TERNARY CORRECTIONS IN THE LIQUID–LIQUID EQUILIBRIA COMPUTATION FOR THREE-COMPONENT SYSTEMS CONTAINING COMPONENTS OF MIXED SOLVENT N-METHYLPYRROLIDONE–ETHYLENE GLYCOL

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Presented are the liquid–liquid (L–L) equilibrium data for three-component heterogeneous systems toluene–N-methylpyrrolidone–ethylene glycol, heptane–N-methylpyrrolidone–ethylene glycol and heptane–toluene–ethylene glycol at 50°C. Equations for the excess Gibbs energy (NRTL. Novák modification of Wilson equation and Redlich–Kister 4th order expansion) extended by ternary universal contribution were employed for correlating the L–L equilibrium data. The binary equation parameters were independently evaluated from the binary equilibrium data. The presented ternary data served for evaluation of parameters of the universal ternary contribution.

Equations for the excess Gibbs energy (G^E-equations) are employed for computing the precise ternary equilibrium data; their parameters can be identified by two different ways. One of them is the identification of all binary parameters of G^E equations (or their parts) from ternary equilibrium L–L data[1,2]. Disadvantage of this method is the usual misinterpretation of the behaviour of binary solutions. The second way is the extention of G^E-equations by ternary elements. An example offers the universal form of ternary contribution suggested by Surový and cowerkers[3] convenient for all types of G^E-equations. The ternary contribution parameters were identified from experimental ternary L–L equilibrium data; the binary parameters remain in the original form at the same time. This method was verified with four systems of the hydrocarbon–hydrocarbon–polar solvent types.

This paper presents the prodceure applied for ternary system containing components of the solvent mixture N-methylpyrrolidone (NMP)–ethylene glycol (EG) with heptane and toluene as model hydrocarbons. The study dealing with reproduction of three-component L–L equilibria is based upon complete binary and ternary equilibrium data. The literature presents relatively little information about systems in question and therefore, measured were sets of experimental data as follows.

THEORETICAL

Activity coefficients in multi-component L–L systems were computed employing the three-parameters G^E-equations:

1. the NRTL equation[4]

$$G^E/RT = \sum_i x_i \sum_j \tau_{ji} G_{ji} x_j / \sum_k G_{ki} x_k \,, \qquad (1)$$

for $i, j, k = 1, 2, \ldots, k$; where $G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$; $\alpha_{ij} = \alpha_{ji}$;

2. the Novák modification of Wilson equation[5]

$$G^E/RT = -\sum_i x_i \ln\left(\sum_j \Lambda_{ij} x_j\right) + \sum_i \sum_j B_{ij} x_i x_j \,, \qquad (2)$$

for $i, j = 1, 2, \ldots, k$; and $B_{ij} = B_{ji}$ and $B_{ii} = B_{jj} = 0$;

3. Redlich–Kister 4th order expension[6]

$$(G^E/RT)_{123} = (G^E/RT)_{12} + (G^E/RT)_{13} + (G^E/RT)_{23} \,, \qquad (3)$$

where $(G^E/RT)_{ij} = x_i x_j [B_{ij} + C_{ij}(x_i - x_j) + D_{ij}(x_i - x_j)^2]$.

The equations were derived from various accesses and therefore, they are not equally suitable for all types of systems. The NRTL equation is one (in addition to UNIQUAC equation[7]) of the most frequented and utilized equations for prediction and reproduction of multi-components L–L equilibria. On the other hand, the classic Wilson equation is unable to predict phase splitting. The Novák modification of this equation can be applied even for a thermodynamic description of the partially miscible systems. The equation is advantageous in that the curve of Gibbs energy of mixing has maximally two inflex points[8]. Further equation, the Redlich–Kister expansion is unsuitable for asymmetric systems and it is virtually not used for the above-mentioned computation type. It is noterworthy that Surový and coworkers[8,3] obtained with this very equation qualitatively most correct predictions for a three-component L–L equilibrium in comparison with the afore-mentioned equations (NRTL and Novák modification of the Wilson equation).

The G^E equations offer results of better quality even when forms extended by universal ternary contribution were employed for computing the activity coefficients. Form of the suggested ternary contribution to the function G^E- derived by Surový and coworkers[3] is

$$\Delta_t G^E/RT = x_1 x_2 x_3 [E_1 x_1 + E_2 x_2 + E_3 x_3] \,. \qquad (4)$$

EXPERIMENTAL

N-Methylpyrrolidone was purified from the technical grade (Slovnaft, Bratislava) by a double

rectification under reduced pressure; the same procedure was applied for ethylene glycol (Loba Chemie, Vienna); the column had c. 10 theoretical plates efficiency. Toluene (p.a. grade, Lachema, Neratovice) and heptane (Loba Chemie, Vienna) were redistilled in an atmospheric column with c. 20 theoretical plates. All solvents were molecular-sieves dried. The chromatographic purities of NMP, EG and heptane were higher than 99·8%, that of toluene 99·6%.

