TERNARY CORRECTIONS IN THE LIQUID-LIQUID EQUILIBRIA FOR FOUR-COMPONENT SYSTEM HEPTANE-TOLUENE-N-METHYLPYRROLIDONE-ETHYLENE GLYCOL

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Prediction for a four-component liquid-liquid equilibrium is based on binary and ternary equilibrium data. Three-parameter equations for the excess Gibbs energy (NRTL equation, Redlich-Kister 4th order expansion and Wilson equation in Novák modification) extended by universal ternary contribution were employed for a thermodynamic description of the four-component system. The computation method was applied for a model four-component system heptane-toluene-N-methylpyrrolidone-ethylene glycol, $t = 50°C$. The computed equilibrium data were compared with experimental ones measured for the weight ratio of the mixture N-methylpyrrolidone per ethylene glycol 20/80, 40/60 and 60/40.

The first theoretical paper concerning the computation of multi-component liquid--liquid equilibria (L-L) employing equations for the excess Gibbs energy (G^E equations) appeared in the sevetieth. Guffey and Wehe[1], Anderson and Prausnitz[2] stressed the fact that a quantitative correspondence between the calculated and experimental equilibrium data is little probable for most systems when using parameters evaluated from binary data only. Therefore, ternary information has to be taken into account to make the computation more precise. At the time being, three independent groups (Ferreira and coworkers. Ruiz and collaborators and Nagata) are investigating the computation of four-component L-L equilibria employing the G^E equation. However, these groups have a diametral access to selection of experimental data and their further processing for evaluation of the G^E equation parameters.

Ferreira and coworkers[3,4] employed a quasi-ternary procedure, the mixed solvent being considered as one component. The model parameters of G^E equation (NRTL) were computed from quasi-ternary data, employing the Sörensen[5] programme resulting in a set of binary parameters, i.e. different model parameters were obtained for any composition of the mixed solvent.

A modified UNIQUAC equation, the binary parameters of which are computed from the binary L-L and V-L (vapour-liquid) equilibrium data was employed by Nagata[6-8] for computation of equilibrium composition. A part of parameters was adjusted according to ternary L–L equilibrium data by the Sörensen programme to improve the prediction of equilibrium data.

Ruiz et al.[10–13] employed the programme proposed by Gomis[14]. A series of twelve binary parameters of the UNIQAUC equation was computed by correlation of quarternary L–L equilibrium data. In order to lower the computing extensiveness the authors evaluated a part of parameters from ternary L–L equilibrium data by the Sörensen programme[5] and eventually also from binary solubilitirs. Paper[13] dealt with various variants for computation of binary parameters from four-, three- and two-component L–L equilibria. It is obvious that the number of possible variants rises with the complexity of a four-component system, and as a result, also the computation of binary parameters becomes more complicated. Therefore, sometimes even simultaneous correlations of sets of ternary data are necessary.

The above-mentioned procedures are very computation extensive. The evaluated parameters of G^E equations are not general, i.e. they are not suited also for other multicomponent systems embodying these subsystems.

This contribution presents another relatively simple access to the thermodynamic solution of the L–L equilibria of a four-component system. In continuation of our preceding paper[15] we extended the application of a universal ternary contribution to the G^E function for a four-component system. This made it possible to evaluate independently the binary parameters of G^E equations from the L–L and V–L equilibrium data. The advantage being the universality of parameters of G^E equations and a good reproducibility not only of the L–L equilibrium, but also of the V–L equilibrium. This cannot be expected from the preceding methods.

EXPERIMENTAL

The equilibrium L–L diagram of the model four-component system heptane–touene–N-methylpyrrolidone (NMP)–ethylene glycol (EG), $t = 50°C$ is outlined in form of an equilateral tetrahedron (Fig. 1*a*) or of a plane projection (Fig. 1*b*). The system consists of three partially miscible binary systems heptane–NMP, heptane–EG, toluene–EG and three completely miscible pairs heptane–toluene, toluene–NMP and NMP–EG. Sides of the tetrahedron are formed by four partially miscible ternary systems of which heptane–toluene–NMP and toluene–NMP–EG are the I type systems containing one partially miscible pair each. Heptane–NMP–EG and heptane–toluene–EG are the II type systems containing thwo partially miscible pairs each.

Equilibrium data for three various weight rations (20/80, 40/60, 60/40) of the mixed solvent NMP/EG were measured for the afore-mentioned L–L model system. A direct analytical method was employed for the measurement, composition of the equilibrated phases was analyzed chromatographically. The analytical procedure and the quality of chemicals used is presented in our previous paper[16]. The experimental equilibrium L–L data are listed in Table I.

