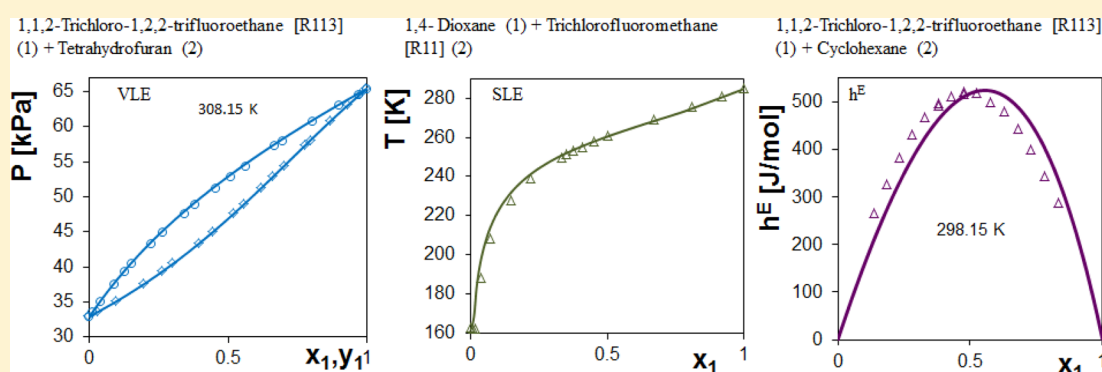


Further Development of Modified UNIFAC (Dortmund): Revision and Extension 6

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ABSTRACT: For process development and simulation, the group contribution concept can be successfully applied for the estimation of the missing pure component and mixture properties. This concept has the great advantage that only a limited number of group interaction parameters is required. With the support of a company consortium founded 1996 at the University of Oldenburg, the group contribution model modified UNIFAC (Dortmund) for the prediction of phase equilibria and excess properties has been continuously revised and extended. Within the consortium the number of available group interaction parameters has been doubled. At the same time, the reliability of the results was greatly improved, and the range of applicability was extended to ionic liquids, polyethers, and so forth, and systems for which no experimental data are available, e.g., reactive systems. In this paper the group interaction parameters for the sulfur groups sulfones, sulfides, and disulfides are given. Furthermore, the current status of the consortium developments is discussed.

■ INTRODUCTION

A reliable knowledge of the real behavior, in particular the phase equilibrium behavior, is of special importance for the development, simulation, and optimization of different processes in the chemical, petrochemical, gas processing, pharmaceutical, food, environmental industry, and so forth. g^E -models and equations of state can be applied to calculate the phase equilibrium behavior using binary parameters only. But in most cases at least a part of the required binary experimental data is missing. Then group contribution methods can be successfully applied.

After the publication of the group contribution model UNIFAC¹ in 1975 different UNIFAC modifications have been proposed to eliminate the weaknesses of original UNIFAC for the prediction of activity coefficients at infinite dilution γ^∞ and the temperature dependence (respectively excess enthalpy h^E), in particular for asymmetric systems. Modified UNIFAC models were developed at the University of Dortmund (modified UNIFAC (Dortmund))^{2,3} and at the University of Denmark (Lyngby) (modified UNIFAC (Lyngby)).^{4,5} To obtain better results for asymmetric systems in both models a different combinatorial part than in original UNIFAC^{1,6} is used. Based on the proposal of Kikic et al.⁷ and Thomas and Eckert,⁸ the

following combinatorial part is applied in modified UNIFAC (Dortmund):

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

where V_i , F_i , and q_i are volume/mole fraction ratios, surface area/mole fraction ratios, and the van der Waals surface area of component i . Besides V_i the following volume/mole fraction ratio V_i' is used:

$$V_i' = \frac{r_i^{3/4}}{\sum_j r_j^{3/4} x_j} \quad (2)$$

where r_i is the relative van der Waals volume of component i and x is the mole fraction. Furthermore, in both models temperature-dependent group interaction parameters are

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introduced, where in modified UNIFAC (Dortmund) the following expression is used:

$$\Psi_{nm} = \exp\left(-\frac{a_{nm} + b_{nm}T + c_{nm}T^2}{T}\right) \quad (3)$$

where the temperature dependence of the group interaction parameter Ψ_{nm} between the functional groups n and m is described using the parameters a_{nm} , b_{nm} , and c_{nm} .

A full description of the modified UNIFAC model (Dortmund) is beyond the scope of this publication. For the equations and parameters of the modified UNIFAC model (Dortmund) the reader is referred to refs 2 and 9 where a full description is given. Revised and extended versions of this method were published in refs 10–15.

In the last years the group contribution method modified UNIFAC (Dortmund) has become a valuable predictive thermodynamic model for the development and simulation of industrial processes, because of the reliable results obtained and

its large range of applicability. With the definition of new groups, the range of applicability was extended to refrigerants, ionic liquids, polyethers, and so forth.

Modified UNIFAC (Dortmund) has become an important thermodynamic model for process development.¹⁶ With the help of modified UNIFAC (Dortmund) various process alternatives can be compared, separation problems in multi-component systems can be detected, and suitable solvents for separation processes like extraction, azeotropic, and extractive distillation can be selected. Furthermore, the influence of solvents on chemical equilibrium conversion and flash points of flammable liquid mixtures can be predicted, the fate of a chemical in the environment or working place can be estimated, the construction of residue curve maps is directly possible, and so forth.

Since the reliability of the results depends on the quality of the group interaction parameters and the range of applicability mainly depends on the size of the parameter matrix, the continuous extension and revision of the group interaction parameter matrix of modified UNIFAC (Dortmund) is most important.

A relevant prerequisite for the further development of predictive methods is the direct access to a comprehensive database. For the further development of modified UNIFAC (Dortmund), the Dortmund Data Bank (DDB) is used. With ca. 7.2 million data tuples stored, DDB¹⁷ is the worldwide largest factual data bank for thermophysical properties, when compared with other data banks, e.g., the NIST data bank with ca. 4.8 million data tuples.¹⁸ Both data banks are continuously updated. In the case of DDB approximately 250 data sets (approximately 1800 data tuples) are added per working day. For fitting the required group interaction parameters of modified UNIFAC (Dortmund) the available database has been enlarged by systematic measurements of missing data in our

Table 1. Thermodynamic Phase Equilibrium Data and Excess Properties Stored in DDB for Nonelectrolyte Systems (February, 2016)

type of thermodynamic mixture data	number of data sets (data points)
VLE (normal boiling points of all components above 0 °C)	37 300
activity coefficients at infinite dilution, γ^∞	(89 000)
excess enthalpies, h^E	22 800
excess heat capacities, c_p^E	6 400
LLE	30 540
SLE	55 300
(a)zeotropic data	(56 500)

