PHASE EQUILIBRIA IN THE WATER–METHYL ALCOHOL–METHYL TERT-BUTYL ETHER–ETHYLENE GLYCOL SYSTEM

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Liquid–liquid equilibria were measured at 20 °C in the W–MeOH–MTBE–EG quaternary system (W is water, MeOH is methyl alcohol, MTBE is methyl tert-butyl ether, and EG is ethylene glycol) and in the W–MeOH–MTBE, W–MTBE–EG and MeOH–MTBE–EG ternary systems. In the W–MeOH–MTBE–EG, W–MeOH–MTBE, and MeOH–MTBE–EG systems, the vapour–liquid equilibria at atmospheric pressure were also measured. The experimental data of the quaternary system were compared with those modelled by superposition of the Wilson and Redlich–Kister equations with the ternary term, whose parameters were determined based on the corresponding binary and, in some cases, ternary systems. A very good agreement was obtained for both the liquid–liquid and vapour–liquid equilibria.

The W(1)–MeOH(2)–MTBE(3)–EG(4) system (W is water, MeOH is methyl alcohol, MTBE is methyl tert-butyl ether, and EG is ethylene glycol) at 20 °C is a four-component system whose two subsystems, viz. W–MTBE and MTBE–EG, are heterogeneous. As a consequence, the three ternary subsystems (W–MeOH–MTBE, W–MTBE–EG and MeOH–MTBE–EG) are heterogeneous as well (Fig. 1); out of these, the W–MTBE–EG system is type II system in Treyball's classification whereas the remaining two are type I systems.

Data of the vapour–liquid equilibria in the W–MeOH, W–EG, MeOH–MTBE and MeOH–EG binary systems have been published[1]. The W–MTBE system (liquid–liquid equilibrium) has been studied by Zikmundová and coworkers[2]. No phase equilibrium data could be found in the literature for the MTBE–EG system or for any of the ternary systems.

The results of this work should serve as data for designing a separatory equipment for this mixture; they were also employed in the investigation of feasibility of estimating the liquid–liquid equilibria (henceforth LLE) and vapour–liquid equilibria (henceforth VLE) in quaternary systems based on known binary and/or ternary data.

EXPERIMENTAL

Chemicals

Methyl tert-butyl ether: The chemical supplied by the Synthetic Rubber Research Institute in Kralupy was dried with sodium and rectified on a packed column (40 theoretical plates) particularly in order to remove residues of dimethyl ether. The distillate was additionally dried with the Dusimo S4 molecular sieve. The water content, as determined by the Karl Fischer method[3], was 0.005 wt.%. The parameters of the chemical so treated were as follows: $\rho(20\ °C) = 0.7403\ g\ cm^{-3}$ (ref.[4]: $0.7405\ g\ cm^{-3}$), $n_D(20\ °C) = 1.3688$ (ref.[4]: 1.3689).

Methyl alcohol: The chemical of reagent grade purity (Lachema, Czechoslovakia) was dried with iodine-activated magnesium and rectified on a packed column (40 theoretical plates). The compound so treated was stored above the Dusimo S4 molecular sieve. The water content according to Karl Fischer measurements was 0.026 wt.%. The parameters were $\rho(20\ °C) = 0.7912\ g\ cm^{-3}$ (ref.[5]: $0.79129\ g\ cm^{-3}$), $n_D(20\ °C) = 1.3285$ (ref.[5]: 1.32840).

Ethylene glycol: The chemical of reagent grade purity supplied by Lachema was used as received; it was stored above the Dusimo S4 molecular sieve and its water content was monitored by the Karl Fischer method during the measurement; values about 0.1 wt.% were observed. The parameters were as follows: $\rho(25\ °C) = 1.1095\ g\ cm^{-3}$ (ref.5: $1.1100\ g\ cm^{-3}$), $n_D(20\ °C) = 1.4297$ (ref.[5]: 1.4318).

Water: Doubly redistilled water with a specific conductivity of $1.481 \cdot 10^{-4}\ S\ m^{-1}$ was used.

Determination of the Liquid–Liquid Equilibrium

Direct analytical method[6]. The heterogeneous mixture was added to the equilibrium cell thermostatted to 20 ± 0.05 °C and stirred vigorously with a magnetic stirrer for 3 to 4 h. After clarification (about 2 h), phase samples were taken and submitted to chromatographic analysis. A CHROM 5 gas chromatograph equipped with a CI 100 integrator (Laboratorní přístroje, Prague) was employed. The conditions of analysis for the various systems are given in Table I. The internal standardization method[7] was used. If the sample analyzed contained water in a low concentrations, the chromatographic analysis was supplemented with the Karl Fischer measurements[3].

TABLE I

Survey of chromatographic analysis conditions; glass columns 1.5 m long, i.d. 2.5 mm

System	Column packing	Detector	Column temperature, °C	Carrier gas
MTBE–EG	Porapak N	TCD	200	hydrogen
W–MeOH–MTBE	Chromosorb 102	TCD	170	hydrogen
W–MTBE–EG	Porapak N	TCD	200	hydrogen
MeOH–MTBE–EG	Porapak N	FID	200	nitrogen
W–MeOH–MTBE–EG	Chromosorb 102	TCD[b]	170	hydrogen
W–MeOH–MTBE–EG	Porapak N	FID[c]	200	nitrogen

[a] Flow rate $40\ cm^3\ min^{-1}$; [b] for the determination of the water–methyl alcohol ratio; [c] for the determination of the methyl alcohol–MTBE–ethylene glycol ratio.

Titrimetric method[6]. Binodal data were obtained in the same cell as used for the above measurements, also at 20 ± 0.05 °C. In the MTBE–EG binary system, one compound was added to a known amount of the other until haze appeared. The concentration coordinates of the binodal curve point could then be determined from the known amounts of the two components at the given temperature. In the ternary systems, one component was added to a known mixture of the other two components until haze appeared or vanished. The amount added was determined by weighing, and the composition corresponding to the binodal curve point was calculated. For the quaternary system, two procedures were applied. In the one, sections on the binodal plane corresponding to certain ratios of two components were established. For this, heterogeneous mixtures of two components, for instance (1) + (2), were titrated with a (homogeneous) solution of the remaining two components, i.e. (3) + (4) in the example, until haze disappeared. In the other procedure, the "height" of the heterogeneous region above the W–MTBE–EG ternary mixture was determined by adding MeOH to the heterogeneous mixture prepared (titration). During titrations, the components (solutions) were added dropwise by using syringes, and the amounts added were determined by differential weighing of the syringes.

