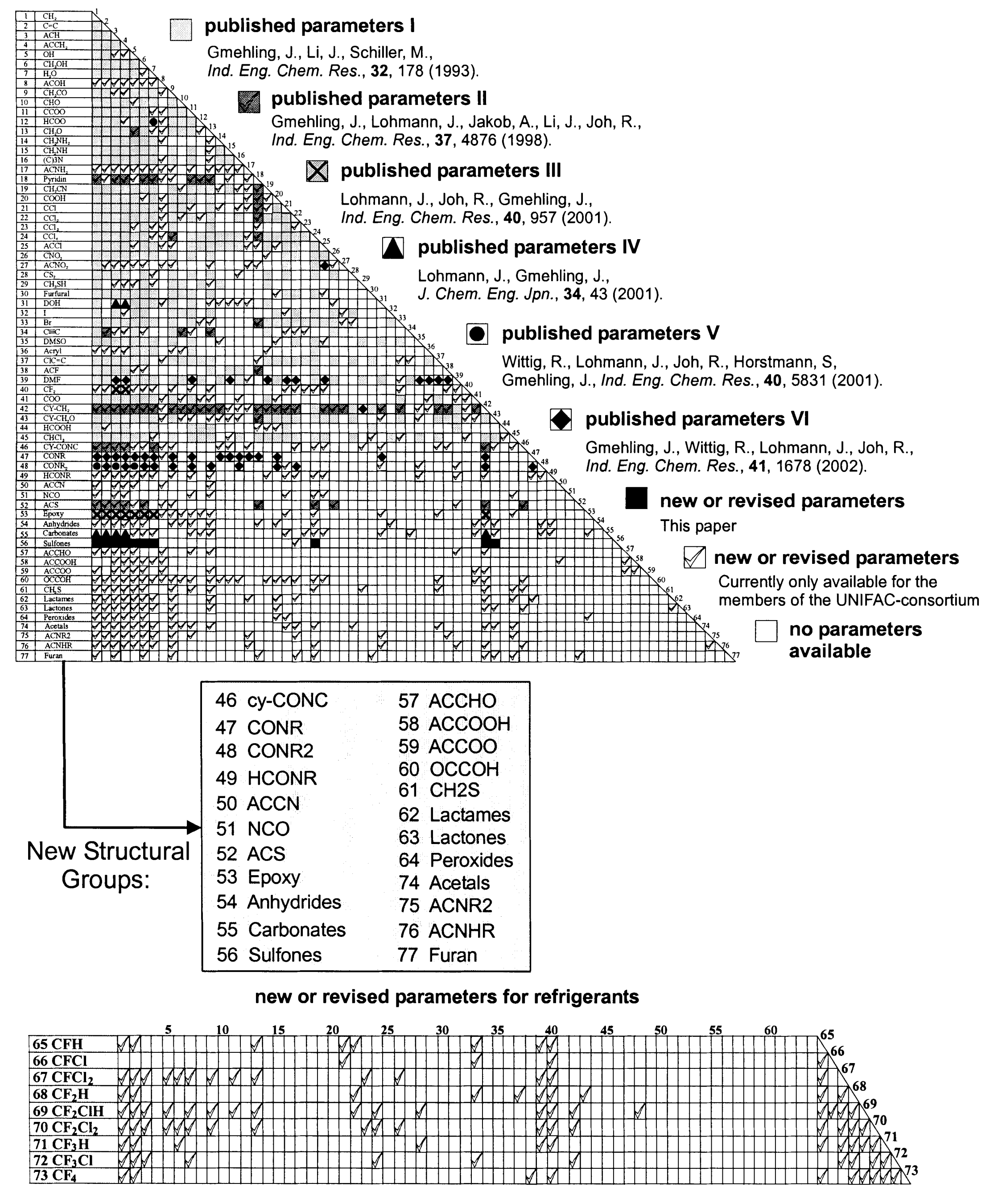

**Figure 11. Current parameter matrix including the refrigerant submatrix of modified UNIFAC (Dortmund) (Apr. 2002).**

industrial interest, which can help chemical engineers during their daily work. Because of ongoing research work, the range of applicability of modified UNIFAC (Dortmund) will be further enlarged and the reliability continually improved.

