

S-GTASQUAC – A Group Contribution Method Based on a New Version of the *quasi*-Chemical Theory

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Summary. In this paper, a group contribution method based on a new *quasi*-chemical method (S-GTASQUAC) is introduced. This group contribution method has a precise physical back-ground and works with small number of model parameters for the description of excess functions. The group interaction parameters were determined for a collection of groups. On the basis of these parameters, the phase equilibria, enthalpies of mixing, and γ_{∞} -values of mixtures containing aliphatic, aromatic, and cyclic hydrocarbons, nitriles, and ketones can be calculated. The potency of S-GTASQUAC was tested by comparing its results with those of the models UNIFAC and mod. UNIFAC (Dortmund).

Keywords. Group contribution method; VLE data; Thermodynamic excess functions; *quasi*-Chemical method; Thermodynamics of mixtures.

S-GTASQUAC – Eine auf einer neuen Version der *quasi*-chemischen Theorie basierende Gruppenbeitragsmethode

Zusammenfassung. In dieser Arbeit wird eine Gruppenbeitragsmethode auf der Basis einer neuen Version der *quasi*-chemischen Methode vorgestellt. Diese Gruppenbeitragsmethode hat eine präzise physikalische Basis und benötigt nur eine geringe Zahl von Modellparametern für die Beschreibung der Exzess-Funktionen. Für eine Reihe von Gruppen wurden die Gruppen-Wechselwirkungsparameter bestimmt. Mit diesen Parametern lassen sich die Phasengleichgewichte, Mischungsenthalpien und γ_{∞} -Werte von Mischungen mit aliphatischen, aromatischen und cyclischen Kohlenwasserstoffen, Nitrilen und Ketonen berechnen. Die Leistungsfähigkeit der Gruppenbeitragsmethode S-GTASQUAC wurde durch Vergleich ihrer Ergebnisse mit jenen der UNIFAC- und mod. UNIFAC Modelle (Dortmund) getestet.

Introduction

Group contribution methods for the calculation of the excess *Gibbs* free energy of a liquid mixture are particularly attractive, because they allow to predict properties of mixtures for which no experimental data exists. The concept that a chemical molecule is an aggregate of functional groups was first proposed in thermochemistry

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for the correlation and prediction of heats of formation of molecules. Its extension to mixtures is based on the assumption that a mixture of individual chemical compounds can be treated with reasonable accuracy as a mixture of functional groups constituting these compounds. Instead of parameters characterizing binary interactions between chemical compounds, a smaller number of parameters characterizing the binary interactions between functional groups is frequently used. The number of functional groups is much smaller than the number of chemical compounds; therefore, thousands of liquid mixtures can be described using a few dozen functional groups.

A fundamental assumption is the additivity of contributions, i.e. a contribution from one group is assumed to be independent of those exerted by any other group within a molecule.

Theory

In a previous paper, we presented the S-TASQUAC model which is based on a new version of the *quasi*-chemical theory [1, 2]. It has been shown that S-TASQUAC is particularly suited for the calculation and prediction of phase equilibria from binary information for mixtures of organic compounds. The S-TASQUAC formalism also allows the development of a group contribution method.

In principle, a mixture of functional groups is treated with the same thermodynamic models as a mixture of components. It must then be taken into account that the pure compounds also represent mixtures of groups. The excess functions are obtained by taking the difference between the mixing part and the pure component part, because hetero-contacts between different groups can occur within a pure component. Then the enthalpy of mixing ΔH^E and the excess *Gibbs* free energy ΔG^E are calculated using the following general expression (solution of groups – concept by *Wilson*):

$$\Delta X^E = \Delta X_G^{E,M} - \sum_K x_K \cdot \Delta X_G^{E,P} \quad (1)$$

(M: mixture, P: pure compound, G: group), and the chemical potential is determined according to Ref. [3] where v_G^K is the number of groups of type G in component K:

$$\Delta \mu_K^E = \sum_G v_G^K \cdot (\mu_G^{E,M} - \mu_G^{E,P}) \quad (2)$$

From Eqs. (1) and (2) and on the basis of the model equations of S-TASQUAC [1, 2], the new expressions of excess functions of S-GTASQUAC can be derived as

$$\begin{aligned} \Delta H^E = & \bar{Z} \cdot N \cdot \sum_{\alpha\beta} \left(X^{\alpha\beta} + \sum_{\gamma\delta} \left(X_{\gamma\delta}^{\alpha\beta} \cdot (\eta_{\gamma\delta}^G - 1) \right. \right. \\ & \left. \left. + \frac{1}{2} \cdot \sum_{\varepsilon\zeta} X_{\gamma\delta,\varepsilon\zeta}^{\alpha\beta} \cdot (\eta_{\gamma\delta}^G - 1) \cdot (\eta_{\varepsilon\zeta}^G - 1) \right) \right)^M \cdot \Delta h_{\alpha\beta} \\ & - \sum_K \left(x_K \cdot Z_K \cdot N \cdot \sum_{\alpha\beta} \left(X^{\alpha\beta} + \sum_{\gamma\delta} \left(X_{\gamma\delta}^{\alpha\beta} \cdot (\eta_{\gamma\delta}^G - 1) \right. \right. \right. \\ & \left. \left. \left. + \frac{1}{2} \cdot \sum_{\varepsilon\zeta} X_{\gamma\delta,\varepsilon\zeta}^{\alpha\beta} \cdot (\eta_{\gamma\delta}^G - 1) \cdot (\eta_{\varepsilon\zeta}^G - 1) \right) \right) \right)^P \cdot \Delta h_{\alpha\beta} \quad (3) \end{aligned}$$