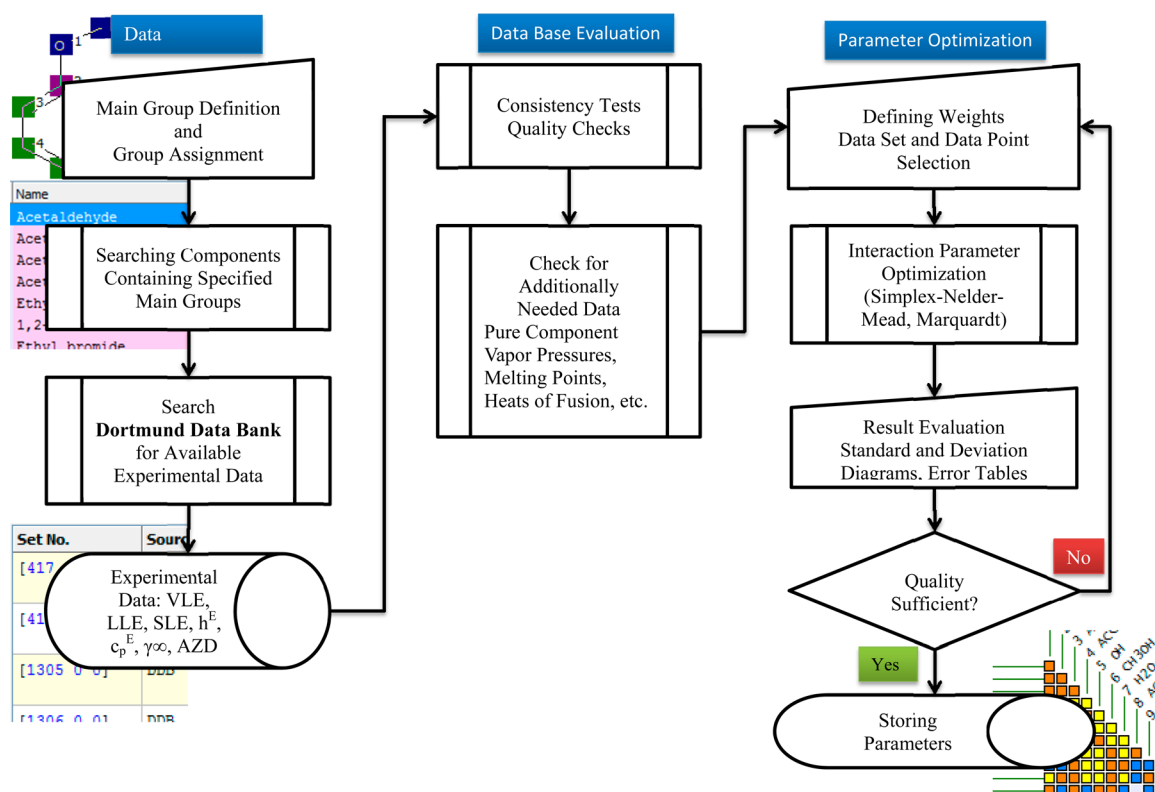
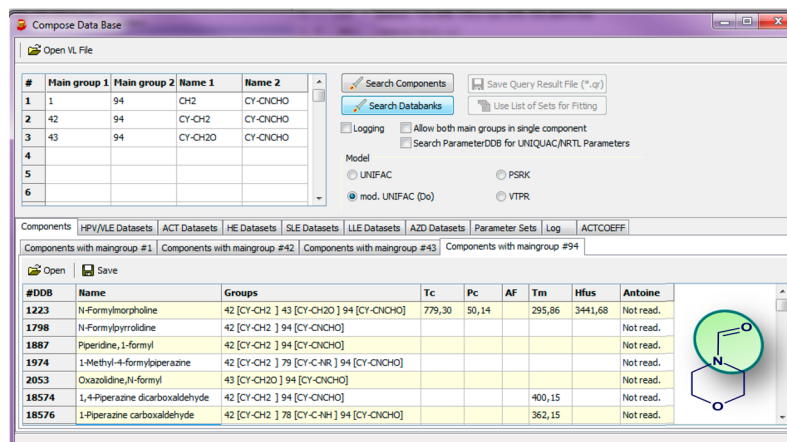
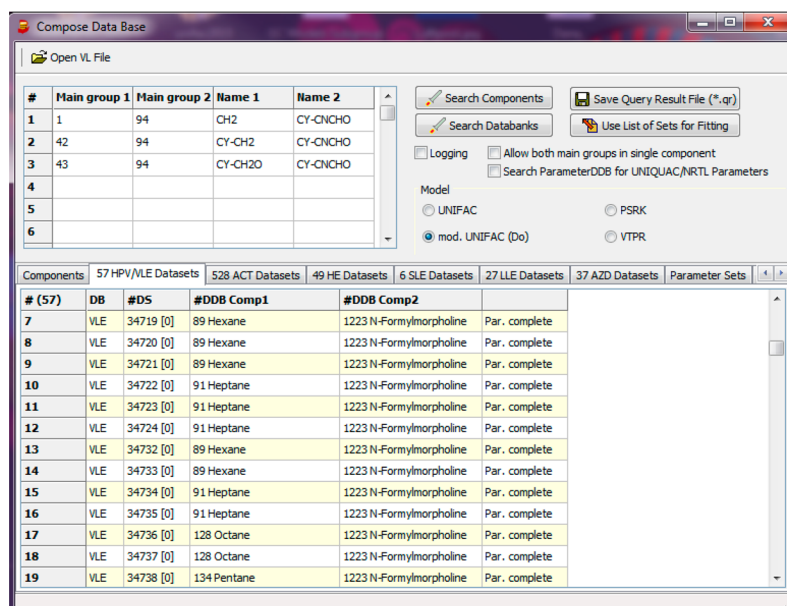


Figure 1. Flow diagram for fitting the required group interaction parameters of the group contribution method modified UNIFAC (Dortmund).

a)



b)



c)

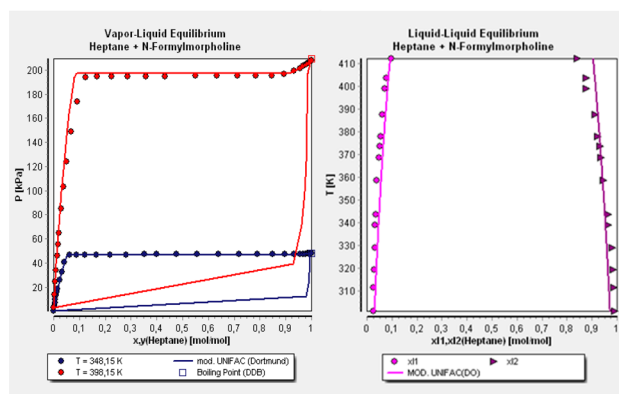


Figure 2. Screenshots from the software developed for the simultaneous parameter fit of group interaction parameters for three different group pairs.

laboratory. Furthermore, sponsors of the consortium¹⁹ provided confidential company data for the development work.

Recently, a comprehensive new modified UNIFAC (NIST) parameter matrix, based on the same formulations used for modified UNIFAC (Dortmund), has been published.²⁰ In most cases, the authors used the same main and subgroups and van der Waals properties as in modified UNIFAC (Dortmund).

The required group interaction parameters were fitted for 984 group pairs using vapor–liquid equilibria (VLE), h^E , and γ^∞ data stored in the NIST databank.

■ FITTING OF MODEL PARAMETERS

In the case of modified UNIFAC (Dortmund) the required group interaction parameters are fitted not only to VLE

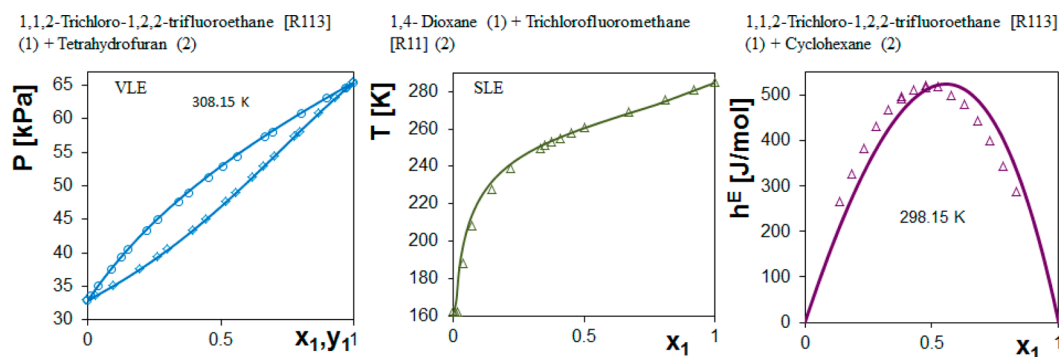


Figure 3. Experimental VLE,²⁸ SLE,²⁹ h^E ,³⁰ and calculated results obtained from a simultaneous fit to three group combinations simultaneously: 42 (cy-CH₂) and 67 (CFCl₂), 43 (cy-CH₂O) and 67 (CFCl₂), 43 (cy-CH₂O) and 70 (CF₂Cl₂).

