THE CALCULATION OF TERNARY LIQUID-LIQUID (L-L) EQUILIBRIUM DATA USING A TERNARY CORRECTION TO THE EXCESS GIBBS FREE ENERGY

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A universal form is proposed for the ternary correction to G^E, which is based on the MacLaurin fourth-order expansion. With data on four ternary equilibrium liquid systems of the hydrocarbon–hydrocarbon–polar solvent type, it is demonstrated that a very good reproducibility of equilibrium L–L concentrations can be achieved by using this ternary correction. The ternary correction was applied to the NRTL, modified Wilson and Redlich–Kister equations. The correction parameters were determined from ternary L–L data, binary parameters were found from vapour–liquid (V–L) equilibrium data. For the determination of correction parameters with the help of the activity objective function, it is desirable to use weights from the law of the error propagation. For the determination of correction parameters with the help of the concentration objective function, an approximate expression was derived for calculating the probable value of the mole fraction of the solute in one of the equilibrium phases.

It obviously follows from so far published works on the calculation of ternary L–L equilibrium data, that a quantitative agreement between calculated and experimental equilibrium data is improbable for the most systems studied if only binary parameters are employed in equations describing the concentration dependence of G^E. This fact follows already from data reported in the monograph by Renon and coworkers[1] as well as from many other papers reviewed in the series by Sorensen and coworkers[2–4] and also from our earlier work[5]. For an accurate calculation of the composition of equilibrium liquid phases in ternary and multicomponent systems it is therefore necessary to consider experimental L–L equilibrium data during the determination of parameters in equations for G^E.

The adjustment of G^E equations according to ternary equilibrium L–L data can be performed in the two manners:

1) All binary parameters or some of them are replaced with parameters calculated from ternary equilibrium data[1]. Since the number of parameters is rather large (up to 9), their numerical determination is very difficult; due to this reason, binary parameters for partially soluble pairs of liquids determined from solubility data are as a rule preserved[3].

The method outlined is being employed above all in G^E equations based on molecular theories (the local composition concept), where only binary interactions are considered, so that equations for multicomponent systems possess binary parameters only (*e.g.*, the NRTL (ref.[1]), UNIQUAC (ref.[6]) equations, *etc.*). Obviously, it is to be expected that if binary parameters are adjusted according to ternary data, the behaviour of binary solutions will not be described correctly with these equations.

In the prediction of ternary L–L equilibrium data, a better approximation of experimental data can be achieved even on the basis of binary parameters if their values are properly changed within their confidence interval[8]. However, this method solves the problem only partially.

2) G^E equations, which are based on empirical expansions (such as the Wohl or the Redlich–Kister expansion[9]) can be extended by the addition of ternary terms; coefficients at these terms can then be determined from ternary L–L equilibrium data. Original binary coefficients remain unchanged during this procedure. The above cited equations, however, possess the following drawbacks: a lack of the theoretical basis and often a lower flexibility in comparison with equations derived from the molecular theory.

Considering both advantages and disadvantages of the two possible method for adjusting the G^E equations, we want to outline here a possibility of using an universal ternary correction for all types of the G^E equations and to discuss problems encountered at determining parameters in this correction.

THEORETICAL

A Proposal of a Universal Ternary Correction to G^E

If we assume that the difference between an experimentally determined value of the excess Gibbs free energy in a ternary solution, G^E, and the value calculated from binary data, G^E_b, is brought about by ternary interactions, this difference may be approximated by ternary terms in the Mac Laurin series. Using the fourth-order expansion, we get

$$\Delta_t G^E/RT = (G^E - G^E_b)/RT = Ax_1x_2x_3 + Bx_1^2x_2x_3 + Cx_1x_2^2x_3 + Dx_1x_2x_3^2 \,. \qquad (1)$$

