SOME INFORMATION ON CALCULATING THE LIQUID–LIQUID EQUILIBRIUM OF TERNARY SYSTEMS. AN IMPROVEMENT OF PREDICTION OF LIQUID–LIQUID EQUILIBRIUM IN TERNARY SYSTEMS FROM BINARY EQUILIBRIUM DATA

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A possibility is described of improving the prediction of ternary liquid–liquid equilibrium data from binary ones by using three-parameter equations for calculating activity coefficients. The parameters for completely miscible pairs of liquids were determined from their vapour–liquid equilibrium data and those for partially miscible pairs of liquids from their mutual solubilities and from one limiting activity coefficient. A qualitatively correct prediction of the liquid–liquid equilibrium data was achieved in all cases by means of three different equations (NRTL equation, Redlich–Kister equation and Wilson equation modified by Novák and coworkers) in four hydrocarbon–hydrocarbon–polar solvent systems investigated.

Joy and Kyle[1] has already drawn attention to the fact that the calculated values of activity coefficients in homogeneous region are often different according to the type of equations used and have often incorrect values if two-parameter equations whose parameters have been calculated from mutual solubilities are used to express the dependence $G^E = f(x_i)$ of binary liquid solution. This fact can consequently contribute to the inaccuracy of predictions of liquid–liquid equilibrium in three- and multicomponent systems based on the binary parameters only. Only by choosing a suitable type of equations, we can ensure that the prediction will be at least qualitatively correct. According to the surveying work by Sørensen and coworkers[2], the best results of equations with pairs of binary parameters are attained with the UNIQUAC equation[3] which has also the best theoretical basis.

The situation is changed in case of equations with triads of binary parameters. Here, by choosing the third parameter, we can attain that for partially soluble pairs of liquids, the activity coefficients should satisfy the condition of equilibrium

$$\gamma_{ij} x_{ij} = \gamma_{ii} x_{ii} \tag{1}$$

of coexisting liquid phases and simultaneously that the course of dependence $\ln \gamma_i = f(x_i)$ in the homogeneous region should be close to the true course. The effect of the third parameter can be well demonstrated by the values of limiting activity coefficients of components. As an example the system heptane(1)–dimethylformamide(2) is presented. At the temperature of 40°C, the solubilities are $x_{11} = 0.886$, $x_{21} = 0.114$, $x_{12} = 0.116$, $x_{22} = 0.884$. The limiting activity coefficients of both components $\gamma_{ij}^\infty \in \langle 14, 22 \rangle$ correspond to the values of the third parameter of the NRTL equation[4] $\alpha_{12} \in \langle 0.05, 0.40 \rangle$, the Redlich–Kister equation[5] $D_{12} \in \langle 0, 0.50 \rangle$ and

the Wilson equation as modified by Novák and coworkers[10] $B_{12} \in \langle 2\cdot 00, 0\cdot 45 \rangle$. The given ranges of values of the third parameter correspond to the region in which the curve $G^M/RT = f(x_1)$ has only two inflex points (see below). In spite of it the range of calculated values of γ_{ij}^{∞} is considerable. Similarly it looks in case of other partially miscible liquids.

The properties of partially miscible pairs of liquids have the predominant influence on the properties of ternary and multicomponent heterogeneous liquid systems. The considerable effect of the third parameter no the values of limiting activity coefficients indicates therefore simultaneously its effect on the calculated ternary L–L equilibrium data. The effect of the parameter α_{ij} on the shape of ternary L–L diagrams calculated in terms of the NRTL equation is discussed by Renon[6] and Soares and coworkers[7] in their works. Owing to the lack of experimental data, Sørensen and coworkers[2] recommend to use the value $\alpha_{ij} = 0\cdot 3$ in the NRTL equation for partially miscible components, which is the optimum average value for the systems studied by them. Heinrich and Dojčanský[15] recommend for ternary systems with open binodal curve to adjust the NRTL parameter α_{ij} of partially miscible pair of liquids according to the limiting activity coefficients of components.

