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Status and results of group contribution methods

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Abstract - Group contribution methods, such as UNIFAC or ASOG can be successfully applied to the prediction of the real behavior of non - electrolyte mixtures. Therefore these methods are used worldwide in the different process simulators for the synthesis and design of separation processes. Since the well known group contribution methods still show some weaknesses a modified version of the UNIFAC method has been developed. Furthermore the solution of groups concept has been applied to equations of state. This allows the simultaneous description of sub and supercritical compounds and at the same time the prediction of other important properties, such as densities, enthalpies, etc. .

INTRODUCTION

The knowledge of the real behavior of fluid mixtures plays an important role in different fields of application, such as for the synthesis, design and optimization of separation processes, the selection of selective solvents for extractive distillation, extraction and absorption, the calculation of chemical equilibrium compositions, the estimation of flash points of flammable liquid mixtures, etc. . For the description of the real behavior of non - electrolyte mixtures equations of state or g^E - models can be used. Both permit the behavior of multicomponent systems to be calculated using binary data alone.
When no experimental data are available, group contribution methods can be applied. For fitting reliable group interaction parameters a comprehensive data base is required. This was the reason for which the Dortmund Data Bank (DDB) was started in 1973. Today the Dortmund Data Bank contains, besides the required pure component properties, the most important mixture data in unified, evaluated and computer readable form. With the help of this data bank different well known group contribution methods, such as UNIFAC (ref. 1), ASOG (ref. 2), modified UNIFAC (ref. 3, 4) and PSRK (Predictive Soave - Redlich - Kwong equation of state) (ref. 5) have been developed in our group, partly in collaboration with other research groups.

MODIFIED UNIFAC METHOD

Although the UNIFAC or ASOG method is used worldwide, both methods still show some weaknesses, such as poor results for activity coefficients at infinite dilution (γ^∞) or excess enthalpies (h^E) and systems with compounds very different in size. This is not surprising, since the data base (nearly only VLE data) used for fitting the interaction parameters of these methods only covered a limited concentration range (5 - 95 %) and mostly compounds of similar size. Furthermore no quantitative information about the temperature dependence was used.
To eliminate most of the above mentioned weaknesses a modified UNIFAC method has been developed (ref. 3, 4). In the modified UNIFAC method the combinatorial part has been slight-

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ly changed, new main groups have been defined and at the same time temperature dependent parameters were introduced :

$$A_{nm} = a_{nm} + b_{nm} T + c_{nm} T^2 \qquad (1)$$

$$\Psi_{nm} = \exp (- A_{nm}/T) \qquad (1a)$$

To obtain reliable results the parameters (a_{nm}, b_{nm}, c_{nm}) have been fitted simultaneously to different thermodynamic properties using a very large data base. Besides experimental vapor - liquid equilibrium (VLE) data heats of mixing data and activity coefficients at infinite dilution were also included in the data base. In a few cases liquid - liquid equilibrium data (LLE) and excess heat capacities c_P^E data have also been taken into account.

All the required pure component and mixture data were taken directly from the Dortmund Data Bank (DDB)(ref. 6). The present status of the Dortmund Data Bank is given in Table 1.

TABLE 1. Current status of the Dortmund Data Bank (DDB)

Pure component properties for approximately 3200 compounds Mixture data from approximately 8000 references	Number of isotherms or isobars
Vapor - Liquid Equilibria	14700
Liquid - Liquid Equilibria	6600
Heats of Mixing	8500
Activity Coefficients at Infinite Dilution	29000 values
Gas Solubilities	5800
Excess Heat Capacities	650
Azeotropic Data	32500 values
Solid - Liquid Equilibria	1100
integrated:	
Vapor - Liquid Equilibria for Low Boiling Substances	8200 (ref. 7)

For fitting the required group interaction parameters the Simplex - Nelder - Mead algorithm in combination with the Marquardt method has been used to minimize the following objective function F:

$$F (a_{nm}, b_{nm}, c_{nm}, R_k, Q_k) = \Sigma \Delta VLE + \Sigma \Delta\gamma^{\infty} + \Sigma \Delta h^E + \Sigma \Delta c_P^E + \Sigma \Delta LLE \stackrel{!}{=} \min \qquad (2)$$

For one group pair often more than 3000 experimental data points were used. The contribution of the different data types to the objective function was influenced by using weighting factors.

