LIQUID–LIQUID EQUILIBRIUM IN THE WATER–METHYL TERT-BUTYL ETHER–NITROMETHANE–ETHYLENE GLYCOL SYSTEM

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The liquid–liquid equilibrium was measured at 20 °C in the title quaternary system and in the three nitromethane-containing ternary subsystems. The data were compared with those predicted by a superposition of the Wilson and Redlich–Kister equations including the ternary parameters. The agreement between the observed and calculated data is very good both for the quaternary system and for the three ternary systems.

The water (W)–methyl tert-butyl ether (MTBE)–nitromethane (NM)–ethylene glycol (EG) quaternary system consists of four heterogeneous binary subsystems, viz. W–MTBE, W–NM, MTBE–EG and NM–EG, at 20 °C. The four ternary subsystems are heterogeneous, each involving two sparingly miscible binary systems (Fig. 1). The W–MTBE–EG, W–MTBE–NM and W–NM–EG ternary systems are type II in Treyball's classification, whereas the MTBE–NM–EG system has two separate heterogeneous regions at 20 °C.

The W–MTBE–EG ternary system has been studied previously[1]. The isobaric vapour–liquid equilibrium in the MTBE–NM system has been measured by Lázničková and Kubíček[2]. The liquid–liquid equilibrium data in the NM–EG system have been published by Francis[3], Sazonov and Filipov[4] and by Markuzin and Nikanorova[5]. The isothermal vapour–liquid equilibrium in the W–NM system has been investigated by Filipov and coworkers[6] and by Schuberth[7]. Data of the binodal curve in this system have been reported by Riddick and Bunger[8]. No data concerning the quaternary system or the three nitromethane-containing ternary systems have been found in available literature.

EXPERIMENTAL

Methyl tert-butyl ether was obtained from the Synthetic Rubber Research Institute in Kralupy nad Vltavou; the substance was dried with sodium and rectified on a packed column (40 theoretical plates) particularly to remove dimethyl ether. The distillate was dried with a Dusimo S4 molecular sieve. The water content, as determined by the Karl Fischer method, was 0.005%. The physical parameters of the product were as follows: $\rho(20\ °C) = 0.7403\ g\ cm^{-3}$ (ref.[9]: $0.7405\ g\ cm^{-3}$), $n_D(20\ °C) = 1.3688$ (ref.[9]: 1.3689).

Nitromethane from Xenon Lodz was also dried with sodium and rectified on a packed column with 40 theoretical plates. The distillate was subjected to fractional crystallization and stored over Dusimo S4 molecular sieve. The parameters were as follows: $\rho(20\ °C) = 1.1382\ g\ cm^{-3}$ (ref.[8]: $1.13816\ g\ cm^{-3}$), $n_D(20\ °C) = 1.3820$ (ref.[8]: 1.38188).

Ethylene glycol supplied by Lachema was used as received. The substance was stored over Dusimo S4 molecular sieve and its water content was monitored by the Karl Fischer method during the measurement. The parameters were as follows: $\rho(20\ °C) = 1.1095\ g\ cm^{-3}$ (ref.[8]: $1.1100\ g\ cm^{-3}$), $n_D(20\ °C) = 1.4297$ (ref.[8]: 1.4318).

Water was doubly redistilled, specific conductivity $1.481 \cdot 10^{-4}\ S\ m^{-1}$.

Data were obtained titrimetrically[10] and by the direct analytical method[10]. The procedure was as in our previous work[1]. The conditions of chromatographic analysis using a CHROM 5 gas chromatograph interfaced to a CI 100 integrator (Laboratorní přístroje, Praha) are given in Table I. The error in the concentrations was 0.2 mole %.

RESULTS

The Ternary Systems

In the W–MTBE–NM system the two heterogeneous binary systems (W–MTBE, W–NM) exhibit a very low mutual miscibility at 20 °C, and the ternary system exhibits a single two-phase region. The course of the longer segment of the binodal curve was determined by titration of MTBE–NM solutions (in various proportions) with water. One point was also determined titrimetrically on the shorter segment of the binodal by titration of a heterogeneous mixture of approximately 8 wt.% MTBE in water with an approximately 5 wt.% solution of NM in water to the vanishing of turbidity. The equilibrium data were also obtained by the direct analytical method. Both the equilibrium and titrimetric data at 20 °C are shown in Fig. 2 and summarized in Table II.

