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Liquid–Liquid and Vapor–Liquid Phase Equilibria for 1-Butanol + Water + 2-Propanol at Ambient Pressure

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The liquid–liquid and the vapor–liquid phase equilibria of the ternary system 1-butanol + water + 2-propanol have been measured at ambient pressure. Compositions along the binodal curve have been determined gravimetrically at 0, 20, 50, and 60 °C. Tie lines were determined for 0, 20, and 60 °C. The data were compared to reported measurements at 80 °C. Furthermore, the vapor–liquid equilibrium at ambient pressure has been measured for both one-phase and two-phase liquid mixtures using a recirculation still proposed by Röck and Sieg.

Introduction

The system 1-butanol + water + 2-propanol is used for the investigation of the convection drying of porous media wetted with a liquid mixture that is not entirely miscible. This system is appropriate since it has a large miscibility gap. To elucidate the mechanisms and come up with a quantitative model to describe the drying process, information about the phase equilibrium of the above system is necessary. Therefore, the binodal curve has been measured at 0, 20, 50, and 60 °C, and tie lines have been measured at 0, 20, and 60 °C. Additionally, the vapor–liquid equilibrium has been determined for 80 different one-phase and 16 two-phase mixtures.

Experimental Section

Both organic components, 1-butanol and 2-propanol, were supplied by Carl Roth GmbH & Co., Karlsruhe. 1-Butanol was obtained at ≥99.5% p.a. purity and 2-propanol at ≥99.9 mass % purity. They were used without further purification. The water was distilled twice.

For the gravimetric determination of the composition along the binodal curve, an electronic balance, Sartorius LC 1200 S, measuring to 0.001 g was used. To determine the tie lines and the vapor–liquid equilibrium, the compositions of the mixtures were measured with a Perkin-Elmer Sigma I gas chromatograph with a packed column (Perkin-Elmer Poropak QS) and an FID detector. The compositions were measured with an accuracy of 0.1 mol %. The carrier gas used was helium. The oven temperature was increased from 100 to 200 °C according to a temperature program. To obtain the chromatographic response factors, standard mixtures were analyzed.

Temperatures were measured with a mercury-in-glass thermometer with an accuracy of 0.1 K. For the vapor–liquid equilibrium measurements, the local pressure was determined with a mercury manometer.

Liquid–Liquid Equilibrium at 0, 20, 50, 60, and 80 °C

Experimental Procedure. The compositions along the binodal curve were determined as follows. A 100 g portion of a two-phase mixture of 1-butanol and water with the content of 1-butanol in the range of mass fractions from 0.07 to 0.90 was weighed. The temperature of the mixture was set to the system temperature in a water bath and kept within 0.1 K. Sufficient 2-propanol to dissolve the two-phase mixture at the system temperature was added by titration. The mass added was noted and the composition (mass fraction) calculated. This was done for at least 10 mixtures at 0, 20, 50, and 60 °C.

The tie lines were determined by making up mixtures with overall compositions lying within the two-phase region, and after being shaken well and allowed to settle at the system temperature (water bath), samples were carefully taken from each phase and their compositions analyzed in the gas chromatograph.

Vapor–Liquid Equilibrium at Ambient Pressure

Experimental Setup. The vapor–liquid equilibrium measurments were carried out in an all-glass equilibrium still with circulation of both the vapor and the liquid phase. An apparatus of this type was proposed first by Gillespie (*5*). The measurements were performed in an apparatus of this type as modified by Röck and Sieg (*6*). The apparatus is shown in a schematic diagram (Figure 2) and described in the following. The boiling flask (2) is heated electrically by a jacketed heater (1). The flask (2) is filled to the Cottrell pump (3) with the liquid mixture. The arising vapor bubbles agitate the liquid in the flask on their way up and entrain liquid drops while passing the Cottrell pump. This provides good mixing between the liquid and the vapor phase. The vapor entrains the liquid up to point 4, where the two phases separate from each other. The liquid is collected in the receiver (10), from where it flows back into the boiling flask. Small liquid drops that still might be carried along in the rising vapor are retained by the shield (5). The vapor is condensed totally in a water-cooled coil (6). After passing point 7, the condensate is collected at point 8 and returned to the flask. Before entering the flask, the condensate and the liquid from the receiver (10) mix at point 9, where they are heated again by thermostated oil in a jacket. The boiling flask, the Cottrell pump, and the rest of the apparatus containing vapor are also thermostated within ±0.1 K by oil circulating in a jacket. The temperature of the the oil is kept up to 0.1 K higher than the equilibrium temperature to prevent partial condensation in the vapor chamber.