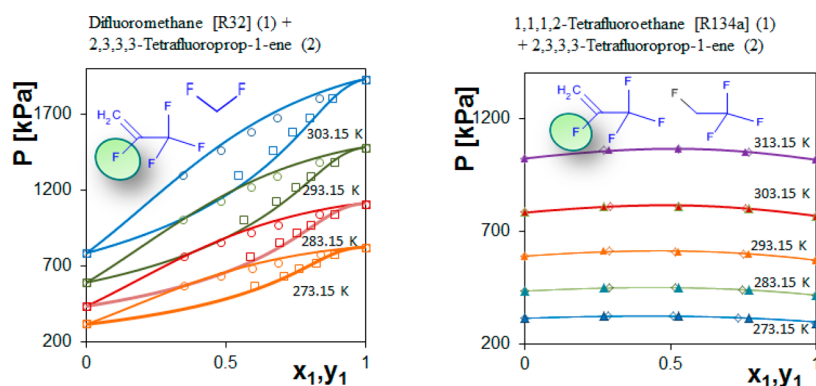


Figure 4. Experimental³¹ and calculated results obtained from a simultaneous fit to four group combinations: 2 (C=C) and 95 (F-C=C), 40 (CF₂) and 95 (F-C=C), 68 (CF₂H) and 95 (F-C=C), 65 (CFH) and 95 (F-C=C).

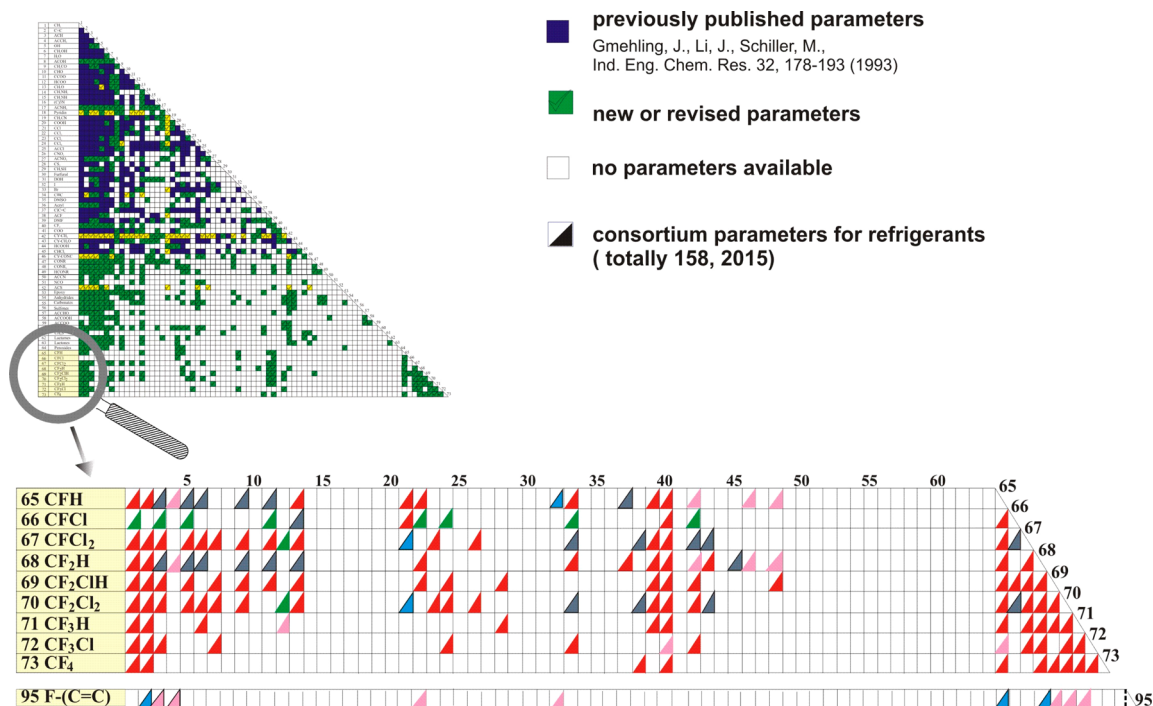


Figure 5. Modified UNIFAC (Dortmund) parameter submatrix for refrigerants.

data as in original UNIFAC, but also to other reliable phase equilibrium data (LLE, solid–liquid equilibria (SLE) of simple eutectic systems, azeotropic data (γ^∞), and excess properties (excess enthalpies h^E , excess heat capacities c_p^E)

of nonelectrolyte subcritical systems in a wide temperature range.²

Table 1 gives an idea about the current number of mixture data for nonelectrolyte systems stored in DDB, which can be

Table 2. Modified UNIFAC (Dortmund) R_k and Q_k Parameters Together with the Group Assignments for the Main Groups of Sulfones (No. 56), Sulfides (No. 61), and Disulfides (No. 93)

main group	subgroup	no.	R_k	Q_k	sample	group assignment
56 sulfone	$(\text{CH}_2)_2 \text{SOO}$	110	2.6870	2.1200	sulfolane	1 $(\text{CH}_2)_2 \text{SOO}$, 2 cy- CH_2
	$\text{CH}_2 \text{SOOCH}$	111	2.4600	1.8080	2,4-dimethylsulfolane	1 $\text{CH}_2 \text{SOOCH}$, 2 CH_3 , 1 cy- CH_2 , 1 cy-CH
61 sulfides	$\text{CH}_3 \text{S}$	122	1.6130	1.3680	dimethyl sulfide	1 CH_3 , 1 $\text{CH}_3 \text{S}$
	$\text{CH}_2 \text{S}$	123	1.3863	1.0600	diethyl sulfide	2 CH_3 , 1 CH_2 , 1 $\text{CH}_2 \text{S}$
	CHS	124	1.1589	0.7480	diisopropyl sulfide	4 CH_3 , 1 CH , 1 CHS
93 disulfides	$-\text{S}-\text{S}-$	201	1.0678	2.2440	dimethyl disulfide	2 CH_3 , 1 $-\text{S}-\text{S}-$

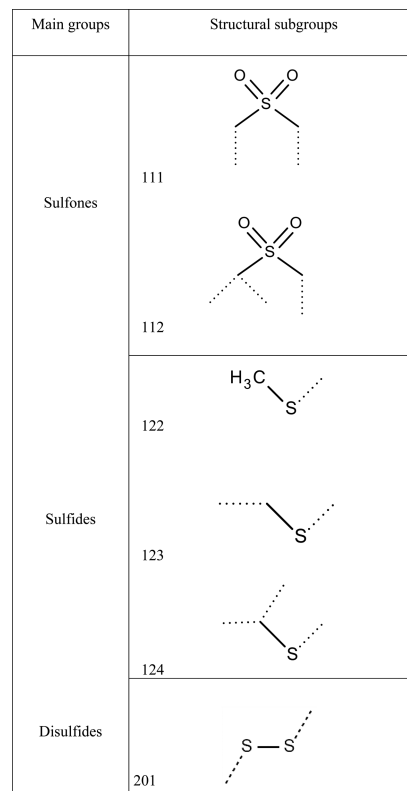
used for fitting the required group interaction parameters of modified UNIFAC (Dortmund). Besides these data, DDB¹⁷ contains data for systems with supercritical compounds, electrolyte systems, polymers, transport, and PvT properties, etc.