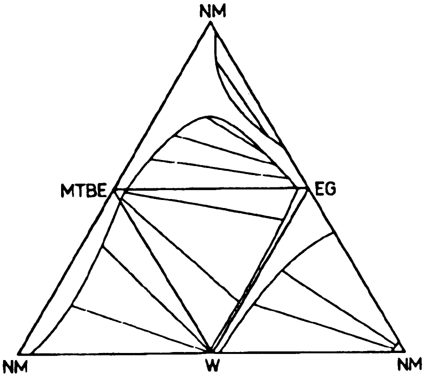

FIG. 1

Heterogeneous region of the W–MTBE–NM–EG system

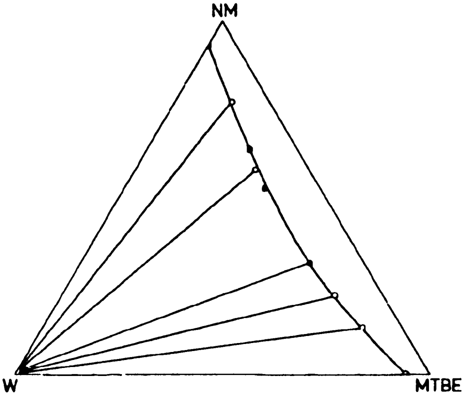

FIG. 2

Phase diagram of the W–MTBE–NM ternary system. Method of determination: ○ analytical, ● titrimetric

In the shape of the heterogeneous region, the W–NM–EG system resembles the above ternary system. It contains two sparingly miscible binary subsystems at 20 °C, viz. W–NM and NM–EG, and forms a single two-phase heterogeneous region. The course of the longer segment of the binodal curve was established by titration of solutions of water in EG at various NM concentrations. In addition, one point on the shorter segment of the binodal was determined by titrating a heterogeneous W–NM–EG

TABLE I
Conditions of chromatographic analysis; glass columns 2.5 mm i.d., carrier gas flow rate 40 cm^3 min^{-1}

System	Column packing	Column temperature, °C	Carrier gas	Detector	Column length, m
W–MTBE–NM	Chromosorb 102	160	hydrogen	TCD	1.5
W–NM–EG	Porapak N	200	hydrogen	TCD	1.5
MTBE–NM–EG	Chromosorb 102	170	nitrogen	FID	1.5
W–MTBE–NM–EG	Sferon SDA	180	hydrogen	TCD	3.0

TABLE II
Liquid–liquid equilibrium in the W(1)–MTBE(2)–NM(3) system at 20 °C

a) Direct analytical method

Aqueous phase			Ether (nitromethane) phase		
x_1	x_2	x_3	z_1	z_2	z_3
0.980	0.010	0.010	0.096	0.776	0.128
0.976	0.009	0.015	0.115	0.660	0.225
0.972	0.009	0.019	0.128	0.551	0.321
0.967	0.006	0.027	0.125	0.296	0.579
0.965	0.004	0.031	0.097	0.135	0.768

b) Titrimetric method

x_1	0.132	0.126	0.111	0.984
x_2	0.545	0.353	0.201	0.011
x_3	0.323	0.521	0.688	0.005

mixture of known composition with pure nitromethane. The equilibrium data were also determined by the direct analytical method; the water content of the nitromethane phase was found by the Karl Fischer method. The data were all measured at 20 °C and are shown in Fig. 3 and summarized in Table III.

The MTBE–NM–EG system also involves two heterogeneous binary subsystems but it exhibits two separate heterogeneous regions. The two-phase regions starting from the sparingly miscible binary systems, MTBE–EG and NM–EG, do not merge and the two heterogeneous regions possess critical points, which lie relatively close to one another. The two binodal curves were first established by the titrimetric method, and measurement of seven connecting lines by the direct analytical method followed. The equilibrium and solubility data of this system at 20 °C are given in Table IV and shown in Fig. 4.