Reassuming the latter work we wish in this work to investigate in detail the extent of the effect of adjusting the third parameter of the partially miscible pairs of liquids in terms of the limiting activity coefficient on the accuracy of prediction of the L–L equilibrium in the hydrocarbon–hydrocarbon–polar solvent systems. No less interesting is the question whether such an adjustment makes it possible to predict L–L equilibrium even in terms of such equations for G^E which are considered in the literature as less suitable for this purpose.

THEORETICAL

Equations for G^E Used

NRTL *equation*[4]. This equation has the form

$$G^E/RT = \sum_i x_i \sum_j \tau_{ji} G_{ji} x_j / \sum_l G_{li} x_1 \; ; \quad i, j, l = 1, 2, ..., K \, , \qquad (2)$$

where

$$G_{ji} = \exp\left(-\alpha_{ji}\tau_{ji}\right) ; \quad \alpha_{ij} = \alpha_{ji}$$

and is considered to be the most suitable three-parameter equation for the qualitative prediction of L–L equilibrium of multicomponent systems on the basis of binary data, which was verified using several tens of mainly ternary L–L systems most extensively in the work by Sørensen and coworkers[2]. A drawback of the equation is a comparatively difficult identification of parameters from the L–G equilibrium data[8]. For higher α_{ij} values, the NRTL equation can yield incorrect values of com-

position of the equilibrium liquid phases owing to the occurrence of more than two inflex points on the curve $G^M = f(x_i)$ of binary systems[9]. For binary symmetric systems ($\tau_{ij} = \tau_{ji}$) there are four inflex points on the G^M curve for $\alpha_{ij} > 0.426$. Therefore we have chosen the values $\alpha_{ij} \leqq 0.4$ for partially miscible binary solutions of systems studied.

Redlich–Kister expansion[5]. The fourth-order equation derived from the Redlich–Kister expansion with binary parameters has the following form for a three-component system

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

where

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

The equation is considered as not very much suitable for predicting the ternary and multicomponent L–L equilibria from binary data[2]. As many as four inflex points can occur on the $G^M = f(x_i)$ curves of binary systems. Therefore we have investigated the conditions of their occurrence in binary symmetric systems ($C_{ij} = 0$):

For the Gibbs energy of mixing of binary symmetric systems we get in agreement with Eq. (3)

$$G^M/RT = x_i x_j \left[B_{ij} + D_{ij}(x_i - x_j)^2\right] + x_i \ln x_i + x_j \ln x_j. \tag{4}$$

By means of Eq. (4) and the condition of existence of inflex point, $\partial^2(G^M/RT)/\partial x^2 = 0$, it is possible to show that for $B_{ij} + D_{ij} > 0$, *i.e.* for systems with limiting activity coefficients larger than unity, the curve of Gibbs energy of mixing (Eq. (4)) exhibits in the interval $x_i \in (0, 1)$

no inflex point if $D_{ij} + 2 > B_{ij} < \sqrt{(48D_{ij})} - 5D_{ij}$,

two inflex points if $B_{ij} > D_{ij} + 2$,

four inflex points if $D_{ij} + 2 > B_{ij} > \sqrt{(48D_{ij})} - 5D_{ij}$.

The cubic term in Eq. (4), which is non-zero in asymmetric systems, acts rather in the direction of smoothing the course of G^M curve so that the condition of existence of two inflex points in symmetric systems

$$B_{ij} > D_{ij} + 2 \tag{5}$$

can be applied to unsymmetric systems, too.

The Wilson equation modified by Novák and coworkers[10] was obtained by combining the Wilson equation[11] with the quadratic term of the Redlich–Kister equation.

For a multicomponent system, the modified Wilson equation takes the form

$$G^E/RT = -\sum_{i=1}^{K} x_i \ln \left[\sum_{j=1}^{K} \Lambda_{ij} x_j \right] + \sum_{i=1}^{K} \sum_{j=1}^{K} B_{ij} x_i x_j \; ; \quad B_{ii} = 0 \; ; \quad B_{jj} = 0 \; . \quad (6)$$

The activity coefficient of the first component in a ternary solution is

$$\ln \gamma_1 = 1 - \ln \left(x_1 + x_2 \Lambda_{12} + x_3 \Lambda_{13} \right) - \frac{x_1}{x_1 + x_2 \Lambda_{12} + x_3 \Lambda_{13}} -$$

$$- \frac{x_2 \Lambda_{21}}{x_1 \Lambda_{21} + x_2 + x_3 \Lambda_{23}} - \frac{x_3 \Lambda_{31}}{x_1 \Lambda_{31} + x_2 \Lambda_{32} + x_3} + B_{12} x_2 (1 - x_1) -$$

$$- B_{23} x_2 x_3 + B_{31} x_3 (1 - x_1) \, . \quad (7)$$

The equations for components 2 and 3 are obtained by a cyclic permutation of indices.