While VLE data provide the information about the composition dependence, excess enthalpies deliver the most reliable information about the temperature dependence of the activity coefficients via the Gibbs–Helmholtz equation.²¹ Information about the dilute range and strong asymmetric systems is taken into account using reliable activity coefficients at infinite dilution. For systems with strong deviations from Raoult's law often liquid–liquid equilibrium data deliver the required reliable information. For fitting temperature-dependent parameters, supporting data at low and high temperatures are most important. While solid–liquid equilibria of simple eutectic systems provide this information at low temperature, excess enthalpies are used as supporting data at high temperatures (>363 K). Unfortunately, most published excess enthalpy data were measured around room temperature. Therefore, using an isothermal flow calorimeter, more than 1100 h^E -data sets at higher temperatures (60–140 °C) were measured in our laboratory. Furthermore, a large number of important data such as VLE (more than 1250 data sets), activity coefficients at infinite dilution, SLE for simple eutectic systems, and so forth were systematically measured for the further development of the modified UNIFAC (Dortmund) model. In a few cases also confidential data provided by our sponsors were used for fitting the required group interaction parameters.

The contribution of the different types of data to the objective function F is taken into account with the help of weighting factors w_i :

$$\begin{aligned}
 F = & w_{\text{VLE}} \sum \Delta \text{VLE} + w_{\text{AZD}} \sum \Delta \text{AZD} \\
 & + w_{\gamma^\infty} \sum \Delta \gamma^\infty + w_{h^E} \sum \Delta h^E \\
 & + w_{c_p^E} \sum \Delta c_p^E + w_{\text{SLE}} \sum \Delta \text{SLE} + w_{\text{LLE}} \sum \Delta \text{LLE}
 \end{aligned} \quad (4)$$

For fitting the temperature-dependent parameters simultaneously to the different types of data, a sophisticated software package was developed. With the help of this software package, the components with the desired functional groups can directly be selected, since in DDB the structures of all the components are stored in form of connection tables and can be divided directly into the functional groups. In the next step, the mixture data for the selected components are taken from the Dortmund Data Bank and checked for thermodynamic consistency and plausibility. The software allows also an equal distribution of the data sets over the different binary systems, compositions, temperatures (pressures), and searches for the required pure component properties, such as vapor pressure, enthalpy of fusion, melting temperature, and so forth. For fitting the group interaction parameters of modified UNIFAC (Dortmund), the

**Figure 6.** Structure of the subgroups for the main groups of sulfones (No. 56), sulfides (No. 61), and disulfides (No. 93).

Simplex–Nelder–Mead method²² is employed first because of its robustness. Close to the minimum of the objective function F , the regression is continued using the Marquardt method²³ which provides a much faster convergence. A flow diagram of the software package is shown in Figure 1.

NEW FITTING TOOL FOR GROUP CONTRIBUTION INTERACTION PARAMETERS

To be able to obtain the most reliable parameters and to use most of the data stored in DDB for fitting the parameters of the different predictive models, our software package has been rewritten and extended. Besides the general tasks of the fitting procedure described above and illustrated in Figure 1, the current software package allows the simultaneous parameter fit to more than two different group pairs. This possibility allows extending the database, since data sets which previously could not be used, can now be used.

Exemplarily this advantage is shown in three screenshots (Figure 2) for fitting the parameters of systems with *N*-formylmorpholine. The group assignment of this molecule contains three different groups (42, 43, 94, as shown in Figure 2a). With the extended software package the group interaction

Table 3. Selected New and Revised Modified UNIFAC (Dortmund) Group Interaction Parameters for the Main Groups of Sulfones (No. 56), Sulfides (No. 61), and Disulfides (No. 93)

<i>n</i>	<i>m</i>	<i>a_{nm}</i> (K)	<i>b_{nm}</i>	<i>c_{nm}</i> (K ⁻¹)	<i>a_{nm}</i> (K)	<i>b_{nm}</i>	<i>c_{nm}</i> (K ⁻¹)
1	9	488.98	0.0292		226.94	-0.8893	
1	61	860.51	-1.9600		-309.94	0.6486	
1	93	468.40	-2.5567		2660.16	-6.8651	
2	61	324.32			-156.46		
2	93	-740.24			232.90		
3	61	454.32	-1.2194		-388.19	1.0430	
3	93	-630.42			-72.27		
4	61	629.46	-1.3904		-305.27	0.6691	
4	93	-478.07			15.05		
5	61	1105.94	-1.6876		1343.95	-2.1649	
5	93	-367.32			34.71		
6	61	34.79			641.04		
6	93	1216.71	-5.4483		-386.35	3.7787	
7	43	-75.75	-0.9851	0.3332×10^{-2}	717.48	-1.4851	-0.7438×10^{-15}
7	61	1038.30			-270.53		
7	93	4878.28	-6.3876		-444.62	-0.7765	
9	42	437.74	-2.7983	0.3640×10^{-2}	364.42	2.1022	-0.4653×10^{-2}
9	56	609.50	-3.9013	0.6091×10^{-2}	-537.41	3.8038	-0.5986×10^{-2}
9	61	1154.43	-6.2811	0.7969×10^{-2}	-921.65	5.3930	-0.6859×10^{-2}
11	56	-1336.2	6.7742	-0.8200×10^{-2}	1915.20	-9.9994	0.1260×10^{-1}
11	61	-1366.59	5.9067	-0.7325×10^{-2}	2622.04	-11.7013	0.1347×10^{-1}
13	56	-209.21	-0.4704	0.6918×10^{-2}	1163.91	-7.1332	0.8390×10^{-2}
13	93	-584.73			178.50		
14	56	190.88			14.91		
15	56	1178.79	-9.9991	0.2076×10^{-1}	1667.89	-7.5870	0.8006×10^{-2}
16	42	324.15	-1.4264		-198.32	1.4520	
16	56	2662.02	-13.9855	0.1774×10^{-1}	-1780.41	5.7197	-0.1650×10^{-2}
18	42	268.23	-1.4137		-5894.1	13.088	
18	56	-354.35	-1.8371	0.1040×10^{-1}	-1838.89	-9.6529	0.2730×10^{-1}
19	56	-50.84	-0.02529		180.81	-0.0642	
21	56	842.49	-1.8434		-313.20	0.4139	
22	56	262.14			-229.08		
23	42	289.08	-0.5852		-69.60	-0.4274	
23	56	401.70			157.63		
25	42	207.16	-1.2206		223.78	-0.5826	
25	56	270.24			452.30		
33	56	2459.0			-271.23		
42	50	426.64	1.1963		125.39	-1.1810	
42	52	313.43	0.0911		-30.56	-0.2455	
42	61	509.27	-0.5337		-108.17	-0.1325	
42	93	246.35	-1.9006		1120.89	-3.1028	
45	56	184.79			-76.14		
50	56	271.02	-0.6847		-59.04	0.4820	
52	56	-299.38	1.2901		359.06	-0.7256	
53	56	912.22	-2.0231		-604.90	1.0475	
55	56	-9.632	0.5554	-6.5000×10^{-5}	125.53	0.2892	-0.9690×10^{-3}
56	61	200.04	0.1979	-0.1600×10^{-2}	742.31	-4.1234	0.7800×10^{-2}

parameters (e.g., 42 with 94, 43 with 94) and an additional further functional group, e.g., main group 1 (alkanes) with the specified main group 94, can now be fitted simultaneously to NFM-alkane systems, when the additionally required group interaction parameters between the other groups (1–42, 1–43, 42–43) are already available. Figure 2b) shows the extent of the database (57 VLE, 49 h^E , 27 LLE, etc.) which, through this procedure, can be used to fit the required parameters. In Figure 2c) typical VLE and LLE results for the system *n*-heptane–*N*-formylmorpholine are shown.