On substituting

$$A = A(x_1 + x_2 + x_3)\,,$$

relation (*1*) changes to

$$\Delta_t G^E/RT = x_1x_2x_3(E_1x_1 + E_2x_2 + E_3x_3)\,, \qquad (2)$$

where E_1, E_2, E_3 are parameters dependent on temperature and pressure. The correction to activity coefficients of components is obtained from Eq. (*2*) by a common procedure employed in calculations of partial molar quantities. For component 1 it is given by

$$\ln \gamma_1 - \ln \gamma_{1b} = \Delta_t \ln \gamma_1 = x_2x_3[E_1x_1(2 - 3x_1) + E_2x_2(1 - 3x_1) + E_3x_3(1 - 3x_1)] \qquad (3)$$

The correction to activity coefficients of components 2 and 3 is readily obtained from relation (*3*) by a cyclic change of its indexes.

By using the Redlich–Kister fourth-order expansion[9] containing the ternary terms

$$\Delta_t G^E/RT = x_1 x_2 x_3 (C + D_1 x_1 + D_2 x_2) \quad (4)$$

relations (*2*) and (*4*) become identical and it holds

$$E_1 = D_1 + C\,; \quad E_2 = D_2 + C\,; \quad E_3 = C\,. \quad (5)$$

The Determination of the Ternary Correction Parameters

a) *The concentration objective function.* For the determination of parameters in G^E equations from ternary equilibrium L–L data, the minimization of the concentration or activity objective function is usually employed. In the case of the concentration objective function, the sum of squares of differences between experimental and calculated mole fractions of components in the equilibrium phases is minimized. The objective function assumes the form

$$F(E)_x = \sum_l \sum_j \sum_i w_{il}^j (x_{il}^j - \hat{x}_{il}^j)^2 \quad (6)$$

for $i = 1, 2, 3$; $j = \mathrm{I}, \mathrm{II}$; $l = 1, 2, \ldots, m$,
with the constraints

$$\Delta \hat{a}_{il} = \hat{a}_{il}^{\mathrm{I}} - \hat{a}_{il}^{\mathrm{II}} = 0\,; \quad \sum_i \hat{x}_{il}^j = 1\,. \quad (7)$$

There are five constraints (3 + 2) for each tie line, *i.e.*, one of the $\hat{x}_{il}^j$'s is an independent variable. In earlier works, *e.g.*, by Renon[1], one of the $\hat{x}_{il}^j$'s is set equal to the experimental value, most often it is

$$\hat{x}_{21}^{\mathrm{II}} = x_{21}^{\mathrm{II}}\,. \quad (8)$$

In recent works, however, the parameters are determined by the maximum likelihood method, *e.g.*, by Várhegyi and Eon[7] of Sørensen and coworkers[3], who minimize the objective function not only with respect to parameters in G^E equations, but also with respect to incidental parameters — independent variables $\hat{x}_{il}^j$ (from now on $\hat{x}_{21}^{\mathrm{II}}$). An improved iterative minimization procedure has been developed by Sørensen and coworkers[3,4]. In the first step, the function $F(E)_x$ is minimized with given values of the incidental parameters, in the second step individual $\hat{x}_{21}^{\mathrm{II}}$'s are corrected so that for each tie line the value of the function

$$F(\hat{x}_{21}^{\mathrm{II}}) = \sum_i \sum_j w_{il}^j (x_{il}^j - \hat{x}_{il}^j)^2 \quad (9)$$

assume its minimum. This procedure is repeated if necessary. Sørensen and coworkers; propose to interpolate $\hat{x}^{II}_{21}$ from a series of calculated equilibrium concentrations. Here we use the iterative method for calculating $\hat{x}^{II}_{21}$ at the minimum of function (9). although this procedure is approximate, its accuracy is satisfactory.