Determination of the Vapour–Liquid Equilibrium

The vapour–liquid equilibrium data were measured by the circulation method in Kay's modification of the Gillespie apparatus[8]. The measurements were performed in the isobaric mode at atmospheric pressure, which was measured with a station barometer at a precision of ± 15 Pa. The apparatus was connected with ambient air through a freezer cooled with ethanol containing solid CO_2. The boiling temperature was measured with a calibrated platinum resistance thermometer connected to an F26 resistance bridge (Automatic Systems Labs.) at a precision of ± 0.02 °C. The equilibrium was allowed to establish for 2 to 3 h; its attaining was indicated by a constant boiling temperature. Thereafter the phases were taken for analysis. The analytical procedures were as in the liquid-liquid measurements.

The experiments were performed at the actual atmospheric pressure, $p = p_{atm}$. The temperatures in tables are values related to standard pressure p_{st} = 101 325 Pa; activity coefficients of the components were assumed to be constant, hence, correction ΔT given by the relation

$$p_{st} = p_{atm} + \sum_i x_i (\gamma_i)\, p_{atm} \left(\partial \ln p_i^0 / \partial T\right) \Delta T \qquad (1)$$

was added to the experimental values.

The properties of the pure substances (molar volumes, Antoine's equation constants) for calculating the vapour pressure, as well as the constants of the dependence of the second virial coefficient on temperature according to the relation

$$B = \alpha_B + \beta_B / T \qquad (2)$$

are given in Table II. For the cross virial coefficients, the relation

$$B_{ij} = -\left(|B_{ii}|\, |B_{jj}|\right)^{1/2}. \qquad (3)$$

was employed.

RESULTS

The MTBE(3)–EG(4) Binary System

For this system, the mutual solubility of the two substances was measured at 20 °C by the analytical method and by the titrimetric method; the mole fractions obtained are $x_3 = 0.058$, $z_3 = 0.947$.

Ternary Systems

For the W(1)–MeOH(2)–MTBE(3) system, VLE was measured at atmospheric pressure (Table III) in the region where both the liquid and the condensed vapour phases are homogeneous. LLE was determined by the titrimetric method and by the direct analytical method. The data are shown in Fig. 2 and given in Table III.

The W(1)–MTBE(3)–EG(4) system involves two partly miscible subsystems at 20 °C (Fig. 3). The mutual miscibility of components in the two binary systems is very low, due to which the homogeneous regions in the ternary system are small. For this reason, only the LLE was measured for this system. The direct analytical method solely was applied, and water in the organic phase was quantitated by the Karl Fischer method. The results are summarized in Table IV.

For the MeOH(2)–MTBE(3)–EG(4) system, the VLE was also measured in the homogeneous region at normal pressure (Table V). LLE at 20 °C was determined titrimetrically as well as by the direct analytical method. The results are summarized in Table V and shown in Fig. 4.

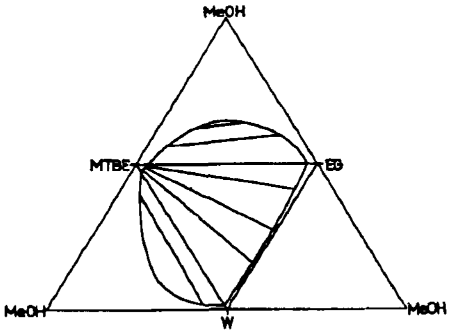


FIG. 1
The W–MeOH–MTBE–EG system

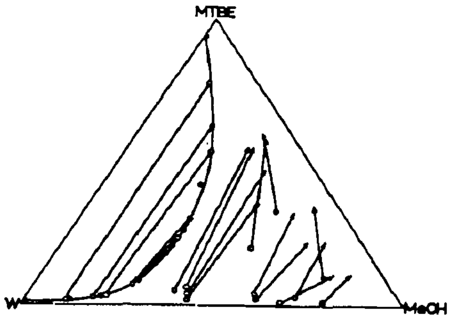


FIG. 2
Phase diagram of the W–MeOH–MTBE system; ○ LLE equilibrium point, ● LLE titration point, ○ → VLE equilibrium pair

The W(1)–MeOH(2)–EG(4) system is homogeneous and no measurements were performed in it.

The W(1)–MeOH(2)–MTBE(3)–EG(4) Quaternary System

The LLE heterogeneous region is qualitatively shown in Fig. 1. In the homogeneous region, VLE was measured at atmospheric pressure. The data are given in Table VI. The analysis was chromatographic. Low water contents were quantitated by the Karl Fischer method. The heterogeneous (LLE) region was established particularly by the titrimetric method, by determining three sections through the binodal plane. The experimental setup was such that MTBE + EG heterogeneous mixtures were titrated with water–methyl alcohol solutions at mass ratios of 3 : 7, 1 : 1 and 7 : 3 until homogeneous mixtures emerged. The results are presented in Fig. 5 and in Table VI. Figure 5 demonstrates that with the $w_1/w_2 = 7/3$ mixture, homogeneous systems are not always obtained. Table VI also includes results from the titrimetric measurements, in which methyl alcohol was added to W(1)–MTBE(3)–EG(4) heterogeneous mixtures whose compositions lay on the connecting line which emerges from the projection of the critical points to the W(1)–MeOH(2)–EG(4) system (Fig. 1). Moreover, the composition of the coexisting phases was determined by the direct analytical method for 16 connodes.