THEORETICAL

Surový and coworkers[15] extended the relation to the excess Gibbs energy of a three-

-component system by a universal ternary contribution

$$\Delta_t G^E/RT = G^E/RT - (G^E/RT)_b = x_1 x_2 x_3 (E_1 x_1 + E_2 x_2 + E_3 x_3)\,. \qquad (1)$$

The ternary contributions could also be applied for a four-component system. Considering the assumption that the difference between the experimentally estimated value for the excess Gibbs energy in a four-component solution G^E and the computed one from binary data G^E_b is due to ternary molecular interactions and the quaternary interactions could be neglected, then the ternary contribution for a four-component system $\Delta_t G^E$ can be computed as a sum of ternary contributions of four ternary subsystems of the four-component system

$$\begin{aligned} \Delta_t G^E/RT = G^E/RT - (G^E/RT)_b &= x_1 x_2 x_3 (E_{14} x_1 + E_{24} x_2 + E_{31} x_3) + \\ &+ x_1 x_2 x_4 (E_{13} x_1 + E_{23} x_2 + E_{43} x_4) + x_1 x_3 x_4 (E_{12} x_1 + E_{32} x_3 + E_{42} x_3) + \\ &+ x_2 x_3 x_4 (E_{21} x_2 + E_{31} x_3 + E_{41} x_4)\,. \end{aligned} \qquad (2)$$

The ternary contribution to an activity coefficient of a four-component solution $\Delta_t \ln \gamma_i$ can be obtained by a routine procedure according to rule

$$\Delta_t \ln \gamma_i = Q + (\partial Q/\partial x_i)_{T,P,x_{j \neq i}} - \sum_{j=1}^{k} x_j (\partial Q/\partial x_j)_{T,P,x_{k \neq j}}\,, \qquad (3)$$

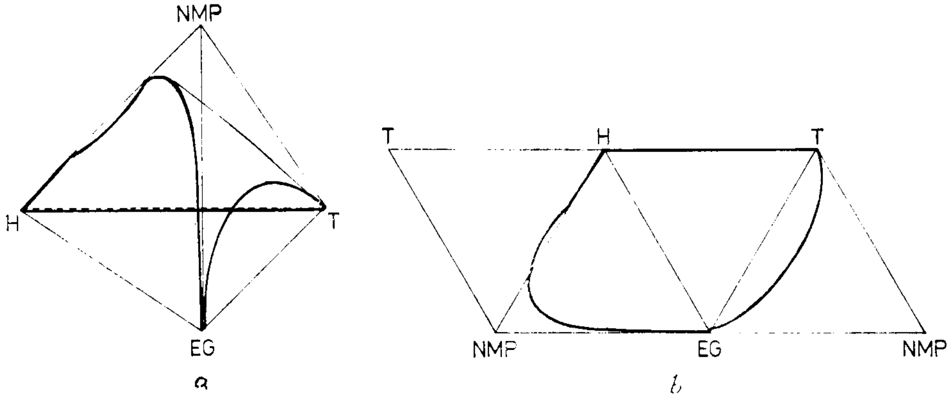

FIG. 1

The L–L equilibrium diagram for the model four-component system heptane–toluene–NMP–EG, t = 50°C; *a* by an equilateral tetrahedron projection, *b* by a plane projection

TABLE I

Experimental and computed L–L equilibrium composition for the four-component system heptane (1)–toluene(2)–NMP(3)–EG(4), $t = 50°C$ at various ratios of the mixed solvent NMP/EG as computed by Redlich–Kister 4th order equation and the corresponding residual F of molar fractions x_{ij} of the particular tie lines

