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Prediction of Free Excess Enthalpy and Excess Enthalpy of Nonelectrolyte Mixtures with the Modified TASQUAC Model

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Summary. Using the known models for liquid mixtures (NRTL, UNIQUAC,...), the excess free enthalpy and the heats of mixing cannot be calculated simultaneously in good agreement with experimental data using only two parameters (or three for NRTL) per temperature and binary system. The excess enthalpy can be estimated only qualitatively but not quantitatively. There is also much doubt about the sign of the predicted H^E data if the absolute value of H^E is small [1]. In this work, we examined the possibilities of modified TASQUAC in simultaneous prediction of *VLE* and H^E data and the thermodynamic consistency of experimental data.

Keywords. *VLE* data; Mixing heat; Thermodynamic consistency; Lattice model.

Vorhersage von freier Exzessenthalpie und Exzessenthalpie von Nichtelektrolytmischungen mit Hilfe des modifizierten TASQUAC-Modells

Zusammenfassung. Mit Hilfe der bekannten Modelle für flüssige Mischungen (NRTL, UNIQUAC,...) können die freie Exzeßenthalpie und die Mischungswärme nicht gleichzeitig in guter Übereinstimmung mit experimentellen Daten berechnet werden. Die Exzeßenthalpie kann, ausgehend von Parametern, die aus *VLE*-Daten erhalten wurden, nur qualitativ, nicht quantitativ beschrieben werden. Weiterhin ist das berechnete Vorzeichen der Mischungswärme bei betraglich kleinen Werten der Exzeßenthalpie unsicher [1]. In dieser Arbeit werden die Möglichkeiten des modifizierten TASQUAC-Modells zur simultanen Beschreibung von *VLE*- und H^E-Daten untersucht sowie die thermodynamische Konsistenz der verwendeten Daten überprüft.

Introduction

Modified TASQUAC calculates the excess enthalpies ΔH^E and free excess enthalpies ΔG^E by summarizing the products of the number of hetero-contacts N_{AB} multiplied with the belonging interchange energy ΔW_{AB} (for details, see Refs. [2–6]).

$$\Delta H^E_{TASQUAC} = \bar{Z} \cdot N \cdot \sum_{AB} \left[X^{AB} + \sum_{CD} \left(X^{AB}_{CD} \cdot (\eta_{CD} - 1) + \frac{1}{2} \cdot \sum_{EF} X^{AB}_{CD,EF} \cdot (\eta_{CD} - 1) \cdot (\eta_{EF} - 1) \right) \right] \cdot \Delta W_{AB} \qquad 1$$

$$\begin{aligned}\Delta G^{E}_{TASQUAC} = \bar{Z}\cdot N\cdot\sum_{AB}\Bigg[& X^{AB}\cdot T\cdot\int_{0}^{1/T}\Delta W_{AB}\cdot\left(\frac{1}{T}\right)\\ & +\sum_{CD}\Bigg(X^{AB}_{CD}\cdot T\cdot\int_{0}^{1/T}(\eta_{CD}-1)\cdot\Delta W_{AB}\cdot d\left(\frac{1}{T}\right)\\ & +\frac{1}{2}\cdot\sum_{EF}X^{AB}_{CD,EF}\cdot T\cdot\int_{0}^{1/T}(\eta_{CD}-1)\cdot(\eta_{EF}-1)\cdot\Delta W_{AB}\cdot d\left(\frac{1}{T}\right)\Bigg)\Bigg]\end{aligned} \qquad 2$$

$$\left(\eta=\exp\left(-\frac{2\cdot\Delta W}{k\cdot T}\right),\ \bar{Z}=\sum_{L}Z_{L}\cdot x_{L},\ N=\sum_{L}n_{L}\cdot N_{Avogadro}=n_{tot}\cdot N_{Avogadro}\right)$$

For the description of the temperature dependence of the interchange parameter ΔW_{AB}, we used the two parameter form proposed in Ref. [7]:

$$\Delta W/k = a_1 + a_2\cdot\left(\frac{T_0}{T}-1\right).$$

a_1 and a_2 can be obtained by fitting *VLE*- and H^E data or other thermodynamic properties of binary systems.