Function (9) can be rewritten as

$$F(\hat{x}^{II}_2) = \sum_{j=I}^{II} [(x^j_1 - \hat{x}^j_1)^2 + (x^j_2 - \hat{x}^j_2)^2 + (x^j_3 - \hat{x}^j_3)^2] \qquad (10)$$

with

$$\hat{x}^j_3 = 1 - \hat{x}^j_2 - \hat{x}^j_1 \; ; \quad x^j_3 = 1 - x^j_2 - x^j_1 \, . \qquad (11)$$

(Subscript l has been omitted to simplify the equations.) On inserting (11) into relation (10), we get

$$F(\hat{x}^{II}_2) = 2 \sum_{j=I}^{II} [(x^j_1 - \hat{x}^j_1)^2 + (x^j_2 - \hat{x}^j_2)^2 + (x^j_1 - \hat{x}^j_1)(x^j_2 - \hat{x}^j_2)] \, . \qquad (12)$$

The mole fractions in phase I are given by

$$\hat{x}^I_i = k_i \hat{x}^{II}_i \; ; \quad (i = 1, 2, 3) \qquad (13)$$

and the $\hat{x}^{II}_1$, according to Rod[10], by

$$\hat{x}^{II}_1 = \frac{1 - k_3 + (k_3 - k_2)\,\hat{x}^{II}_2}{k_1 - k_3} \, , \qquad (14)$$

where k_1, k_2, k_3 are reciprocals of distribution coefficients. By substituting

$$(1 - k_3)/(k_1 - k_3) = a \; ; \quad (k_3 - k_2)/(k_1 - k_3) = b \qquad (15)$$

and inserting into (12), we obtain

$$\begin{aligned} F(\hat{x}^{II}_2) = 2[(x^{II}_1 - a - b\hat{x}^{II}_2)^2 + (x^{II}_2 - \hat{x}^{II}_2)^2 + (x^{II}_1 - a - b\hat{x}^{II}_2)(x^{II}_2 - \hat{x}^{II}_2) + \\ + (x^I_1 - k_1 a - k_1 b\hat{x}^{II}_2)^2 + (x^I_2 - k_2\hat{x}^{II}_2)^2 + \\ + (x^I_1 - k_1 a - k_1 b\hat{x}^{II}_2)(x^I_2 - k_2\hat{x}^{II}_2)] \, . \end{aligned} \qquad (16)$$

If we assume that the distribution coefficients, within the range of differences between experimental and calculated equilibrium concentrations, are independent of composition, the minimization of function (*16*) is very simple. From the condition

$$\mathrm{d}F(\hat{x}_2^{\mathrm{II}})/\mathrm{d}\hat{x}_2^{\mathrm{II}} = 0$$

we get

$$\hat{x}_2^{\mathrm{II}} = \frac{(x_1^{\mathrm{I}} - k_1 a)(2k_1 b + k_2) + x_2^{\mathrm{I}}(k_1 b + 2k_2) + (x_1^{\mathrm{II}} - a)(2b + 1) + x_2^{\mathrm{II}}(b + 2)}{k_1 b(2k_1 b + k_2) + k_2(k_1 b + 2k_2) + b(2b + 1) + (b + 2)} . \tag{17}$$

Since, at the beginning of the computation, calculated distribution coefficients of $\hat{x}_2^{\mathrm{II}}$ are not known, the computations are performed in an iterative manner and experimental values of k_i are used as the first approximation. Mole fractions of other components are calculated, *e.g.*, by the isoactivity method. The accuracy of $\pm 2 \,.\, 10^{-4}$ in determination of $\hat{x}_2^{\mathrm{II}}$ is usually achieved after 5–6 iterations.