No.	Phase I				Phase II				F_b F
	x_1^I	x_2^I	x_3^I	x_4^I	x_1^{II}	x_2^{II}	x_3^{II}	x_4^{II}	
NMP/EG = 20/80									
1.	0·804[a]	0·190	0·006	0·000	0·004	0·016	0·127	0·853	
	0·801[b]	0·187	0·011	0·001	0·002	0·008	0·132	0·858	0·49
	0·801[c]	0·187	0·011	0·001	0·002	0·015	0·128	0·855	0·26
2.	0·693	0·297	0·010	0·000	0·003	0·023	0·126	0·848	
	0·690	0·294	0·015	0·001	0·002	0·012	0·131	0·855	0·56
	0·691	0·295	0·031	0·000	0·002	0·023	0·126	0·849	0·16
3.	0·486	0·500	0·014	0·000	0·003	0·037	0·120	0·840	
	0·480	0·495	0·022	0·003	0·002	0·019	0·128	0·851	0·89
	0·483	0·497	0·017	0·003	0·002	0·035	0·121	0·842	0·25
4.	0·330	0·636	0·022	0·012	0·002	0·047	0·116	0·835	
	0·331	0·638	0·027	0·004	0·001	0·024	·0127	0·848	1·03
	0·334	0·641	0·021	0·004	0·001	0·045	0·117	0·837	0·41
5.	0·185	0·791	0·016	0·008	0·001	0·058	0·098	0·843	
	0·180	0·787	0·028	0·005	0·001	0·029	0·111	0·859	1·38
	0·184	0·790	0·021	·0005	0·001	0·050	0·102	0·847	0·40
NMP/EG = 40/60									
1.	0·811	0·172	0·017	0·000	0·010	0·031	0·273	0·686	
	0·805	0·168	0·026	0·001	0·004	0·011	0·285	0·700	1·10
	0·806	0·168	0·025	0·001	0·005	0·024	0·278	0·693	0·56
2.	0·679	0·295	0·026	0·000	0·010	0·050	0·263	0·677	
	0·672	0·291	0·035	0·002	0·004	0·018	0·281	0·697	1·58
	0·674	0·293	0·032	0·001	0·005	0·040	0·270	0·685	0·65
3.	0·510	0·433	0·034	0·013	0·010	0·076	0·252	0·662	
	0·505	0·443	0·049	0·003	0·003	0·037	0·268	0·692	2·34
	0·509	0·447	0·042	0·002	0·004	0·058	0·263	0·675	1·03
4.	0·327	0·597	0·054	0·023	0·010	0·111	0·238	0·641	
	0·326	0·630	0·066	0·005	0·003	0·037	0·277	0·683	3·40
	0·332	0·609	0·055	0·004	0·003	0·078	0·258	0·661	1·74

TABLE I
(*Continued*)

				NMP/EG = 60/40					
1.	0·814	0·148	0·038	0·000	0·026	0·051	0·432	0·491	
	0·803	0·143	0·053	0·001	0·008	0·015	0·458	0·519	2·08
	0·804	0·146	0·050	0·000	0·017	0·026	0·448	0·509	1·40
2.	0·683	0·257	0·050	0·010	0·029	0·089	0·408	0·474	
	0·672	0·256	0·071	0·001	0·008	0·026	0·447	0·519	3·27
	0·674	0·259	0·066	0·001	0·015	0·045	0·435	0·505	2·32
3.	0·521	0·391	0·070	0·018	0·032	0·128	0·388	0·452	
	0·507	0·392	0·098	0·003	0·007	0·040	0·440	0·513	4·49
	0·531	0·391	0·076	0·002	0·010	0·064	0·388	0·538	3·95
4.[d]	0·334	0·506	0·115	0·045	0·041	0·213	0·332	0·414	

[a] Experimental data; [b] computed from binary data; [c] computed from binary and ternary data; [d] experimental data only; equations have trivial solution.

where $Q = \Delta_t G^E/RT$. Then

$$\begin{aligned}\Delta_t \ln \gamma_1 = {} & x_2x_3[E_{14}x_1(2 - 3x_1) + E_{24}x_2(1 - 3x_1) + E_{34}x_3(1 - 3x_1)] + \\ & + x_3x_4[E_{12}x_1(2 - 3x_1) + E_{32}x_3(1 - 3x_1) + E_{42}x_4(1 - 3x_1)] + \\ & + x_2x_4[E_{13}x_1(2 - 3x_1) \times E_{23}x_2(1 - 3x_1) + E_{43}x_4(1 - 3x_1)] - \\ & - 3x_2x_3x_4(E_{21}x_1 + E_{31}x_1 + E_{41}x_1)\,. \end{aligned} \tag{4}$$

Contributions to activity coefficients of further components could be obtained by cyclic permutation of indices in the relationship (*4*) as

$$\begin{tikzcd} 1 \arrow[r] & 2 \arrow[d] \\ 4 \arrow[u] & 3 \arrow[l] \end{tikzcd}$$