Results and Discussion

Based on the mixing heat data sets listed in Tables 2a–9a, one parameter set a_1, a_2 is fitted to every binary system (see Table 1). For that purpose, the function

$$Min=\sum^{I}\frac{1}{N_I}\sqrt{\sum^{N_I}(H_{calc}-H_{exp})^2}$$

is minimized by the NAG-routine E04FDF. The quality of the calculated H^E data can be estimated with the help of the relative deviations.

$$\delta H=\sqrt{\frac{1}{N_I}\sum^{N_I}\left(\frac{H_{calc}-H_{exp}}{H_{exp}}\right)^2}\cdot 100.$$

In a previous paper [6], we have reported about the results of describing *VLE* data with modified TASQUAC. Table 1 shows a comparison of interchange energy parameters a_1, a_2 obtained from *VLE* respectively H^E data. In most cases there are considerable differences between the results. Therefore we tried to check the thermodynamic consistency of the data base. The correlation between excess free enthalpy and excess enthalpy is

$$\frac{\partial\dfrac{G^E}{T}}{\partial T}=-\frac{H^E}{T^2}.$$

The calculation of G^E from experimental data was carried out without taking real-gas corrections into account [6]. Experimental G^E and H^E data were interpolated with a *Redlich–Kister*-equation ($G^E = x_1\cdot x_2[A + B\cdot(x_1 - x_2) + C\cdot(x_1 - x_2)^2 + D\cdot(x_1 - x_2)^3]$) to the molefractions $x_1 = 0.2$, 0.4, 0.6 and 0.8. Starting from $G = H + T\cdot S = H_0 + \int c_p dT + T\cdot S = H_0 + \int(a + b\cdot T + cT^2)dT + T\cdot S$, the temperature dependence of G^E can be expressed as

$$\frac{G^E}{T}=\frac{H_0}{T}+a+\frac{1}{2}\cdot b\cdot T+\frac{1}{3}\cdot c\cdot T^2+S \quad \text{and} \quad H=-\left(-\frac{H_0}{T^2}+\frac{1}{2}\cdot b+\frac{2}{3}\cdot c\cdot T\right)\cdot T^2.$$

It was found that the H^E data calculated in this way are not in good agreement with experimental data. Only for the system benzene-cyclohexane (see Tables 5a–c) the thermodynamic consisty test yields an acceptable result. The increase (or decrease) of H^E with temperature can be calculated correctly from *VLE* data but the absolute values are quite different from experimental data. *Paul et al*, reported that they also could find only a qualitative correlation between their *VLE* and H^E data [8, 9]. We do not say that there is no consistency between experimental G^E and H^E data (altough we consider the results of the test as a valuable and interesting information) because of two reasons:

(i) in many cases the number of *VLE* data is quite small and
(ii) the temperature range of *VLE* data is small; therefore we cannot expect to calculate the correct temperature dependence of G^E.

An additional problem is the use of data sets from different authors.

For every isothermal data set there is one optimal interchanging parameter ΔW_{AB}. This parameter can be realized for a known temperature by many different combinations of a_1 and a_2. Therefore we obtain the picture of a ditch in a 3-dimensional graphic (Figs. 1, 2).

Taking more data sets into account, the absolute minimum results from the point of intersection of these ditches. In many cases these ditches run nearly parallel or in a small angle; there is no sharp minimum for a_1 and a_2 using only few data sets (*VLE* or H^E data only). Because of this reason it seems ingenious to extend the data base for a_1 and a_2 and to fit these parameters simultaneously to *VLE* and H^E data. To combine the deviations in pressure and mixing heat, we minimized the sum of the relative deviations:

$$Min=\sum_{i=1}^{M}\frac{1}{N_i}\sqrt{\sum_{j=1}^{N_i}\left(\frac{\theta_{calc}-\theta_{exp}}{\theta_{exp}}\right)^2} \qquad (\theta=P \text{ or } H^E).$$