Today the modified UNIFAC parameter matrix is of similar size (ref. 4) as the one for UNIFAC (ref. 1). A comparison of the results of the different group contribution methods shows in most cases advantages for the modified UNIFAC method. This is illustrated in the following Tables and Figures.

In Table 2 the calculated mean deviations in vapor phase mole fraction, temperature and pressure for 2200 thermodynamically consistent isothermal or isobaric VLE data sets are given together with the deviations obtained by a direct fit of the VLE data using the UNIQUAC method. From the deviations between direct fit and prediction it can be seen that the error is reduced by nearly a factor of 2.5 for all three quantities when modified UNIFAC instead of UNIFAC is used.

TABLE 2. Mean deviations between experimental and predicted and fitted binary VLE - data
(data base: 2200 consistent isothermal or isobaric data sets)

group contribution method	Δy	ΔT [K]	ΔP [mm Hg]
UNIFAC	0.0141	1.06	12.56
modified UNIFAC	0.0088	0.68	6.55
UNIQUAC	0.0058	0.42	4.14

Similar improvements are obtained for heats of mixing data or activity coefficients at infinite dilution. Table 3 shows a comparison of the mean deviations calculated by UNIFAC and modified UNIFAC for 6000 isothermal heats of mixing data sets and 14000 γ^{∞} values. Again it can be seen that the deviations obtained by modified UNIFAC are at least a factor of two smaller than the results of the original UNIFAC method.

TABLE 3. Mean deviations between experimental and predicted binary h^E and γ^{∞} data.
(data base : a) h^E: 6000 isothermal data sets; b) γ^{∞}: 14000 data points)

group contribution method	Δh^E [J/mol]	Δh^E_{rel}* [%]	$\Delta\gamma^{\infty}$**	$\Delta\gamma^{\infty}_{rel}$ ** [%]
UNIFAC	335.0	88.8	2.09	28.15
modified UNIFAC	103.8	30.0	1.06	15.56

* $\Delta h^E_{rel} = |(h^E_{exp} - h^E_{calc})/h^E_{exp,max}| \cdot 100$ [%] ** exp. γ^{∞} values < 100

Fig. 1 shows experimental and predicted azeotropic points for different alcohol - benzene systems in the temperature range 273 to 373 K. The knowledge of these data is of special importance during the synthesis and the design of rectification columns. As can be seen, good agreement is obtained again, which means that the modified UNIFAC method can be used as an important and reliable tool for process synthesis.

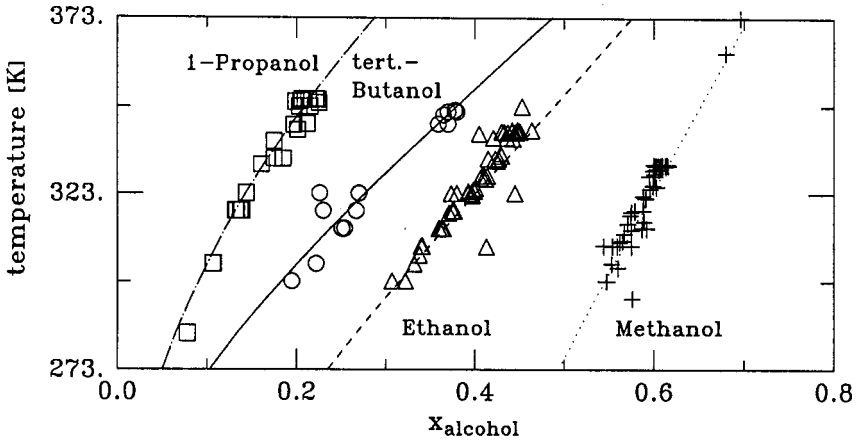

Fig. 1 Experimental and predicted azeotropic data for different alcohol - benzene systems