Composition of the equilibrium liquid phases of the four-component system was computed by an isoactivity method through minimization of the objective function

$$F = \sum_i (\hat{a}_i^{II} - \hat{a}_i^{I})^2 \quad i = 1, 2, \ldots, 4 \tag{5}$$

for $\hat{x}_3^{II} = x_3^{II}$ and $\hat{x}_4^{II} = x_4^{II}$; or $\hat{x}_2^{I} = x_2^{I}$ and $\hat{x}_3^{II} = x_3^{II}$ by the Newton–Raphson method. In sense of the Gibbs phase rule two mole fractions habe to be chosen when computing the composition. Two above-mentioned variants were applied; results of better quality were achieved in the second case, i.e. when experimental mole fractions x_2^{I} and x_3^{II} were introduced. The statistical character of these experimental mole fractions was considered via comparison the experimental composition with the calculated one. Their values were adjusted by a process based on the maximum likelihood method. Here, the mole fractions $\hat{x}_3^{\mathrm{II}}$, $\hat{x}_4^{\mathrm{II}}$ or $\hat{x}_2^{\mathrm{I}}$, $\hat{x}_3^{\mathrm{II}}$ were the incidental parameters; they used to be selected so as the objective function

$$F(\hat{x}_3^{\mathrm{II}}, \hat{x}_4^{\mathrm{II}}) = \sum_{\mathrm{i}} \sum_{\mathrm{j}} (x_{\mathrm{ij}} - \hat{x}_{\mathrm{ij}})^2 \quad i = 1, 2, 3, 4 \quad j = \mathrm{I.\ II} \tag{6}$$

would be minimal for each couple of equilibrium phases.

A simple iteration procedure for computation of probable values $\hat{x}_3^{\mathrm{II}}$ and $\hat{x}_4^{\mathrm{II}}$ based on the Rod relations[17] was worked out. Employing the relation

$$\hat{x}_{\mathrm{i}}^{\mathrm{I}} = k_{\mathrm{i}} \hat{x}_{\mathrm{i}}^{\mathrm{II}} \,, \tag{7}$$

where k_{i} are the reciprocal values of distribution coefficients, then the $\hat{x}_2^{\mathrm{II}}$ can be expressed as a functional dependence of mole fractions $\hat{x}_3^{\mathrm{II}}$ and $\hat{x}_4^{\mathrm{II}}$

$$\hat{x}_2^{\mathrm{II}} = a + b\hat{x}_3^{\mathrm{II}} + c\hat{x}_4^{\mathrm{II}} \,. \tag{8}$$

Substitutions a, b, c equal

$$a = (1 - k_1)/(k_2 - k_1) \; b = (k_1 - k_3)/(k_2 - k_1) \; c = (k_1 - k_4)/(k_2 - k_1) . \tag{9}$$

Introduction of bonding conditions

$$\hat{x}_{1\mathrm{j}} = 1 - \hat{x}_{2\mathrm{j}} - \hat{x}_{3\mathrm{j}} - \hat{x}_{4\mathrm{j}} \quad x_{1\mathrm{j}} = 1 - x_{2\mathrm{j}} - x_{3\mathrm{j}} - x_{4\mathrm{j}} \tag{10}$$

and relationship (*8*) the function (*6*) can be transformed as

$$\begin{aligned} F(\hat{x}_3^{\mathrm{II}}, \hat{x}_4^{\mathrm{II}}) = 2 \big[& (\hat{x}_2^{\mathrm{I}} - k_2 a - k_2 b \hat{x}_3^{\mathrm{II}} - k_2 c \hat{x}_4^{\mathrm{II}})^2 + (x_3^{\mathrm{I}} - k_3 \hat{x}_3^{\mathrm{II}})^2 + (x_4^{\mathrm{I}} - k_4 \hat{x}_4^{\mathrm{II}})^2 + \\ & + (x_2^{\mathrm{I}} - k_2 a - k_2 b \hat{x}_3^{\mathrm{II}} - k_2 c \hat{x}_4^{\mathrm{II}}) (x_3^{\mathrm{I}} - k_3 \hat{x}_3^{\mathrm{II}}) + (x_3^{\mathrm{I}} - k_3 \hat{x}_3^{\mathrm{II}}) \,. \\ & \cdot (x_4^{\mathrm{I}} - k_4 \hat{x}_4^{\mathrm{II}}) + (x_4^{\mathrm{I}} - k_4 \hat{x}_4^{\mathrm{II}}) (x_2^{\mathrm{I}} - k_2 a - k_2 b \hat{x}_3^{\mathrm{II}} - k_2 c \hat{x}_4^{\mathrm{II}}) + \\ & + (x_2^{\mathrm{II}} - a - b \hat{x}_3^{\mathrm{II}} - c \hat{x}_4^{\mathrm{II}})^2 + (x_3^{\mathrm{II}} - \hat{x}_3^{\mathrm{II}})^2 + (x_4^{\mathrm{II}} - \hat{x}_4^{\mathrm{II}})^2 + \\ & + (x_2^{\mathrm{II}} - a - b \hat{x}_3^{\mathrm{II}} - c \hat{x}_4^{\mathrm{II}}) (x_3^{\mathrm{II}} - \hat{x}_3^{\mathrm{II}}) + (x_3^{\mathrm{II}} - \hat{x}_3^{\mathrm{II}}) (x_4^{\mathrm{II}} - \hat{x}_4^{\mathrm{II}}) + \\ & + (x_4^{\mathrm{II}} - \hat{x}_4^{\mathrm{II}}) (x_2^{\mathrm{II}} - a - b \hat{x}_3^{\mathrm{II}} - c \hat{x}_4^{\mathrm{II}}) \big] \,. \end{aligned} \tag{11}$$