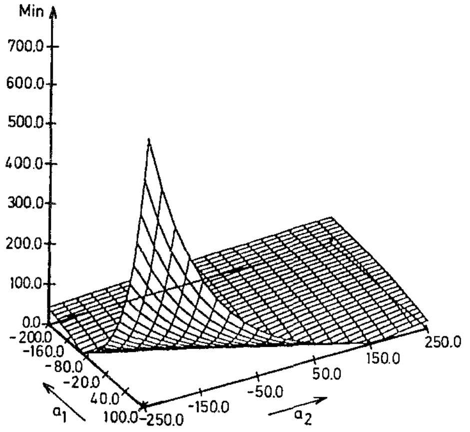

Fig. 1. Deviation of pressure as a function of a_1 and a_2; x-axis: a_1, y-axis: a_2, z-axis: mean relative deviation of pressure

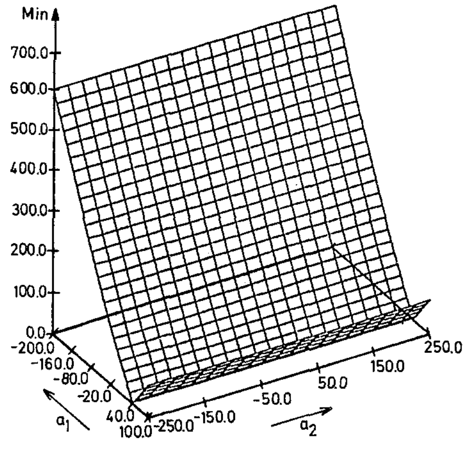

Fig. 2. Deviation of H^E as a function of a_1 and a_2; x-axis: a_1, y-axis: a_2, z-axis: mean relative deviation of mixing heat

Regardless of the number of data-points per set N_i the same weight was attributed to each data set in the optimizing procedure.

We must make some critical remarks of this fit. The dependence of the relative deviations as a function of a_1 and a_2 is not known for all examples. For the system

Table 1. Interchange parameters from different data sources

Component A	Component B	a_1, a_2 from *VLE* data		a_1, a_2 from H^E data		a_1, a_2 from *VLE* and H^E data	
		a_1 [K]	a_2 [K]	a_1 [K]	a_2 [K]	a_1 [K]	a_2 [K]
Chloroform	Tetrachloromethane	2.29	0.82	4.29	−73.25	4.30	4.68
Tetrachloromethane	Cyclohexane	1.46	0.17	2.55	2.82	2.49	2.58
Tetrachloromethane	Toluene	12.61	22.60	0.27	1.10	−0.08	−1.74
Benzene	Cyclohexane	14.58	17.47	13.95	17.84	13.68	14.58
Benzene	Aniline	31.58	39.07	14.59	28.50	13.97	10.13
Cyclohexane	Toluene	13.56	17.91	9.21	7.48	8.53	7.91
Cyclohexane	Chlorobenzene	8.54	6.69	11.90	14.54	11.11	13.15
Toluene	Aniline	28.54	31.50	17.63	75.99	16.54	18.34

Table 2a. Results for chloroform/tetrachloromethane mixtures

Literatue	Temp. [K]	a_1, a_2 from			
		H^E and *VLE* data		H^E data	
		Mean [%]	Max [%]	Mean [%]	Max [%]
[10]	297.85	4.68	11.79	4.00	9.66
[11]	298.15	4.33	9.92	4.34	10.00

Table 2b. Results for chloroform/tetrachloromethane mixtures (isothermal data sets)