The Quaternary System

Owing to the fact that the W–MTBE–NM–EG system includes four very sparingly miscible binary subsystems, the extent of the heterogeneous region in the quaternary system is considerable. This is one of the reasons why only the liquid–liquid equilibrium was measured in this work. Three of the sparingly miscible ternary subsystems possess one band-shaped heterogeneous region each (type II according to Treyball), whereas only the fourth ternary subsystem, viz. MTBE–NM–EG, involves two separate heterogeneous regions and hence, two critical points. On the line connecting the critical points in the quaternary system, three points were determined at 20 °C by titrating homogeneous MTBE–NM–EG mixtures with water to the appearance of turbidity. The

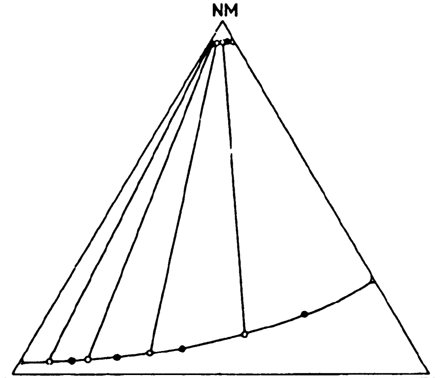

FIG. 3

Phase diagram of the W–NM–EG ternary system. Method of determination: ○ analytical, ● titrimetric

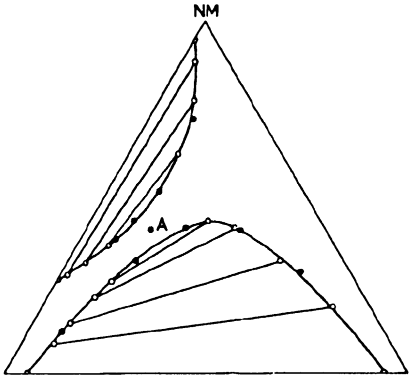

FIG. 4

Phase diagram of the MTBE–NM–EG ternary system. Method of determination: ○ analytical, ● titrimetric. Point A (see Appendix)

TABLE III
Liquid–liquid equilibrium in the W(1)–NM(2)–EG(3) system at 20 °C

a) Direct analytical method

Glycol (aqueous) phase			Nitromethane phase		
x_1	x_2	x_3	z_1	z_2	z_3
0.382	0.115	0.503	0.029	0.946	0.025
0.642	0.057	0.301	0.046	0.941	0.013
0.797	0.041	0.162	0.058	0.936	0.006
0.896	0.035	0.069	0.066	0.932	0.002

b) Titrimetric method

x_1	0.217	0.559	0.735	0.839	0.018
x_2	0.169	0.074	0.048	0.040	0.947
x_3	0.614	0.367	0.217	0.121	0.035

TABLE IV
Liquid–liquid equilibrium in the MTBE(1)–NM(2)–EG(3) system at 20 °C

a) Direct analytical method

Ether (nitromethane) phase			Glycol phase		
x_1	x_2	x_3	z_1	z_2	z_3
0.717	0.189	0.094	0.079	0.080	0.841
0.526	0.322	0.152	0.096	0.141	0.763
0.361	0.412	0.227	0.117	0.217	0.666
0.291	0.429	0.280	0.133	0.261	0.606
0.035	0.877	0.088	0.015	0.281	0.704
0.087	0.773	0.140	0.042	0.311	0.647
0.122	0.625	0.253	0.078	0.368	0.554

b) Titrimetric method

x_1	0.082	0.123	0.111	0.103	0.243	0.166	0.367	0.081	0.589
x_2	0.121	0.523	0.718	0.441	0.408	0.316	0.413	0.383	0.291
x_3	0.797	0.354	0.171	0.456	0.349	0.518	0.220	0.536	0.120

equilibrium liquid–liquid data were determined by the direct analytical method. In the low-water content phases, water was quantitated by the Karl Fischer method. The results of the liquid–liquid equilibrium measurements are given in Table V.