Providing the distribution coefficients are not a function of composition within the deviation of equilibrium concentrations measured and computed, then from condition

$$\frac{\partial F(\hat{x}_3^{II}, \hat{x}_4^{II})}{\partial \hat{x}_3^{II}} = 0 \quad \frac{\partial F(\hat{x}_3^{II}, \hat{x}_4^{II})}{\partial \hat{x}_4^{II}} = 0 \tag{12}$$

one can obtain a system of two linear equations of two unknowns $\hat{x}_3^{II}$ and $\hat{x}_4^{II}$. This computing scheme can be utilized in original form even for minimization of the objective function (*6*) for probable $\hat{x}_2^{I}$ and $\hat{x}_3^{II}$; the $\hat{x}_2^{I}$ value was enumerated using relations (*7*) and (*8*).

RESULTS

Prediction for the equilibrium composition of a model four-component system was done through three-parameter G^E equations (NRTL), Redlich–Kister 4th order expansion and the Novák modification of Wilson equation). the binary parameters of which were evaluated on the basis of binary L–L and V–L data only and also by using the above-mentioned equations extended by the universal ternary contribution. The form of the G^E equation employed, binary parameters of equations and parameters of ternary contributions are presented in our preceding paper[16]. Values of the ternary contribution of G^E equations were high with the system tolurne–-NMP–EG, $t = 50°C$; the course of the computed binodal curve[16] was unreal in the region with a higher NMP content. The high parameter values of ternary contributions of the given system (and also of heptane–toluene–EG, $t = 50°C$) influenced unfavourably (from the convergence viewpoint) complelation of the four--component L–L equilibrium. Therefore, the set of relatively lower values was withdrawn from that of ternary parameters generated by the simplex method. Thus, e.g. sets representing more realistic the form of the heterogeneous region with a higher NMP content were withdrawn from the system toluene–NMP–EG, $t = 50°C$ even though the three-component L–L equilibrium was weaker reproduced. Selection of parameters in the three-component L–L equilibrium did virtually not affect the quality of reproduction of the system heptane–toluene–EG, $t = 50°C$. Parameters of ternary contributions are listed in Table II.

The L–L equilibrium compositions of the model four-component system computed e.g. by the Redlich–Kister equation are presented in Table I.

Quality of the prediction for the four-component L–L equilibrium is judged on the basis of mole fraction residuals F computed according to relation

$$F = 100[\sum_m \sum_j \sum_i (x_{ijm} - \hat{x}_{ijm})^2 / 2KM]^{1/2} . \tag{13}$$

$$i = 1, 2, \ldots, 4; \quad j = \mathrm{I}, \mathrm{II}; \quad m = 1, 2, \ldots, K .$$

Results of the prediction for an L–L equilibrium for various weight ratios of the mixed solvent NMP/EG are give in Table III.