Literature	Temp. [K]		a_1, a_2 from			
			H^E and *VLE* data		*VLE* data	
			δP	δy	δP	δy
[12]	298.15	Mean	0.16	0.0037	0.21	0.0037
		Max	0.42	0.0068	0.61	0.0067
[12]	313.15	Mean	0.76	0.0029	0.68	0.0029
		Max	1.32	0.0053	1.23	0.0053
[13]	318.15	Mean	1.05	0.0024	0.90	0.0026
		Max	2.03	0.0044	1.81	0.0046
[12]	328.15	Mean	0.93	0.0036	0.69	0.0038
		Max	2.23	0.0078	1.49	0.0082

Table 2c. Results for chloroform/tetrachloromethane mixtures (isobaric data sets)

Literature	Pressure [mmHg]		a_1, a_2 from			
			H^E and *VLE* data		*VLE* data	
			δT	δy	δT	δy
[14]	747.00	Mean	0.10	0.0030	0.08	0.0030
		Max	0.23	0.0064	0.15	0.0069

Table 3a. Results for tetrachloromethane/cyclohexane mixtures

Literature	Temp. [K]	a_1, a_2 from			
		H^E and *VLE* data		H^E data	
		Mean [%]	Max [%]	Mean [%]	Max [%]
[15]	283.15	9.52	15.34	12.23	18.42
[16]	288.15	5.68	7.43	3.31	5.07
[17]	293.15	4.69	6.81	2.79	4.55
[18]	293.15	4.13	7.82	2.42	5.58
[15]	298.15	6.71	8.21	9.01	10.71
[19]	298.15	6.54	10.08	5.18	8.00
[16]	298.15	5.24	6.65	3.07	4.49
[20]	298.15	5.52	6.48	3.71	4.33
[17]	298.15	6.81	8.10	4.72	5.97
[21]	298.15	3.29	4.08	1.14	1.87
[15]	313.15	7.82	10.51	9.86	12.67
[22]	313.15	7.70	11.84	9.66	14.02
[18]	313.15	9.57	11.11	7.82	9.38
[16]	318.15	3.55	4.51	1.81	2.76
[15]	328.15	7.12	9.33	8.77	11.07

Table 3b. Results for tetrachloromethane/cyclohexane mixtures (isothermal data sets)

Literature	Temp. [K]		a_1, a_2 from			
			H^E and *VLE* data		*VLE* data	
			δP	δy	δP	δy
[23]	283.15	Mean	1.12	0.0141	1.11	0.0142
		Max	2.02	0.0241	1.99	0.0240
[24]	313.15	Mean	1.97	0.0026	1.03	0.0025
		Max	3.61	0.0034	3.07	0.0051
[23]	333.15	Mean	2.55	0.0017	1.24	0.0029
		Max	5.38	0.0075	4.26	0.0096
[25]	343.15	Mean	2.43	0.0010	1.93	0.0027
		Max	4.66	0.0022	3.72	0.0046
[24]	343.15	Mean	2.32	0.0007	1.91	0.0021
		Max	4.37	0.0026	2.39	0.0035

Table 3c. Results for tetrachloromethane/cyclohexane mixtures (isobaric data sets)

Literature	Pressure [mmHg]		a_1, a_2 from			
			H^E and *VLE* data		*VLE* data	
			δT	δy	δT	δy
[26]	760.00	Mean	0.30	0.0008	0.13	0.0022
		Max	0.48	0.0025	0.26	0.0038
[27]	760.00	Mean	0.09	0.0032	0.24	0.0049
		Max	0.17	0.0100	0.39	0.0134
[28]	760.00	Mean	0.32	0.0059	0.13	0.0060
		Max	0.46	0.0143	0.29	0.0172

Table 4. Results for tetrachloromethane/toluene mixtures (isothermal data sets)

Literature	Temp. [K]		a_1, a_2 from			
			H^E and *VLE* data		*VLE* data	
			δP	δy	δP	δy
[29]	308.15	Mean	0.74	0.0025	0.82	0.0030
		Max	1.96	0.0047	1.87	0.0063
[29]	313.15	Mean	1.35	0.0020	1.32	0.0016
		Max	3.69	0.0047	3.73	0.0033
[29]	318.15	Mean	1.05	0.0024	0.54	0.0009
		Max	1.80	0.0063	1.23	0.0023
[29]	328.15	Mean	2.36	0.0032	0.62	0.0010
		Max	3.63	0.0077	2.50	0.0022
[29]	338.15	Mean	4.99	0.0040	0.48	0.0025
		Max	7.31	0.0111	1.43	0.0044