The L–L data of ternary systems (toluene–NMP–EG, heptane–NMP–EG and heptane–toluene–EG) at $t = 50°C$ were measured by a direct analytical method, the complete composition of the equilibrium phases was analyzed chromatographically. A diluting component functioning as an

TABLE I

Experimental data of L–L equilibria for three-component systems, $t = 50°C$

x_i^I	x_j^I	x_k^I	x_i^{II}	x_j^{II}	x_k^{II}
		Heptane–Toluene–EG			
0·99948	—	0·00052	0·00159	—	0·99841
0·883	0·117	0·000	0·001	0·005	0·994
0·749	0·251	0·000	0·001	0·008	0·991
0·633	0·367	0·000	0·001	0·011	0·988
0·456	0·544	0·000	0·001	0·015	0·984
0·359	0·641	0·000	0·001	0·018	0·981
0·248	0·751	0·001	0·000	0·021	0·979
—	0·9958	0·0042	—	0·0239	0·9761
		Heptane–NMP–EG			
0·99948	—	0·00052	0·00159	—	0·99841
0·992	0·008	0·000	0·002	0·110	0·888
0·990	0·010	0·000	0·004	0·216	0·780
0·983	0·017	0·000	0·011	0·321	0·668
0·982	0·018	0·000	0·017	0·411	0·572
0·968	0·032	0·000	0·033	0·548	0·419
0·933	0·067	0·000	0·060	0·680	0·260
0·895	0·105	0·000	0·101	0·746	0·153
0·713	0·2866	—	0·3222	0·6778	—
		Toluene–NMP–EG			
0·9958	—	0·0042	0·0239	—	0·9761
0·956	0·026	0·018	0·052	0·066	0·882
0·934	0·036	0·030	0·063	0 086	0·852
0·911	0·053	0·036	0·084	0·116	0·800
0·905	0·059	0·036	0·089	0·121	0·790
0·893	0·069	0·038	0·106	0·137	0·757
0·872	0·078	0·050	0·127	0·156	0·717

internal standard in chromatographic analysis and simultaneously ensuring the homogeneity of phases analyzed was added to the equilibrium phases. The column was packed with a stationary phase 10% neopentyl glycol succinate and the sample was analyzed at 160°C with an accuracy ±0·5 mole%, or higher. Results of measurements are listed in Table I. The equilibrium L–L data for the system heptane–toluene–NMP, $t = 50$°C were not determined because of a narrow geterogeneous range. The binodal curve for the above-mentioned system apperaed in paper[9].

Binary solubilities of partially miscible pairs with a smaller heterogeneous region (toluene–EG, heptane–NMP) were measured by a turbidity method in a narrow temperature range 50 ± 5°C. The relationship $x_{ij} = (f(t)$ was drawn by the least squared method by means of quadratic polynomial and the solubility was interpolated for $t = 50$°C. Composition of the equilibrium phases of the system heptane–EG, $t = 50$°C was determied by chromatographic analysis due to a very small mutual solubilities as follows: the hydrocarbon phase was extracted with water and the aqueous extract was analyzed chromatographically. Prior to analysis the glycol phase was diluted with amyl alcohol. Solubilities of binary mixtures are listed in Table II for a 95% confidence interval.

The isothermal equilibrium data liquid–vapour ($t = 50$°C) for two-component homogeneous binary systems toluene–NMP and heptane–toluene have not been reported and therefore, they were determined as follows: toluene–NMP by a static method[10], heptane–toluene by a circulation method[11]; both equilibrium data are detailed in ref.[9]. The equilibrium data for the mixed solvent méasured by a differential method are reported in ref.[12].

RESULTS AND DUSCUSSION

The binary parameters of G^E equations were independently evaluated from binary solubilities and liquid–vapour equilibrium data. Employed were following procedures: Computation of binary parameters of G^E equations for partially miscible pairs was based on results by Surový and coworkers[8]. The third parameter (α_{ij} for NRTL equation, B_{ij} for Wilson–Novák equation and D_{ij} for Redlich–Kister expansion) was adjusted according to the limiting activity coefficient of the hydrocarbon in the solvent.