$$\begin{aligned}
\Delta G^E = & \bar{Z} \cdot N \cdot \sum_{\alpha\beta} \left(X^{\alpha\beta} \cdot (\Delta h_{\alpha\beta} - T \cdot \Delta s_{\alpha\beta}) \right. \\
& + \sum_{\gamma\delta} \left(X_{\gamma\delta}^{\alpha\beta} \cdot (\Delta h_{\alpha\beta} \cdot \Theta_{\gamma\delta}^G - T \cdot \Delta s_{\alpha\beta} \cdot \sigma_{\gamma\delta}) \right. \\
& \left. \left. + \frac{1}{2} \cdot \sum_{\varepsilon\zeta} X_{\gamma\delta,\varepsilon\zeta}^{\alpha\beta} \cdot (\Delta h_{\alpha\beta} \cdot \Theta_{\gamma\delta,\varepsilon\zeta}^G - T \cdot \Delta s_{\alpha\beta} \cdot \sigma_{\gamma\delta,\varepsilon\zeta}) \right) \right)^M \\
& - \sum_K \left(x_K \cdot Z_K \cdot N \cdot \sum_{\alpha\beta} \left(X^{\alpha\beta} \cdot (\Delta h_{\alpha\beta} - T \cdot \Delta s_{\alpha\beta}) \right. \right. \\
& + \sum_{\gamma\delta} \left(X_{\gamma\delta}^{\alpha\beta} \cdot (\Delta h_{\alpha\beta} \cdot \Theta_{\gamma\delta}^G - T \cdot \Delta s_{\alpha\beta} \cdot \sigma_{\gamma\delta}) \right. \\
& \left. \left. + \frac{1}{2} \cdot \sum_{\varepsilon\zeta} X_{\gamma\delta,\varepsilon\zeta}^{\alpha\beta} \cdot (\Delta h_{\alpha\beta} \cdot \Theta_{\gamma\delta,\varepsilon\zeta}^G - T \cdot \Delta s_{\alpha\beta} \cdot \sigma_{\gamma\delta,\varepsilon\zeta}) \right) \right)^P \quad (4)
\end{aligned}$$

$$\begin{aligned}
\Delta \mu_K^E = & \sum_G v_G^K \cdot Z_G \cdot \sum_{\alpha\beta} \left({}_G Y^{\alpha\beta} \cdot (\Delta h_{\alpha\beta} - T \cdot \Delta s_{\alpha\beta}) \right. \\
& + \sum_{\gamma\delta} \left({}_G Y_{\gamma\delta}^{\alpha\beta} \cdot (\Delta h_{\alpha\beta} \cdot \Theta_{\gamma\delta}^G - T \cdot \Delta s_{\alpha\beta} \cdot \sigma_{\gamma\delta}) \right. \\
& \left. \left. + \frac{1}{2} \cdot \sum_{\varepsilon\zeta} {}_G Y_{\gamma\delta,\varepsilon\zeta}^{\alpha\beta} \cdot (\Delta h_{\alpha\beta} \cdot \Theta_{\gamma\delta,\varepsilon\zeta}^G - T \cdot \Delta s_{\alpha\beta} \cdot \sigma_{\gamma\delta,\varepsilon\zeta}) \right) \right)^M \\
& - \sum_G v_G^K \cdot Z_G \cdot \sum_{\alpha\beta} \left({}_G Y^{\alpha\beta} \cdot (\Delta h_{\alpha\beta} - T \cdot \Delta s_{\alpha\beta}) \right. \\
& + \sum_{\gamma\delta} \left({}_G Y_{\gamma\delta}^{\alpha\beta} \cdot (\Delta h_{\alpha\beta} \cdot \Theta_{\gamma\delta}^G - T \cdot \Delta s_{\alpha\beta} \cdot \sigma_{\gamma\delta}) \right. \\
& \left. \left. + \frac{1}{2} \cdot \sum_{\varepsilon\zeta} {}_G Y_{\gamma\delta,\varepsilon\zeta}^{\alpha\beta} \cdot (\Delta h_{\alpha\beta} \cdot \Theta_{\gamma\delta,\varepsilon\zeta}^G - T \cdot \Delta s_{\alpha\beta} \cdot \sigma_{\gamma\delta,\varepsilon\zeta}) \right) \right)^P \quad (5)
\end{aligned}$$

$$\gamma_K^{S\text{-GTASQUAC.res}} = \exp(\Delta \mu_K^E / k \cdot T) \quad (6)$$

The form of the concentration functions X and Y is preserved on the basis of groups and have been explained in detail in a previous paper [4, 5].