It has been reported[10] that if a four-component system involves four (or more) heterogeneous binary subsystems, the formation of a three-phase or four-phase region can be expected. Tentative titrations of various MTBE–NM–EG mixtures with water were therefore performed with the aim to find whether more than two liquid phases emerge; this was actually not observed.

TABLE V

Liquid–liquid equilibrium in the W(1)–MTBE(2)–NM(3)–EG(4) system at 20 °C

a) Titration with water on the connecting line of the critical points of the MTBE–NM–EG subsystem

x_1	0.017	0.019	0.016
x_2	0.170	0.154	0.134
x_3	0.394	0.412	0.450
x_4	0.419	0.415	0.400

b) Direct analytical method

Phase one				Phase two			
x_1	x_2	x_3	x_4	z_1	z_2	z_3	z_4
0.041	0.632	0.260	0.067	0.298	0.045	0.062	0.595
0.047	0.407	0.443	0.103	0.265	0.050	0.108	0.577
0.042	0.256	0.585	0.117	0.219	0.049	0.153	0.579
0.056	0.662	0.236	0.046	0.475	0.028	0.038	0.459
0.073	0.407	0.456	0.064	0.479	0.026	0.065	0.430
0.067	0.309	0.559	0.065	0.438	0.026	0.082	0.454
0.083	0.696	0.206	0.015	0.775	0.012	0.017	0.196
0.099	0.459	0.420	0.022	0.768	0.011	0.028	0.193
0.082	0.252	0.646	0.020	0.754	0.008	0.038	0.200
0.089	0.703	0.202	0.006	0.898	0.006	0.013	0.083
0.102	0.476	0.413	0.009	0.876	0.008	0.023	0.093
0.102	0.258	0.631	0.009	0.865	0.006	0.030	0.099

DISCUSSION

Thermodynamic Description of the Systems

The systems were described thermodynamically by using a superposition of the Wilson and Redlich–Kister equations including the ternary term. The correlation equations as well as the temperature dependences were as in the previous work[1].

$$Q = G^E/(RT) = Q_{RK} + Q_{Wilson} + Q_{tern} \,. \tag{1}$$

For an N-component system we have

$$Q_{Wilson} = -\sum_{i=1}^{N} x_i \ln \sum_{j=1}^{N} x_j A_{ij} \,, \tag{2}$$

$$A_{ij} = (V_j^L/V_i^L)\exp(-a_{ij}/T) \,, \tag{3}$$

$$Q_{RK} = -\sum_{i=1}^{N-1} \sum_{j>i}^{N} x_i x_j \sum_{k=1}^{n_{ij}} A_{ijk} (x_i - x_j)^{k-1} \,, \tag{4}$$

$$Q_{tern} = \sum_{i=1}^{N-2} \sum_{j>i}^{N-1} \sum_{k>j}^{N} x_i x_j x_k \left[C_{ijki} x_i + C_{ijkj} x_j + C_{ijkk} x_k\right] \,, \tag{5}$$

where n_{ij} is the number of terms (parameters) in the i–j binary system.

The binary parameters a_{ij} and A_{ijk} are generally assumed to be temperature dependent,

$$a_{ij} = \alpha_{ij} + \beta_{ij} T + \gamma_{ij} T^2 \,, \tag{6}$$

$$A_{ijk} = \alpha_{ijk} + \beta_{ijk}/T + \gamma_{ijk}/T^2 \,, \tag{7}$$

whereas the parameters C_{ijk} are regarded as temperature independent.

The Binary Systems

The description of the W–MTBE, W–EG and MTBE–EG systems was taken from ref.[1].

MTBE–NM system. The parameters of the correlation equation were calculated by using the isobaric data of the vapour–liquid equilibrium[2] (p = 101.325 kPa); the deviation in the composition used was $\sigma_x = \sigma_y = 0.001$. The constants of the Wilson and

Redlich–Kister equations were calculated. The former equation afforded better results, both with the temperature independent parameters and with parameters where the temperature dependence is taken into account. Since the use of the temperature dependent parameters did not lead to improvement, the constants of the Wilson equation with temperature independent energetic parameters were employed for the subsequent calculations in multicomponent systems.