THERMODYNAMIC DESCRIPTION OF THE SYSTEMS STUDIED

The thermodynamic description of the equilibrium data was based on the superposition of the Wilson and Redlich–Kister equations with a ternary term, suggested previously[2,9]

$$Q = G^{E}/(RT) = Q_{RK} + Q_{Wilson} + Q_{tern}\ . \qquad (4)$$

TABLE II
Used constants of the pure substances

Substance	V cm^3 mol^{-1}	Antoine's equation[a] constants			Constants for the calculation of the 2nd virial coefficient	
		A	B	C	α_B	β_B, K
MTBE	119.04[b] (20 °C)	14.03185[c]	2 701.23[c]	231.795[c]	1 390[d]	$-8.371\ .\ 10^{5}$[d]
MeOH	40.73[b] (20 °C)	16.56404[e]	3 627.72[e]	239.19[e]	2 568[f]	$-1.276\ .\ 10^{6}$[f]
EG	55.92[b] (20 °C)	16.08275[g]	4 439.57[g]	189.70[g]	–	–
W	18.07[b] (20 °C)	16.32931[h]	3 841.72[h]	228.00[h]	1 510[f]	$-7.583\ .\ 10^{5}$[f]

[a] Antoine's equation: $\ln p = A - B/(t + C)$ (values for p in kPa); [b] ref.[1]; [c] ref.[29]; [d] calculated following Pitzer and Curl[33]; [e] ref.[21]; [f] ref.[30]; [g] ref.[31]; [h] ref.[32] .

TABLE III

Observed equilibrium compositions for the W(1)–MeOH(2)–MTBE(3) system

a) Liquid–liquid equilibrium at 20 °C – direct analytical method

x_1	x_2	x_3	z_1	z_2	z_3
0.869	0.114	0.017	0.137	0.094	0.769
0.794	0.179	0.027	0.191	0.174	0.635
0.759	0.204	0.037	0.240	0.216	0.544
0.669	0.255	0.076	0.419	0.279	0.302
0.645	0.261	0.094	0.477	0.280	0.243

b) Liquid–liquid equilibrium at 20 °C – titrimetric method

x_1	0.322	0.463	0.505	0.546	0.644	0.771	0.855
x_2	0.253	0.279	0.277	0.275	0.260	0.195	0.127
x_3	0.425	0.258	0.218	0.179	0.096	0.034	0.018

c) Vapour–liquid equilibrium at standard pressure (101 325 Pa)

t, °C	x_1	x_2	x_3	y_1	y_2	y_3
65.40	0.194	0.787	0.019	0.079	0.810	0.111
65.63	0.373	0.601	0.026	0.135	0.641	0.224
63.42	0.368	0.591	0.041	0.126	0.549	0.325
64.48	0.558	0.420	0.022	0.163	0.483	0.354
60.68	0.541	0.415	0.044	0.138	0.389	0.473
58.33	0.574	0.376	0.050	0.129	0.318	0.553
57.91	0.534	0.402	0.064	0.123	0.326	0.551
63.74	0.265	0.698	0.037	0.097	0.678	0.225
53.35	0.174	0.497	0.329	0.074	0.327	0.599
55.08	0.300	0.501	0.199	0.091	0.337	0.572
58.98	0.155	0.742	0.103	0.056	0.591	0.353

TABLE IV
Observed liquid–liquid equilibrium data of the W(1)–MTBE(3)–EG(4) system at 20 °C

x_1	x_3	x_4	z_1	z_3	z_4
0.007	0.944	0.049	0.173	0.050	0.777
0.026	0.939	0.035	0.453	0.030	0.517
0.042	0.943	0.015	0.679	0.016	0.303
0.056	0.939	0.005	0.861	0.011	0.128

TABLE V
Observed equilibrium compositions for the MeOH(2)–MTBE(3)–EG(4) system

a) Liquid–liquid equilibrium at 20 °C – direct analytical method

x_2	x_3	x_4	z_2	z_3	z_4
0.078	0.845	0.077	0.155	0.089	0.756
0.119	0.794	0.087	0.206	0.106	0.688
0.159	0.709	0.132	0.239	0.140	0.621
0.251	0.546	0.203	0.280	0.238	0.482

b) Liquid–liquid equilibrium at 20 °C – titrimetric method

x_2	0.082	0.145	0.247	0.272	0.278	0.268	0.198
x_3	0.075	0.082	0.158	0.203	0.315	0.363	0.633
x_4	0.843	0.773	0.595	0.525	0.407	0.389	0.169

c) Vapour–liquid equilibrium at standard pressure (101 325 Pa)

t, °C	x_2	x_3	x_4	y_2	y_3	y_4
54.29	0.484	0.358	0.158	0.369	0.631	0
57.15	0.700	0.214	0.086	0.534	0.466	0
58.95	0.752	0.163	0.085	0.603	0.397	0
60.16	0.869	0.073	0.058	0.720	0.280	0
61.92	0.878	0.055	0.067	0.790	0.210	0
63.05	0.904	0.034	0.062	0.849	0.151	0

For an N-component system we have

$$Q_{\mathrm{Wilson}} = -\sum_{i=1}^{N} x_i \ln \sum_{j=1}^{N} x_j A_{ij} \,, \tag{5}$$

$$A_{ij} = (V_j^L / V_i^L) \exp(-a_{ij}/T) \,, \tag{6}$$

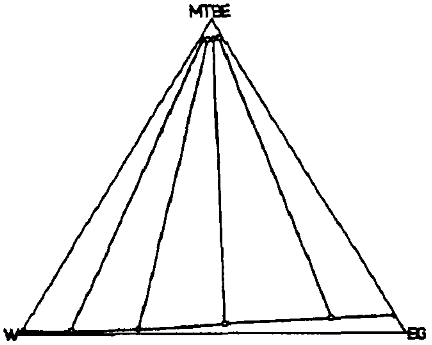
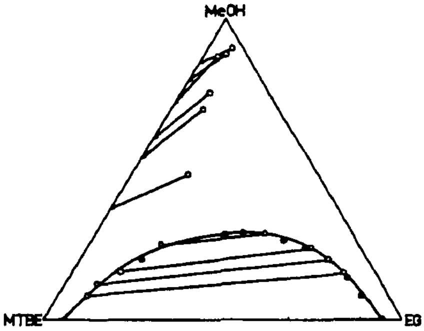