The mole fraction is therefore defined as

$$x_G = \frac{\sum_K N_K \cdot v_G^K}{\sum_G \sum_K (N_K \cdot v_G^K)} \quad (7)$$

$$x_G^K = \frac{v_G^K}{\sum_G v_G^K} \quad (8)$$

(x_G : mole fraction in the mixture, x_G^K : mole fraction in the pure component). Instead of mole fractions, coordination fractions were introduced to describe the asymmetrical course of mixing functions and to take into account the different sizes and shapes of components.

$$\kappa_G = \frac{Z_G \cdot x_G}{\sum_G Z_G \cdot x_G} \quad (9)$$

$$\kappa_G^K = \frac{Z_G \cdot x_G^K}{\sum_G Z_G \cdot x_G^K} \quad (10)$$

Z_G is the coordination number of a group and is calculated according to Eq. (11) where $A_{W,Bondi}$ is the surface area of groups determined by the *Bondi* method [6] (cf. Table 1).

$$Z_G = \frac{A_{W,Bondi}}{A_{WS}} \quad A_{WS} = 2.5 \cdot 10^8 \text{ cm}^2 \cdot \text{mol}^{-1} \quad (11)$$

Analogous to the S-TASQUAC model, the temperature functions Θ_{CD}^G and the entropy functions σ_{CD} are applied to functional groups:

$$\Theta_{\gamma\delta}^G = \frac{\eta_{\gamma\delta}^S \cdot (\eta_{\gamma\delta}^H - 1)}{\ln \eta_{\gamma\delta}^H} - 1 \quad (12)$$

$$\Theta_{\gamma\delta,\varepsilon\zeta}^G = \frac{\eta_{\gamma\delta}^S \cdot \eta_{\varepsilon\zeta}^S \cdot (\eta_{\gamma\delta}^H \cdot \eta_{\varepsilon\zeta}^H - 1)}{\ln(\eta_{\gamma\delta}^H \cdot \eta_{\varepsilon\zeta}^H)} - \frac{\eta_{\gamma\delta}^S \cdot (\eta_{\gamma\delta}^H - 1)}{\ln \eta_{\gamma\delta}^H} - \frac{\eta_{\varepsilon\zeta}^S \cdot (\eta_{\varepsilon\zeta}^H - 1)}{\ln \eta_{\varepsilon\zeta}^H} + 1 \quad (13)$$

$$\sigma_{\gamma\delta} = \frac{\eta_{\gamma\delta}^S - 1}{\ln \eta_{\gamma\delta}^S} - 1 \quad (14)$$

$$\sigma_{\gamma\delta,\varepsilon\zeta} = \frac{\eta_{\gamma\delta}^S \cdot \eta_{\varepsilon\zeta}^S - 1}{\ln(\eta_{\gamma\delta}^S \cdot \eta_{\varepsilon\zeta}^S)} - \frac{\eta_{\gamma\delta}^S - 1}{\ln \eta_{\gamma\delta}^S} - \frac{\eta_{\varepsilon\zeta}^S - 1}{\ln \eta_{\varepsilon\zeta}^S} + 1 \quad (15)$$

This method interprets the activity coefficient γ_K of a component K in a mixture as the sum of combinatorial (comb) and residual (res) contributions. The combinatorial (entropic) part represents the differences in size and shape of the molecules and is computed from pure-component properties, whereas the residual part (group interaction contribution) is due to intermolecular forces and is computed from the properties of the mixture.

$$\ln \gamma_K = \ln \gamma_K^{\text{comb}} + \ln \gamma_K^{\text{S-GTASQUAC,res}} \quad (16)$$

The combinatorial part is described by the Flory-Huggins expression including the *Kikic* modification [7] for the athermal entropy of mixing:

$$\ln \gamma_K^{\text{comb}} = \ln \left(\frac{\phi_K}{x_K} \right) + 1 - \frac{\phi_K}{x_K} \quad (17)$$

$$\text{with } \phi_K = \frac{r_K^{2/3} \cdot x_K}{\sum_L r_L^{2/3} \cdot x_L}, \quad r_K = \frac{V_{W,Bondi}}{V_{WS}}, \quad \text{and } V_{WS} = 15.17 \text{ cm}^3 \cdot \text{mol}^{-1} \quad (18)$$

Division of Groups

The number of groups is a result of a compromise. The number of functional groups must remain small but should not neglect significant effects of molecular structure on the mixture properties. To decrease the number of parameter fittings, one has to rely on the increment concept of the mod. UNIFAC model [8, 9] with the division of molecules in functional groups. An assortment of functional groups with corresponding volumes and surface areas as well as examples for the division into groups are summarized in Table 1.

Real System Calculations

For the determination of reliable group interaction parameters, the optimization of parameters must be carried out on a large data basis. This could be guaranteed by using the *Dortmunder Data Base* which includes many kinds of mixture data types (VLE, ΔH^E , γ_∞ , LLE, etc.) as well as a high number of systems and data sets.