Further results of this approach are shown in Figures 3 and 4, where the parameters for three (Figure 3) and four (Figure 4)

group pairs were fitted simultaneously to systems containing components from the important class of refrigerants. With the help of the extended software package, for example, the existing parameter matrix for refrigerants (Figure 5) was distinctly extended. In this submatrix, the defined groups are now available for fluorocarbons, hydrofluorocarbons, hydrochlorocarbons as well as for chlorofluorocarbons, hydrochlorofluorocarbons, and vinylfluoride. Today, the actual refrigerant matrix comprises group interaction parameters for 158 group pairs, as shown in Figure 5.

By the way, with the help of the new software package not only the group interaction parameters of modified UNIFAC

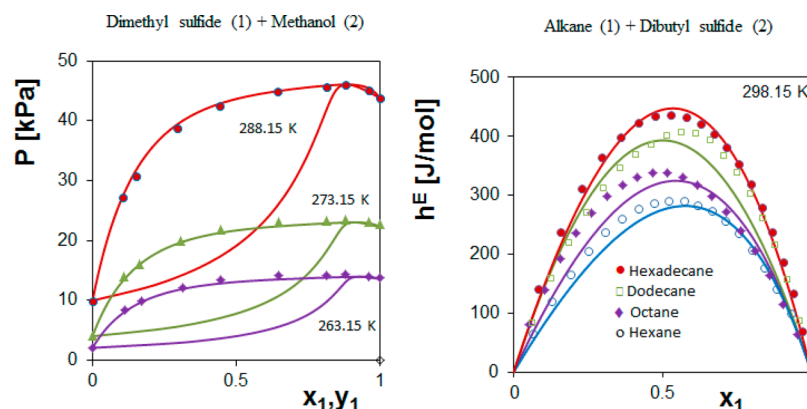


Figure 7. Experimental^{34,35} and predicted VLE and h^E using modified UNIFAC (Dortmund) for various binary systems with dimethyl sulfide and dibutyl sulfide.

(Dortmund), and original UNIFAC,⁶ but also the required parameters of the group contribution equations of state PSRK^{24,25} and VTPR^{26,27} can be fitted. In the future the consideration of ternary and higher systems should be enabled in the simultaneous parameter fit.

RESULTS

A. Modified UNIFAC (Dortmund)—Extension. Sulfolane, because of its high selectivity in altering the activity coefficients at infinite dilution of aromatics and aliphatics, can be used as selective solvent for the separation of aromatics from aliphatics by extraction or extractive distillation. Because of its industrial importance, missing parameters for the sulfone group were fitted within the consortium. A sulfone main group (Table 2, Figure 6) has been introduced to describe systems with sulfolane. The group has been defined according to Wu and Sandler³² and introduced in the modified UNIFAC (Dortmund) model. For the sulfone group the parameters for 10 group pairs have already been published.³³ For fitting additional sulfone parameters exclusively VLE and excess enthalpy data of sulfolane systems measured in our laboratory were used. Table 3 contains the newly fitted group interaction parameters (typically fitted in the temperature range from -10 °C to 120 °C) for the sulfone group. Furthermore, the group interaction parameters for the main group sulfides and disulfides and a few other main groups are listed in Table 3. The structures of the subgroups of these main groups are shown in Figure 6.

Typical results for phase equilibria and excess enthalpies using modified UNIFAC (Dortmund) for systems with sulfides (main group 61) are shown in Figure 7. As can be seen not only the VLE but also h^E -data are in good agreement with experimental findings.

Different scientists^{20,36} tried to use the published group interaction parameters of the sulfide group also for the prediction of systems with disulfides, what was not intended. They found out that poor agreement with the experimental data was obtained (see red lines in Figure 8). Only with the introduction of a disulfide main group a reliable description of the phase equilibrium behavior and excess properties has been reached (see blue lines in Figure 8).

B. Modified UNIFAC (Dortmund): Revision. Another objective of the consortium work is the continuous verification of the current parameters and, if necessary, the revision of these parameters. During the last 20 years, approximately 300 published or consortium parameters have been revised.

This development was possible by the steady growth of the number of data stored in the DDB, as exemplarily shown in Table 4 for water with cyclic ethers. The revision of the old parameters leads to a distinct improvement of the results. For systems with water and cyclic ethers, the results using the old and the new parameters are shown in Figure 9.

The current status of the modified UNIFAC (Dortmund) parameter matrix is shown in Figure 10.

Today group interaction parameters for 1721 group pairs are available for 103 main groups. As can be seen, modified UNIFAC (Dortmund) can now even be applied for systems with peroxides, cyclic thioethers, imidazoles, morpholines, pyrroles, acrolein, cycloalkylamines, disulfides, *N*-formylmorpholine, mercury, polyethylene glycols, pyrazine, ionic liquids,⁴⁰ etc. This enormous development was only possible with the help of the steadily growing Dortmund Data Bank, the systematic measurement of missing VLE, γ^∞ , h^E , SLE and azeotropic data and the support of more than 50 companies of the company consortium.

A comprehensive comparison⁴¹ of the results of different UNIFAC methods for 10 360 isothermal VLE data sets is shown in Figure 11, where the percentages of VLE data that can be predicted within a certain error, in this case relative pressure deviation, are shown. Figure 11 shows again the improved results of the modified UNIFAC versions compared to original UNIFAC. As expected, modified UNIFAC (NIST), which is mathematically identical with modified UNIFAC (Dortmund), shows a similar performance. Both models predict approximately 90% of the data within a relative deviation <10%. But modified UNIFAC (Dortmund) has the great advantage that the range of applicability is much larger because of the distinctly higher number of available group interaction parameters.

Results of various modified UNIFAC (Dortmund) applications have been published recently.⁴² Another recent publication shows⁴³ that modified UNIFAC (Dortmund), when compared to UNIFAC, leads to distinctly better results for the calculation of initial normal boiling points, and for flash points of flammable liquid mixtures of polyurethane raw material. This can be explained due to the introduction of the new main group CH_2OCH_2 (instead of the alkyl group CH_2 and the ether group CH_2O), which lead to improved results for the investigated mixtures.

C. Modified UNIFAC (Dortmund): Filling Gaps Using COSMO-RS (OI). Despite of the reliability and simple applicability of group contribution methods, there are some well-known weaknesses described in detail in ref 21. The main