FIG. 3
Phase diagram of the W–MTBE–EG ternary system



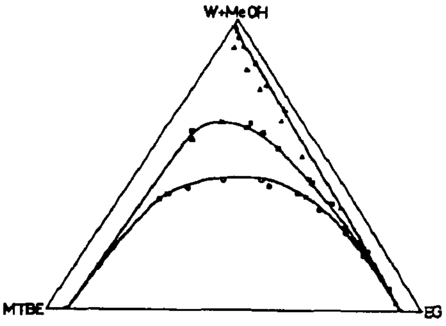


FIG. 4
Phase diagram of the MeOH–MTBE–EG system; ○ LLE equilibrium point, ● LLE titration point, ○ → VLE equilibrium pair

FIG. 5
Sections of the heterogeneous region in the W–MeOH–MTBE–EG system. W–MeOH ratio, calculated (full) point, experimental (empty) point: 3 : 7, ●, ○; 1 : 1, ■, □; 7 : 3, ▲, △

$$Q_{\mathrm{RK}} = \sum_{i=1}^{N-1} \sum_{j>i}^{N} x_i x_j \sum_{k=1}^{n_{ij}} A_{ijk} (x_i - x_j)^{k-1} , \tag{7}$$

$$Q_{\mathrm{tern}} = \sum_{i=1}^{N-2} \sum_{j>i}^{N-1} \sum_{k>j}^{N} x_i x_j x_k (C_{ijki} x_i + C_{ijkj} x_j + C_{ijkk} x_k) , \tag{8}$$

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

The binary parameters a_{ij} and A_{ijk} are considered to be temperature dependent following the equations

$$a_{ij} = \alpha_{ij} + \beta_{ij} T + \gamma_{ij} T^2 \tag{9a}$$

$$A_{ijk} = \alpha_{ijk} + \beta_{ijk}/T + \gamma_{ijk}/T^2 \tag{9b}$$

The relations for the activity coefficients and $\partial \ln \gamma_i / \partial x_j$ are given elsewhere[9,10]. Parameters C_{ijkl} were assumed to be temperature independent.

The data reduction (correlation) procedure was as follows: The best possible description of the binary systems was obtained based on binary vapour–liquid and liquid–liquid equilibrium data[11]. The predicted heat of mixing was also taken into account when assessing the quality of the parameters[12]. Exceptionally, when the volume of data was small or their accuracy was low, ternary data were also included. Using the binary parameters obtained, the ternary parameters were also determined for the heterogeneous ternary systems. For the homogeneous ternary system, the corresponding binary parameters were assumed to be sufficient for its description.

Correlation of Equilibrium Data of Binary Systems

The W(1)–MeOH(2) system. This system exhibits relatively small deviations from Raoult's law, and $H^E(x_1) < 0$ at 25 °C (at $x_1 = 0.5$ and $t = 25$ °C, $H^E = -783$ to -840 J mol^{-1}, ref.[12]). The vapour–liquid equilibrium for this system has been examined by many authors – see ref.[1]. Data by those authors were employed for calculating the parameters (also taking into account the thermodynamic consistency tests reported in the monograph[1]); the values of $\sigma_T = 0.05$ and $\sigma_p = 0.002\,p^e$ were used (p^e is the pressure value). The published data are as follows: $\sigma_x = 0.0005$, $\sigma_y = 0.001$ at 25 °C, ref.[13]; $\sigma_x = \sigma_y = 0.0005$ at 60 °C, ref.[14]; $\sigma_x = \sigma_y = 0.001$ at 100 °C, ref.[15]; isobaric data: $\sigma_x = \sigma_y = 0.001$ at 101.32 kPa, ref.[16] as well as ref.[17]. In the correlation, Wilson's equation parameters a_{12}, a_{21} were assumed to be temperature independent in the first version, and linearly dependent on temperature in the second version (four parameters were determined based on the equilibrium data). In the former approach, the description of

TABLE VI
Observed equilibrium data of the W(1)–MeOH(2)–MTBE(3)–EG(4) system

1. Liquid–liquid equilibrium at 20 °C

a) Sections through the binodal plane

x_1	x_2	x_3	x_4
	W–MeOH mass ratio 3 : 7		
0.082	0.107	0.065	0.746
0.172	0.225	0.120	0.483
0.198	0.259	0.208	0.335
0.195	0.255	0.314	0.236
0.185	0.242	0.415	0.158
0.167	0.220	0.512	0.101
	W–MeOH mass ratio 1 : 1		
0.393	0.221	0.312	0.074
0.410	0.230	0.226	0.134
0.402	0.226	0.155	0.217
0.362	0.203	0.114	0.321
0.289	0.162	0.081	0.468
0.188	0.105	0.060	0.647
	W–MeOH mass ratio 7 : 3		
0.479	0.116	0.322	0.083
0.618	0.149	0.037	0.196
0.561	0.135	0.036	0.268
0.754	0.182	0.034	0.030
0.730	0.176	0.029	0.065
0.769	0.185	0.026	0.020
0.683	0.164	0.025	0.128
0.787	0.189	0.021	0.003

TABLE VI
(*Continued*)

b) Section on the line connecting the critical points of the heterogeneous ternary subsystems

x_1	x_2	x_3	x_4
0.000	0.267	0.415	0.318
0.244	0.252	0.320	0.284
0.383	0.255	0.263	0.099
0.465	0.280	0.217	0.038
0.531	0.292	0.177	0.000

c) Direct analytical method

Phase one				Phase two			
x_1	x_2	x_3	x_4	z_1	z_2	z_3	z_4
0.013	0.034	0.881	0.072	0.060	0.077	0.056	0.807
0.020	0.063	0.834	0.083	0.040	0.131	0.074	0.755
0.013	0.104	0.781	0.102	0.037	0.181	0.108	0.674
0.019	0.224	0.525	0.232	0.026	0.281	0.225	0.468
0.014	0.040	0.886	0.060	0.066	0.078	0.064	0.792
0.016	0.072	0.847	0.065	0.057	0.120	0.076	0.747
0.017	0.119	0.755	0.109	0.052	0.181	0.108	0.659
0.036	0.177	0.633	0.154	0.051	0.253	0.156	0.540
0.027	0.121	0.740	0.112	0.099	0.178	0.090	0.633
0.138	0.122	0.717	0.023	0.698	0.162	0.021	0.119
0.169	0.195	0.581	0.055	0.503	0.227	0.070	0.200
0.106	0.086	0.783	0.025	0.731	0.115	0.016	0.138
0.089	0.087	0.775	0.049	0.603	0.131	0.027	0.239
0.057	0.082	0.815	0.046	0.363	0.122	0.050	0.465
0.028	0.092	0.794	0.086	0.147	0.148	0.076	0.629