The selection and compilation of a suitable data basis was carried out very thoroughly in order to acquire a reliable parameter matrix for the prediction of vapour-liquid equilibria, enthalpies of mixing, and infinite dilution activity coefficients. For this purpose, testing consistency was carried out by the VLE

Table 1. Volume and surface parameters for the S-GTASQUAC model

Main group	Subgroup	$V_W/\text{cm}^3 \cdot \text{mol}^{-1}$	$10^{-9} A_W/\text{cm}^2 \cdot \text{mol}^{-1}$	Examples	Increment concept
1 CH ₂	1 CH ₃	13.67	2.12	Hexane	2 CH ₃ , 4 CH ₂
	2 CH ₂	10.23	1.35	Octane	2 CH ₃ , 6 CH ₂
	3 CH	6.78	0.57	2-Methylpropane	3 CH ₃ , 1 CH
	4 C	3.33	0.00	Neopentane	4 CH ₃ , 1 C
3 ACH	9 ACH	8.06	1.00	Benzene	6 ACH
	10 AC	4.74	0.21	Styrene	1 CH ₂ =CH, 5 ACH, 1 AC
4 ACCH ₂	11 ACCH ₃	19.21	2.42	Toluene	5 ACH, 1 ACCH ₃
	12 ACCH ₂	15.77	1.65	Ethylbenzene	1 CH ₃ , 5 ACH, 1 ACCH ₂
	13 ACCH	12.32	0.87	Isopropylbenzene	2 CH ₃ , 5 ACH, 1 ACCH
9 CH ₂ CO	18 CH ₃ CO	25.37	3.72	2-Butanone	1 CH ₃ , 1 CH ₂ , 1 CH ₃ CO
	19 CH ₂ CO	21.93	2.95	3-Pentanone	2 CH ₃ , 1 CH ₂ , 1 CH ₂ CO
19 CCN	40 CH ₃ CN	28.37	4.31	Acetonitrile	1 CH ₃ CN
	41 CH ₂ CN	24.93	3.54	Propionitrile	1 CH ₃ , 1 CH ₂ CN
42 cyc-CH ₂	78 cyc-CH ₂	10.23	1.35	Cyclohexane	6 cyc-CH ₂
	79 cyc-CH	6.78	0.57	Methylcyclohexane	1 CH ₃ , 5 cyc-CH ₂ , 1 cyc-CH
	80 cyc-C	3.33	0.00	1,1-Dimethylcyclohexane	2 CH ₃ , 5 cyc-CH ₂ , 1 cyc-C

data reduction. Then, data sets which did not comply with the testing consistency were taken out. Enthalpies of mixing and infinite dilution activity coefficients were analyzed graphically. The temperature dependency of ΔH^E and γ_∞ was checked, and scattered values or non-plausible data sets were sorted out.

In the course of this work, the computer programs of the S-GTASQUAC model were integrated into the software of the *Dortmunder Data Base*. The selection of experimental data and the determination of group interchange parameters were carried out at the university of Oldenburg (Lehrstuhl fur Technische Chemie, group of Prof. J. Gmehling).

The group interaction parameters were obtained by minimizing the residual sum of squares [10] of VLE, ΔH^E and γ_∞ simultaneously. Here, the choice of the starting point has no influence on the result of adjustable parameters (W_i^p , W_j^h , $W_k^{\gamma_\infty}$ evaluation factors). The results are summarized in Table 2.

$$\begin{aligned} \min = & \sum_i \left(W_i^p \cdot (p_{\text{exp}} - p_{\text{calc}})^2 \right) + \sum_j \left(W_j^h \cdot (\Delta H_{\text{exp}}^E - \Delta H_{\text{calc}}^E)^2 \right) \\ & + \sum_k \left(W_k^{\gamma_\infty} \cdot (\gamma_{\text{exp}}^\infty - \gamma_{\text{calc}}^\infty)^2 \right) \end{aligned} \quad (19)$$

With these parameters, the deviation between experimental and calculated values for all group contribution methods can be determined in the same way:

$$\text{Mean } \delta X_{\text{abs}} = \frac{1}{N} \cdot \sum_{i=1}^N |X_{\text{calc}} - X_{\text{exp}}| \quad X = p, T, y, \gamma_\infty, \Delta H^E \quad (20)$$

$$\text{Mean } \delta X_{\text{rel}} = \frac{1}{N} \cdot \sum_{i=1}^N \left| \frac{X_{\text{calc}} - X_{\text{exp}}}{X_{\text{exp}}} \right| \quad X = p, T, y, \gamma_\infty \quad (21)$$

$$\text{Mean } \delta \Delta H_{\text{rel}}^E = \frac{1}{N} \cdot \sum_{i=1}^N \frac{|\Delta H_{\text{calc}}^E - \Delta H_{\text{exp}}^E|}{|\Delta H_{\text{exp}}^E|_{\text{max}}} \quad (22)$$