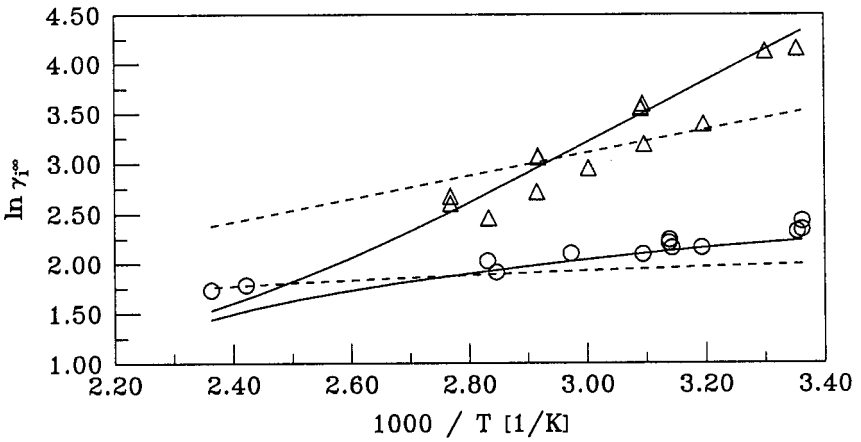

Fig. 2 Experimental and predicted γ^{∞} - values for the system ethanol - cyclohexane
(experimental: o γ^{∞} of cyclohexane, Δ γ^{∞} of ethanol)
(prediction : - - - - UNIFAC, ——— modified UNIFAC)

In Fig. 2 the experimental and predicted logarithms of the activity coefficients at infinite dilution for the system ethanol - cyclohexane (important for ethanol dehydration) are given as a function of temperature (1/T). Clearly it can be recognized that in contrast to UNIFAC the modified UNIFAC method predicts the correct temperature dependence. That is not only true at low temperatures but also at approximately 423 K, where by accident original UNIFAC shows a better agreement with the experimental data. However, from the reliable description of the temperature dependence the h^E data (see Fig. 4) it can be concluded that the reported experimental γ^{∞} - values for cyclohexane in ethanol at this temperature are too high.

Only in a few cases have LLE data been used to fit the required group interaction parameters. With the improved description of the temperature dependence a better description of the LLE behavior as function of temperature should be obtained. Fig. 3 shows experimental LLE data together with the predicted results using the original and the modified UNIFAC method for different methanol - alkane systems (not included in the data base). Although the modified UNIFAC method is not able to describe the flat behavior near the upper critical point the improved prediction is obvious, in particular when compared with the results of the original UNIFAC method.

With the objective to describe the real behavior over the whole concentration and temperature ranges all available information from the Dortmund Data Bank has been used for fitting reliable parameters. The most important information about the temperature dependence is provided by heats of mixing data. Although a lot of data are available (see Table 1), unfortunately most of the authors have measured their h^E data between 283 and 323 K (> 95 % of all data sets). This means that although h^E data are much better described using modified UNIFAC (see Table 3), because of the often limited temperature range of the h^E data base, extrapolations to temperatures not covered by the data base (typically 273 - 398 K) can still lead to erroneous results. Fig. 4 illustrates this situation with the help of experimental and predicted h^E data for the system ethanol - cyclohexane. When the group interaction parameters between the cyclic alkane and the alcohol group were fitted first, only h^E data were available between 283 and 318 K (case a). Later on, using an isothermal flow calorimeter h^E measurements at 363 K and 416 K were performed and the data obtained were added to the data base for refitting the parameters.