The accuracy of x_2^{II} values computed in this manner is lowest for systems with a small heterogeneous region in the vicinity of the plait point. However, even in these cases the value of the expression

$$[\sum_{\mathrm{l}} F(\hat{x}_{2\mathrm{l}}^{\mathrm{II}})]^{1/2}$$

was at most by 10% higher than that obtained during the more exact calculation.

b) *The activity objective function.* If the activity objective function is employed, the minimized function is the sum of squares of differences between activities in experimental equilibrium phases

$$F(E)_{\mathrm{a}} = \sum_{\mathrm{l}} \sum_{\mathrm{i}} w_{\mathrm{il}}(a_{\mathrm{il}}^{\mathrm{I}} - a_{\mathrm{il}}^{\mathrm{II}})^2 . \tag{18}$$

Since the objective function (*18*) contains only experimental concentrations (the actual difference between the activities equals zero), the algorithm for the determination of parameters is substantially simpler than that with the concentration objective function (*6*). However, it is true that calculated concentrations of equilibrium phases based on the activity objective function are less accurate. Different variants employed for the objective function differ from each other by the value of the statistical weight. They are reviewed by Sørensen[3]. The most often used expressions are

$$w_{\mathrm{il}} = 1 \tag{19}$$

$$w_{\mathrm{il}} = (a_{\mathrm{il}}^{\mathrm{I}} + a_{\mathrm{il}}^{\mathrm{II}})^{-2} \tag{20}$$

and the logarithmic objective function

$$F(E)'_a = \sum_l \sum_i (\ln a^{I}_{il} - \ln a^{II}_{il})^2 \quad (21)$$

which is practically equivalent to weight (*20*). One may object that such a choice of weight is empirical and theoretically little justified. If we take into account that one of the mole fractions of components is constrained by the relation $\sum_i x_i = 1$, the law of propagation of errors leads to the following expression for the statistical weight

$$w_{il} = \frac{\sigma^2}{\sum_{j=1}^{II} [(\partial a_i/\partial x_1)^2_{x_2} \sigma^2_{x_1} + (\partial a_i/\partial x_2)^2_{x_1} \sigma^2_{x_2}]_{jl}}, \quad (22)$$

where σ is an arbitrarily selected constant. By assuming that the standard deviation σ_{x_i} is identical for both components 1 and 2 during all experiments, relation (*22*) simplifies to

$$w_{il} = \frac{1}{\sum_{j=1}^{II} [(\partial a_i/\partial x_1)^2_{x_2} + (\partial a_i/\partial x_2)^2_{x_1}]_{jl}}. \quad (23)$$

The easiest way for determining the weight is numerical differentiation.

The effect of the choice of weight will be demonstrated on the example of the determination of parameters for the ternary correction to the NRTL equation describing the liquid heptane(1)–toluene(2)–DMFA(3) system at 40°C. Experimental ternary equilibrium L–L data as well as parameters in the NRTL equation for the heptane–to-

TABLE I

Coefficients in the ternary correction to the NRTL equation and the residuals for the heptane–toluene–DMFA system at 40°C ($\hat{x}^{II}_{21} = x^{II}_{21}$)

Weight	E_1	E_2	E_3	F_x	F_{K2}
(*19*)	−0·5123	−4·1817	0·0919	0·61	0·095
(*20*)	−2·5117	5·3298	0·0947	2·14	0·037
(*23*)	−0·7916	−3·9788	0·2606	0·77	0·063

luene and toluene–DMFA pairs are given in Tables I and II of our earlier paper[5]. The following parameters

$$\tau_{31} = 1{\cdot}9642\,; \quad \tau_{13} = 1{\cdot}9790\,; \quad \alpha_{13} = 0{\cdot}360$$

were employed for the partially soluble heptane–DMFA system. Coefficients in the ternary correction with weights according to (*19*), (*20*), or (*23*) are given in Table I together with the residuals of equilibrium mole fractions

$$F_x = 100\sqrt{\left[\sum_l \sum_i \sum_j (x^j_{il} - \hat{x}^j_{il})^2/6m\right]} \quad (i = 1, 2, 3;\ j = \mathrm{I}, \mathrm{II};\ l = 1, 2, \ldots, m) \qquad (24)$$