Table 2. Group interaction parameters for the S-GTASQUAC model

Main group 1	Main group 2	$\Delta h_{\alpha\beta} k^{-1}/\text{K}$	$10^3 \Delta s_{\alpha\beta} k^{-1}$
1 CH ₂	3 ACH	32.54	62.39
1 CH ₂	4 ACCH ₂	4.18	0.17
1 CH ₂	9 CH ₂ CO	263.15	569.81
1 CH ₂	19 CCN	66.84	32.41
1 CH ₂	42 cyc-CH ₂	2.95	6.28
3 ACH	4 ACCH ₂	42.29	107.79
3 ACH	9 CH ₂ CO	323.11	872.81
3 ACH	19 CCN	29.24	-26.61
3 ACH	42 cyc-CH ₂	23.71	37.06
4 ACCH ₂	9 CH ₂ CO	194.67	331.34
4 ACCH ₂	19 CCN	29.29	-37.99
4 ACCH ₂	42 cyc-CH ₂	17.59	41.54

Table 3. Description of $\delta\Delta H^E$ (%) of binary mixtures with the S-GTASQUAC model and comparison with other group contribution methods

Model	UNIFAC	UNIFACDO	S-GTASQUAC	N_i
CH ₂ ↔ACH	52	7	8	73
CH ₂ ↔ACCH ₂	45	14	15	93
CH ₂ ↔ <i>cyc</i> -CH ₂	77	109	78	294
CH ₂ ↔CH ₂ CO	29	5	20	102
CH ₂ ↔CCN	33	13	33	67
ACH↔ACCH ₂	126	22	28	74
ACH↔ <i>cyc</i> -CH ₂	50	4	10	96
ACH↔CH ₂ CO	92	125	79	15
ACH↔CCN	15	4	3	11
ACCH ₂ ↔ <i>cyc</i> -CH ₂	51	13	16	49
ACCH ₂ ↔CH ₂ CO	89	83	117	38
ACCH ₂ ↔CCN	55	12	19	26

Non-ideal behaviour in the gas phase was calculated employing the subroutines PHIS and BIJS taken from *Prausnitz et al.* [11].

The results of S-GTASQUAC were compared to those of other group contribution methods like UNIFAC [3] and mod. UNIFAC (Dortmund) [8, 9].

The UNIFAC model requires two temperature independent parameters ω_{AB} and ω_{BA} per group combination for the calculation of excess function. The following expression for the interchange energy is used for the mod. UNIFAC model.

$$\frac{\Delta\omega_{\alpha\beta}}{k} = \exp\left(-\frac{a_1 + a_2 \cdot T + a_3 \cdot T^2}{T}\right) \neq \frac{\Delta\omega_{\beta\alpha}}{k} \quad (23)$$

Consequently, six group interaction parameters per hetero-contact must be fitted, whereas S-GTASQUAC only requires two parameters ($\Delta h_{\alpha\beta}$ and $\Delta s_{\alpha\beta}$) for each group combination. Table 3 shows the results of $\delta\Delta H_{rel}^E$ for the three group contribution methods. The values for $\delta\gamma_\infty$, δy , δp , and δT are available on request from the corresponding author (cf. Ref. [1]).

Results and Discussion

With the exception of mixtures containing a CCN or CH₂CO group, the agreement between experimental and calculated data is good in the S-GTASQUAC model. In comparison to UNIFAC and mod. UNIFAC (Dortmund), S-GTASQUAC provided results of the same quality for groups with exclusive dispersion interactions for the description of vapour-liquid equilibria and enthalpies of mixing. This is significant, because mod. UNIFAC requires six parameters per group contact (S-GTASQUAC two parameters) and therefore is of a higher mathematical flexibility.

Infinite dilution activity coefficients were described only inadequately by all group contribution methods. The reason for this is the quality of experimental data. The agreement between the γ_∞ values at the same temperature is often not given by different authors, or there is only one γ_∞ value per system (cf. Fig. 1).