In Fig. 4 the resulting parameters (data base: VLE, h^E, γ^{∞}) together with the predicted h^E results using the different data bases are shown. It is obvious that with a limited h^E data base (case a) the results at higher temperatures are very poor. Using the h^E data measured at 363

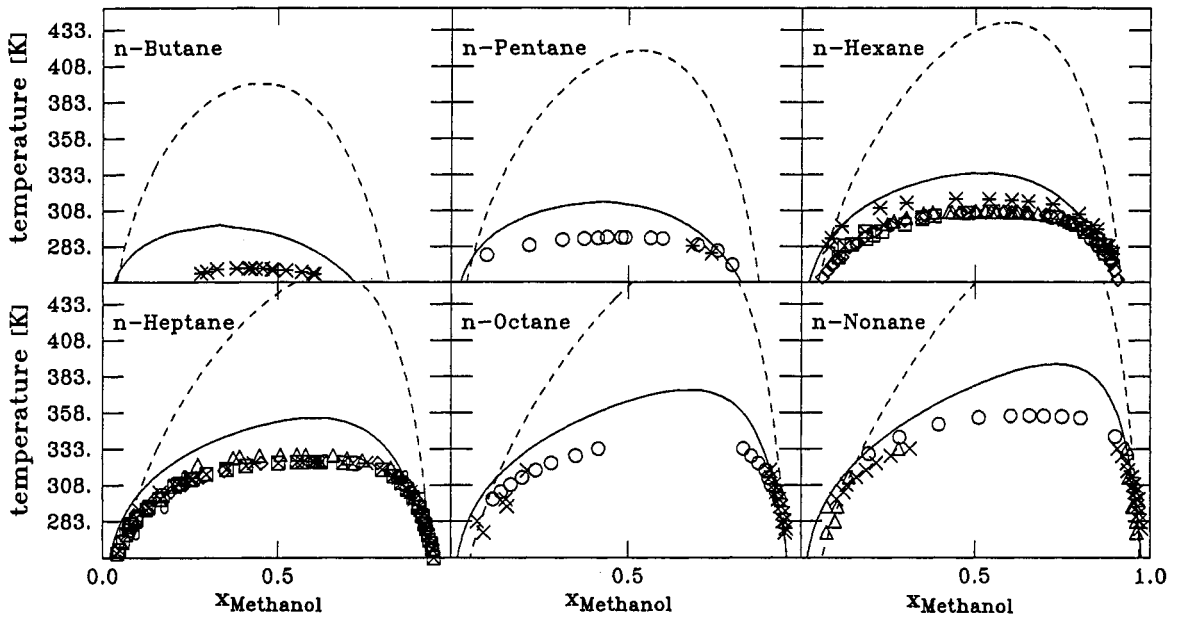

Fig. 3 Experimental and predicted liquid - liquid equilibrium data for different methanol - n - alkane systems – – – UNIFAC, ——— modified UNIFAC