Table 5a. Results for benezene/cyclohexane mixtures

Literatue	Temp. [K]	a_1, a_2 from			
		H^E and *VLE* data		H^E data	
		Mean [%]	Max [%]	Mean [%]	Max [%]
[30]	280.15	5.26	10.25	4.30	7.35
[20]	288.15	7.05	13.21	4.84	10.92
[31]	293.15	4.08	6.43	2.78	4.30
[32]	293.15	14.54	35.64	16.20	38.76
[20]	298.15	3.66	5.62	4.70	7.63
[33]	298.15	5.92	11.86	5.41	10.14
[34]	298.15	5.32	9.78	4.05	8.03
[35]	298.15	6.50	10.19	5.22	8.45
[36]	298.15	5.76	10.31	4.83	8.57
[37]	298.15	4.24	9.53	3.67	7.78
[38]	298.15	5.93	11.93	5.13	10.21
[39]	298.15	6.22	11.56	5.02	9.85
[40]	298.15	5.49	10.79	4.08	9.07
[41]	298.15	6.65	15.14	5.36	13.49
[42]	298.15	8.57	18.17	7.36	16.58
[43]	298.15	3.47	6.47	3.58	8.52
[30]	298.15	5.05	11.65	4.10	9.93
[30]	298.15	6.64	12.15	5.76	10.44
[44]	303.15	7.04	16.03	6.18	14.70
[45]	303.15	8.48	13.12	7.62	11.74
[20]	308.15	10.75	11.32	12.08	12.66
[46]	308.15	9.47	15.17	9.72	16.57
[47]	308.15	17.95	20.23	16.96	19.26
[46]	313.15	20.76	42.58	21.24	43.80
[48]	313.15	3.89	6.26	3.69	7.16
[46]	318.15	15.43	28.89	15.67	29.53
[37]	323.15	3.33	7.95	3.26	7.83
[49]	323.15	5.90	10.95	5.86	10.83
[50]	323.15	4.19	8.40	4.14	8.29
[30]	323.15	5.42	9.65	5.38	9.53
[48]	328.15	5.18	9.10	5.18	9.31
[46]	331.55	10.10	17.65	10.37	18.05
[30]	348.15	5.26	7.94	5.57	9.30
[58]	363.15	17.93	37.03	15.24	33.16
[30]	373.15	5.24	8.50	6.04	10.95
[30]	393.15	5.98	11.37	6.28	10.66

shown in Figs. 1 and 2 (benzene/cyclohexane), the relative deviations are of the same magnitude, but this is not necessarily the case. Nevertheless, the description of *VLE* (Tables 2b–9b, 2c–9c) and mixing heat data (Tables 2a–9a) succeeds with relative small deviations; therefore we can justify this fit.

Table 5b. Results for benzene/cyclohexane mixtures (isothermal data sets)