An advantage of Eq. (6) compared to the classical Wilson equation is that it is able to describe with $B_{ij} > 0$ the partially miscible system in a thermodynamically correct way. In case of completely miscible pairs of liquids, $B_{ij} = 0$ is then chosen so that it is possible to use for their thermodynamic description the parameters Λ_{ij} of the classical two-parameter Wilson equation which are relatively extensively tabulated[12,13]. In addition, the fact is not certainly negligible that the G^M curve for binary solutions has at most two inflex points for the case of this modification of the Wilson equation.

Calculation Procedures Used in Predicting Ternary L–L Equilibria

Adjustment of the third parameter (α_{ij} for NRTL, B_{ij} for the Wilson and D_{ij} for the Redlich–Kister equation) in terms of the limiting activity coefficient of hydrocarbon in solvent was made for the partially miscible pairs of liquids in the following way: Different values of the third parameter were chosen and the values of the remaining two parameters were calculated by numerical solution of the system of equations derived from the condition of equilibrium (1) and then the value of limiting activity coefficient was calculated from the corresponding equation. More precision was then given to the third parameter according to the experimental data on limiting activity coefficient by using the binary bisection method.

The composition of ternary equilibrium phases was calculated by the isoactivity method by minimizing the function

$$F(\hat{x}_i) = \sum_{i=1}^{3} (\hat{a}_i^{II} - \hat{a}_i^{I})^2 \quad (8)$$

for $\hat{x}_2^{II} = x_2^{II}$. The minimization was carried out by the Newton–Raphson method. The partial derivatives were calculated numerically.

Coordinates of the plait point were calculated as an arithmetic mean of the coordinates of tie-line very close to the plait point. If we choose the difference of mole fractions of one of components in equilibrium phases

$$\hat{x}_i^I - \hat{x}_i^{II} = \delta\hat{x}_i , \qquad (9)$$

the tie-line lying in the vicinity of the plait point is uniquely determined when choosing suitably the component i. We chose $\delta\hat{x}_1 = 10^{-2}$ for the systems studied in this work. The values of three equilibrium mole fractions $\hat{x}_1^{II}, \hat{x}_2^{II}, \hat{x}_2^I$ were calculated by minimizing function (8) by the Newton–Raphson method on using the restraining conditions

$$\hat{x}_3^{II} = 1 - \hat{x}_1^{II} - \hat{x}_2^{II}; \ \hat{x}_3^I = 1 - \hat{x}_1^I - \hat{x}_2^I; \ \hat{x}_1^I = \hat{x}_1^{II} + \delta\hat{x}_1 . \qquad (10)$$

The linear approximation of the difference of activities in function (8) has then the form

$$a_i^{II} - a_i^I \approx (a_i^{II} - a_i^I)^0 + \left[(\partial a_i^{II}/\partial x_1^{II})_{x_2^{II}}^0 - (\partial a_i^I/\partial x_1^I)_{x_2^I}^0\right] \Delta x_1^{II} +$$
$$+ (\partial a_i^{II}/\partial x_2^{II})_{x_1^{II}}^0 \Delta x_2^{II} - (\partial a_i^I/\partial x_2^I)_{x_1^I}^0 \Delta x_2^I . \qquad (11)$$

(Superscript ^{0} denotes the values for x_i from foregoing approximation.) With regard to a small difference of activities in the vicinity of plait point it is necessary to use a computer with at least 12 significant digits and to finish the computations at $F(\hat{x}_i) \leq 10^{-15}$. The coordinates of tie-line in close proximity of the assumed plait point were chosen as the first estimate. The partial derivatives were calculated numerically.

