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Liquid−Liquid Equilibrium and Critical Phenomena in the Ternary System Water + 2-Methoxyethanol + Toluene in the Temperature Range 283 K to 383 K

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Liquid−liquid equilibrium and critical phenomena in the ternary system water + 2-methoxyethanol (methylcellosolve) + toluene have been studied by means of the visual polythermal method under saturation pressure in the temperature range from 283 K to 383 K. The system is characterized, at all temperatures, by the presence of a two-phase liquid−liquid equilibrium. The solubility data for twelve temperatures are presented. The mutual solubility of the components increases with increasing temperature. The temperature dependence of the critical solution (plait) point composition has been established.

Introduction

The widespread use of nonaqueous and mixed solvents in science and technology requires the knowledge of the temperature dependence of the component mutual solubility in ternary liquid systems. The composition at the critical solution (plate) point is an important part of the solubility diagram of a ternary system with a liquid−liquid equilibrium (LLE) because its position on the LLE isotherm characterizes the solubility and the interactions between the components in the system. However, few experimental data have been reported in the literature on how temperature affects the composition at the critical solution point. In previous papers we have studied liquid−liquid equilibria and critical phenomena in the ternary systems water + propan-2-ol + octane,[1] water + propan-2-ol + heptane,[2,3] water + propan-2-ol + toluene,[4] water + pyridine + hexane,[5] and water + propan-1-ol + dodecane.[6]

2-Methoxyethanol is a highly polar and amphiphilic solvent with a considerable homogenizing and solvent ability. It is widely used in semiconductor manufacturing industries, as an agent for separation of aromatic compounds from petroleum fractions by azeotropic distillation and extraction, and also as a de-icing additive in military and general aviation jet fuel.[7−9]

We are not aware of any investigations of the system water + 2-methoxyethanol + toluene.

The objectives of the present work are as follows: to determine the mutual component solubility of the ternary system water + 2-methoxyethanol + toluene in the temperature range from 283 K to 383 K at saturation pressure and to establish the temperature dependence of the critical solution (plait) point composition in the same temperature range.

Experimental Section

Materials. Ordinary bidistilled water was used. 2-Methoxyethanol (Mikrotechna N.P. Praha 4, Czechia) was dried over molecular sieves 4A and fractionally distilled with a 0.6 m column, discarding the first 10% of volume. No impurities were found by GLC. The chromatography was executed on the gas chromatograph LHM-80 (Russia). A thermal conductivity detector was used at 353 K. The colomn was a 3 m long and 3 mm diameter steel tube packed with Chromoton-N with static phase Apiezon L (LaChema, s.p.Brno, Prague, Czechia) in an amount 15 mass %. Helium at the flow rate 35 mL/min was used as carrier gas. The measured properties of 2-methoxyethanol were in good agreement with the literature values: T_b (101 325 Pa)/K = 397.65 (397.75[10]); n_D (298.15 K) = 1.4000 (1.4002[10]); ρ(298.15 K)/kg·m^{-3} = 960.15 (960.24[10]). Toluene (Reakhim, Shostka, Russia) "pure for analysis" grade material was dried over molecular sieves 4A and used without further purification. No impurities were found by GLC (at 333 K, Chromoton-N with static phase PEG-400 (LaChema, s.p.Brno, Prague, Czechia) in an amount 15 mass %). The measured properties of toluene were in good agreement with the literature values: T_b (101 325 Pa)/K = 383.85 (383.78[10]); n_D (298.15 K) = 1.4942 (1.494 13[10]); ρ(298.15 K)/kg·m^{-3} = 862.4 (862.19[10]).

Apparatus and Procedure. Phase transitions in the ternary system from two liquid phases to a homogeneous liquid phase, or vice-versa, were determined by the visual polythermal method while heating and cooling the samples in sealed glass ampules under the saturation pressure. The temperature T was maintained constant to within 0.1 K using a Mechanik Medingen U-10 ultrathermostat and was measured with the same accuracy by means of a calibrated Hg thermometer.

Mixtures of known compositions were prepared by mass, with an accuracy of 0.0001 g. The compositions of the ternary mixtures varied on several selected sections of the composition triangle. The mixtures on each section are characterized by a varying content of one component and a constant mass ratio of the two other components. Using the reproducibility of the results (measuring the phase transition temperatures in ternary mixtures with the same composition), equilibrium between the phases with constant mixing was found to be achieved within 0.5 h. The relative error in solubility determinations was 0.5% to 1.0%.