Literature	Temp. [K]		a_1, a_2 from			
			H^E and *VLE* data		*VLE* data	
			δP	δy	δP	δy
[52]	281.15	Mean	0.28	0.0044	0.14	0.0025
		Max	0.62	0.0086	0.29	0.0056
[53]	283.15	Mean	0.48	0.0053	0.23	0.0038
		Max	0.93	0.0100	0.40	0.0068
[52]	287.15	Mean	0.41	0.0044	0.18	0.0025
		Max	0.92	0.0086	0.32	0.0056
[52]	293.15	Mean	0.58	0.0044	0.24	0.0023
		Max	1.27	0.0082	0.39	0.0053
[54]	298.06	Mean	1.16	0.0051	0.27	0.0036
		Max	1.51	0.0085	0.58	0.0054
[55]	298.15	Mean	2.01	0.0092	0.95	0.0055
		Max	2.73	0.0141	1.51	0.0089
[54]	313.10	Mean	2.21	0.0059	0.55	0.0039
		Max	3.22	0.0085	1.03	0.0056
[24]	313.14	Mean	2.32	0.0074	0.56	0.0040
		Max	3.20	0.0132	1.05	0.0091
[56]	313.14	Mean	2.30	0.0074	0.55	0.0040
		Max	3.15	0.0132	1.06	0.0091
[57]	313.15	Mean	2.50	0.0078	0.61	0.0048
		Max	3.49	0.0142	1.22	0.0100
[58]	313.15	Mean	2.46	0.0043	0.45	0.0030
		Max	2.86	0.0077	0.89	0.0049
[59]	313.15	Mean	3.24	0.0034	0.97	0.0037
		Max	4.08	0.0082	1.65	0.0064
[60]	313.15	Mean	1.98	0.0056	0.62	0.0025
		Max	3.28	0.0087	0.95	0.0079
[61]	318.15	Mean	1.68	0.0058	1.18	0.0028
		Max	3.32	0.0106	3.08	0.0053
[61]	328.15	Mean	2.27	0.0054	2.34	0.0036
		Max	3.87	0.0097	4.00	0.0067
[54]	328.20	Mean	3.93	0.0053	1.64	0.0031
		Max	11.46	0.0077	7.85	0.0045
[53]	333.15	Mean	4.20	0.0055	1.16	0.0024
		Max	5.99	0.0088	2.20	0.0049
[24]	343.13	Mean	6.16	0.0063	1.44	0.0031
		Max	8.49	0.0110	2.60	0.0078
[62]	343.15	Mean	11.09	0.0021	4.03	0.0056
		Max	12.25	0.0044	7.06	0.0099
[63]	343.15	Mean	12.38	0.0083	5.32	0.0116
		Max	14.41	0.0199	7.96	0.0224
[64]	343.15	Mean	6.01	0.0066	1.35	0.0037
		Max	8.80	0.0118	3.48	0.0128

Table 5c. Results for benzene/cyclohexane mixtures (isobaric data sets)

Literature	Pressure [mmHg]		a_1, a_2 from			
			H^E and *VLE* data		*VLE* data	
			δT	δy	δT	δy
[65]	760.00	Mean	0.46	0.0048	0.06	0.0026
		Max	0.57	0.0097	0.17	0.0064
[66]	760.00	Mean	0.22	0.0037	0.26	0.0021
		Max	0.29	0.0097	0.33	0.0051
[67]	760.00	Mean	0.35	0.0053	0.08	0.0017
		Max	0.50	0.0077	0.19	0.0040
[68]	760.00	Mean	0.39	0.0061	0.09	0.0028
		Max	0.53	0.0100	0.23	0.0050
[69]	760.00	Mean	0.28	0.0044	0.13	0.0026
		Max	0.38	0.0089	0.25	0.0056
[70]	760.00	Mean	0.39	0.0061	0.09	0.0029
		Max	0.53	0.0100	0.23	0.0050
[71]	760.00	Mean	0.53	0.0064	0.12	0.0029
		Max	0.74	0.0092	0.36	0.0059

Table 6a. Results for benzene/aniline mixtures

Literatue	Temp. [K]	a_1, a_2 from			
		H^E and *VLE* data		H^E data	
		Mean [%]	Max [%]	Mean [%]	Max [%]
[72]	293.15	25.60	32.51	21.95	28.08
[73]	298.15	10.76	17.97	14.59	23.14
[74]	298.15	11.35	14.90	10.90	19.30
[75]	303.15	9.54	22.93	9.11	21.19
[74]	308.15	21.38	49.29	21.46	49.51

Table 6b. Results for benzene/aniline mixtures (isothermal data sets)

Literature	Temp. [K]		a_1, a_2 from			
			H^E and *VLE* data		*VLE* data	
			δP	δy	δP	δy
[76]	298.15	Mean	0.82		2.40	
		Max	2.89		6.81	
[76]	308.15	Mean	2.44		1.59	
		Max	7.21		7.84	