TABLE VI
(*Continued*)

2. Vapour–liquid equilibrium at 101 325 Pa

t, °C	Liquid phase				Vapour phase			
	x_1	x_2	x_3	x_4	y_1	y_2	y_3	y_4
64.51	0.096	0.821	0.026	0.057	0.059	0.814	0.127	0.000
65.63	0.205	0.717	0.024	0.054	0.078	0.758	0.164	0.000
66.00	0.371	0.560	0.024	0.045	0.131	0.602	0.267	0.000
69.48	0.522	0.428	0.011	0.039	0.213	0.554	0.233	0.000
73.33	0.592	0.369	0.004	0.035	0.235	0.613	0.152	0.000
68.25	0.565	0.390	0.009	0.036	0.182	0.531	0.287	0.000
68.83	0.602	0.347	0.009	0.042	0.199	0.504	0.297	0.000
69.69	0.576	0.366	0.008	0.050	0.211	0.514	0.275	0.000
69.39	0.572	0.377	0.008	0.043	0.186	0.530	0.284	0.000
62.50	0.543	0.394	0.025	0.038	0.151	0.374	0.475	0.000

the equilibrium data was somewhat poorer ($S_x = 0.067$, $S_y = 0.0061$) and the prediction of H^E was inadequate altogether ($H^E(x_1) > 0$). This fact is consistent with the analysis of Wilson's equation performed previously[18], which demonstrated that $H^E > 0$ is obtained for systems having $G^E > 0$. In the second version the equilibrium data description was better ($S_y = 0.0031$, $S_x = 0.0041$) and also the agreement of the predicted heats of mixing was good ($H^E = -892$ J mol^{-1} at $x_1 = 0.5$, $T = 298.15$ K). The parameters are given in Table VII.

The W(1)–MTBE(3) system. The parameters were taken from ref.[2] and are given in Table VII.

The W(1)–EG(4) system. Although this system has been measured several times, the published data are controversial. Gmehling and coworkers[1], for instance, report the two thermodynamic consistency tests positive only for the data by Trimbley and Potts[19] measured at a pressure of 228 Torr, the deviation in the vapour phase composition being as high as 0.12. In view of the wide temperature region used, the temperature dependence of G^E should also be taken into account. The application of Wilson's equation with both temperature independent and temperature dependent parameters was unsatisfactory, and therefore the Redlich–Kister equation was employed. With regard to the low precision of the equilibrium data, the dependence of the heat of mixing (in J mol^{-1}) on composition at 298.15 K, published by Christensen and coworkers[12],

$$H^E = x_1 x_2 [-2\,709.5 - 1\,770(x_1 - x_2) - 1\,386(x_1 - x_2)^2]$$

TABLE VII
Survey of binary parameters

System	Labelling *i–j*	*ij*	α_{ij}, K	β_{ij}	γ_{ij}, K^{-1}	*k*	α_{ijk}	β_{ijk}, K	γ_{ij}, K^{2}
W–MeOH	1–2	12	364.04	-0.30378	–		–	–	–
		21	-988.68	2.9444	–		–	–	–
W–MTBE	1–3	13	1 522.8	-1.6331	–	1	2.45	-507	–
		31	-2 044.5	8.6966	–		–	–	–
W–EG	1–4	14	–	1.1297[a]	–	1	0.5245	-110.76	-32 076
		41	–	-1.1297[a]	–	2	0.63788	-212.93	–
						3	0.23776	-166.7	–
MeOH–MTBE	2–3	23	578.8	–	–		–	–	–
		32	-128.6	–	–		–	–	–
MeOH–EG	2–4	24	–	0.31696[a]	–	1	-0.047	64.11	–
		42	–	-0.31696[a]	–	2	0.0992	13.4	–
MTBE–EG	3–4	34	428.6	–	–	1	0.5	–	–
		43	898.1	–	–		–	–	–

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

was used, employing the approximate relation for C_p^E (in J mol^{-1} k^{-1})

$$C_p^E = 6 x_1 x_2 ,$$

obtained from the H^E data at 298.15 and 318.15 K (ref.[12]). Based on the two dependences, the β_{141}, γ_{141}, β_{142}, β_{143} parameters were determined (Table VII). The remaining parameters, α_{141}, α_{142}, α_{143}, were determined based on the VLE data. In the calculations, the data of ref.[20] were used; these have been measured at 25, 50 and 100 Torr and cover the temperature region of 30 °C to 133 °C. The mean deviation in the phase composition was $S_{x_1} = 0.0056$ and $S_{y_1} = 0.0049$ (the values of $\sigma_x = \sigma_y = 0.001$ were used).

The MeOH(2)–MTBE(3) system. This system exhibits positive deviations from Raoult's law and probably also $H^E > 0$. This suggests that application of Wilson's equation to this system should be successful[18], which was also confirmed. The data of ref.[21], $\sigma_x = \sigma_y = 0.0005$ at normal pressure; of ref.[22], $\sigma_x = \sigma_y = 0.001$ at $p = 588$ Torr; and the $t - x_1$ data of ref.[23], $\sigma_x = 0.001$, were used. The parameters, which are given in Table VII, provided values of $S_{x_1} = 0.0042$ and $S_{y_1} = 0.0043$. The predicted value of H^E is 527 J mol^{-1} at 298.15 K, $x^1 = 0.5$. (For the methyl alcohol–diethyl ether system, which can be looked upon as similar, Christensen and coworkers[12] report a value of 440 J mol^{-1} at 298.15 K.)