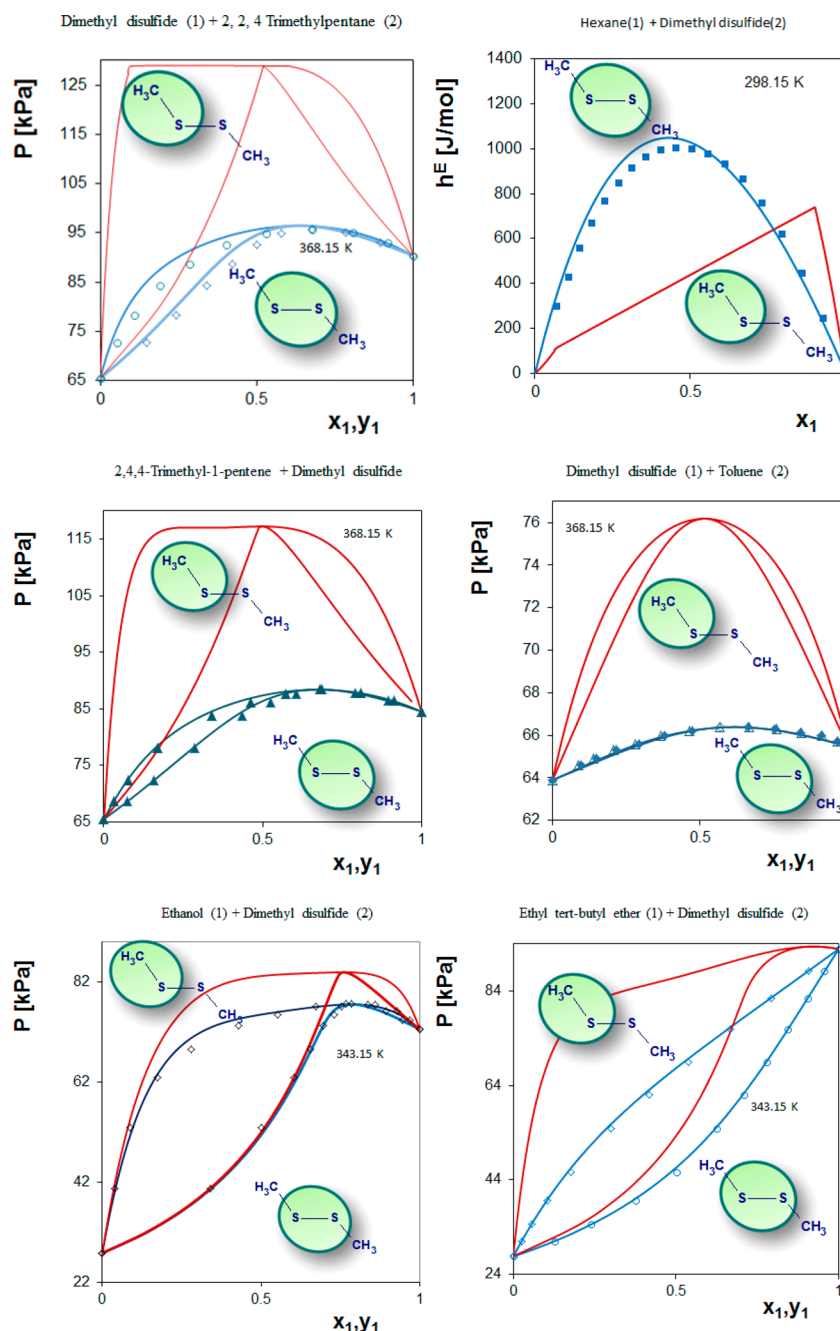


Figure 8. Experimental^{35,37,38} and predicted isothermal VLE and h^E data using modified UNIFAC (Dortmund) with different group assignments for various systems with dimethyl disulfide.

drawback is that at least a minimum of experimental data is required for fitting the group interaction parameters. For strongly reactive systems such as isocyanates with alcohols, experimental phase equilibrium data cannot be measured but can be estimated with the help of quantum chemical methods such as COSMO-RS (OI).⁴⁴ These estimated data can then be used as pseudoexperimental data in order to fill the gaps in the modified UNIFAC (Dortmund) matrix, e.g., to be able to predict the real behavior of a multicomponent system with the reactive compounds. Although this method was developed initially only for reactive systems, it has been extended to other systems when experimental binary data are missing. To check the quality of the predictions, in a few publications^{45–47} the calculated data were compared with the experimental data

Table 4. Number of Data Used for the Fitting the Group Interaction Parameters between the Main Groups 7 (H_2O) and 43 (cy- CH_2O)

data sets (points) used for fitting	VLE	h^E	LLE	γ^∞	azeotropic data	c_p^E
old parameters	81	46	not considered	(15)	not considered	5
new parameters	126	54	46	(67)	(137)	25

measured later. In most cases a good agreement was obtained. Consequently, gaps in the modified UNIFAC (Dortmund) parameter matrix can be filled with the parameters derived from COSMO-RS (OI) predictions, to be able to predict the real behavior of the considered system. In the last 10 years

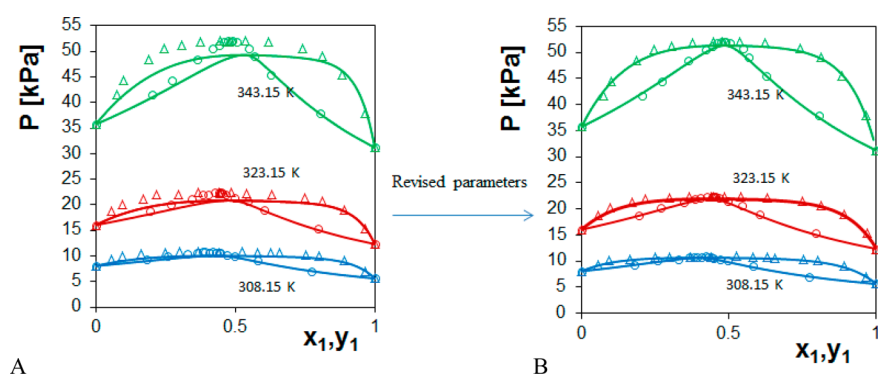


Figure 9. Experimental³⁹ and predicted VLE data for the system water (1) + 1,4-dioxane (2): (A) published modified UNIFAC (Dortmund) group interaction parameters.⁹ (B) revised modified UNIFAC (Dortmund) group interaction parameters (main groups 7 and 43).

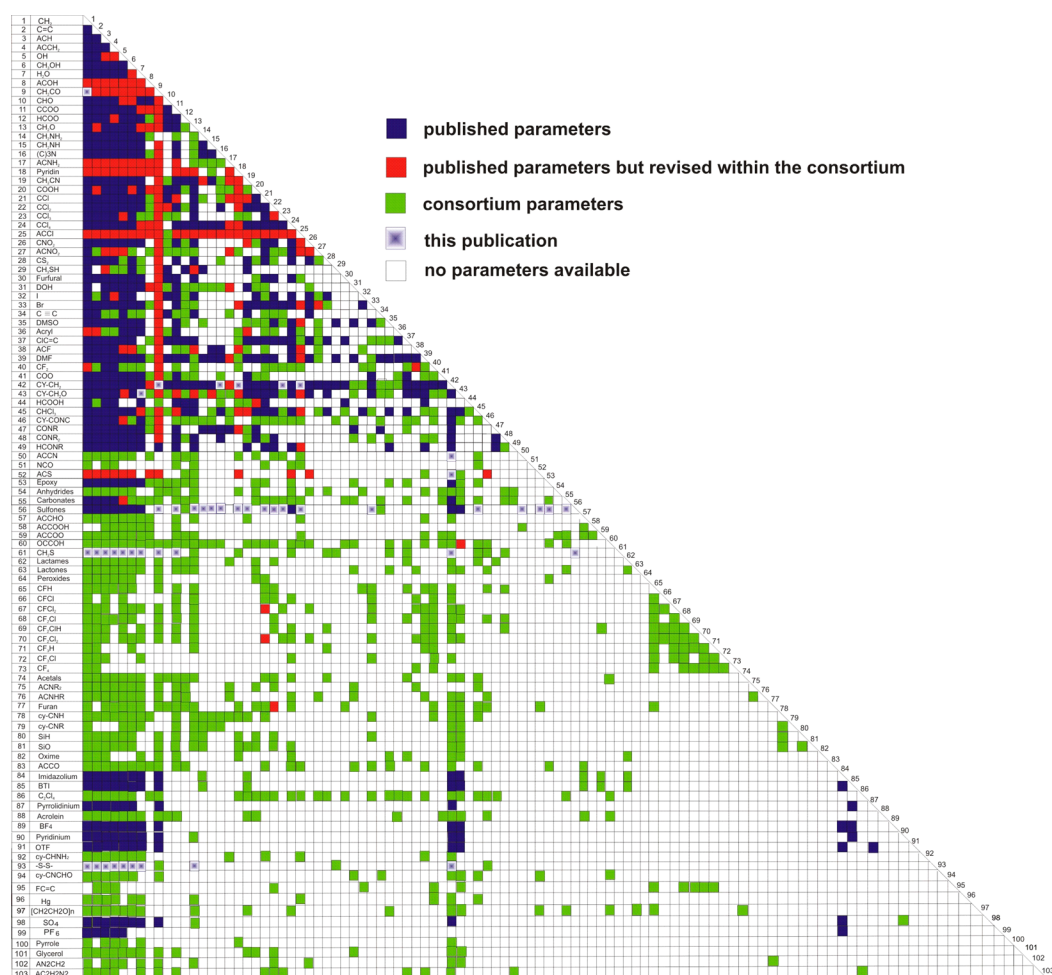


Figure 10. Current group interaction parameter matrix of modified UNIFAC (Dortmund) (February 2016).

for approximately 300 group pairs group interaction parameters have been determined this way, e.g. for isocyanates (main group 51), peroxides (main group 64), furanes (main group 77), refrigerants (main groups 71 and 72), oximes (main group 82), cyclic amines (main group 79), lactones (main group 63), etc. Exemplarily, the results for two reactive alcohol–methylisocyanate systems are shown in Figure 12.