(Continued)

Table 6b. (*Continued*)

Literature	Temp. [K]		a_1, a_2 from			
			H^E and VLE data		VLE data	
			δP	δy	δP	δy
[76]	318.15	Mean	3.17		2.51	
		Max	6.03		9.37	
[77]	323.15	Mean	2.32	0.0003	0.45	0.0001
		Max	5.24	0.0005	1.29	0.0004
[78]	343.15	Mean	6.57	0.0018	10.78	0.0023
		Max	17.53	0.0071	25.99	0.0098
[77]	343.15	Mean	5.72	0.0008	1.30	0.0003
		Max	11.06	0.0034	3.21	0.0011
[77]	363.13	Mean	7.47	0.0009	1.85	0.0012
		Max	9.08	0.0016	3.08	0.0019
[79]	392.45	Mean	16.01	0.0026	13.09	0.0024
		Max	25.53	0.0067	21.10	0.0059

Table 6c. Results for benzene/aniline mixtures (isobaric data sets)

Literature	Pressure [mmHg]		a_1, a_2 from			
			H^E and VLE data		VLE data	
			δT	δy	δT	δy
[80]	760.00	Mean	1.18	0.0080	1.09	0.0100
		Max	5.62	0.0782	5.69	0.0810
[81]	760.00	Mean	1.28	0.0219	0.61	0.0168
		Max	4.34	0.0713	2.73	0.561

Table 7a. Results for cyclohexane/toluene mixtures

Literatue	Temp. [K]	a_1, a_2 from			
		H^E and VLE data		H^E data	
		Mean [%]	Max [%]	Mean [%]	Max [%]
[82]	293.15	10.62	16.47	4.78	10.06
[83]	298.15	13.87	19.97	9.06	13.67
[84]	298.15	55.31	69.38	67.47	82.70
[36]	298.15	15.54	22.88	9.96	16.78
[85]	298.15	13.56	19.06	7.77	12.65
[44]	303.15	13.61	21.45	7.98	15.05

Table 7b. Results for cyclohexane/toluene mixtures (isothermal data sets)

Literature	Temp. [K]		a_1, a_2 from			
			H^E and *VLE* data		*VLE* data	
			δP	δy	δP	δy
[86]	293.15	Mean	0.23		0.20	
		Max	0.55		0.44	
[87]	298.15	Mean	0.69	0.0027	0.69	0.0028
		Max	1.83	0.0151	1.83	0.0150
[86]	298.15	Mean	0.25		0.24	
		Max	0.57		0.55	
[86]	303.15	Mean	0.28		0.27	
		Max	0.62		0.67	
[86]	308.15	Mean	0.38		0.38	
		Max	0.65		0.89	
[86]	313.15	Mean	0.60		0.63	
		Max	1.11		1.43	
[88]	323.15	Mean	2.41	0.0102	1.49	0.0076
		Max	4.51	0.0274	3.00	0.0213

Table 7c. Results for cyclohexane/toluene mixtures (isobaric data sets)

Literature	Pressure [mmHg]		a_1, a_2 from			
			H^E and *VLE* data		*VLE* data	
			δT	δy	δT	δy
[89]	200.00	Mean	0.29	0.0090	0.31	0.0064
		Max	0.49	0.0281	0.63	0.0193
[89]	300.00	Mean	0.24	0.0095	0.18	0.0066
		Max	0.65	0.0330	0.46	0.0228
[90]	760.00	Mean	0.67	0.0074	0.14	0.0025
		Max	1.03	0.0149	0.30	0.0088
[91]	760.00	Mean	0.52	0.0107	0.13	0.0063
		Max	0.84	0.0202	0.31	0.0116
[65]	760.00	Mean	0.48	0.0085	0.12	0.0042
		Max	0.86	0.0222	0.26	0.0087
[92]	760.00	Mean	0.39	0.0063	0.13	0.0035
		Max	0.87	0.0190	0.24	0.0057