The MeOH(2)–EG(4) system. The three published data sets could not be described successfully with a single set of parameters. A procedure similar to that used for the W–EG system was ultimately applied. The H^E data of ref.[12] at 298.15 K (in J mol^{-1}) were correlated by means of the equation

$$H^E = x_1 x_2 [533 + 111.5 (x_1 - x_2)].$$

The α_{241} and α_{242} values were determined based on equilibrium data of ref.[24] at 40 °C ($\sigma_x = 0.001$, $\sigma_y = 0.005$). All parameters are given in Table VII; they provided the values of $S_x = 0.0016$, $S_y = 0.0002$.

The MTBE(3)–EG(4) system. The modified Wilson's equation with $\alpha_{341} = 0.5$ was used for the thermodynamic description (LLE). By solving the $\bar{a}_i = \bar{\bar{a}}_i$ set ($i = 1, 2$), the a_{12} and a_{21} parameters were determined based on the mutual solubility of the components at 20 °C (Table VII). The value of $\alpha_{341} = 0.5$ was chosen based on previous experience and also with regard to the fact that the equilibrium data of the corresponding ternary systems (see below) were relatively well predicted.

Correlation of LLE Data for the Ternary Systems

A special approach[5,25 – 28] must be applied to obtain a good description of the liquid–liquid equilibrium, prediction based on binary parameters solely being insufficient. For a better fit, Surovy and coworkers[28] suggested the addition of a ternary term containing three parameters, which are determined from the LLE data in the ternary system. A computer program was developed for the calculation of the parameters; this program minimizes the target function

$$F_{tot} = [(\sum_{k=1}^{n_L} F_k)/6n_L]^{1/2} , \tag{10}$$

where

$$F_k = \sum_{i=1}^{3} [(x_{i,exp} - x_{i,calc})^2 + (z_{i,exp} - z_{i,calc})^2] \tag{11}$$

and n_L is the number of pairs of equilibrium points (connodes); $x_{i,calc}$ and $z_{i,calc}$ are calculated equilibrium pairs of points (determined by the procedure given in the Appendix), obtained so that for each experimental point and for the given set of parameters, the F_k value was minimized by the Newton method. The ternary parameters for the three heterogeneous ternary systems, along with the F_{tot} value, are given in Table VIII. The mean square deviations of the mole ratios are given in Table IX.

Since only the solubility at 20 °C is known for the MTBE(3)–EG(4) system, several series of calculations with different α_{341} values were performed for the MeOH(2)–MTBE(3)–EG(4) system. The value of $\alpha_{341} = 0.5$, which provided relatively good results for this system, was ultimately chosen. On the other hand, the equilibrium data calculation for the W(1)–MTBE(3)–EG(4) system were virtually unaffected by the a_{341} parameter.

VLE and LLE Prediction in the Ternary Systems and in the Quaternary System Based on Binary and Ternary Data

First, summarize the results of VLE predictions based on the binary and ternary data. Table IX demonstrates that the prediction which is based on the binary parameters

TABLE VIII
Survey of ternary parameters

System (*i*–*j*–*k*)	C_{ijki}	C_{ijkj}	C_{ijkk}	F_{tot}, %
W–MeOH–MTBE	1.85	-5.32	-1.75	1.37
MeOH–MTBE–EG	-0.93	0.11	1.99	1.25
W–MTBE–EG	0.99	-3.08	-0.79	0.23
W–MeOH–EG	0.0	0.0	0.0	–

TABLE IX
Standard deviations in the correlation of experimental data

System	Equilibrium	B	Standard deviations of x_i of liquid phase one				Standard deviations of x_i of liquid phase two or vapour phase				Standard deviations of temperature and pressure in VLE	
			S_{x_1}	S_{x_2}	S_{x_3}	S_{x_4}	S_{x_1}	S_{x_2}	S_{x_3}	S_{x_4}	S_T (°C)	S_p (kPa)
W(1)–MeOH(2) –MTBE(3)	LLE	0	0.172	0.061	0.112	–	0.173	0.036	0.191	–	–	–
		3	0.014	0.014	0.017	–	0.014	0.014	0.007	–	–	–
	VLE	0	0.005	0.005	0.007	–	0.006	0.008	0.005	–	0.12	0.36
		3	0.021	0.016	0.036	–	0.011	0.022	0.019	–	0.40	0.94
W(1)–MTBE(3) –EG(4)	LLE	0	0.004	–	0.007	0.007	0.005	–	0.003	0.003	–	–
		3	0.004	–	0.002	0.004	0.0002	–	0.0002	0.0002	–	–
MeOH(2)–MTBE(3)– EG(4)	LLE	3	–	0.016	0.008	0.017	–	0.014	0.005	0.009	–	–
	VLE	0	–	0.015	0.022	0.012	–	0.006	0.006	0	0.08	0.10
		3	–	0.015	0.019	0.013	–	0.006	0.006	0	0.01	0.19
W(1)–MeOH(2)– MTBE(3)–EG(4)	LLE	6[a]	0.009	0.007	0.016	0.013	0.007	0.021	0.015	0.034	–	–
		9[b]	0.007	0.010	0.010	0.012	0.005	0.019	0.015	0.029	–	–
	VLE	0	0.005	0.007	0.006	0.005	0.013	0.009	0.004	0	0.24	0.56
		6[a]	0.005	0.005	0.015	0.013	0.011	0.007	0.004	0	0.16	0.41
		9[b]	0.005	0.005	0.015	0.013	0.011	0.007	0.004	0	0.15	0.41

B number of ternary parameters. [a] Ternary parameters of the W(1)–MeOH(2)–MTBE(3) and MeOH(2)–MTBE(3)–EG(4) systems; [b] zero ternary parameters used for the W(1)–MeOH(2)–EG(4) system only.

solely, with zero ternary parameters, is very good. For the W(1)–MeOH(2)–MTBE(3) system it is even considerably better than with the use of the ternary data determined from LLE. This fact has been observed before[9] and it has been found that this is due to the neglecting of the temperature dependence of the ternary parameters which, as also follows from the LLE measurements, in their absolute value decrease rapidly with temperature[9].