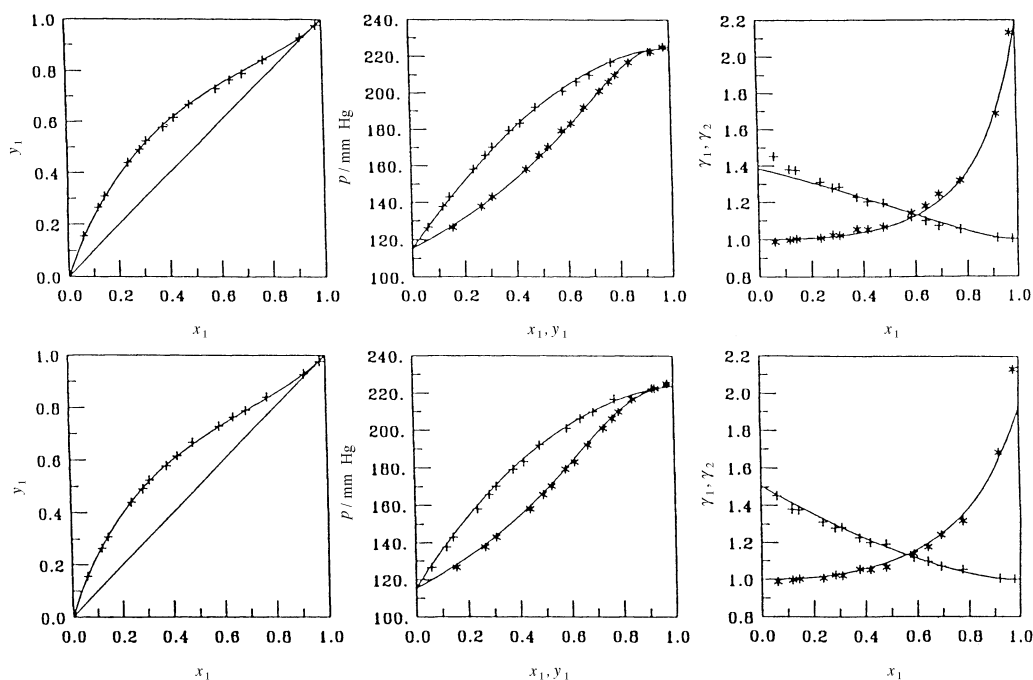


Fig. 1. Comparison of the results obtained from mod. UNIFAC (above) and S-GTASQUAC (below) with VLE data sets for the system benzene-heptane

There were clear differences with respect to the description of enthalpies of mixing. The UNIFAC model described the ΔH^E -values worse than mod. UNIFAC and S-GTASQUAC, because here enthalpies of mixing were not taken into account in the optimization of parameters. The mod. UNIFAC model is only superior to S-GTASQUAC for mixtures of alkanes with ketones and nitriles.

An explanation for the poor results of mixtures with ketones and nitriles might be the dipole moment of the compounds. This is not surprising, since the model assumptions are based on the *quasi*-chemical theory. The *quasi*-chemical model only takes into account interactions between the nearest neighbours. Dipole-dipole interactions are long-range interactions and therefore outside of assumption for a successful application of the *quasi*-chemical approximation. Therefore, the model equations of S-GTASQUAC must be extended by explicitly taking into account the dipole-dipole interactions for the calculation of interaction energy [12] (cf. Fig. 2).

Investigations directed to the prediction of thermodynamic properties of binary information are likewise interesting and important. Furthermore, the prediction of thermodynamic properties on the basis of binary information was investigated for five ternary systems. The respective thermodynamic excess functions were calculated as real predictions using parameters obtained from the fitting of binary experimental data (VLE , ΔH^E , γ_∞). These results were compared to those of the mod. UNIFAC model.

The benzene-heptane-acetonitrile system (see Table 4), with a strong deviation from ideal behaviour, can only be described insufficiently by the S-GTASQUAC

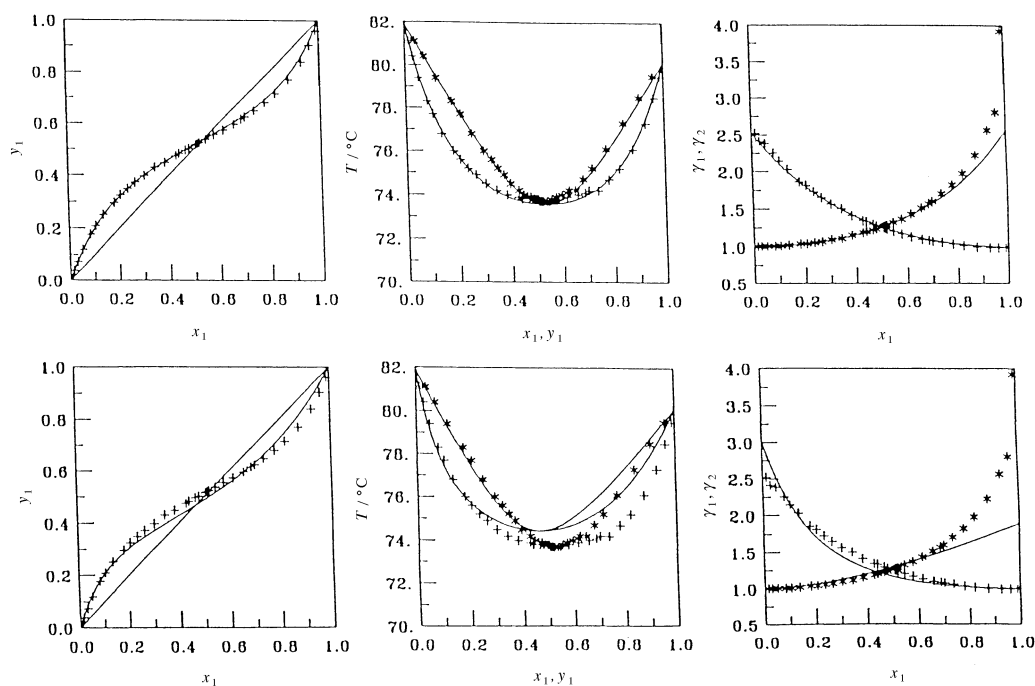


Fig. 2. Comparison of the results obtained from mod. UNIFAC (above) and S-GTASQUAC (below) with VLE data sets for the system benzene-acetonitrile

model. The problem of describing binary mixtures containing the CCN group has already been discussed. The poor result for this ternary mixtures is not surprising. For the other systems (see Tables 5–8), S-GTASQUAC provides results of the same quality as mod. UNIFAC. Superiority of one model cannot be established. This