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Table 1. Phase Transition Temperatures, T/K, against the Toluene Content (100w_3, mass %) in the Mixtures with Mass Ratio w_1/w_2 in the Ternary System Water (1) + 2-Methoxyethanol (2) + Toluene (3)

$w_1/w_2 = 70.00/30.00$		$w_1/w_2 = 53.00/47.00$		$w_1/w_2 = 42.00/58.00$		$w_1/w_2 = 30.00/70.00$	
100w_3	T/K	100w_3	T/K	100w_3	T/K	100w_3	T/K
0.28	280.75	0.47	280.95	1.78	282.25	4.28	282.75
0.40	300.15	0.51	285.75	2.72	311.45	6.13	301.35
0.59	320.55	0.72	302.55	3.60	338.15	8.41	321.55
0.82	336.55	0.97	317.95	4.58	353.65	10.32	334.95
1.20	356.35	1.37	334.05	5.58	364.35	12.84	346.95
1.54	370.35	1.96	352.15	6.62	372.85	15.98	360.15
2.10	385.45	2.41	363.95	8.12	387.75	18.98	371.45
		3.00	375.45			23.41	383.75
		3.72	385.85				

Table 2. Phase Transition Temperatures, T/K, against the Water Content (100w_1, mass %) in the Mixtures with Mass Ratio w_2/w_3 in the Ternary System Water (1) + 2-Methoxyethanol (2) + Toluene (3)

$w_2/w_3 = 11.86/88.14$		$w_2/w_3 = 22.00/78.00$		$w_2/w_3 = 36.51/63.49$		$w_2/w_3 = 49.99/50.01$		$w_2/w_3 = 62.99/37.01$		$w_2/w_3 = 78.00/22.00$	
100w_1	T/K	100w_1	T/K	100w_1	T/K	100w_1	T/K	100w_1	T/K	100w_1	T/K
21.09	281.35	15.80	282.25	10.50	281.45	6.94	279.35	4.05	280.75	1.48	281.45
23.75	299.35	16.01	286.15	11.07	291.65	7.84	302.95	4.40	299.75	1.55	296.15
25.62	311.95	16.96	297.55	12.00	307.75	8.00	323.05	4.58	307.35	1.70	311.15
27.79	325.35	19.00	319.85	13.02	320.75	9.74	338.55	5.00	322.55	1.97	326.05
30.57	340.35	22.19	343.95	13.98	332.35	11.18	358.95	5.60	339.45	2.43	351.95
33.82	356.85	25.03	362.25	15.43	348.05	12.07	368.75	6.00	349.05	3.04	374.95
		29.24	383.45	17.45	364.55	13.13	379.95	6.70	365.45	3.78	392.35
				19.30	378.35	14.35	391.45	7.28	375.65		
				20.73	393.45	15.60	401.45	7.90	385.05		
								8.51	393.05		

The compositions corresponding to the critical solution points were determined experimentally by the phase-volume ratio method.[11] These measurements were carried out by cooling graduated ampules filled with mixtures of compositions selected to split in phases of equal volumes at the critical state. The relative error in determination of the critical solution point compositions was 5%.

Results

Binary Systems. The components of the binary system water + toluene are practically immiscible. The components of the binary systems water + 2-methoxyethanol and toluene + 2-methoxyethanol are completely miscible in the studied temperature range.

Ternary System Water + 2-Methoxyethanol + Toluene. The compositions of the ternary (water + 2-methoxyethanol + toluene) mixtures varied along 10 mass ratios (I−X) of the composition triangle. The mixtures along mass ratios I−IV are characterized by a varying content of toluene and a constant water to 2-methoxyethanol mass ratio: 70.00/30.00 (I), 53.00/47.00 (II), 42.00/58.00 (III), and 30.00/70.00 (IV). The mixtures along mass ratios V−X are characterized by a varying content of water and a constant toluene to 2-methoxyethanol mass ratio: 11.86/88.14 (V), 22.00/78.00 (VI), 36.51/63.49 (VII), 49.99/50.01 (VIII), 62.99/37.01 (IX), and 78.00/22.00 (X). The direct experimental data of the phase transition temperatures in the mixtures of the components along mass ratios I−X are given in Tables 1 and 2. The phase transition temperatures against the content of the variable component in the ternary mixtures for all mass ratios were plotted (the figures are not represented).

The compositions and temperatures of the critical solution points in the ternary system water + 2-methoxyethanol + toluene (Table 3) were determined by investigation of the mixtures along five additional mass ratios of the composition triangle. These mixtures are characterized by a varying content of water and a constant toluene to 2-methoxyethanol mass ratio: 49.09/50.91, 48.21/51.79, 47.70/52.30, 46.98/53.02, and 46.15/53.85. The critical phenomena in the mixtures were accompanied by intense blue opalescence at the moment of the phase transition. The temperature dependences of water and toluene contents at the critical solution points are presented in Figure 1.