In the quaternary system the effect of the ternary parameters did not appear to such an extent. Table IX includes evaluation for three variants. In variant I, all ternary parameters are assumed to be zero. The deviations are somewhat lower than in variants II and III. In variant II, the ternary parameters were only included for the W(1)–MeOH(2)–MTBE(3) and MeOH(2)–MTBE(3)–EG(4) systems, hence for systems that in Treyball's classification are type I (systems with a critical point). In variant III, all the calculated ternary parameters were included, i.e., also those of the W(1)–MTBE(3)–EG(4) system. The differences between variants II and III are negligible.

For the liquid–liquid equilibrium, efforts were made to perform the calculations for the same three variants as in VLE, differing in the use of the ternary parameters. However, the variant with all ternary parameters equal to zero was inapplicable because the trivial solution was thus obtained in several cases. Variant II, where the ternary parameters concern systems that are type I in Treyball's classification, gave nearly the same results and variant III, for which the ternary parameters of all the ternary subsystems involved were used.

CONCLUSIONS

The LLE and, to a lower extent, VLE was measured for the W–MeOH–MTBE–EG system and its heterogeneous ternary subsystems. Experimental data correlation was made using a superposition of the Wilson and Redlich–Kister equations with a ternary term. For VLE, it turned out that the multicomponent system data can be predicted based on the binary data, without the use of the ternary parameters (determined from the LLE data).

When modelling LLE it is necessary to use the ternary parameters of ternary systems possessing a critical point (Type I in Treyball's classification). The ternary parameters of ternary systems without a critical point (Type II in Treyball's classification) can be omitted, particularly if the heterogeneous region dominates, as is the case with the W–MTBE–EG system under study. For the quaternary system, also, it is necessary to use the ternary parameters of those ternary subsystems that possess a critical point.

APPENDIX

The agreement of the predicted and observed compositions of the equilibrium liquid phases of the four-component system was assessed in terms of the quantity S (considering a single experimental point)

$$S = \sum_{i=1}^{6} (\hat{\varphi}_i - \varphi_i^e)^2 \;, \tag{A1}$$

where $\varphi_i = x_1, x_2, x_3, z_1, z_2, z_3$; φ_i^e are the experimental values and $\hat{\varphi}_i$ values corresponding to the "nearest" point, which were determined by the following procedure (extension of that given in the monograph[5]). The nearest point is defined as that point giving the least S value and satisfying the equilibrium conditions.

A four-component two-phase system possesses two degrees of freedom at a given temperature and pressure. The x_1, x_2 values can be regarded as independent variables and the remaining mole fractions, as dependent variables. Knowing some equilibrium compositions x_i^0 and z_i^0 we can write for some other (changed) equilibrium composition

$$\begin{aligned} &x_1 = x_1^0 + \Delta x_1 \qquad x_2 = x_2^0 + \Delta x_2 \\ &x_3 = x_3^0 + (\partial x_3/\partial x_1)\Delta x_1 + (\partial x_3/\partial x_2)\Delta x_2 \\ &z_1 = z_1^0 + (\partial z_1/\partial x_1)\Delta x_1 + (\partial z_1/\partial x_2)\Delta x_2 \\ &z_2 = z_2^0 + (\partial z_2/\partial x_1)\Delta x_1 + (\partial z_2/\partial x_2)\Delta x_2 \\ &z_3 = z_3^0 + (\partial z_3/\partial x_1)\Delta x_1 + (\partial z_3/\partial x_2)\Delta x_2 \,. \end{aligned} \tag{A2}$$

By inserting Eq. (*A2*) in Eq. (*A1*) we obtain from the conditions

$$\partial S/\partial(\Delta x_1) = 0 \,, \quad \partial S/\partial(\Delta x_2) = 0 \tag{A3}$$

the set

$$\Delta x_1 [1 + \sum_{k=1}^{4} (\partial\varphi_k/\partial x_1)^2] + \Delta x_2 \sum_{k=1}^{4} (\partial\varphi_k/\partial x_1)(\partial\varphi_k/\partial x_2) =$$

$$= x_1^e - x_1^0 + \sum_{k=1}^{4} (\varphi_k^e - \varphi_k^0)(\partial\varphi_k/\partial x_1)$$

$$\Delta x_1 \sum_{k=1}^{4} (\partial\varphi_k/\partial x_1)(\partial\varphi_k/\partial x_2) + \Delta x_2 [1 + \sum_{k=1}^{4} (\partial\varphi_k/\partial x_2)^2] =$$

$$= x_2^e - x_2^0 + \sum_{k=1}^{4} (\varphi_k^e - \varphi_k^0)(\partial\varphi_k/\partial x_2) \;,$$

where $\varphi_k = x_3, z_1, z_2, z_3$.

The values of $\partial x_3/\partial x_j$, $\partial z_1/\partial x_j$, $\partial z_2/\partial x_j$, $\partial z_3/\partial x_j$, $j = 1, 2$ are obtained by differentiating the equilibrium conditions:

$$(\partial \ln \bar{\bar{a}}_i/\partial z_1)(\partial z_1/\partial x_j) + (\partial \ln \bar{\bar{a}}_i/\partial z_2)(\partial z_2/\partial x_j) + (\partial \ln \bar{\bar{a}}_i/\partial z_3)(\partial z_3/\partial x_j) -$$
$$- (\partial \ln \bar{a}_i/\partial x_3)(\partial x_3/\partial x_j) = \partial \ln \bar{a}_i/\partial x_j \quad (j = 1, 2) \; . \qquad (A5)$$

The calculation procedure is such that first, based on the experimental values of x_j^e, z_i^e, the variables x_3^0, z_1^0, z_2^0, and z_3^0 are calculated by solving the equilibrium conditions $\bar{\bar{a}}_i = \bar{a}_i$ (in this step, $x_1^e = x_1^0, x_2^e = x_2^0$). By solving the system (*A3*), the $\partial\varphi_k/\partial x_j$ values are determined; calculation of the increments Δx_1, Δx_2 and, consecutively, of the remaining increments Δz follows (Eq. (*A2*)). For sufficiently low increments the calculation is terminated, otherwise a next composition approximation is determined by means of Eq. (*A2*) and the calculation is repeated.