An advantage of this method in comparison with the Gibbs method of calculation of critical points, used by other authors[19,20] is the fact that the program for calculating tie-lines can be used nearly without changing it for calculating the plait point.

EXPERIMENTAL

The prediction of ternary liquid–liquid equilibria was verified using four systems hydrocarbon––hydrocarbon–polar solvent chosen so that the shape and size of the heterogeneous region in equilibrium diagrams should be different. The experimental liquid–liquid equilibrium data of these systems are given in Table I. The binary solubilities for all the systems are our measurements carried out in the following way: The temperature of turbidity appearence was established for 5—7 solutions of known composition in sealed ampoules. The dependence $x_{ij} = f(t)$ was made up by the least-squares method in terms of a quadratic polynomial and from it the solubility was interpolated for the given temperature. Our measurements of the ternary L–L equilibrium data

TABLE I

Composition of equilibrium liquid phases

x_1^{I}	x_2^{I}	x_3^{I}	x_1^{II}	x_2^{II}	x_3^{II}
Heptane(1)–toluene(2)–DMFA(3), 40°C					
0·886	—	0·114	0·116	—	0·884
0·847	0·025	0·128	0·127	0·018	0·855
0·814	0·046	0·140	0·134	0·036	0·830
0·786	0·060	0·154	0·146	0·047	0·806
0·754	0·077	0·169	0·156	0·062	0·782
0·699	0·102	0·199	0·177	0·084	0·739
0·657	0·116	0·227	0·198	0·100	0·702
0·581	0·137	0·282	0·239	0·122	0·639
			$0·393^a$	$0·153^a$	$0·454^a$
Heptane(1)–cyclohexane(2)–DMFA(3), 25°C					
0·927	—	0·073	0·084	—	0·916
0·741	0·185	0·074	0·075	0·029	0·896
0·634	0·291	0·075	0·067	0·047	0·886
0·553	0·369	0·078	0·062	0·061	0·877
0·448	0·473	0·079	0·054	0·084	0·862
0·356	0·562	0·082	0·045	0·102	0·853
0·239	0·680	0·081	0·034	0·136	0·830
0·122	0·795	0·083	0·019	0·168	0·813
—	0·918	0·082	—	0·201	0·799
Cyclohexane(1)–benzene(2)–furfural(3), 25°C (ref.[14])[b]					
0·948	—	0·052	0·137	—	0·863
0·875	0·054	0·071	0·157	0·039	0·804
0·825	0·089	0·086	0·171	0·072	0·757
0·773	0·123	0·104	0·190	0·104	0·706
0·715	0·156	0·129	0·215	0·136	0·649
0·648	0·187	0·165	0·249	0·169	0·582
—	—	—	0·409	0·213	0·378
Heptane(1)–benzene(2)–DMSO(3), 40°C (ref.[15])					
0·9925	—	0·0075	0·0140	—	0·9860
0·881	0·109	0·010	0·017	0·055	0·928
0·785	0·200	0·015	0·022	0·111	0·867
0·698	0·280	0·022	0·028	0·167	0·805
0·618	0·351	0·031	0·037	0·222	0·741
0·553	0·401	0·046	0·043	0·264	0·693
0·485	0·446	0·069	0·051	0·296	0·653

[a] Determined by graphical extrapolation; [b] in case of repeated measurements performed by the authors, the arithmetic mean of mole fractions of components from these measurements is given.

are given in the first two parts of Table I. They were obtained by the analytical method so that, after separating the equilibrium liquid phases, the solvent was extracted by water. The composition of both phases was calculated from the composition of aqueous extract and of the hydrocarbon

TABLE II

Parameters of the NRTL, Wilson and Redlich–Kister equations for completely miscible pairs of liquids