Since the use of reliable experimental data for fitting group interaction parameters is preferable, the group interaction parameters derived from COSMO-RS (OI) predictions should be considered as “second-class-parameters”.

CONCLUSIONS

The accuracy of the results and the range of applicability of group contribution methods mainly depend on the quality of the parameters and the size of the group interaction parameter matrix. Therefore, with the help of the Dortmund Data Bank and the further developed software package, different group contribution methods are steadily revised and extended.

In this paper new parameters, e.g., for 38 group pairs for the sulfon, sulfide, and disulfide group, and revised parameters for 8 group pairs, e.g., for cyclic ethers–water, etc., are given. Furthermore, it is shown how missing parameters can be obtained

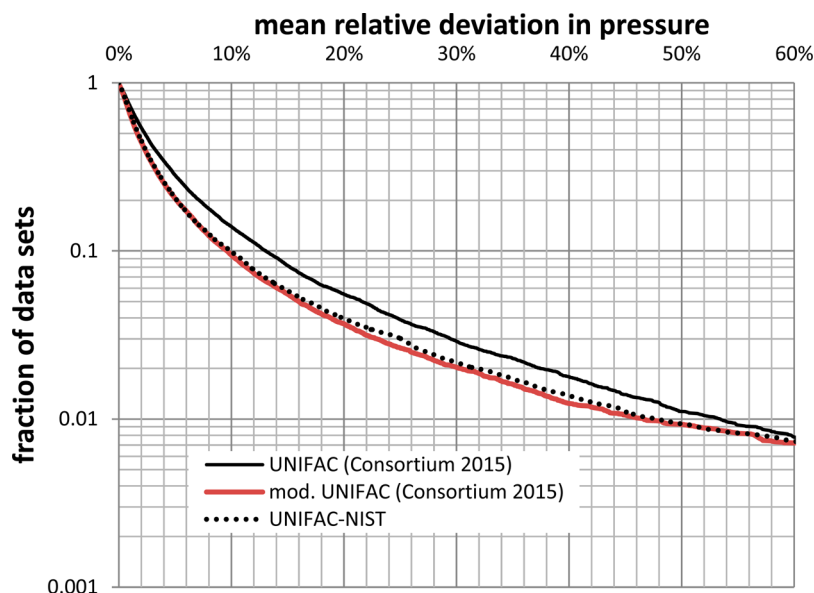


Figure 11. Fraction of the data sets estimated with a certain relative pressure deviation.

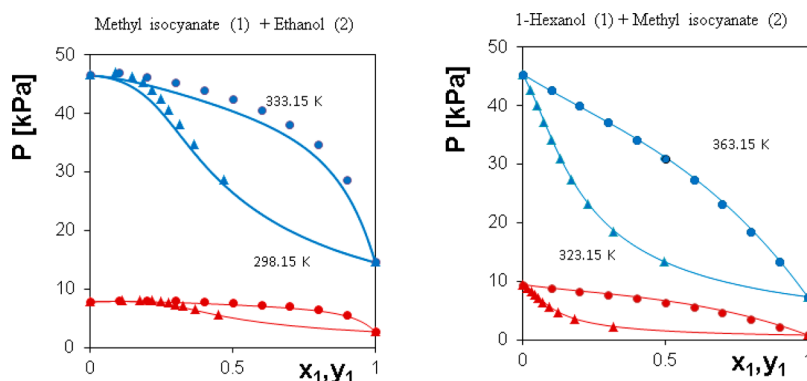


Figure 12. Pseudoexperimental and calculated VLE data for alcohol–methyl isocyanate systems predicted by COSMO-RS (Ol) (●, ▲) and modified UNIFAC (Dortmund) (continuous line).

when experimental data are missing, as for reactive systems such as isocyanates with alcohols.

A comparison of the predicted VLE results using a comprehensive database shows again the advantage of the modified UNIFAC methods compared to original UNIFAC. The current status of the different group interaction parameter matrices is always available via Internet.¹⁹

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REFERENCES

- (1) Fredenslund, Aa.; Jones, R. L.; Prausnitz, J. M. Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures. *AIChE J.* **1975**, *21*, 1086–1099.
- (2) Weidlich, U.; Gmehling, J. A modified UNIFAC model, Part I Prediction of VLE, h^E and γ^∞ . *Ind. Eng. Chem. Res.* **1987**, *26*, 1372–1381.
- (3) Weidlich, U. *Experimentelle und theoretische Untersuchungen zur Erweiterung der Gruppenbeitragsmethode UNIFAC*. PhD Thesis, University of Dortmund, Germany, 1985.
- (4) Larsen, B. L. *Predictions of phase equilibria and heat effects of mixing with a modified UNIFAC model*. PhD Thesis, Institutet for Kemiteknik, The Technical University of Denmark, Denmark, 1986.
- (5) Larsen, B. L.; Rasmussen, P.; Fredenslund, Aa. A modified UNIFAC group-contribution model for prediction of phase equilibria and heats of mixing. *Ind. Eng. Chem. Res.* **1987**, *26*, 2274–2286.
- (6) Fredenslund, Aa.; Gmehling, J.; Rasmussen, P. *Vapor-Liquid Equilibria Using UNIFAC*; Elsevier: Amsterdam, 1977.
- (7) Kikic, I.; Alessi, P.; Rasmussen, P.; Fredenslund, Aa. On the Combinatorial Part of the UNIFAC and UNIQUAC Models. *Can. J. Chem. Eng.* **1980**, *58*, 253.