and with the residuals of solute (toluene) distribution coefficients

$$F_{K2} = \sqrt{\left[\sum_l (K_2 - \hat{K}_2)^2/m\right]}\,. \qquad (25)$$

It follows from this table that by far the highest value of F_x is obtained with weight (*20*), which is obvious also from Fig. 1, where binodal curves calculated from sets of coefficients E in Table I are compared with experimental data. A somewhat higher value of F_x with weight (*23*) in comparison with weight (*19*) is due to the different shape of the binodal curve neat the plait point. If the point lying near the point is omitted during the calculation of F_x, we obtain $F_x = 0{\cdot}64$ with weight (*19*) and $F_x = 0{\cdot}42$ with weight (*23*). During investigation the possibility of using the ternary correction in the NRTL, Wilson and Redlich–Kister equations for all systems reported in our earlier paper[5] and with different sets of binary coefficients, weight (*23*) proved unambiguously as the most suitable one. The value of F_x with weight (*23*)

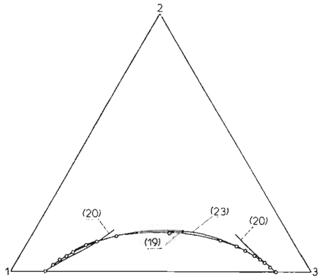

FIG. 1

Calculated courses of the binodal curve in the heptane(1)–toluene(2)–DMFA(3) system with weights (*19*), (*20*), (*23*) in the activity objective function. ○ — experimental points was in 34 out of 39 cases lower than with a less accurate weight of $w_{i1} = 1$. The use of weight (*23*), resp. (*22*), is supported also by the fact that the residuals of solute distribution coefficients are lower than those with $w_{i1} = 1$. This occurs because the calculated weight of the component 2 is always higher than the weights of the remaining two components, according to the system and its composition up to 1 000 times, on the average 5 – 10 times.

RESULTS AND DISCUSSION

The suitability of using the ternary correction to the excess Gibbs free energy (*2*) was tested in calculations of ternary equilibrium liquid–liquid concentrations in the systems: *a*) heptane(1)–toluene(2)–DMFA(3) at 40°C, *b*) heptane(1)–cyclohexane(2)–DMFA(3) at 25°C, *c*) cyclohexane(1)–benzene(2)–fural(3) at 25°C, *d*) heptane(1)–benzene(2)–DMSO(3) at 40°C.
In the calculations, the function G_b^E was approximated by the NRTL, Wilson (as modified by Novák and coworkers) or Redlich–Kister equations. Parameters in the ternary correction were determined from experimental equilibrium data reported in our earlier paper[5]. This paper also contains expressions employed for G_b^E, resp. corresponding references, and parameters in these equations for completely miscible pairs of components determined from vapour–liquid equilibrium data.

In the first step, parameters in the ternary correction were determined by minimizing the activity objective function (*18*) with weight (*23*). The minimization was performed by the Newton–Raphson method. The computations converged rapidly. Five iterations were necessary on the average to reach the minimum of $F(E)_a$ with an accuracy of $\pm 10^{-9}$ and from initial values of parameters $E_i = 0$. (The accuracy of $\pm 10^{-9}$ in $F(E)_a$ corresponds to the accuracy of $\pm 10^{-3} - 10^{-4}$ in E_i.)

The inverse calculation of equilibrium mole fractions was performed by the isoactivity method, namely by minimizing the function

$$F(\hat{x}_i) = \sum_{i=1}^{3} (\hat{a}_i^{II} - \hat{a}_i^{I})^2 \qquad (26)$$

for individual $\hat{x}_{21}^{II}$'s at the minimum of function (*9*). Values of $\hat{x}_{21}^{II}$ were calculated by an iterative method based on relation (*17*). Calculated equilibrium data were evaluated on the basis of the residuals of mole fractions (*24*) as well as on the basis of the residuals of solute distribution coefficients

$$F'_{K2} = 100 \sqrt{\sum_l \left(\frac{K_2 - \hat{K}_2}{K_2}\right)_l^2 \cdot \frac{1}{m}} \qquad (27)$$

with $K_2 = x_2^{II}/x_2^{I}$ and $\hat{K}_2 = \hat{x}_2^{II}/\hat{x}_2^{I}$.