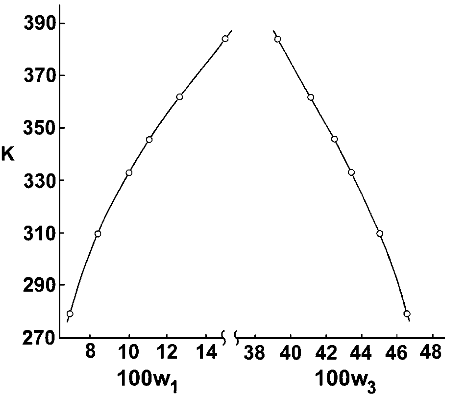

Figure 1. Temperature dependences of the water and toluene contents (mass %) at the critical solution points of the ternary system water (1) + 2-methoxyethanol (2) + toluene (3).

Table 3. Compositions (mass %) and Temperatures, T/K, of the Critical Solution Points in the Ternary System Water (1) + 2-Methoxyethanol (2) + Toluene (3)

100w_1	100w_2	100w_3	T/K
6.94	46.54	46.52	279.45
8.39	46.64	44.97	310.05
10.00	46.61	43.39	333.15
11.05	46.52	42.43	345.75
12.63	46.32	41.05	362.05
15.03	45.76	39.21	384.25

The direct experimental polythermal data (Tables 1−3) were used to estimate the component solubilities and the critical solution point compositions at twelve temperatures in Table 4.

Discussion and Conclusions

The two-liquid-phase binodal surface in the temperature range from 283 K to 383 K is plotted in the temperature−concentration prism of the ternary system water + 2-meth-

Table 4. Mutual Component Solubility (mass %) in the Ternary System Water (1) + 2-Methoxyethanol (2) + Toluene (3)

T/K	$100w_1$	$100w_2$	$100w_1$	$100w_2$	$100w_1$	$100w_2$
283.15	69.79	29.92	21.45	69.23	7.07	46.48
	52.74	46.77	15.84	65.64	4.09	35.49
	41.24	56.95	10.60	56.76	1.49	21.67
	28.69	66.99	7.1[a]	46.5[a]		
293.15	69.76	29.89	22.87	67.98	7.43	46.29
	52.68	46.73	16.56	65.08	4.27	35.43
	41.09	56.76	11.15	56.41	1.53	21.66
	28.41	66.29	7.5[a]	46.6[a]		
298.15	69.73	29.88	23.58	67.36	7.63	46.19
	52.65	46.69	17.01	64.73	4.37	35.39
	41.03	56.66	11.42	56.24	1.56	21.66
	28.25	65.95	7.8[a]	46.6[a]		
303.15	69.70	29.87	24.30	66.72	7.85	46.08
	52.61	46.66	17.45	64.39	4.48	35.35
	40.96	56.57	11.70	56.06	1.60	21.65
	28.10	65.58	8.0[a]	46.6[a]		
313.15	69.64	29.85	25.80	65.40	8.36	45.83
	52.53	46.59	18.33	63.70	4.73	35.26
	40.84	56.39	12.40	55.62	1.73	21.62
	27.77	64.81	8.6[a]	46.6[a]		
323.15	69.57	29.81	19.37	62.89	5.02	35.15
	52.43	46.49	13.22	55.10	1.91	21.58
	40.72	56.24	9.4[a]	46.6[a]		
	27.41	63.98	8.91	45.55		
333.15	69.46	29.77	26.99	63.00	9.44	45.29
	52.29	46.37	20.66	61.88	5.36	35.03
	40.58	56.04	14.05	54.57	2.10	21.54
	29.19	62.41	10.0[a]	46.6[a]		
343.15	69.34	29.72	26.40	61.62	10.02	45.00
	52.13	46.22	22.07	60.78	5.75	34.88
	40.38	55.75	14.94	54.00	2.27	21.50
	31.14	60.69	10.8[a]	46.5[a]		
353.15	69.20	29.66	25.70	60.00	10.71	44.65
	51.94	46.06	23.55	59.63	6.17	34.73
	40.09	55.37	16.00	53.33	2.45	21.46
	33.20	58.88	11.7[a]	46.5[a]		
363.15	69.06	29.59	24.98	58.31	6.59	34.57
	51.74	45.88	17.26	52.53	2.68	21.41
	39.71	54.84	12.8[a]	46.3[a]		
	25.19	58.35	11.55	44.23		
373.15	68.86	29.51	24.13	56.34	7.13	34.37
	51.48	45.66	18.64	51.66	2.98	21.34
	39.20	54.14	13.8[a]	46.1[a]		
	27.10	56.86	12.48	43.77		
383.15	68.60	29.40	23.04	53.78	7.77	34.13
	51.13	45.35	19.82	50.91	3.37	21.26
	38.77	53.54	14.9[a]	45.8[a]		
	29.18	55.24	13.45	43.28		

[a] Critical solution point.