NM–EG system. The parameters of the correlation equation were calculated based on the data of refs[3,4] which cover the region of 0 – 40 °C. The data by Markuzin and Nikanorova[5] were not employed because of their apparent disagreement with the other data. Therefore, the data by Francis[3] and by Sazonov and Filipov[4], which are in a perfect mutual agreement, were plotted in an auxiliary diagram from which the course of the binodal curve was established and the equilibrium compositions were found for the various temperatures. In the calculation of the parameters by the maximum likelihood method, these points read from the plot were assigned a five-fold higher deviation in the determination of composition ($\sigma_x = 0.005$). A five-fold lower weight was also regarded for the critical point. The data so prepared were then used to determine the parameters of the correlation equation. The Wilson energetic parameters were considered linearly temperature-dependent. In the Redlich–Kister term, only the first constant was taken into account and its parameters α_{341} and β_{341} were calculated.

W–NM system. The parameters of the correlation equation were optimized by simultaneous correlation of two kinds of equilibrium, viz. the liquid–liquid equilibrium and the liquid–vapour equilibrium. Smoothed data by Riddick and Bunger[8] concerning the mutual solubility of water and nitromethane over the region of 0 – 105 °C were used for this. The values of $\sigma_x = \sigma_z = 0.0005$ were considered, only for the isotherm at 100 °C we had $\sigma_x = \sigma_z = 0.005$ and for the critical point composition (105 °C) we had $\sigma_x = \sigma_z = 0.05$. The isothermal data by Filipov and coworkers[6] at 23 °C and by Schuberth[7] at 50 °C were employed for the vapour–liquid equilibrium. For all of the points of this equilibrium, the same error in composition was considered, viz. $\sigma_x = \sigma_y = 0.001$. The parameters α_{13}, β_{13}, α_{31}, β_{31}, α_{131} and β_{131} were optimized, whereby a satisfactory description of both kinds of equilibrium was reached.

The calculated binary parameters, as further employed, are given in Table VI. When using calculations by the maximum likelihood method, the temperature and pressure deviations considered were $\sigma_T = 0.05$ K and $\sigma_p = 0.002\ p_0$, respectively, where p_0 is the experimental pressure value.

The Ternary Systems

The parameters for the thermodynamic description of the W–MTBE–EG system were taken from ref.[1] Optimization of the ternary parameters in the W–MTBE–NM and W–NM–EG ternary systems was performed by the same procedure and using the same objective function F_{tot} as in ref.[1]. A specific approach had to be adopted for the MTBE–

TABLE VI
Survey of binary parameters

System	*i–j* labelling	*ij*	α_{ij}/K	β_{ij}	γ_{ij}/K^{-1}	*k*	α_{ijk}	β_{ijk}/K	γ_{ijk}/K^2	Ref.
W–MTBE	1–2	12	1 522.8	−1.6331	–	1	2.45	−507	–	1
		21	−2 044.5	8.6966	–		–	–	–	
W–NM	1–3	13	2 350.6	−4.8113	–	1	1.0935	−184.61	–	
		31	710.84	−0.6946	–		–	–	–	
W–EG	1–4	14	–	1.1297[a]	–	1	0.5245	−110.76	−32 076	1
		41	–	−1.1297[a]	–	2	0.63788	−212.93	–	
						3	0.23776	−166.70	–	
MTBE–NM	2–3	23	75.16	–	–		–	–	–	
		32	445.65	–	–		–	–	–	
MTBE–EG	2–4	24	428.6	–	–	1	0.5	–	–	1
		42	898.1	–	–		–	–	–	
NM–EG	3–4	34	1 888.9	−5.0664	–	1	1.2838	−302.80	–	
		43	5 596.6	−15.771	–		–	–	–	

[a] In this case the contribution of the Wilson equation is zero and the condition $A_{ij} = 1$ leads to the relation $\beta_{ij} = \ln (V_j^L/V_i^L)$.