A lot of gaps in the modified UNIFAC (Dortmund) parameter matrix were already filled with the help of the huge amount of thermodynamic phase equilibria and excess properties continuously stored in the DDB or measured in our laboratory.

The main group for sulfones is just one example for a new introduced substance class in modified UNIFAC (Dortmund). Many other main groups of industrial interest have already been introduced into the parameter matrix of modified UNIFAC (Dortmund) within the UNIFAC consortium project: monoalkylated formamides, aromatic nitriles, isocyanates, anhydrides, aromatic aldehydes, aromatic acids, aromatic esters, sulfides, cyclic amides, cyclic esters, peroxides, refrigerants, acetals, furan, mono- and dialkylated anilines.

The present status of the group interaction parameter matrix is given in Figure 11.

The most actual status of the research work is always available on the Web at http://www.uni-oldenburg.de/tchemie/consortium.

## Outlook

In the future, it is planned to further introduce main groups for components of industrial interest: aromatic ethers (such as anisole), cyclic amines (such as piperidine), cyclic sulfides (such as tetrahydrothiophene), and cyclic carbonates (such as propylene carbonate). However, due to the lack of data for these compounds, a large number of additional measurements of $VLE$, $\gamma^\infty$, $h^E$, $SLE$, and azeotropic data have to be performed before.

Furthermore, the well-known weaknesses of group contribution methods (isomer and proximity effects) will be examined and hopefully be minimized in the near future.

In the future, 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. This approach will also provide densities and enthalpies for both the liquid and the vapor phase as a function of temperature, pressure, and composition. These are important thermophysical properties for process simulation, which are required as additional information in the $\gamma$-$\varphi$-approach.

Additionally, the effects of strong electrolytes on the phase equilibrium behavior (LIFAC) (Yan et al., 1999) will be combined with modified UNIFAC (Dortmund).

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## Notation

$a_{nm}$, $b_{nm}$, $c_{nm}$ = modified UNIFAC (Dortmund) group interaction parameters between main groups $n$ and $m$
$c_p^E$ = molar excess heat capacity, $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
$F$ = objective function
$F_i$ = auxiliary property for component $i$ (surface fraction/mole fraction)
$f_i^0$ = standard fugacity of component $i$, kPa
$h^E$ = molar excess enthalpy, $\text{J} \cdot \text{mol}^{-1}$
$i$, $j$ = components
$n$,$m$ = main groups
$K$ = chemical equilibrium constant
$LLE$ = liquid-liquid equilibrium
$P$ = pressure, kPa
$P_i^S$ = saturation vapor pressure of component $i$, kPa
$q_i$ = relative van der Waals surface area of component $i$
$Q_k$ = relative van der Waals surface area of subgroup $k$
$r_i$ = relative van der Waals volume of component $i$
$R_k$ = relative van der Waals volume of subgroup $k$
$SLE$ = solid-liquid equilibrium
$T$ = absolute temperature, K
$T_{trs}$ = transition temperature, K
$V_i$ = auxiliary property for component $i$ (volume fraction/mole fraction)
$V_i'$ = empirically modified $V_i$-value
$VLE$ = vapor-liquid equilibrium
$w$ = weighting factor
$x_i$ = mole fraction of component $i$ in the liquid phase
$X_m$ = mole fraction of group $m$ in the liquid phase
$y_i$ = mole fraction of component $i$ in the vapor phase

### *Greek letters*

$\gamma_i$ = activity coefficient of component $i$
$\gamma^\infty$ = activity coefficient at infinite dilution
$\Gamma_k$ = group activity coefficient of group $k$ in the mixture
$\Gamma_k^{(i)}$ = group activity coefficient of group $k$ in the pure substance
$\Theta_m$ = surface fraction of group $m$ in the liquid phase
$\nu_k^{(i)}$ = number of structural groups of type $k$ in molecule $i$
$\varphi_i$ = fugacity coefficient of component $i$
$\Psi_{nm}$ = modified UNIFAC (Dortmund) - temperature term (Eq. 1)

### *Subscript*

calc = calculated

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