System	NRTL			Wilson[a]		Redlich–Kister		
	τ_{ij}	τ_{ji}	α_{ij}	$\varLambda_{ij}$	$\varLambda_{ji}$	B_{ij}	C_{ij}	D_{ij}
Heptane(1)– –toluene(2) 40°C	0·0878	0·3614	0·4097	0·7280	0·8901	0·3869	−0·0458	0·0045
Toluene(2)– –DMFA(3), 40°C	1·1255	−0·1286	0·4001	0·9917	0·3574	0·7386	0·2049	−0·0056
Heptane(1)–cyclo- hexane(2), 25°C	−0·8646	1·0198	0·0664	1·4922	0·5290	0·0946	0·0336	0·0319
Cyclohexane(1)– –benzene(2), 25°C	0·0031	0·5589	0·2341	0·5949	0·9237	0·5496	−0·0594	−0·1446
Benzene(2)– –furfural(3), 25°C	1·1164	0·4213	0·8696	0·8805	0·3115	0·9628	0·2138	0·0967
Heptane(1)– –benzene(2), 40°C	−0·4936	1·1863	0·2499	0·4651	1·1253	0·4816	−0·1161	−0·0171
Benzene(2)– –DMSO(3), 40°C	1·2671	0·5790	0·6422	0·6859	0·2759	1·2376	0·2215	0·1349

[a] $B_{ij} = 0$.

TABLE III

Experimental values of limiting activity coefficients γ_{13}^{∞} of hydrocarbons in solvents

System	γ_{13}^{∞}
Heptane(1)–DMFA(3), 40°C	18·8
Heptane(1)–DMFA(3), 25°C	23·3
Cyclohexane(2)–DMFA(3), 25°C	12·7[a]
Cyclohexane(1)–furfural, 25°C	15·9
Heptane(1)–DMSO(3), 40°C	79·6

[a] γ_{23}^{∞}.

part determined refractometrically. The accuracy of measurements of binary solubilities was ± 0.1 mol% and in the system in the last part of Table I ± 0.05 mol%. The accuracy of the ternary equilibrium data was better than ± 0.5 mol%. The third part of Table I was made up on the basis of the ternary equilibrium data by Henty and coworkers[14] and the last part of Table I from the data by Heinrich and Dojčanský[15].

The binary parameters of Eqs (2), (3) and (6) for completely miscible pairs were calculated from the P-x vapour–liquid equilibrium data which were taken from the work of Heinrich[16] for the pairs of the first and last parts of Table I and for the remaining pairs were obtained from our own measurements. The data were measured by a static method in the apparatus described by Surový and coworkers[17]. The evaluation of all the three parameters was carried out simultaneously, minimizing the function

$$F(\pi_1, \pi_2, \pi_3) = \sum_{l=1}^{m} \{[P - \hat{P}(\pi_1, \pi_2, \pi_3)]/P\}_l^2 . \qquad (12)$$

The values of the parameters are given in Table II.

To establish the third parameter of the G^E equations of partially miscible pairs of liquids it is necessary to know a value of one limiting activity coefficient. The value of those limiting activity coefficient of hydrocarbon in solvent was determined because its error of determination was lower. The determination in systems of the first three parts of Table I was made by the Carlson––Colburn method[18] by means of the P-x equilibrium data in homogeneous region. The extrapolation of apparent activity coefficients was carried out in terms of regression equations of the dependence $\ln \gamma_i' = f(x_i)$.

Because of low solubility of heptane in dimethyl sulphoxide the limiting activity coefficient of heptane was calculated from the solubility and from the experimental vapour pressure in heterogeneous region by means of the relation

$$\gamma_{ij}^{\infty} = \left[(P_{het} - P_j^0 x_{jj})/P_i^0 x_{ij}\right]^{x_{jj}^{-2}} . \qquad (13)$$

(The relation was derived on the assumption that the simple dependence $\ln \gamma_{ij} = A x_{jj}^2$ holds for the activity coefficient of dissolved component, the vapour phase behaves as an ideal gas and the activity coefficient of solvent is unity.) The values of limiting activity coefficients are given in Table III.

RESULTS AND DISCUSSION

The most important data for evaluating the results of prediction of ternary L–L equilibria for four systems investigated and for the NRTL, Wilson and Redlich––Kister equations are given in Tables IV and V. The basis of evaluating form the residuals given by the formula[2]

$$F_x = 100 \sqrt{\left(\sum_l \sum_i \sum_j (x_{ijl} - \hat{x}_{ijl})^2/6m\right)} , \qquad (14)$$

where $i = 1, 2, 3$; $j = $ I, II; $l = 1, 2, \ldots, $ m and $\hat{x}_2^{II} = x_2^{II}$.