TABLE II

Values of parameters of ternary contributions E_i and mole fraction residuals F, for the NRTL equation. Redlich–Kister 4th order expansion and the Novák modification of Wilson equation; $t = 50$°C

Type of the G^E equation	E_1	E_2	E_3	F
	Heptane–NMP–EG			
NRTL	−0·2394	−5·3491	−0·2351	0·33
Redlich–Kister	13·4983	−10·8298	2·9332	0·36
Wilson–Novák	7·4551	−5·3758	1·1216	0·30
	Toluene–NMP–EG			
NRTL	−0·0363	2.5181	−8·7624	2·96
Redlich–Kister	−1·5126	3·7327	−7·2193	2·76
Wilson–Novák	−3·0705	6·6215	−7·4817	2·61
	Heptane–Toluene–EG			
NRTL	6·400	23·4380	−30·090	0·08
Redlich–Kister	18·1460	35·1672	−46·6910	0·06
Wilson–Novák	7·8400	30·0100	−36·8400	0·06

TABLE III

Values of average residuals of mole fractions $\langle F \rangle$, for various weight rations of the mixed solvent NMP/EG as computed by G^E equations; the parameters were evaluated from: I binary data, II binary data and L–L data of two ternary systems (toluene–NMP–EG, heptane–NMP–EG), III complete binary and ternary data

Weight ratio NMP/EG	Redlich–Kister 4th order expansion			NRTL equation			Wilson–Novák equation		
	I	II	III	I	II	III	I	II	III
20/80	0·87	0·30	0·31	0·94	0·40	0·53	0·80	0·26	0·29
40/60	2·10	1·00	0·32	2·51	1·10	0·63	2·12	1·03	0·32
60/40	3·28	2·56	0·91[a]	3.83	2·09	1·05[a]	3·39	2·49	1·16[a]
Average	1·88	1·09	0·41[a]	2·19	1·06	0·66[a]	1·88	1·07	0·49[a]

[a] Partial results.

It is obvious that the quality of prediction for a four-component L–L equilibrium from binary data decreased with an increasing content of NMP in the mixed solvent and the mean residual values for mole fractions $\langle F_b \rangle$ rose. We suppose the differences between the experimental and predicted heterogeneous region were due to a synergetic effect of component interactions of the mixed solvent[9]. The average values of mole fraction residual were $\langle F_b \rangle = 2{\cdot}19$, 1·88 and 1·88 according to NRTL. Wilson–Novák and Redlich–Kister equations, respectively. The prediction for a four-component L–L equilibrium changed for better when employing the ternary contributions of ternary systems toluene–NMP–EG and heptane–NMP–EG (eventually also the heptane–toluene–EG). The average values of residuals become lower when applying the NRTL equation $\langle F \rangle = 1{\cdot}06$ (0·66), the Wilson–Novák equation $\langle F \rangle = 1{\cdot}07$ (0·49) and the Redlich–Kister expansion $\langle F \rangle = 1{\cdot}09$(0·41); the numbers in parentheses are valid when also ternary correction parameters for the system heptane–toluene–EG was used.

So far, the analytical computation of four-component L–L equilibria employing the G^E equatlions has been applied to systems of the I and II types, i.e. systems containing one or two partially miscible pairs. The four-component system under study contained three partially miscible pairs, the most complicated of systems analyzed. Nevertheless, the prediction for a four-component L–L equilibrium is satisfactory when making use of the afore-mentioned method. It is believed taht reproduction of the ternary system toluene–NMP–EG, $t = 50°C$ could be improved and consequently, the prediction for a four-component L–L equilibrium of the model system turns to be of better quality.

The proposed method based upon binary and ternary information is characterized by a low computation extensiveness, good reproductivility of binary V–L and also two-, three- and four-component L–L equilibria. Notable is also the universality of the computed model parameters and those of the ternary contribution to G^E equations; what means their utilization also for other systems, where the corresponding binary and ternary subsystems are included; this was impossible with the preceding methods.

LIST OF SYMBOLS

a	activity
a, b, c	substitutions
B	the third parameter of the modified Wilson equation
B, C, D	binary parameters of the Redlich–Kister expansion
E	parameters of the thernary contribution
F	objective function, residual of mole fractions
G^E	molar excess Gibbs energy
K	total number of componens
k	reciprocal value of the distribution coefficient

M	total number of experiments
R	gas constant
t, T	temperature, absolute temperature
x_i, $\hat{x}_i$	mole fraction of the component in the liquid phase (experimental, respectively computed)
Q	function for the excess Gibbs energy
α	binary parameter of the NRTL equation
γ	activity coefficient
Δ_t	ternary contribution
Λ	binary parameter of the modified Wilson equation
τ	binary parameter of the NRTL equation

Superscripts

$\wedge$	calculated value
I, II	designation of phases

Subscripts

b	calculated from binary data
i, j, k	designation of the component
1, 2, 3	designation of the component
j	designation of the phase
m	designation of the experimental measurement

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