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Liquid−Liquid Equilibrium in Ternary Systems Containing Ethylene Glycol, Monofunctional Benzene Derivative, and Ethyl Acetate

Jana Dreiseitlová, Karel Řehák,* and Pavel Morávek

Department of Physical Chemistry, Institute of Chemical Technology, Prague, 166 28 Praha 6, Czech Republic

ABSTRACT: Liquid−liquid equilibrium (LLE) data in ternary systems ethylene glycol + toluene + ethyl acetate, ethylene glycol + anisole + ethyl acetate, and ethylene glycol + acetophenone + ethyl acetate were measured at 298.15 K. The experimental data were utilized to adjust the parameters of the nonrandom two-liquid (NRTL) equation. The Othmer−Tobias plot of the LLE data shows that the system ethylene glycol + acetophenone + ethyl acetate exhibits a less common behavior.

INTRODUCTION

Systematic measurements of phase equilibria in small systems containing core structures are very desirable for the evaluation of group contribution parameters in models describing activity coefficients (e.g., UNIFAC). Such group contribution models can be then used for the estimation of solubilities of compounds with more complex structures such as drugs. In our previous work we studied mutual solubilities in binary systems containing monofunctional derivatives of benzene and ethylene glycol.[1]

Ethylene glycol, that is, ethane-1,2-diol, is widely used in industry. It is an important coolant and heat transfer agent, precursor in the plastic industry, and hydrate inhibitor for the natural gas transport. Ethylene glycol serves also as a minor ingredient in many cosmetic and drug products. Its usage as a solvent is not frequent so that data on mutual miscibility with many other liquids are rare. Nevertheless, in solvent selection procedures (e.g., for drug production), ethylene glycol can be considered as a cosolvent or antisolvent. For this reason we extended our previous work to ternary systems. In this work, experimental data on the liquid−liquid equilibrium (LLE) in three ternary systems at 298.15 K are reported. The systems studied are ethylene glycol + toluene + ethyl acetate, ethylene glycol + anisole + ethyl acetate, and ethylene glycol + acetophenone + ethyl acetate. No literature data on the LLE for the mentioned ternary systems were found.

EXPERIMENTAL SECTION

Ethylene glycol (i.e., ethane-1,2-diol), toluene, anisole (i.e., methoxybenzene), acetophenone (i.e., 1-phenylethanone), and ethyl acetate were supplied by Sigma-Aldrich with mass fraction purities greater than 0.997 and 0.99 (in the case of acetophenone only). Specifications of chemicals used in this work are given in Table 1. Mass fractions of water in the chemicals were determined by coulometric Karl Fischer titration using a Metrohm KF coulometer 831. Because of the high hydrophilicity of ethylene glycol, most manipulations with it were performed in a drybox. Densities of the used reagents were measured at 298.15 K by a density meter Anton Paar DMA 5000 and compared to those taken from literature (see Table 1).

Mutual solubility data for the three ternary systems were acquired using a direct analytical method, which consisted in a direct analysis of the conjugated phases. Heterogeneous mixtures for sampling were prepared in an equilibrium cell which was thermostatted by means of a Lauda RC6 CP Edition 2000 thermostat to the required temperature (± 0.05 K). The mixture inside the cell was agitated for 6 h and then left to stand for at least 12 h to allow the two phases to separate. To gain sufficient amount of data for determination of tie-lines, samples taken from the both liquid phases were analyzed by means of spectrophotometry and gas chromatography.

Spectrophotometry was utilized for the determination of concentration of benzene derivative in both liquid phases of all systems. A Varian Cary Bio 50 UV−visible spectrophotometer was used. An appropriate wavelength for measuring absorbance was chosen (namely, 256.0 nm for toluene, 271.0 nm for anisole, and 279.5 nm for acetophenone). The spectophotometer was calibrated with methanol solutions of known concentrations of the selected benzene derivative. Parameters of a calibration equation were then fitted to the measured absorbance data. Samples taken from the equilibrium cell were diluted with methanol so that their compositions matched approximately that of calibration mixtures. Finally, using the calibration equation and a mass balance, compositions of benzene derivative in the both equilibrium phases were calculated.

Next information needed for determination of tie-lines in the studied ternary systems were obtained by means of an HP 6890 gas chromatograph with a flame ionization (FID) detector. The analyses were performed using an HP-INNOWAX (cross-linked polyethylene glycol) capillary column (30 m × 0.32 mm × 0.25 μm). Analyses of samples pertaining to the first (i.e., glycol-rich) phase and to the second (i.e., organics-rich) phase were carried out in a different way. The ethylene glycol-rich phase was analyzed for the composition ratio of benzene derivative and ethyl acetate. In the organic-rich phase, the content of ethylene glycol was measured. For the former analyses, the chromatograph was calibrated with ethanol solutions of known compositions of benzene derivative and ethyl acetate.