The data for $3-4$ values of the third parameter of partially miscible pairs of liquids, π_3, are given for each equation. The data corresponding to the experimental value

Table IV

Evaluation of the prediction of ternary L–L equilibria

Equation	$(\pi_3)_{13}$	γ_{13}^∞	γ_{31}^∞	F_x
	Heptane(1)–toluene(2)–DMFA(3), 40°C			
	0·200	14·8	15·0	4·40
NRTL	0·300	16·4	16·7	4·02
	0·360	*18·8*	*19·1*	*3·37*
	0·400	22·4	22·7	2·62
	1·500	14·5	14·8	3·98
Wilson	0·900	16·5	16·7	3·76
	0·630	*18·8*	*19·1*	*3·36*
	0·450	21·8	22·2	2·80
	0	14·0	14·3	3·89
Redlich–Kister	0·200	16·6	16·8	2·68
	0·355	*18·8*	*19·0*	*0·57*
	0·500	21·2	21·4	—^{a}
	Cyclohexane(1)–benzene(2)–furfural(3), 25°C			
	0·200	12·0	27·6	4·10
NRTL	*0·353*	*15·9*	*32·8*	*3·13*
	0·400	20·8	37·9	3·97
	1·500	12·4	31·0	2·83
Wilson	*0·580*	*15·9*	*42·3*	*1·71*
	0·300	21·6	59·1	0·91
	0·100	11·9	26·9	2·52
Redlich–Kister	*0·371*	*15·9*	*29·9*	*1·48*
	0·600	20·3	32·7	7·08
	Heptane(1)–benzene(2)–DMSO(3), 40°C			
	0·100	*79·6*	*143·9*	*1·37*
NRTL	0·300	100·0	158·3	1·12
	0·350	110·6	170·1	2·87
	3·500	*79·5*	*144·8*	*0·86*
Wilson	1·450	90·5	167·4	0·53
	1·100	99·1	183·9	0·70
	0·100	*79·7*	*143·8*	*0·66*
Redlich–Kister	0·700	85·2	149·0	0·94
	1·250	90·5	153·6	4·49

^{a} The predicted heterogeneous region covers only a part of the true heterogeneous region.

of limiting activity coefficient of hydrocarbon in solvent (Tables IV and V) are printed in italics.

The calculated binodal curves of the systems are compared with experimental data in Figs 1a–d for the third parameters of partially miscible pairs adjusted by means of the experimental limiting activity coefficients.

On comparing the results in Tables IV and V we can see that the adjustment of the third parameter of partially miscible components in terms of the limiting activity coefficient is undoubtedly useful, the residuals F_x being in this case always relatively near to the minimum of the dependence $F_x = f[(\pi_3)_{13}]$, or $F_x = f[(\pi_3)_{13}, (\pi_3)_{23}]$. On the contrary, a random choice of the third parameter can cause a considerable worsening of the prediction of ternary L–L equilibria. As to the accuracy of the equilibrium data prediction with adjusted third parameter it is necessary to state that for the given systems it was qualitatively correct for all the types of equations used which can be seen in Figs 1a–d, too.

A more detailed evaluation of individual equations for G^E is not well possible owing to a small number of ternary systems investigated. The overall mean value of F_x for the individual types of equations is

NRTL: $\bar{F}_x = 2\cdot1$
Wilson: $\bar{F}_x = 1\cdot8$
Redlich–Kister: $\bar{F}_x = 1\cdot4$

TABLE V
Evaluation of the prediction of ternary L–L equilibria for the heptane(1)–cyclohexane(2)––DMFA(3) system, 25°C

Equation	$(\pi_3)_{13}$	γ_{13}^∞	γ_{31}^∞	$(\pi_3)_{23}$	γ_{23}^∞	γ_{32}^∞	F_x
	0·200	18·4	20·8	0·200	9·2	19·9	1·62
NRTL	0·356	23·3	25·9	0·366	12·7	24·4	0·65
	0·400	28·3	30·8	0·400	15·6	27·3	0·60
	1·500	18·3	20·9	1·500	9·7	23·0	2·01
Wilson	0·690	23·3	26·8	0·480	12·7	32·4	1·44
	0·450	28·2	32·6	0·300	15·7	41·1	1·26
	0	17·5	19·8	0	8·0	18·4	2·78
Redlich–Kister	0·462	23·3	25·3	0·300	12·7	21·9	2·83
	0·600	25·4	27·3	0·430	15·5	23·6	5·59