- (8) Thomas, E. R.; Eckert, C. A. Prediction of Limiting Activity Coefficients by a Modified Separation of Cohesive Energy Model and UNIFAC. *Ind. Eng. Chem. Process Des. Dev.* **1984**, *23*, 194–209.
- (9) Gmehling, J.; Li, J.; Schiller, M. A Modified UNIFAC Model 2. Present Parameter Matrix and Results for Different Thermodynamic Properties. *Ind. Eng. Chem. Res.* **1993**, *32*, 178–193.
- (10) Lohmann, J.; Joh, R.; Gmehling, J. From UNIFAC to Modified UNIFAC (Dortmund). *Ind. Eng. Chem. Res.* **2001**, *40*, 957–964.
- (11) Gmehling, J.; Lohmann, J.; Jakob, A.; Li, J.; Joh, R. A Modified UNIFAC (Dortmund) Model. 3. Revision and Extension. *Ind. Eng. Chem. Res.* **1998**, *37*, 4876–4882.
- (12) Gmehling, J.; Wittig, R.; Lohmann, J.; Joh, R. A Modified UNIFAC (Dortmund) Model. 4. Revision and Extension. *Ind. Eng. Chem. Res.* **2002**, *41*, 1678–1688.
- (13) Wittig, R.; Lohmann, J.; Joh, R.; Horstmann, S.; Gmehling, J. Vapor-Liquid Equilibria and Enthalpies of Mixing in a Temperature Range from 298.15 to 413.15 K for the Further Development of Modified UNIFAC (Dortmund). *Ind. Eng. Chem. Res.* **2001**, *40*, 5831–5838.
- (14) Lohmann, J.; Gmehling, J. Modified UNIFAC (Dortmund): Reliable Model for the Development of Thermal Separation Processes. *J. Chem. Eng. Jpn.* **2001**, *34*, 43–54.
- (15) Jakob, A.; Grensemann, H.; Lohmann, J.; Gmehling, J. Further Development of Modified UNIFAC (Dortmund): Revision and Extension 5. *Ind. Eng. Chem. Res.* **2006**, *45*, 7924–7933.
- (16) Gmehling, J. Present Status and Potential of Group Contribution Methods for Process Development. *J. Chem. Thermodyn.* **2009**, *41*, 731–747.
- (17) Dortmund Data Bank, <http://www.ddbst.com> (March 30, 2016).
- (18) <http://trc.nist.gov/tde.html> (March 30, 2016).
- (19) UNIFAC consortium. <http://www.unifac.org>.
- (20) Kang, J. W.; Diky, V.; Frenkel, M. New Modified UNIFAC Parameters Using Critically Evaluated Phase Equilibrium Data. *Fluid Phase Equilib.* **2015**, *388*, 128–141.
- (21) Gmehling, J.; Kolbe, B.; Kleiber, M.; Rarey, J. *Chemical Thermodynamics for Process Simulation*; Wiley-VCH: Weinheim, 2012.
- (22) Nelder, J. A.; Mead, R. A Simplex Method for Function Minimization. *Comp. J.* **1965**, *7*, 308–313.
- (23) Marquardt, D. W. An Algorithm for Least-Squares Estimation of Nonlinear Parameters. *J. Soc. Ind. Appl. Math.* **1963**, *11*, 431–441.
- (24) Holderbaum, T.; Gmehling, J. PSRK: A Group-Contribution Equation of State Based on UNIFAC. *Fluid Phase Equilib.* **1991**, *70*, 251–265.
- (25) Horstmann, S.; Fischer, K.; Gmehling, J. PSRK Group Contribution Equation of State: Revision and Extension III. *Fluid Phase Equilib.* **2000**, *167*, 173–186.
- (26) Ahlers, J.; Gmehling, J. Development of a Universal Group Contribution Equation of State. III. Prediction of Vapor-Liquid Equilibria, Excess Enthalpies, and Activity Coefficients at Infinite Dilution with the VTPR Model. *Ind. Eng. Chem. Res.* **2002**, *41*, 5890–5899.
- (27) Schmid, B.; Gmehling, J. The Universal Group Contribution Equation of State VTPR: Present Status and Potential for Process Development. *Fluid Phase Equilib.* **2011**, *302*, 213–219.
- (28) Fenclova, D.; Dohnal, V. (Vapour + Liquid) Equilibria and Excess Molar Volumes of {1,1,2-Trichlorotrifluoroethane (Freon 113) + an Oxygenated Solvent of n-Hexane}. *J. Chem. Thermodyn.* **1991**, *23*, 911–921.
- (29) Ott, J. B.; Goates, J. R.; Mangelson, N. F. Solid Compound Formation in the CCl₄ Mixtures of p-Dioxane with CCl₄, CBrCl₃, and CFCl₃. Solid-Liquid Phase Equilibria in Binary and CFCl₃ Systems. *J. Chem. Eng. Data* **1964**, *9* (2), 203–206.
- (30) Dohnal, V.; Patterson, D. Excess Molar Enthalpies of {1,1,2-Trichlorotrifluoroethane (Freon 113) + an Oxygenated Solvent or a Hydrocarbon}. *J. Chem. Thermodyn.* **1989**, *21*, 727–730.
- (31) Kamiaka, T.; Dang, C.; Hihara, E. Vapor-Liquid Equilibrium Measurements for Binary Mixtures of R1234yf with R32, R125, and R134a. *Int. J. Refrig.* **2013**, *36* (3), 965–971.
- (32) Wu, H. S.; Sandler, S. I. Use of ab Initio Quantum Mechanics Calculations in Group Contribution Methods: 1. Theory and the Basis for Group Identifications. *Ind. Eng. Chem. Res.* **1991**, *30*, 881–889.
- (33) Wittig, R.; Lohmann, J.; Gmehling, J. Prediction of Phase Equilibria and Excess Properties for Systems with Sulfones. *AIChE J.* **2003**, *49* (2), 530–537.
- (34) Jackowski, A. W. Vapor-Liquid Equilibria in Binaries Composed of Methanol, Methanethiol, and 2-Thiapropane. *Polym. J. Chem.* **1980**, *54*, 1765–1773.
- (35) Philippe, R.; Ferhat-Hamida, Z. *Int. Data Series Sel. Data Mixtures Ser. A* **1977**, *2*, 116–137.
- (36) Gmehling, J. Letter to the editor: About “New Modified UNIFAC Parameters Using Critically Evaluated Phase Equilibrium Data” by Jeong Won Kang, Vladimir Diki, Michael Frenkel. *Fluid Phase Equilib.* **2015**, *388*, 128–141.
- (37) Sapei, E.; Uusi-Kyyny, P.; Keskinen, K. I.; Pokki, J.-P.; Alopaeus, V. Phase Equilibria for Systems Containing Dimethyl Disulfide and Diethyl Disulfide with Hydrocarbons at 368.15 K. *Fluid Phase Equilib.* **2010**, *293* (2), 175–181.
- (38) Uusi-Kyyny, P.; Sapei, E.; Pokki, J.-P.; Pakkanen, M.; Alopaeus, V. Vapor-Liquid Equilibrium for Dimethyl Disulfide + Butane, + trans-But-2-ene, + 2-Methylpropane, + 2-Methylpropene, + Ethanol, and 2-Ethoxy-2-methylpropane. *J. Chem. Eng. Data* **2011**, *56* (5), 2501–2510.
- (39) Kortuem, G.; Valent, V. Thermodynamische Mischungseffekte der Systeme Wasser (1)-1,4-Dioxan (2) und Methanol (1)-1,4-Dioxan (2); ein Vergleich. *Ber. Bunsen-Ges. Phys. Chem.* **1977**, *81* (8), 752–761.
- (40) Hector, T.; Gmehling, J. Present Status of the Modified UNIFAC Model for the Prediction of Phase Equilibria and Excess Enthalpies for Systems with Ionic Liquids. *Fluid Phase Equilib.* **2014**, *371*, 82–92.
- (41) Rarey, J. Private communication.
- (42) Gmehling, J.; Constantinescu, D.; Schmid, B. Group Contribution Methods for Phase Equilibrium Calculations. *Annu. Rev. Chem. Biomol. Eng.* **2015**, *6*, 267–292.
- (43) Peper, S.; Dohrn, R.; Konejung, K. Methods for the Prediction of Thermophysical Properties of Polyurethane Raw Material Mixtures. *Fluid Phase Equilib.* **2016**, *10.1016/j.fluid.2015.12.020*.
- (44) Grensemann, H.; Gmehling, J. Performance of a Conductor-Like Screening Model for Real Solvents Model in Comparison to Classical Group Contribution Methods. *Ind. Eng. Chem. Res.* **2005**, *44*, 1610–1624.
- (45) Mu, T.; Rarey, J.; Gmehling, J. Group Contribution Prediction of Surface Charge Density Profiles for COSMO-RS(OI). *AIChE J.* **2007**, *53* (3), 3231–3240.
- (46) Constantinescu, D.; Rarey, J.; Gmehling, J. Application of COSMO-RS Type Models to the Prediction of Excess Enthalpies. *Ind. Eng. Chem. Res.* **2009**, *48*, 8710–8725.
- (47) Xue, Z.; Mu, T.; Gmehling, J. Comparison of the a Priori COSMO-RS Models and Group Contribution Methods: Original UNIFAC, Modified UNIFAC(Do), and Modified UNIFAC(Do). *Ind. Eng. Chem. Res.* **2012**, *51*, 11809–11817.