TABLE II

Parameters in the NRTL, Wilson and Redlich–Kister equations for partially soluble liquid pairs

Components			NRTL equation			Wilson equation			Redlich–Kister equation		
i	j	$t/°C$	τ_{ij}	τ_{ji}	α_{ij}	Λ_{ij}	Λ_{ji}	B_{ij}	B_{ij}	C_{ij}	D_{ij}
Heptane	DMFA	40	1·7395	1·7190	0·2850	0·2057	0·2012	0·5850	2·6038	0·0056	0·2500
Heptane	DMFA	25	2·2541	2·1387	0·3560	0·1972	0·1663	0·6900	2·7281	0·0416	0·4620
Cyclohexane	DMFA	25	2·3153	1·5494	0·3660	0·3129	0·0991	0·4800	2·5156	0·2724	0·3000
Cyclohexane	fural	25	2·6582	0·7223	0·1600	1·0118	0·1760	1·7000	2·7859	0·4098	0·0950
Heptane	DMSO	40	4·1180	3·6368	0·3500	0·0670	0·0350	0·9750	3·4298	0·2628	1·3500

The computations of the minimum of the objective function (*18*) with different values of the third parameters of partially soluble liquid pairs indicated that the third parameter is closely correlated with the minimum of the objective function and that the correlation curve passes through a minimum for all systems and equations investigated. Due to this fact, the third parameters were determined by interpolation at this minimum and the remaining two parameters of partially soluble components were calculated from solubility data by the method described in our earlier paper[5]. The only exception was the benzene–cyclohexane–DMFA system, for which – due to an extremely low value of the objective function – the third parameters of partially soluble pairs were calculated from experimental values of limit-

TABLE III

Coefficients in the ternary correction E_i, the residuals of mole fractions of components and residuals of solute distribution coefficients for different types of the G^E equations. The objective function is based on activities (*18*)

Equation	E_1	E_2	E_3	F_x [a]	F'_{K2} [a]
		Heptane–toluene–DMFA, 40°C			
NRTL	−1·3026	−5·1972	−0·6076	0·386	8·44
Wilson	−0·6347	−4·0336	−0·0735	0·252	7·74
Redlich–Kister	−0·2686	−3·4116	−0·0672	0·348	8·57
		Heptane–cyclohexane–DMFA, 25°C			
NRTL	0·0485	−0·2479	0·0327	0·158	2·39
Wilson	0·1883	−0·2014	0·6608	0·241	3·49
Redlich–Kister	1·7700	1·1412	−0·6900	0·180	2·26
		Cyclohexane–benzene–fural, 25°C			
NRTL	−3·0455	−2·2615	−1·0082	0·217	6·63
Wilson	−1·5866	−0·3888	−0·4654	0·332	7·72
Redlich–Kister	−1·5931	−0·7695	−0·5655	0·123	3·94
		Heptane–benzene–DMSO, 40°C			
NRTL	3·0614	−2·5741	3·0758	0·160	2·55
Wilson	3·7786	−3·5223	1·9748	0·213	4·85
Redlich–Kister	4·7015	−1·3347	2·7013	0·235	2·42

[a] Mean values of the residuals $\bar{F}_x$ and $\bar{F}'_{K2}$: NRTL — 0·230 and 5·00; Wilson — 0·260 and 5·95; Redlich–Kister — 0·222 and 4·30.

ing activity coefficients[5]. The sets of parameters employed for partially soluble liquid pairs are given in Table II.