The difference between single $\bar{F}_x$ is not large enough to enable to draw unambiguous conclusions. In spite of it, it is necessary to note that for the systems with one pair of immiscible liquids, the prediction on the basis of the Redlich–Kister equation was best with mean value of $\bar{F}_x = 0.9$. However, this equation has been the most sensitive to the adjustment of the third parameter of partly miscible components of all the equations investigated.
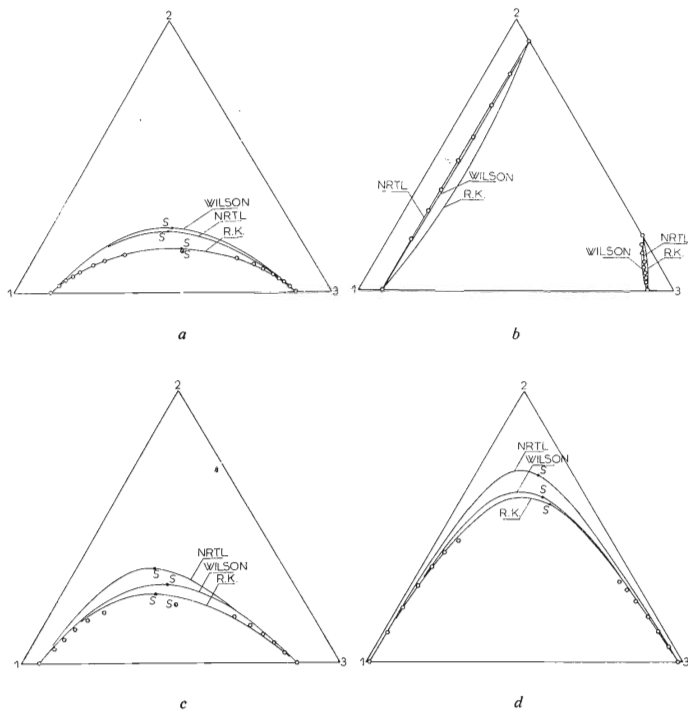

Fig. 1

Comparison of the predicted binodal curves with experimental data for the systems: *a* heptane(1)–toluene(2)–DMFA(3), 40°C; *b* heptane(1)–cyclohexane(2)–DMFA(3), 25°C; *c* cyclohexane(1)–benzene(2)–furfural(3), 25°C; *d* heptane(1)–benzene(2)–DMSO(3), 40°C

LIST OF SYMBOLS

a_i	activity of i-th component
B_{ij}	third binary parameter of modified Wilson equation
B_{ij}, C_{ij}, D_{ij}	first, second and third binary parameter of Redlich–Kister equation
F	objective function, residual
G^E	excess Gibbs energy
G^M	Gibbs energy of mixing
K	total number of components
m	number of experiments
P	saturated vapour pressure
R	gas constant
t	temperature (centigrade scale)
T	absolute temperature
x_i, x_j	mole fraction of i-th and j-th component
x_{ij}	solubility of component i in liquid j expressed in mole fractions
α_{ij}	third parameter of NRTL equation
γ_i	activity coefficient
γ_{ij}	activity coefficient of component i in saturated solution of liquid j
$\Lambda_{ij}, \Lambda_{ji}$	first and second binary parameter of Wilson equation
π_n	n-th parameter of equation for G^E
$(\pi_n)_{ij}$	n-th parameter of equation for G^E in binary solution $i—j$
τ_{ij}, τ_{ji}	first and second binary parameter of NRTL equation

Superscripts

∞	infinitely diluted solution
$\circ$	pure component, estimated value
$\wedge$	calculated value
I, II	phase designation
—	mean value

Subscripts

i	i-th component
j	j-th component, j-th phase
l	l-th experiment
m	number of experiments
n	n-th parameter
1, 2, 3	ordinal number of component
het	heterogeneous region

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