NM–EG system. The calculation of the ternary parameters for this system was the key point in the correlation of the quaternary system. In fact, the shape of the calculated heterogeneous region is exceedingly sensitive to the values of the correlation equation parameters. When calculating the parameters, the algorithm usually converged to an end but either the heterogeneous regions were too small (when using the binary parameters solely) or one heterogeneous region emerged. Therefore, the procedure described in Appendix was adopted. In this manner, a set of constants was obtained permitting both heterogeneous regions of the system to be successfully modelled.

A survey of the obtained ternary parameters for the four ternary systems, along with the corresponding F_{tot} values, is given in Table VII.

Prediction of the Liquid–Liquid Equilibria in the Ternary Systems and in the Quaternary System Based on the Binary and Ternary Data

Table VII demonstrates that the F_{tot} values are lower for the systems that are type II according to Treyball than for the MTBE–NM–EG system. For the W–NM–EG system, this value increases to 0.48% if the ternary constants are put equal to zero, which also implies a very good agreement of the calculated and observed compositions. The agreement is considerably poorer if the ternary constants are chosen zero for the W–MTBE–NM system (F_{tot} = 2.48%), particularly in the non-aqueous phase; calculation which includes the ternary parameters leads to an appreciable improvement (F_{tot} = 0.18%). Hence, for the W–MTBE–NM system the use of the ternary constants is desirable. For the MTBE–NM–EG system the course of the two binodal curves cannot be modelled successfully unless the ternary constants are used. These constants are much more difficult to calculate in this case; Table VII, however, demonstrates that if the special calculation procedure is used, a very good agreement between the observed and calculated values of the equilibrium phase composition is again reached (F_{tot} = 1.06%).

Prediction of the liquid–liquid equilibrium in the quaternary system based on the binary parameters solely was unsuccessful and in some instances the nearest point was not established. If the ternary constants of the MTBE–NM–EG subsystem were

TABLE VII
Survey of ternary parameters

i–j–k System	C_{ijki}	C_{ijkj}	C_{ijkk}	F_{tot}, %
W–MTBE–EG[a]	0.99	-3.08	-0.79	0.23
W–MTBE–NM	-1.78	-2.13	-0.94	0.18
W–NM–EG	0.85	-0.43	-0.27	0.31
MTBE–NM–EG	-0.75	-0.93	-1.31	1.06

[a] Ref.[1].

included, the calculation for parts of the connodes converged to an end, the agreement between the calculated and observed equilibrium concentrations, however, was very poor. The agreement improved appreciably by including the ternary constants of the W–MTBE–NM subsystem. Presumably, this improvement was due to the fact that in the latter subsystem itself the agreement of the calculated and observed equilibrium compositions is considerably poorer if the ternary constants are omitted than if they are involved. Inclusion of the ternary constants of the remaining two ternary subsystems, viz. W–MTBE–EG and W–NM–EG, brought about a minor improvement in the prediction of the liquid–liquid equilibrium in the quaternary system.

Conclusions that can be drawn based on the results of this work confirm those of our previous work[1]:

1. Generally, the ternary constants must be employed when describing the two-phase heterogeneous region in a four-component system. The description then is satisfactory within experimental errors, and the quaternary constants need not be included.

2. The ternary constants can be omitted for those ternary subsystems whose ternary data can also be described with a sufficient accuracy without these constants.

3. In principle, superposition of the Wilson and Redlich–Kister equations is capable of describing the liquid–liquid phase equilibrium in quaternary systems sufficiently well.

APPENDIX

Calculation of the ternary parameters for the MTBE–NM–EG system based on data of the composition of the coexisting phases provided the parameters

$$C^0_{1231} = -0.750, \quad C^0_{1232} = -0.884, \quad C^0_{1233} = -1.294, \qquad (A1)$$

which predict a single heterogeneous region for this system. This drawback in the correlation could be eliminated neither by changes in the first approximation of the ternary parameters nor by changes in the increments ΔC_i in the various iteration steps.

The following procedure was chosen to refine the parameters. Using the parameter values (*A1*), the stability determinant D was calculated in point A (Fig. 4) lying approximately on the connecting line of the critical points of the two heterogeneous regions:

$$D = \left[\left(\frac{\partial^2 G_m}{\partial x_1^2}\right)_{T,p,x_2}\left(\frac{\partial^2 G_m}{\partial x_2^2}\right)_{T,p,x_1} - \left(\frac{\partial^2 G_m}{\partial x_1 \partial x_2}\right)^2_{T,p}\right]/(RT)^2 = -0.0126. \qquad (A2)$$

This confirmed that the above parameters in this point predict splitting into two liquid phases.