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Table 1. Purity ω, Water Mass Fraction $\omega(H_2O)$, and Density ρ at T = 298.15 K of the Compounds Used

	purity[a]		ρ (298.15 K)/g·cm^{-3}	
compound	100 ω	100 $\omega(H_2O)$	this work	literature data
ethylene glycol	99.8	0.008	1.10990	1.11000[2]
acetophenone	99.0	N/A	1.02300	1.0231[5]
anisole	99.7	0.006	0.98913	0.98929[4]
toluene	99.8	0.008	0.86227	0.86219[3]
ethyl acetate	99.8	0.004	0.89440	0.89455[2]

[a] Declared by the manufacturer.

Table 2. Experimental Data on the LLE in Ternary Systems Ethylene Glycol (1) + Benzene Derivative (2) + Ethyl Acetate (3) at Temperature 298.15 K. Mole Fractions of Components in the Glycol-Rich Phase (x'_i), Mole Fractions of Components in the Organic-Rich Phase (x''_i), and Root-Mean-Square Deviation Given by eq 4 (δ_{rms})

x'_1	x'_2	x'_3	x''_1	x''_2	x''_3
Ethylene Glycol (1) + Acetophenone (2) + Ethyl Acetate (3)					
0.8669	0.0987	0.0344	0.1718	0.6318	0.1964
0.8549	0.0172	0.1279	0.1336	0.0991	0.7673
0.8537	0.0812	0.0651	0.1711	0.4740	0.3549
0.8532	0.0714	0.0753	0.1654	0.4150	0.4195
0.8509	0.0534	0.0957	0.1640	0.2984	0.5376
0.8501	0.0371	0.1128	0.1432	0.2116	0.6452
0.8839	0.1161	0.0000	0.1440	0.8560	0.0000
0.8602	0.0000	0.1398	0.1236	0.0000	0.8764
δ_{rms} = 0.0040					
Ethylene Glycol (1) + Toluene (2) + Ethyl Acetate (3)					
0.9705	0.0210	0.0085	0.0045	0.9048	0.0906
0.9676	0.0208	0.0116	0.0060	0.8725	0.1216
0.9628	0.0204	0.0168	0.0084	0.8240	0.1676
0.9562	0.0195	0.0243	0.0112	0.7694	0.2195
0.9472	0.0185	0.0342	0.0192	0.6065	0.3743
0.9424	0.0182	0.0395	0.0229	0.5813	0.3958
0.9269	0.0163	0.0568	0.0352	0.4469	0.5179
0.9153	0.0148	0.0699	0.0543	0.3424	0.6032
0.9079	0.0138	0.0783	0.0604	0.2867	0.6529
0.8922	0.0100	0.0979	0.0766	0.1804	0.7430
0.8644	0.0059	0.1297	0.1054	0.0785	0.8161
0.9783	0.0217	0.0000	0.0018	0.9982	0.0000
0.8602	0.0000	0.1398	0.1236	0.0000	0.8764
δ_{rms} = 0.0024					
Ethylene Glycol (1) + Anisole (2) + Ethyl Acetate (3)					
0.9567	0.0320	0.0113	0.0157	0.8559	0.1284
0.9467	0.0304	0.0229	0.0242	0.7435	0.2322
0.9429	0.0291	0.0280	0.0292	0.6529	0.3180
0.9316	0.0264	0.0420	0.0469	0.5272	0.4259
0.9130	0.0221	0.0649	0.0620	0.3761	0.5619
0.9014	0.0168	0.0818	0.0795	0.2732	0.6474
0.8790	0.0109	0.1101	0.0941	0.1385	0.7673
0.8646	0.0070	0.1284	0.1047	0.0921	0.8032
0.9659	0.0341	0.0000	0.0085	0.9915	0.0000
0.8602	0.0000	0.1398	0.1236	0.0000	0.8764
δ_{rms} = 0.0046					

The later analyses utilized 1,3-propanediol as the internal standard, and the chromatograph was calibrated with methanol solutions of known concentrations of ethylene glycol and 1,3-propanediol.