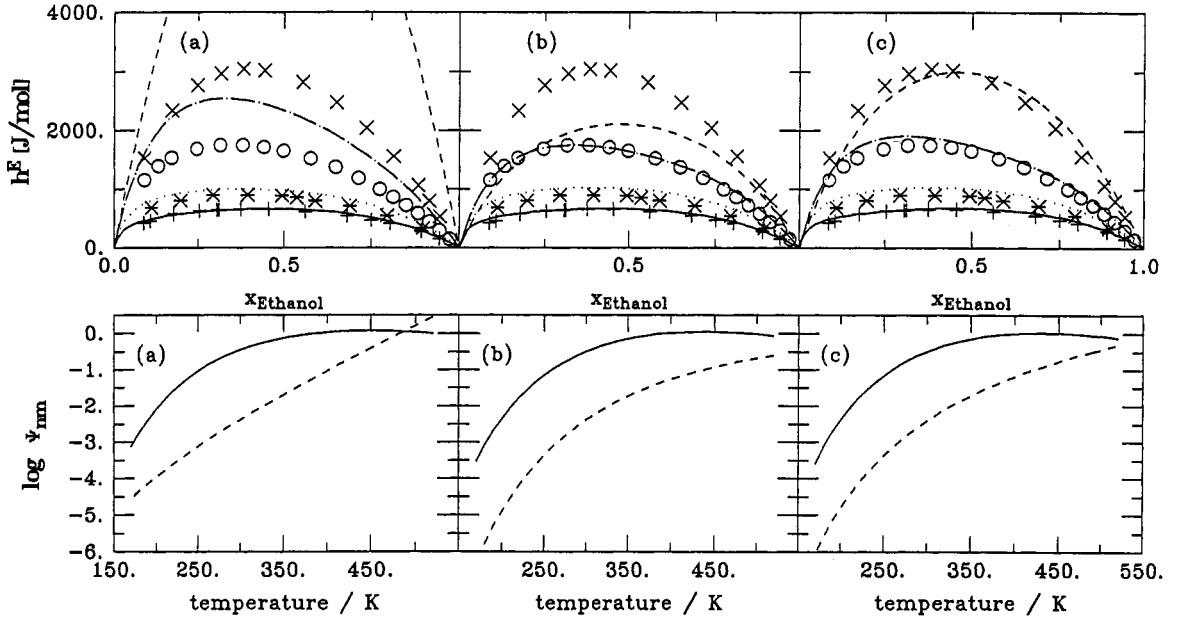

Fig. 4 Group interaction parameters Ψ_{nm} (——— Ψ OH - cycl. CH2, – – – – Ψ cycl. CH2 - OH) obtained from different data bases together with experimental and predicted excess enthalpy data for the system ethanol - cyclohexane at 298 K (+ ———), 318 K (* ·····), 363 K (o –·–·–) and 416 K (x - - - -).

K the results are much better at 363 K but still not good enough at 416 K (case b). Including also the new experimental h^E data at 416 K (case c) satisfying results are obtained for the whole temperature range, whereby it has to be mentioned that the results for VLE and γ^∞ were not worsened.

PSRK MODEL

As already mentioned before, equations of state show different advantages when compared with g^E - models, since because no standard fugacity is required this method can directly be applied to systems with supercritical compounds. At the same time other properties, such as densities, enthalpies, etc. can be calculated directly.

On the other hand use of equations of state with the classical quadratic mixing rules gave only poor results for systems with polar compounds. With the development of the so - called g^E - mixing rules (ref. 9) now a procedure is available which can successfully be applied for strongly polar systems, not only as a correlative but also as a predictive method. In the latter case instead of a g^E - model such as Wilson, NRTL or UNIQUAC, the required excess Gibbs energy is predicted with the help of a group contribution method (ref. 5 , 10).

The direct use of group contribution methods including the already available parameters in so - called g^E - mixing rules (ref. 9) for equations of state is the consequent extension of the solution of groups concept (ref. 10). Different methods have been suggested (e.g. MHV2 (ref. 11), PSRK (ref. 5)). In both methods the zero pressure reference state is used. This reference state in contrast to the infinite pressure reference state has the great advantage that the already available parameters of group contribution methods can be used.

In the PSRK model the Soave - Redlich - Kwong equation of state (ref. 12) plus Mathias - Copeman expression (ref. 13) is used together with the group contribution method UNIFAC. To extend the range of application to supercritical compounds new parameters for supercritical compounds, such as CO_2, CH_4, N_2, H_2S, H_2 and CO were added to the existing parameter table (ref. 5). With these parameters the predicted excess Gibbs energy for the given composition can be used to obtain the required parameter a for the chosen cubic equation of state following eq. 3. The pure component parameters a_{ii} and b_i can be obtained from critical data and the parameter b using the normal mixing rules.

$$a = b \left[\frac{g^E}{A_1} + \Sigma x_i \frac{a_{ii}}{b_i} + \frac{RT}{A_1} \Sigma x_i \ln \frac{b}{b_i} \right] \quad m^6\,Pa\,/\,mol^2 \qquad (3)$$

$$b = \Sigma x_i b_i \quad m^3\,/\,mol \qquad A_1 = -0.64663$$

Fig. 5 and 6 show typical results of this procedure. In Fig. 5 the original UNIFAC parameters (ref. 1) were used to predict the VLE behavior for the system ethanol - water in the temperature range 473 to 623 K. For all temperatures the agreement between experiment and prediction is satisfying.