Table 4. Description of VLE data of the system benzene-heptane-acetonitrile

Isobaric data							
Ref.	N_i	p/mmHg		S-GTASQUAC		mod. UNIFAC	
				δy	$\delta T/\text{K}$	δy	$\delta T/\text{K}$
[13]	36	760.00	Mean	0.0620	5.85	0.0082	0.91
			Max	0.2454	13.53	0.0226	1.84
Isothermal data							
Ref.	N_i	T/K		S-GTASQUAC		mod. UNIFAC	
				δy	$\delta p/\text{mmHg}$	δy	$\delta p/\text{mmHg}$
[14]	53	318.56	Mean	0.0671	50.27	0.0073	6.64
			Max	0.2963	147.80	0.3010	19.10

Table 5. Description of VLE data of the system benzene-cyclohexane-hexane

Isobaric data							
Ref.	N_i	p/mmHg		S-GTASQUAC		mod. UNIFAC	
				δy	$\delta T/\text{K}$	δy	$\delta T/\text{K}$
[15]	109	760.00	Mean	0.0056	0.26	0.0048	0.29
			Max	0.0365	2.19	0.0413	1.68
[16]	110	760.00	Mean	0.0050	0.23	0.0046	0.29
			Max	0.0343	2.18	0.0188	0.65
Isothermal data							
Ref.	N_i	T/K		S-GTASQUAC		mod. UNIFAC	
				δy	$\delta p/\text{mmHg}$	δy	$\delta p/\text{mmHg}$
[17]	10	283.15	Mean	0.0067	0.92	0.0037	0.34
			Max	0.0196	1.47	0.0084	1.50
[17]	10	288.15	Mean	0.0066	1.30	0.0041	0.29
			Max	0.0211	1.95	0.0113	0.94
[17]	12	298.15	Mean	0.0077	1.85	0.0042	0.35
			Max	0.0329	2.49	0.0234	0.81
[17]	6	343.15	Mean	0.0051	7.44	0.0033	1.18
			Max	0.0120	14.84	0.0075	1.76
[18]	24	343.15	Mean	0.0077	4.35	0.0047	7.52
			Max	0.0204	9.92	0.0169	11.65

Table 6. Description of VLE data of the system benzene-methylcyclopentane-hexane

Isobaric data							
Ref.	N_i	p/mmHg		S-GTASQUAC		mod. UNIFAC	
				δy	$\delta T/\text{K}$	δy	$\delta T/\text{K}$
[19]	54	760.00	Mean	0.0040	0.34	0.0045	0.16
			Max	0.0124	0.71	0.0252	0.47
Isothermal data							
Ref.	N_i	T/K		S-GTASQUAC		mod. UNIFAC	
				δy	$\delta p/\text{mmHg}$	δy	$\delta p/\text{mmHg}$
[20]	103	333.15	Mean	0.0038	3.02	0.0044	5.02
			Max	0.0383	8.70	0.0342	8.35

Table 7. Description of VLE data of the system cyclohexane-heptane-toluene

Isobaric data							
Ref.	N_i	p/mmHg		S-GTASQUAC		mod. UNIFAC	
				δy	$\delta T/\text{K}$	δy	$\delta T/\text{K}$
[21]	101	760.00	Mean	0.0041	0.30	0.0032	0.25
			Max	0.0148	0.62	0.0105	0.61
[22]	35	760.00	Mean	0.0037	0.21	0.0031	0.17
			Max	0.0124	0.45	0.0134	0.43

Isothermal data							
Ref.	N_i	T/K		S-GTASQUAC		mod. UNIFAC	
				δy	$\delta p/\text{mmHg}$	δy	$\delta p/\text{mmHg}$
[23]	16	298.15	Mean	0.0055	1.70	0.0050	1.13
			Max	0.0171	4.95	0.0145	3.90

Table 8. Description of isobaric VLE data of the system heptane-methylcyclohexane-toluene

Isobaric data							
Ref.	N_i	p/mmHg		S-GTASQUAC		mod. UNIFAC	
				δy	$\delta T/\text{K}$	δy	$\delta T/\text{K}$
[24]	78	760.00	Mean	0.0059	0.23	0.0056	0.25
			Max	0.0609	0.99	0.0703	1.36

result is interesting because mod. UNIFAC uses six parameters and S-GTASQUAC only two per group contact. Regardless of its higher mathematical flexibility, the group contribution method mod. UNIFAC cannot provide results which are better than those obtained with the new model. Further advantages of S-GTASQUAC are the physically meaningful group interchange parameters and the consistency of parameter sets for the description of multicomponent systems with only two parameters.