The mentioned combination of analytical methods yielded tie-line data of the LLE in the studied systems. They are given in Table 2. The uncertainties of the determined mole fractions were estimated by means of measuring artificially prepared mixtures having known compositions of components. While the absolute values of the expanded uncertainty (U) varied according to the amount of components in the original sample, the relative values (i.e., $U_r = U/x_i$) were found to be more or less constant. The relative expanded uncertainty U_r = 0.015 (for a level of confidence of 95 %) was finally assigned to the determined composition expressed in molar fraction.

■ CORRELATION OF LLE DATA

The experimental results on the LLE were used to describe the ternary systems by the nonrandom two-liquid (NRTL) equation.[6] The systems studied are of the general pattern ethylene glycol (1) + benzene derivative (2) + ethyl acetate (3). Experimental data on the LLE for the systems (1) + (2) have been published and correlated[1] by the NRTL equation with parameters

$$\tau_{12} = \frac{g_{12} - g_{22}}{RT} = \frac{a_{12}}{RT} \qquad \tau_{21} = \frac{g_{21} - g_{11}}{RT} = \frac{a_{21}}{RT} \tag{1}$$

a_{ij} were considered to be temperature-dependent.

$$\frac{a_{ij}}{R} = a_{ij,0} + a_{ij,1}T + a_{ij,2}T^2 \tag{2}$$

where $a_{ij,0}$, $a_{ij,1}$, and $a_{ij,2}$ are temperature-independent adjustable parameters. The NRTL nonrandomness parameters were set arbitrary $\alpha_{ij} = \alpha_{ji} = 0.2$ for all binary systems. The parameters a_{13} and a_{31} in the form of eq 2 were obtained by the same procedure as in ref 1. For this purpose the experimental data on the LLE for the ethylene glycol (1) + ethyl acetate (3) system given in our previous paper[7] were used. This system exhibits the LLE with the upper critical solution temperature T_c = 329.06 K at x_{1c} = 0.5448. The evaluated temperature-dependent parameters a_{13} and a_{31} satisfactorily describe the LLE in the binary system (1) + (3). The calculated critical solution data are $T_{c,calc}$ = 329.07 K and $x_{1c,calc}$ = 0.5443. No experimental data at 298.15 K which can be used for evaluation of parameters a_{23} and a_{32} pertaining to binary systems benzene derivative (2) + ethyl acetate (3) were available. Therefore, these parameters were fit to the ternary LLE data measured in this work. Taking into account no temperature dependence, values $a_{23,0}$ and $a_{32,0}$ were determined by minimization of the objective function

$$F(a_{23,0}, a_{32,0}) = \sum_{i=1}^{n}\sum_{k=1}^{3}[(x'_{k,i} - x'_{k,i,\text{calc}})^2 + (x''_{k,i} - x''_{k,i,\text{calc}})^2] \tag{3}$$

where n is the number of experimentally determined tie-lines. ($x'_{1,i}$, $x'_{2,i}$, $x'_{3,i}$) and ($x''_{1,i}$, $x''_{2,i}$, $x''_{3,i}$) are the mole fractions of the components at the end points of the ith experimental tie-line. These data are given in Table 2. Similarly, ($x'_{1,i,\text{calc}}$, $x'_{2,i,\text{calc}}$, $x'_{3,i,\text{calc}}$) and ($x''_{1,i,\text{calc}}$, $x''_{2,i,\text{calc}}$, $x''_{3,i,\text{calc}}$) are end points of the ith calculated tie-line which lies closest to the mentioned ith experimental tie-line.

The function F is a nonlinear function which could have more than one point of minimum. Therefore, the nonderivative numerical method based on the scanning of two-dimensional rectangular grids in the parameters $a_{23,0}$ and $a_{32,0}$ (lattice point)

Table 3. Constants ($a_{ij,k}$) of Temperature Dependence of the NRTL Equation Parameters Given by eq 2, the NRTL Nonrandomness Parameters (α_{ij})