Table 8a. Results for cyclohexane/chlorobenzene mixtures

Literature	Temp. [K]	a_1, a_2 from			
		H^E and VLE data		H^E data	
		Mean [%]	Max [%]	Mean [%]	Max [%]
[93]	293.15	16.65	26.71	21.29	35.76
[72]	293.15	18.64	23.10	15.17	20.63
[83]	298.15	10.40	17.85	14.35	26.16
[94]	298.15	10.78	18.57	12.37	22.93
[95]	303.15	24.34	26.16	19.13	21.01
[96]	308.65	14.57	33.14	19.41	42.36
[95]	313.15	22.93	29.30	18.16	24.47
[96]	318.15	16.16	34.88	20.93	44.04
[96]	328.15	24.14	59.29	29.24	69.91

Table 8b. Results for cyclohexane/chlorobenzene mixtures (isothermal data sets)

Literature	Temp. [K]		a_1, a_2 from			
			H^E and VLE data		VLE data	
			δP	δy	δP	δy
[97]	348.15	Mean	10.35	0.0072	2.82	0.0051
		Max	14.80	0.0192	5.46	0.0102

Table 8c. Results for cyclohexane/chlorobenzene mixtures (isobaric data sets)

Literature	Pressure [mmHg]		a_1, a_2 from			
			H^E and VLE data		VLE data	
			δT	δy	δT	δy
[98]	760.00	Mean	1.05	0.0089	1.07	0.0128
		Max	10.62	0.0193	9.27	0.0265

Table 9a. Results for toluene/aniline mixtures

Literature	Temp. [K]	a_1, a_2 from			
		H^E and VLE data		H^E data	
		Mean [%]	Max [%]	Mean [%]	Max [%]
[99]	298.15	10.91	17.59	11.02	21.30
[99]	308.65	14.39	28.89	11.95	22.68

Table 9b. Results for toluene/aniline mixtures (isothermal data sets)

Literature	Temp. [K]		a_1, a_2 from			
			H^E and VLE data		VLE data	
			δP	δy	δP	δy
[100]	313.15	Mean	4.64		1.21	
		Max	7.91		3.90	
[101]	353.15	Mean	12.27	0.0108	1.11	0.0013
		Max	19.76	0.0468	2.91	0.0061
[101]	363.15	Mean	16.33	0.0125	1.32	0.0019
		Max	26.97	0.0478	2.49	0.0086
[101]	373.17	Mean	20.45	0.0128	2.29	0.0037
		Max	36.08	0.0431	3.73	0.0124

Conclusions

The prediction of H^E data with interchange parameters a_1 and a_2 fitted to VLE data and *vice versa* does not lead to acceptable results in general. Using the simultaneously fitted parameters, the results are quite satisfactory or even good. It is known from literature [8, 9] that VLE and H^E data are not consistent in many cases. Therefore, there is no expectation that a prediction of thermodynamic properties succeeds in good agreement with experimental results with only one parameters set. One important prerequisite to reach this aim in the improvement of the experimental data base. For the moment, TASQUAC (and we think the other models too) can be used only as a tool for testing the thermodynamic consistency of different kind of thermodynamic data but not for the prediction of all interesting thermodynamic properties with only one parameter set.

Symbols. G^E: excess free enthalpy; H^E: excess enthalpy; M: number of data sets; N: total number of molecules; $N_{Avogadro}$: *Avogadro*-number; N_I: number of data points; N_{AB}: number of contact pairs between molecules of component A and B; P: pressure; T: temperature; ΔW: interchange energy; X: concentration function; Y: concentration function; Z_K: coordination number; $\bar{Z}$: mean coordination number; a_1, a_2: interchange parameter; c_p: heat-capacity; k: *Boltzmann* constant; n_K: number of moles of component K; n_{tot}: total number of moles; x: liquid phase mole fraction; y: vapor phase mole fraction; δ: deviation.

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