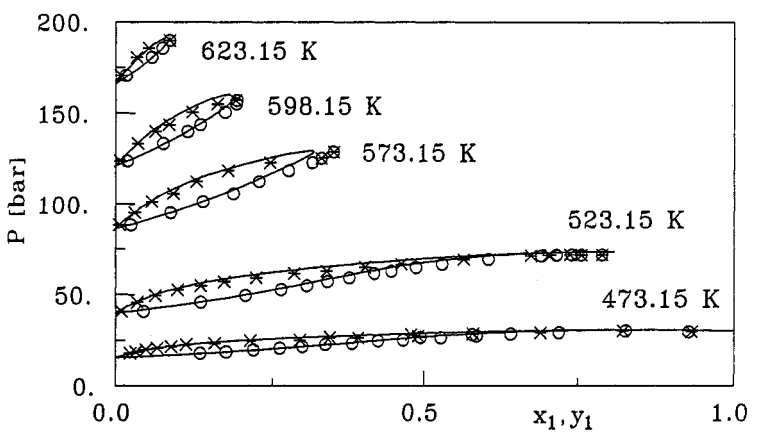

Fig. 5 Experimental and predicted VLE data for the system ethanol(1) - water(2) in the temperature range 473 to 623 K.

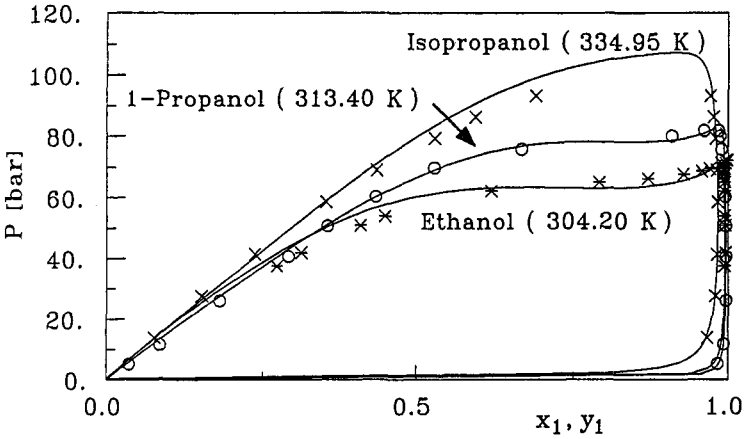

Fig. 6 Experimental and predicted VLE data for different CO_2 - alcohol (ethanol, 1 - propanol, 2 - propanol) systems

For the VLE results given in Fig. 6 for three CO_2 - alcohol systems new group interaction parameters had to be fitted, which describe the interaction between CO_2 and alkanes respectively alcohols. As data, besides high pressure VLE data, gas solubilities for CO_2 - alcohol systems were also used.

CONCLUSIONS

Because of the large parameter matrix and the reliable results obtained for VLE, group contribution methods such as ASOG or UNIFAC have become important tools for the synthesis, design and optimization of separation processes and other applications. Using the modified UNIFAC method much better results are obtained for VLE, LLE, h^E, γ^∞, etc. . However extrapolations to lower or higher temperatures can lead to erroneous results. This situation can only be improved in the future by including experimental information about the real behavior of non - electrolyte systems at low and high temperatures, including solid - liquid equilibria and h^E data at high temperatures (> 398 K). This experimental work is in progress in our research group, but because of the large number of data required the experimental work can not be completed by one group. For a systematic study, help of other research groups would be desirable.

With the development of group contribution equations of state, an ideal way is available in the near future, since this method allows the prediction of not only phase equilibria, but also other properties such as densities, enthalpies, etc. . At the same time it can be applied to systems with supercritical compounds.

Acknowledgement

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SYMBOLS

a_{nm}, b_{nm}, c_{nm}, A_{nm}	group interaction parameters
a, b, a_{ii}, b_i	parameters used in the Soave - Redlich - Kwong equation of state
c_p^E	excess heat capacity
g^E	molar excess Gibbs energy
h^E	molar excess enthalpy
Q_k, R_k	relative van der Waals properties
γ^∞	activity coefficient at infinite dilution
R	general gas constant
T	absolute temperature
x_i	mole fraction of component i in the liquid phase
y_i	mole fraction of component i in the vapor phase

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