The software can be obtained from the corresponding author.

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List of symbols

a_1, a_2, a_3	interaction parameters of the mod. UNIFAC model
A_w	surface parameter
ΔG	<i>Gibbs</i> free energy

$\Delta g_{\alpha\beta}$	<i>Gibbs</i> free energy parameter for the S-GTASQUAC-model
ΔH	enthalpy
$\Delta h_{\alpha\beta}$	enthalpy parameter for the S-GTASQUAC-model
k	<i>Boltzmann</i> constant
N	total number of molecules
N_i	number of data points
N_K	number of molecules of type K
p	pressure
r	volume parameter
ΔS	entropy
$\Delta s_{\alpha\beta}$	entropy parameter for the S-GTASQUAC-model
T	temperature
V_W	volume parameter
ΔW	interchange energy
x	liquid-phase mole fraction
X	concentration function
y	vapour-phase mole fraction
Y	concentration function
Z_G	coordination number
\bar{Z}	mean coordination number
Θ^G	temperature function for the S-GTASQUAC-model
γ	activity coefficient
δ	deviation
$\eta^G = \exp\left(\frac{-2\cdot\Delta g_{\alpha\beta}}{k\cdot T}\right)$	interchange parameter (dimensionless) for the S-GTASQUAC-model
$\eta^H = \exp\left(\frac{-2\cdot\Delta h_{\alpha\beta}}{k\cdot T}\right)$	enthalpy parameter (dimensionless) for the S-GTASQUAC-model
$\eta^S = \exp\left(\frac{2\cdot\Delta s_{\alpha\beta}}{k}\right)$	entropy parameter (dimensionless) for the S-GTASQUAC-model
κ_G	coordination fraction of group G
μ_κ	chemical potential
ν	oscillation frequency
ν_G^K	number of type G groups in component K
ϕ	volume fraction
σ_{KL}	entropy function for the S-GTASQUAC-model
$\omega_{\alpha\beta}$	temperature dependent interaction parameter of the mod. UNIFAC model

References

- [1] Studte A (1996) Beschreibung und Vorhersage der thermodynamischen Eigenschaften von Nichtelektrolytgemischen mit dem S-TASQUAC/S-GTASQUAC Modell. Thesis, TU Braunschweig, Germany
- [2] Lacmann R, Studte A (1999) *Monatsh Chem* **130**: 485
- [3] Fredenslund A, Gmehling J, Rasmussen P (1977) *Vapour-Liquid Equilibria using UNIFAC*. Elsevier, Amsterdam
- [4] Brennecke D (1989) Modellierung des Phasengleichgewichtsverhaltens und der thermodynamischen Eigenschaften von Nichtelektrolytgemischen. Thesis, TU Braunschweig, Germany
- [5] Brennecke D, Lacmann R (1988) *Fluid Phase Equilibria* **43**: 57
- [6] Bondi A (1968) *Physical Properties of Molecular Crystals, Liquids and Glasses*. Wiley, New York, p 450
- [7] Kicic I, Alessi P, Rasmussen P, Fredenslund A (1980) *Can J Chem Eng* **58**: 253

- [8] Weidlich U (1985) Experimentelle und theoretische Untersuchungen zur Erweiterung der Gruppenbeitragsmethode UNIFAC. Thesis, Dortmund, Germany
- [9] Weidlich U, Gmehling J (1987) *Ind Eng Chem Res* **26**: 1372
- [10] Nelder JA, Mead R (1965) *Comp J* **7**: 308
- [11] Prausnitz JM, Grens EA, Eckert CA, Hsieh R, O'Connell JP (1980) *Computer Calculations for Multicomponent Vapour-Liquid and Liquid-Liquid Equilibria*. Prentice-Hall, New Jersey
- [12] Atkins PW (1994) *Physical Chemistry*, 5th edn. Oxford University Press, Oxford Melbourne Tokyo
- [13] Tripathi RP, Asselineau L (1975) *J Chem Eng Data* **20**: 33
- [14] Palmer DA, Smith DB (1972) *J Chem Eng Data* **17**: 71
- [15] Ridgway K, Butler PA (1967) *J Chem Eng Data* **12**: 509
- [16] Butler PA, Ridgway K (1967) *J Appl Chem* **17**: 191
- [17] Li ICP, Polak J, Lu BCY (1974) *J Chem Thermodyn* **6**: 417
- [18] Susarev MP, Chen ST (1963) *Z Fiz Khim* **37**: 1739
- [19] Belknap RC, Weber JH (1961) *J Chem Eng Data* **6**: 485
- [20] Beyer W, Schuberth H, Leibnitz E (1965) *J Prakt Chem* **27**: 276
- [21] Myers HS (1957) *AICHE J* **3**: 467
- [22] Black C (1959) *Ind Eng Chem* **51**: 211
- [23] Katayama T, Sung EK, Lightfoot EN (1965) *AICHE J* **11**: 924
- [24] Wisniak J, Tamir A (1977) *J Chem Eng Data* **22**: 391

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