$a_{12,0}$/K	$a_{12,1}$	$a_{12,2}$/K^{-1}	$a_{21,0}$/K	$a_{21,1}$	$a_{21,2}$/K^{-1}	α_{12}
Ethylene Glycol (1) + Toluene (2)[a]						
328.65	1.1199	0	1960.4	−2.3978	0	0.2
Ethylene Glycol (1) + Anisole (2)[a]						
282.38	0.8307	0	3574.5	−7.7145	0	0.2
Ethylene Glycol (1) + Acetophenone (2)[a]						
483.60	0.22098	$1.1094 \cdot 10^{-4}$	270.68	6.1151	$-1.9575 \cdot 10^{-2}$	0.2
$a_{13,0}$/K	$a_{13,1}$	$a_{13,2}$/K^{-1}	$a_{31,0}$/K	$a_{31,1}$	$a_{31,2}$/K^{-1}	α_{13}
Ethylene Glycol (1) + Ethyl Acetate (3)[b]						
376.95	−1.3703	$5.08 \cdot 10^{-3}$	428.07	6.0404	$-1.9728 \cdot 10^{-2}$	0.2
$a_{23,0}$/K	$a_{23,1}$	$a_{23,2}$/K^{-1}	$a_{32,0}$/K	$a_{32,1}$	$a_{32,2}$/K^{-1}	α_{23}
Toluene (2) + Ethyl Acetate (3)						
602.13	0	0	−410.34	0	0	0.2
Anisole (2) + Ethyl Acetate (3)						
1301.1	0	0	−663.09	0	0	0.2
Acetophenone (2) + Ethyl Acetate (3)						
375.36	0	0	−183.60	0	0	0.2

[a] Values taken from ref 1. [b] Evaluated by correlation of experimental data from ref 7.

was used to determine the minimum of function *F*. The parameters of the NRTL equation describing the LLE in the studied systems are summarized in Table 3. The values of the root-mean-square deviation for *n* number of tie-lines calculated as

$$\delta_{\text{rms}} = \sqrt{\frac{\sum_{i=1}^{n}\sum_{k=1}^{3}\left[(x'_{k,i} - x'_{k,i,\text{calc}})^2 + (x''_{k,i} - x''_{k,i,\text{calc}})^2\right]}{6n}} \tag{4}$$

are given in Table 2.

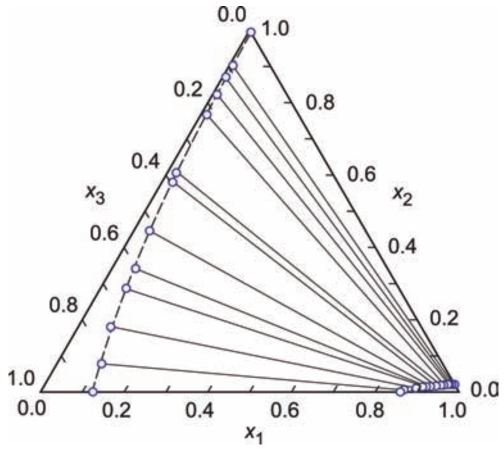

Figure 1. Liquid−liquid equilibrium (LLE) in the system ethylene glycol (1) + toluene (2) + ethyl acetate (3). ○—○, experimental tie-lines; - - -, binodal LLE curve calculated by the NRTL model.

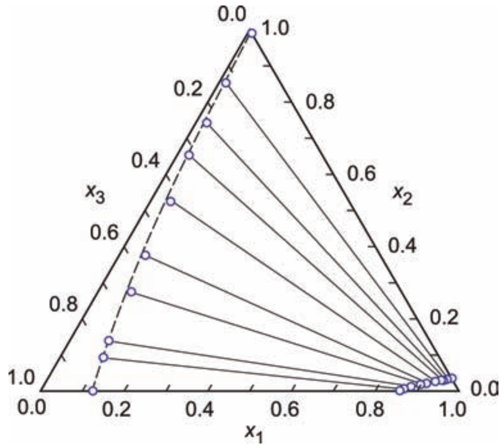

Figure 2. LLE in the system ethylene glycol (1) + anisole (2) + ethyl acetate (3). ○—○, experimental tie-lines; - - -, binodal LLE curve calculated by the NRTL model.

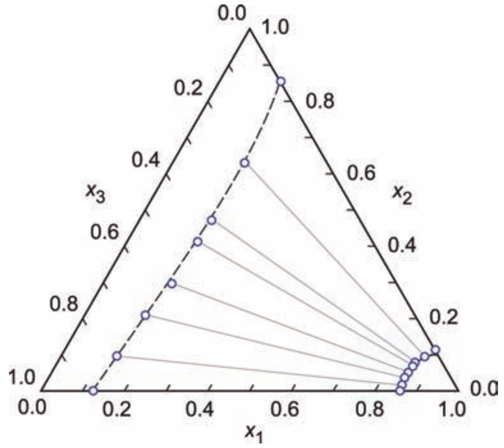

Figure 3. LLE in the system ethylene glycol (1) + acetophenone (2) + ethyl acetate (3). ○—○, experimental tie-lines; - - -, binodal LLE curve calculated by the NRTL model.