SYMBOLS

A_{ij}	Wilson's equation parameter
A_{ijk}	Redlich–Kister equation parameter
a_{ij}	Wilson's equation parameter
a_i	activity of component *i*
B, B_{ij}	second virial coefficient
C_{ijkl}	ternary parameter
C_p^E	excess molar thermal capacity at constant pressure
d	differentiation operator
e	(superscript) experimental value
F_k, F_{tot}	target functions defined by Eqs (*10*), (*11*)
G^E	molar excess Gibbs energy
H^E	molar excess enthalpy
i, *j*, *k*, *l*	summation indices
N	number of components
n_D	refractive index
n_L	number of connodes
n_{ij}	upper summation limit in Eq. (*7*)
p	pressure
p_i^0	saturated vapour pressure of component *i*
Q	dimensionless molar Gibbs energy
Q_{Wilson}	Wilson part of *Q*
Q_{RK}	Redlich–Kister part of *Q*
Q_{tern}	ternary term in relation for *Q*
R	universal gas constant
S	quantity defined by Eq. (*A1*)

$S_v = \sum_{i=1}^{n} [(v_i^e - \hat{v}_i)^2/n]^{1/2}$	mean square deviation of quantity v
T	absolute temperature
t	centigrade temperature
V_i, V_i^L	molar volume of component *i* in the liquid state
x_i	mole fraction of component *i* in the liquid phase
y_i	mole fraction of component *i* in the vapour phase
z_i	mole fraction of component *i* in the liquid phase
α_B	coefficient of temperature dependence of the virial coefficient
β_B	coefficient of temperature dependence of the virial coefficient
α_{ij}, β_{ij}, γ_{ij}	terms in the temperature dependence of Wilson's equation parameters
α_{ijk}, β_{ijk}, γ_{ijk}	terms in the temperature dependence of the Redlich–Kister equation parameters
γ_i	activity coefficient of component *i*
∂	partial differentiation operator
Δ	quantity change
ρ	density
σ	standard deviation estimate
$^-$, $^=$	(bars) phase labelling

REFERENCES

1. Gmehling J., Onken V.: *Vapor–Liquid Equilibrium Data Collection.* Dechema Chemistry Data Series, Frankfurt am Main 1977 – 1984.
2. Zikmundová D., Matouš J., Novák J. P., Kubíček V., Pick J.: Fluid Phase Equil. *54*, 93 (1990).
3. Mitchell J., Smith D. W.: *Aquametry.* Wiley, New York 1948.
4. Evans T. V., Edlund K. R.: Ind. Eng. Chem. *28*, 1186 (1936).
5. Riddick J. A., Bunger W. B.: *Organic Solvents.* Wiley, New York 1970.
6. Novák J. P., Matouš J., Pick J.: *Liquid–Liquid Equilibria.* Academia, Prague; Elsevier, Amsterdam 1987.
7. Mikeš O. (Ed.): *Laboratory Handbook of Chromatographic and Allied Methods.* Ellis Horwood Ltd., Chichester 1979.
8. Kay W. B.: AIChE J. *25*, 179 (1979).
9. Novák J. P., Matouš J., Říčná K., Kubíček V.: Collect. Czech. Chem. Commun. *54*, 586 (1989).
10. Voňka P., Novák J. P.: Chem. Listy *83*, 1233 (1989).
11. Voňka P., Novák J. P., Matouš J.: Collect. Czech. Chem. Commun. *54*, 2823 (1989).
12. Christiansen J. J., Hanks R. V., Izatt R. M.: *Handbook of Heats of Mixing.* Wiley, New York 1982.
13. Hall D. J., Mask C. J., Pemberton R. C.: NPL Report Chem. *95*, January 1979.
14. McGlashan M. L., Williamson A. G.: J. Chem. Eng. Data *21*, 196 (1976).
15. Griswold J., Wong S. Y.: Chem. Eng. Prog., Symp. Ser. 3 *48*, 18 (1952).
16. Kohoutová J., Suška J., Novák J. P., Pick J.: Collect. Czech. Chem. Commun. *35*, 3210 (1970).
17. *Ocon J., Rebolleda F.: An. Real. Soc. Espan. Fis. Y. Quim. 548, 525 (1958).*
18. Voňka P., Novák J. P., Suška J., Pick J.: Chem. Eng. Commun. *2*, 51 (1975).
19. Trimble H. M., Potts W.: Ind. Eng. Chem. *27*, 66 (1935).
20. Sokolov N. M., Tsygankova L. N., Zhavoronkov N. M.: Teor. Osn. Khim. Tekhnol. *5*, 900 (1971).
21. Aim K., Cyprian M.: J. Chem. Eng. Data *25*, 100 (1983).
22. Acosta R. G., Rodriquez E. R., De La Guordia P. M.: Rev. Inst. Mex. Pet. *12*, 40 (1980).
23. Churkin V. N., Gorshkov V. A., Pavlov L. J.: Prom-st. Sint. Kauch. *4*, 2 (1979).
24. Sedletskaya I. S., Kogan V. B.: Zh. Prikl. Khim. *42, 2551 (1989)*.

25. Sörensen J. M., Arlt W.: *Liquid–Liquid Equilibrium Data Collection*. Dechema Chemistry Data Series, Frankfurt am Main 1979, 1980.
26. Pablo J. J., Prausnitz J. M.: AIChE J. *34*, 1595 (1988).
27. Nagata I.: Fluid Phase Equil. *54*, 191 (1990).
28. Surový J., Dojčanský J., Bafrncová S.: Collect. Czech. Chem. Commun. *47*, 1420 (1982).
29. Ambrose D., Ellender J. H., Sprake C. H. S., Townsend R.: J. Chem. Thermodyn. *8*, 165 (1976).
30. Dymond J. H., Smith E. B.: *The Virial Coefficients of Pure Gases and Mixtures*. Clarendon Press, Oxford 1980.
31. Dykyj J., Repáš M.: *Tlak nasýtenej pary organických zlúčenín*. Veda, Bratislava 1979.
32. Dreisbach R. R.: *Chemical Properties of Chemical Compounds* III. Am. Chem. Soc., Washington D. C. 1961.
33. Pitzer K. S., Curl R. F.: J. Am. Chem. Soc. *79*, 2369 (1957).

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