For measuring the equilibrium of a two-phase mixture, two tiny electrical motors are installed on openings of the still over the liquid-phase and the condensed-vapor-phase collectors (10 and 8 respectively). Each motor moves an

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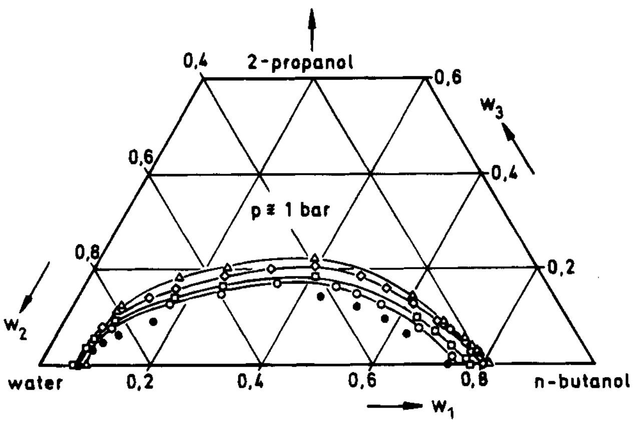

Figure 1. Binodal curves of the system 1-butanol + water + 2-propanol at 0, 20, 50, 60, and 80 °C and ambient pressure: (△) 0 °C, (◇) 20 °C, (□) 50 °C, (○) 60 °C, (●) 80 °C.

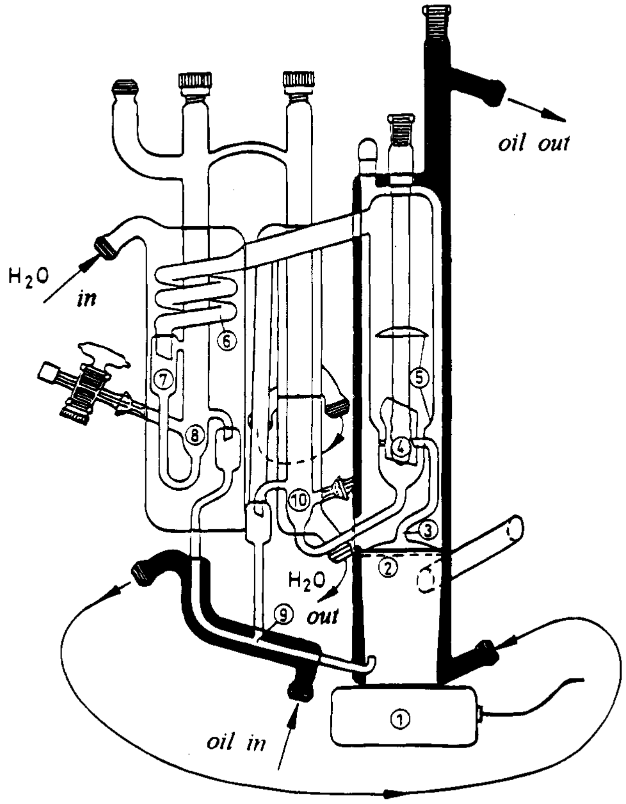

Figure 2. Schematic diagram of the equilibrium still: (1) electrical jacketed heater, (2) boiling flask, (3) Cottrell pump, (5) shield, (6) water-cooled coil, (8) condensed-vapor-phase collector, (10) liquid-phase collector, (4, 7, and 9) described in the text.

Table 1. Mass Fractions *w* along the Binodal Curve for 1-Butanol (1) + Water (2) + 2-Propanol (3) at 0, 20, 50, 60, and 80 °C and Ambient Pressure

t/°C	w_1	w_2	w_1	w_2
0	0.0992	0.9008[a]	0.6849	0.2283
	0.0845	0.8051	0.7405	0.2088
	0.0877	0.7896	0.7613	0.2024
	0.1640	0.6558	0.7725	0.1992
	0.2397	0.5594	0.7822	0.1955
	0.3893	0.3893	0.8069	0.1931[a]
	0.6017	0.2579		
20	0.0781	0.9219[b]	0.3988	0.3988
	0.0736	0.8462	0.4908	0.3273
	0.0818	0.8264	0.5476	0.2949
	0.0890	0.8012	0.6112	0.2620
	0.1223	0.7460	0.6738	0.2368
	0.1291	0.7316	0.6898	0.2300
	0.1687	0.6749	0.7057	0.2228
	0.1854	0.6517	0.7449	0.2101
	0.2448	0.5712	0.7671	0.2039
	0.3205	0.4806	0.7993	0.2007[b]
50	0.0646	0.9354[c]	0.6306	0.2703
	0.0674	0.8948	0.6793	0.2513
	0.0710	0.8755	0.7200	0.2400
	0.0909	0.8177	0.7368	0.2327
	0.1721	0.6886	0.7622	0.2277
	0.2502	0.5840	0.7758	0.2242[c]
	0.4083	0.4083		
60	0.0652	0.9348[c]	0.4578	0.3815
	0.0723	0.8844	0.4995	0.3563
	0.0923	0.8309	0.5549	0.3182
	0.1737	0.7001	0.6482	0.2783
	0.2537	0.5928	0.7357	0.2458
	0.3453	0.4845	0.7638	0.2362[c]

[a] Reference 2. [b] Reference 3. [c] Reference 4.