TABLE II

Solubilities of binary systems at $t = 50$°C evaluated for a 95%-confidence interval, γ_{ij}^{∞} is the limiting activity coefficient of the hydrocarbon in solvent

System i–j	x_{ij}	x_{ji}	γ_{ij}^{∞}
Heptane–EG	$(15{\cdot}9 \pm 0{\cdot}2)\ 10^{-4}$	$(5{\cdot}2 \pm 0{\cdot}2)\ 10^{-4}$	630·8[a]
Toluene–EG	$(23{\cdot}91 \pm 0{\cdot}07)\ 10^{-3}$	$(4{\cdot}18 \pm 0{\cdot}11)\ 10^{-3}$	50·6[a]
Heptane–NMP	$0{\cdot}3222 \pm 7{\cdot}3\ 10^{-3}$	$0{\cdot}2866 \pm 4{\cdot}8\ 10^{-3}$	12·7[b]

[a] Computed from vapour pressure in heterogenesous region according to Surový[8]; [b] determined by the Carlson–Colburn method[15].

TABLE III

Binary parameters of NRTL equation, Redlich–Kister 4th order expansion and Novák modification of Wilson equation for binary systems, $t = 50°C$

System	NRTL equation			Redlich–Kister expansion			Wilson–Novák equation		
	τ_{ij}	τ_{ji}	α_{ij}	B_{ij}	C_{ij}	D_{ij}	Λ_{ij}	Λ_{ji}	B_{ij}
Heptane–toluene	0·0526	0·3940	0·8586	0·3790	−0·0547	0·0083	0·6050	1·0595	0·0
Heptane–NMP	1·7503	1·6606	0·40	2·2926	0·0202	0·2600	0·2480	0·2068	0·3303
Heptane–EG	6·4821	1·1246	0·03	6·9553	0·5540	0·006	1·0337	0·1345	5·60
Toluene–NMP	0·9968	0·4088	1·6899	0·5930	0·1424	0·1759	1·1962	0·2888	−0·1675
Toluene–EG	4·1820	2·1782	0·21	4·2574	0·8117	0·480	0·9846	0·0717	2·95
NMP–EG	0·3114	−0·8143	0·60	−0·6554	−0·1836	0·1967	2·4339	0·6778	0·0

Parameters of G^E equations for completely miscible pairs were evaluated by the iterative procedure of the maximal likelihood method according to Rod and Hančil[13]. (The computing method is given in paper[9].).

The ternary contribution parameters were evaluated by means of the set of independent binary parameters of G^E euquations (Table III) from three-component L–L equilibrium data. The parameters were identified by minimization of the objective function based on mole fractions[3] by a simplex method.

The inverse computation of equilibrium mole fractions was performed by the isoactivity method, by minimization of function

$$F(\hat{x}_i) = \sum_{i=1}^{3} (\hat{a}_i^{II} - \hat{a}_i^{I}) \tag{5}$$

namely for $\hat{x}_2^{II}$, for which the function

$$F(\hat{x}_2^{II}) = \sum_{i} \sum_{j} (x_{ij} - \hat{x}_{ij})^2 \quad i = 1, 2, 3; \; j = I, II \tag{6}$$

is minimal.

Quality of the computed equilibrium data was evaluated on the basis of mole

TABLE IV

Parameter values of ternary contributions E_i and mole fraction residuals computed from binary data (F_b) and from binary and ternary information (F) for NRTL equation, Redlich–Kister 4th order expansion and Novák modification of Wilson equation, $t = 50°C$

Type of the G^E equation	E_1	E_2	E_3	F	F_b
	Heptane–NMP–EG				
NRTL	−0·2394	−5·3491	−0·2351	0·33	1·11
Redlich–Kister	13·4983	−10·8298	2·9332	0·36	0·88
Wilson–Novák	7·4551	−5·3758	1·1216	0·30	0·81
	Toluene–NMP–EG				
NRTL	−14·5596	41·8186	−12·5104	2·32	3·03
Redlich–Kister	−19·2548	30·5702	−8·8953	2·29	3·09
Wilson–Novák	−3·0705	6·6215	−7·4718	2·62	2·93
	Heptane–Toluene–EG				
NRTL	6·400	23·4380	−30·090	0·08	0·11
Redlich–Kister	18·1460	35·1672	−46·6910	0·06	0·15
Wilson–Novák	25·4667	33·6001	−50·5333	0·06	0·13

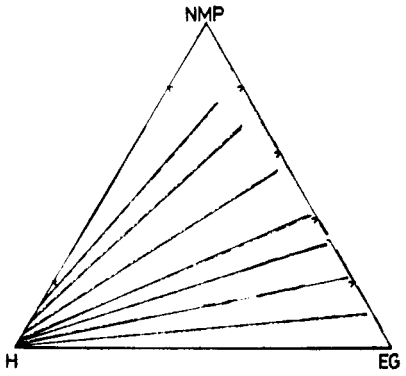

FIG. 1

System heptane–NMP–EG, $t = 50°C$. The L–L equilibrum data: —— experimental, ·-·-· computed by Redlich–Kister equation with ternary correction