Coefficients in the ternary correction (*2*) calculated from objective function (*18*) and the residuals F_x and F'_{K2} for different systems and equations are reported in Table III. Table IV contains results of calculations of equilibrium L–L concentrations evaluated in the same manner for the case when parameters in the ternary correction were determined from the objective function based on mole fractions (*6*) with weights $w^j_{i1} = 1$ and with the binary parameters equal to those employed for the

TABLE IV

Coefficients in the ternary correction E_i, the residuals of mole fractions of components and residuals of solute distribution coefficients for different types of the G^E equations. The objective function is based on mole fractions (*6*)

Equation	E_1	E_2	E_3	F_x[a]	F'_{K2}
		Heptane–toluene–DMFA, 40°C			
NRTL	−1·4341	−3·9436	−0·8059	0·253	5·64
Wilson	−0·7603	−3·3740	−0·1518	0·244	7·48
Redlich–Kister	−0·3448	−2·5463	−0·2142	0·245	9·04
		Heptane–cyclohexane–DMFA, 25°C			
NRTL	0·0705	−0·2070	0·0523	0·155	2·62
Wilson	0·1436	−0·1374	0·5718	0·232	3·86
Redlich–Kister	1·7282	1·1891	−0·7385	0·175	2·54
		Cyclohexane–benzene–fural, 25°C			
NRTL	−2·7785	−3·4147	−0·8602	0·146	6·66
Wilson	−1·2110	−1·9343	−0·2873	0·202	8·03
Redlich–Kister	−1·4482	−1·4450	−0·4719	0·094	3·89
		Heptane–benzene–DMSO, 40°C			
NRTL	3·7388	−3·4221	3·3155	0·139	2·59
Wilson	3·9021	−3·6302	2·0025	0·210	4·93
Redlich–Kister	5·1787	−2·0270	3·0482	0·125	2·05

[a] Mean values of the residuals $\bar{F}_x$ and $\bar{F}'_{K2}$: NRTL — 0·173 and 4·38; Wilson — 0·222 and 6·08; Redlich–Kister — 0·160 and 4·38.

activity objective function. The minimization was performed by the simplex method, with values from Table III taken as the first estimate of parameters E_i.

It obviously follows from the results that an excellent reproducibility of equilibrium concentrations of liquid phases is achieved with the ternary correction to G^E – the standard deviation of mole fractions oscillates about 0·002. The reproducibility of solute distribution coefficients can also be considered as satisfactory, its standard relative deviation is approximately 5%. Even though the modified Wilson equation yields somewhat worse results, no substantial difference can be observed between the different equations employed. A more detailed evaluation of the equations is not possible due to the small number of systems investigated.

If we compare results obtained from the objective function based on activities or mole fractions, resp. (Tables III and IV), we can see that, in accordance with our expectations, the residuals of mole fractions are lower for the objective function (*6*), the difference between both residuals is by far not so large as it could be expected according to results of Sørensen and coworkers[3], which is brought about by using the more accurate expression (*23*) for the weight. The reproducibility of the distribution coefficient K_2 is worse in more than one half of the cases investigated with the objective function (*6*).

LIST OF SYMBOLS

a, b	distribution coefficient functions (*15*)
a_i	activity
C, D_1, D_2	ternary parameters in the Redlich–Kister equation
E_1, E_2, E_{3c}	parameters in the ternary correction to the excess Gibbs free energy
$F(E), F(x_i)$	objective functions
F_x, F_{K2}	residuals
G^E	molar excess Gibbs free energy
G^E_b	molar excess Gibbs free energy calculated from binary parameters
$\Delta_t G^E$	ternary correction to the molar excess Gibbs free energy
k_1, k_2, k_3	reciprocal of distribution coefficients
K_2	solute distribution coefficient
m	number of measurements
R	gas constant
T	absolute temperature
w_i	statistical weight
x_i	mole fraction
$\tau_{ij}, \tau_{ji}, \alpha_{ij}$	parameters in the NRTL equation
γ_i	activity coefficient
σ_x	standard deviation

Superscripts:

j	j-th phase
I, II	symbol of a phase (II — solvent phase)
—	mean value
∧	calculated value

Subscripts

i	i-th component
l	l-th measurement
1, 2, 3	serial component number (2 — solute, 3 — solvent)

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