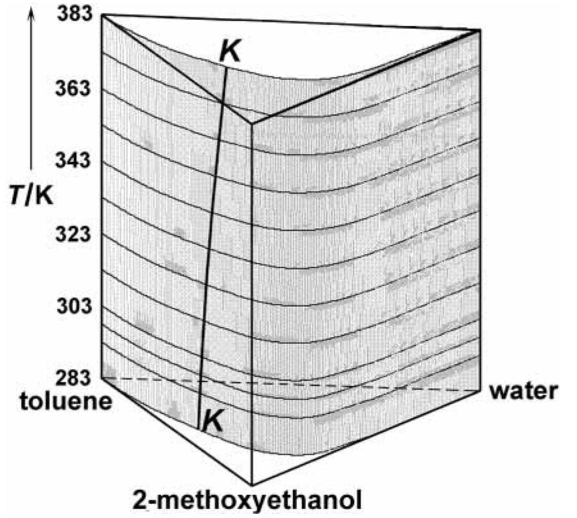

Figure 2. Two-liquid-phase binodal surface in the temperature−concentration prism of the ternary system water + 2-methoxyethanol + toluene.

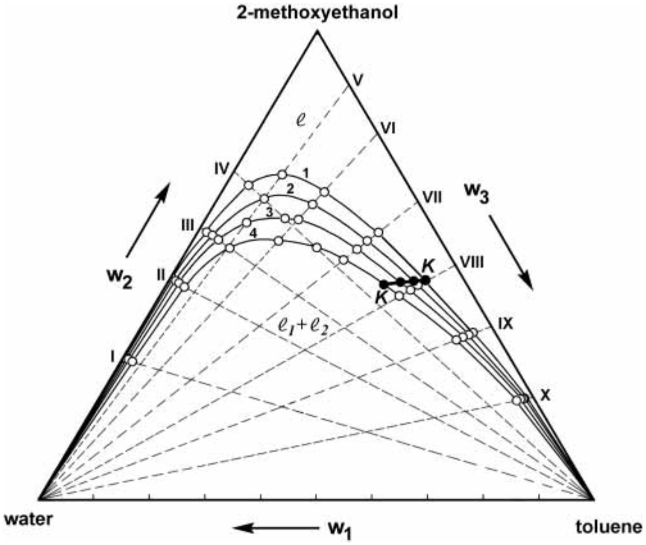

Figure 3. Orthogonal projections of isothermal cuts of the temperature−concentration prism (solubility isotherms, mass %) of the ternary system water (1) + 2-methoxyethanol (2) + toluene (3) onto its basis at the following temperatures (K): 283.15 (curve 1), 323.15 (curve 2), 353.15 (curve 3), and 383.15 (curve 4).

oxyethanol + toluene in Figure 2. The line of the critical solution points (curve KK) lies on this binodal surface. The orthogonal projections of isothermal cuts of the temperature−concentration prism (solubility isotherms) of this ternary system onto its basis at 283.15 K (1), 323.15 K (2), 353.15 K (3), and 383.15 K (4) are presented in Figure 3. The solubility diagram of the ternary system water + 2-methoxyethanol + toluene at all temperatures is characterized by the presence of a two-phase liquid−liquid equilibrium field $l_1 + l_2$, abutting on the water + toluene side of the composition triangle, and of a homogeneous liquid field l. On Figure 3 the curve KK is the projection of the critical point line KK, which lies on the two-liquid-phase binodal surface in the temperature−concentration prism (Figure 2). From Table 4 and Figure 3 it is observed that the mutual solubility in the system increases with temperature.

The composition at the critical solution point varies slightly with temperature. As temperature increases, the water content in the critical mixtures increases, while that of the toluene decreases (Table 3, Figure 1). At all temperatures the critical solution point is turned to the 2-methoxyethanol + toluene side of the concentration triangle (Figure 3). Increasing the temperature leads to a shift of the critical solution point toward the vertex of the binodal curve (Figure 3). This can be regarded as arising from the weakening of molecular interactions between water and 2-methoxyethanol and is apparently related to the destruction of methylcellosolve hydrates. The increase of the enthalpy of mixing in the binary system water + 2-methoxyethanol with temperature[12] supports our conclusion.

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