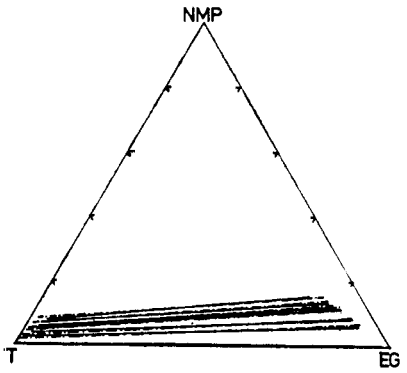

FIG. 2

System toluene–NMP–EG, $t = 50°C$. The L–L equilibruim data: —— experimental, ·-·-· computed by Redlich–Kister equation with ternary correction

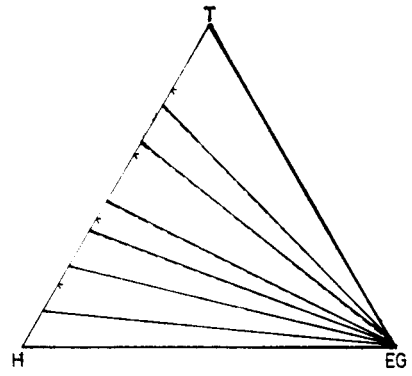

FIG. 3

System heptane–toluene–EG, $t = 50°C$. The L–L equilibrum data: —— experimental, - - - computed by Redlich–Kister equation without ternary correction. (The L–L equilibrium data computed by Redlich–Kister equation with ternary correction merged with the experimental ones.)

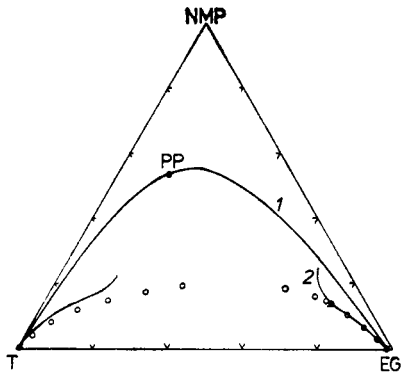

FIG. 4

System toluene–NMP–EG, $t = 50°C$. Binodal curve: o experimental, *1* predicted from binary data of Redlich–Kister equation, 2 correlated by Redlich–Kister equation with ternary correction. PP plait point

fraction residuals

$$F = 100[\sum_{m}\sum_{i}\sum_{j}(x_{ijm} - \hat{x}_{ijm})^2/6M]^{1/2} \qquad (7)$$

where $i = 1, 2, 3$; $j = \text{I, II}$; $m = 1, 2, \ldots, M$.

Results of these computations are summarized in Table IV and plotted in Figs. 1 to 3. The residual values of mole fractions for all G^E equations employed (NRTL and Novák modification of the Wilson equations, respectively and the Redlich–Kister expansion) are comparable. It is, however obvious that the prediction quality of the L–L equilibrium based on binary data (residuals F_b) and correlations of L–L equilibrium arising from ternary data (residuals F) considerably differ for the respective systems. Prediction for the L–L equilibrium from binary data was not of sufficient quality with the system toluene–NMP–EG, $t = 50°C$ (the average mole fractions residual for the G^E equations employed, $\langle F_b \rangle = 3{\cdot}02$). As supposed, the difference in magnitude between the experimental and predicted heterogeneous regions of the system under investigation (Fig. 4). is due to a synergetic effect of component interactions of the solvent mixture with the aromatic hydrocarbon[14]. The reproduction quality of L–L data becomes better only partially by using ternary contributions, the average mole fraction residual $\langle F \rangle = 2{\cdot}41$. Prediction for the system heptane–NMP–EG, $t = 50°C$ is satisfactory ($\langle F_b \rangle = 0{\cdot}93$), with ternary contributions the reproduction quality of L–L data becomes considerably better ($\langle F \rangle = 0{\cdot}33$). Prediction for the L–L data with the system heptane–toluene–EG, $t = 50°C$ based on binary data is very good, the mole fraction residuals are very low ($\langle F_b \rangle = 0{\cdot}13$). Reproduction refinement of the three-component L–L equilibrium of the system under study is veirtually unnecessary.

The evaluated parameters of ternary contributions can be employed for prediction refinement for four-component L–L equilibrium of the model system containing the given components, i.e. heptane–toluene–NMP–EG at $t = 50°C$.

LIST OF SYMBOLS

a	activity
B	the third parameter of the modified Wilson equation
B, C, D	binary parameters of the Redlich–Kister expansion
E	parameters of the ternary contribution
F	objective function, residual of mole fractions
G^E	molar excess Gibbs energy
K	total number of componens
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)

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

∞ infinitely diluted solution
$\wedge$ 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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