The ratio of differences in this point also gave the $\partial D/\partial C_{123i}$ values, viz.

$$\frac{\partial D}{\partial C_{1231}} = -0.048\,, \quad \frac{\partial D}{\partial C_{1232}} = -0.148\,, \quad \frac{\partial D}{\partial C_{1233}} = -0.439\,. \qquad (A3)$$

These values indicate that while the determinant D is nearly insensitive to C_{1231}, the parameters C_{1232} and C_{1233} affect the determinant appreciably, and a small change in their value can bring about division of the heterogeneous region into two parts. It turned out that by using the values

$$C_{1232} = C^0_{1232} - \frac{D}{\partial D/\partial C_{1232}} = -0.884 - \frac{(-0.0126)}{(-0.148)} = -0.969\,, \qquad (A4)$$

$$C_{1233} = C^0_{1233} - \frac{D}{\partial D/\partial C_{1233}} = -1.324\,, \qquad (A5)$$

which on their own only make it possible to achieve a zero value of determinant D, a good description of the binodal curve is obtained in the critical regions without making poorer the quality of the calculated equilibrium compositions corresponding to the experimental points. Subsequent calculations were made using the parameters given in Table VII, which were obtained from the starting set (*A1*) by considering only half corrections for C_{1232} and C_{1233} and by holding $C_{1231} = C^0_{1231}$.

SYMBOLS

A_{ijk}	Redlich–Kister equation parameter
A_{ij}	Wilson equation parameter
a_{ij}	Wilson equation parameter
C_{ijkl}	ternary parameter
C^0_{ijkl}	ternary parameter starting approximation
D	stability determinant
F_{tot}	objective function, ref.[1]
G^E	molar excess Gibbs energy
G_m	molar Gibbs energy of mixing
i, j, k, l	summation subscripts
n_{ij}	number of binary concentration parameters in the Redlich–Kister equation for a system i–j
n_D	refractive index
p	pressure
p_0	experimental pressure value
Q	dimensionless molar excess Gibbs energy, $G_m/(RT) - \sum x_i \ln x_i$
R	universal gas constant
T	absolute temperature
V_i^L	molar volume of i-th component in the liquid phase

x_i	mole fraction of i-th component in the first liquid phase
z_i	mole fraction of i-th component in the second liquid phase
$\alpha_{ij}, \beta_{ij}, \gamma_{ij}$	terms in the temperature dependence of the Wilson equation parameters
$\alpha_{ijk}, \beta_{ijk}, \gamma_{ijk}$	terms in the temperature dependence of the Redlich–Kister equation parameters
∂	partial differentiation operator
σ	standard deviation estimate
ρ	density

REFERENCES

1. Kubíček V., Matouš J., Novák J. P.: Collect. Czech. Chem. Commun. *57*, 2021 (1992).
2. Lázničková R., Kubíček V.: Unpublished results.
3. Francis A. W.: J. Phys. Chem. *60*, 20 (1956).
4. Sazonov V. P., Filipov V. V.: Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol. *18*, 222 (1975).
5. Markuzin N. P., Nikanorova L. A.: Zh. Obshch. Khim. *32*, 3469 (1962).
6. Filipov V. V., Markuzin N. P., Sazonov V. P.: Zh. Prikl. Khim. (Leningrad) *50*, 1321 (1977).
7. Schuberth H.: Z. Phys. Chem. (Leipzig) *225*, 305 (1964).
8. Riddick J. A., Bunger W. B.: *Organic Solvents*. Wiley–Interscience, New York 1970.
9. Evans T. W., Edlund K. R.: Ind. Eng. Chem. *28*, 1186 (1936).
10. Novák J. P., Matouš J., Pick J.: *Liquid–Liquid Equilibria*. Academia, Praha; Elsevier, Amsterdam 1987.

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