RESULTS AND DISCUSSION

Experimental data on the LLE at 298.15 K for systems ethylene glycol (1) + toluene (2) + ethyl acetate (3), ethylene glycol (1) + anisole (2) + ethyl acetate (3), and ethylene glycol (1) + acetophenone (2) + ethyl acetate (3) are summarized in Table 2. All of the systems exhibit the LLE phase diagram of Type 2.[8] Binaries (1) + (2) and (1) + (3) exhibit immiscibility, while the binary (2) + (3) is completely miscible. There are no plait points at the LLE diagrams of the studied system. These diagrams are given in Figures 1, 2, and 3. The tie-lines calculated by the NRTL equation (with parameters given in Table 3) which are closest to the experimental ones cannot be seen because the deviations between experimental and calculated data are below the resolution of the figures. The experimental LLE data were ascertained by the Othmer−Tobias correlation.[9] The data were plotted in coordinates $\ln[(1 - w'_1)/w'_1]$ against $\ln[(1 - w''_3)/w''_3]$, where w'_1 is the mass fraction of ethylene glycol in the ethylene glycol-rich phase and w''_3 is the mass fraction of ethyl acetate in the other organic phase. According to Othmer and Tobias,[9] the majority of the systems exhibit linearity in the mentioned plot. It was found that the systems ethylene glycol (1) + toluene (2) + ethyl acetate (3) and ethylene glycol (1) + anisole (2) + ethyl acetate (3) satisfy this option. The system ethylene glycol (1) + acetophenone (2) + ethyl acetate (3) however exhibits the plot with a significant curvature (see Figure 4). Our opinion is that this behavior is not caused by an inconsistency of the

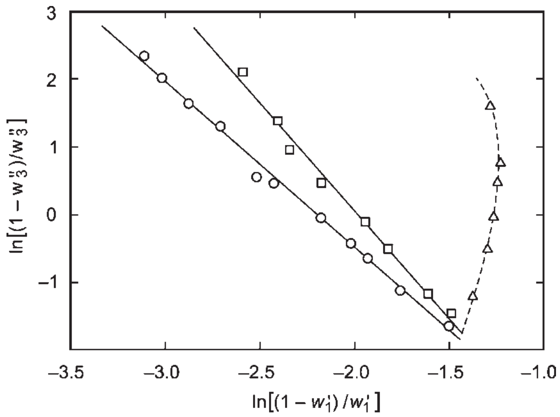

Figure 4. Othmer−Tobias correlation. ○, data for the ethylene glycol (1) + toluene (2) + ethyl acetate (3) system; □, data for the ethylene glycol (1) + anisole (2) + ethyl acetate (3); △, data for the ethylene glycol (1) + acetophenone (2) + ethyl acetate (3). —, linear fit; - - -, line drawn merely to lead the eye.

experimental data, but it is given by the nature of the ternary system. In contrast to the other two systems, the binodal line pertaining to the glycol-rich phase exhibits a strong "non-convex-like" curvature.

No literature data on LLE for the ternary systems were found in literature. The obtained LLE data for binaries can be compared with the previously published results.[1,7] Good agreement with differences in mole fractions below 0.0029 was observed for all binary mutual solubilities except of solubility of acetophenone in ethylene glycol. For that case the discrepancy in mole fraction for an unknown reason reached 0.018.

CONCLUSIONS

The LLE data at 298.15 K were experimentally determined for ternary systems ethylene glycol + toluene + ethyl acetate, ethylene glycol + anisole + ethyl acetate, and ethylene glycol + acetophenone + ethyl acetate.

A thermodynamic description of the ternary systems was established by means of the NRTL equation. For this reason, previously published parameters for binary systems containing ethylene glycol were utilized. They were completed by the NRTL parameters pertaining to binary systems benzene derivative + ethyl acetate which were determined by a numerical optimization procedure utilizing the ternary experimental data. The NRTL model with the presented parameters describes the LLE in the ternary system within the experimental uncertainty. It was found that the LLE in the ternary system ethylene glycol + acetophenone + ethyl acetate does not satisfy the Othmer−Tobias correlation, and consequently this system exhibits an unusual behavior.

AUTHOR INFORMATION

Corresponding Author

*E-mail: karel.rehak@vscht.cz. Address for correspondence: Dr. Karel Řehák, Department of Physical Chemistry, Institute of Chemical Technology, Prague, Technická 5, 166 28 Praha 6, Czech Republic. Tel.: +420 220 444 039.

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