Table 2. Determination of the Tie Lines for 1-Butanol (1) + Water (2) + 2-Propanol (3)

	water rich phase		alcohol rich phase	
t/°C	w_1	w_2	w_1	w_2
0	0.085	0.885	0.733	0.212
	0.084	0.865	0.662	0.238
	0.085	0.825	0.565	0.277
	0.088	0.811	0.500	0.313
	0.089	0.783	0.425	0.365
20	0.071	0.906	0.714	0.223
	0.073	0.881	0.634	0.258
	0.085	0.838	0.531	0.308
60	0.074	0.908	0.671	0.268
	0.083	0.865	0.562	0.312
	0.095	0.834	0.459	0.385

excenter disk which is connected to the upper end of a long metal rod with a metal plate welded to its lower end. The metal plate is emerged in the liquid. By its up-and-down movement the two liquid phases become homogeneous. Thus, it is possible to draw representative samples.

Experimental Procedure. The liquid mixture (300 mL) was poured slowly into the flask. The electrical heating was set to such a power input that the liquid just started boiling. This was done in order to have sufficient circulation and a minimal risk of overheating. The vapor temperature is determined using a mercury-in-glass thermometer (0.1 K divisions). It was assumed that equilibrium was reached after the vapor temperature was constant for 60 min. Then, samples were drawn with a syringe. The removed liquid was replaced by adding an equal amount of liquid, so that the overall composition was changed. The compositions of the samples of the liquid and the condensed vapor are determined using the gas chromatograph. In the case of the two-phase samples methanol was added until the mixture became homogeneous.

Results

The data for the phase diagram of 1-butanol + water + 2-propanol are given in Table 1. Additionally, data measured at 80 °C from ref 1 are listed. The data for the binary mixture 1-butanol + water were taken from ref 2 for 0 °C, from ref 3 for 20°C, and from ref 4 for all other temperatures. In Table 2, the raw data for the tie lines are shown.

For easier comparison of the measured data with the data cited from the literature, all the binodal curves are shown on the triangular diagram, Figure 1, where the compositions are plotted as mass fractions. A qualitative comparison confirms that the tendency of the miscibility gap to become smaller with increasing temperature is continued by the reported data at 80 °C (*1*).

Table 3. Liquid *x* and Vapor *y* Mole Fractions for One-Phase Systems at Ambient Pressure for 1-Butanol (1) + Water (2) + 2-Propanol (3)

p/MPa	t/°C	x_1	x_2	y_1	y_2
0.099 29	87.3	0.3560	0.0408	0.1104	0.0986
0.099 95	87.8	0.3020	0.1463	0.1248	0.1799
0.100 35	95.3	0.5498	0.0307	0.2675	0.0682
0.100 35	92.1	0.4646	0.0253	0.1859	0.0531
0.099 82	89.7	0.3421	0.0258	0.1400	0.0513
0.099 82	88.9	0.3240	0.0286	0.1153	0.0484
0.099 70	87.9	0.2980	0.0507	0.1061	0.0531
0.099 94	86.5	0.2926	0.0295	0.0953	0.0525
0.099 33	110.4	0.8812	0.0151	0.7170	0.0198
0.100 49	107.1	0.8151	0.0132	0.5836	0.0344
0.104 07	105.5	0.7922	0.0148	0.5390	0.0346
0.099 74	102.5	0.7200	0.0165	0.4426	0.0394
0.099 70	101.4	0.7088	0.0131	0.4219	0.0348
0.099 61	97.1	0.5821	0.0052	0.2963	0.0337
0.099 61	96.6	0.5908	0.0150	0.2714	0.0318
0.100 24	95.6	0.5592	0.0211	0.2541	0.0541
0.100 05	116.3	0.9868	0.0051	0.9589	0.0149
0.100 23	109.8	0.8880	0.0087	0.6995	0.0306
0.100 30	108.1	0.8558	0.0096	0.6357	0.0326
0.100 54	113.3	0.9482	0.0105	0.8345	0.0229
0.100 59	110.4	0.8969	0.0080	0.7157	0.0245
0.101 50	107.5	0.8292	0.0074	0.5925	0.0173
0.101 45	105.4	0.8013	0.0084	0.5332	0.0185
0.101 38	102.0	0.7134	0.0095	0.4126	0.0176
0.101 38	99.4	0.6452	0.0078	0.3449	0.0195
0.100 31	93.2	0.4732	0.0097	0.1987	0.0171
0.100 62	89.1	0.3413	0.0102	0.1111	0.1060
0.100 66	87.0	0.2921	0.0099	0.0745	0.0149
0.100 65	83.0	0.0428	0.0092	0.0150	0.0145
0.100 63	82.9	0.0664	0.0076	0.0143	0.0117
0.100 62	84.1	0.1229	0.0101	0.0331	0.0142
0.100 58	83.8	0.1198	0.0095	0.0268	0.0137
0.100 54	84.4	0.1400	0.0093	0.0366	0.0140
0.100 49	85.3	0.1765	0.0091	0.0489	0.0146
0.100 46	85.8	0.1904	0.0097	0.0587	0.0162
0.100 67	86.6	0.2436	0.0103	0.0745	0.0188
0.100 38	105.4	0.7884	0.0039	0.5205	0.0105
0.100 33	103.1	0.7415	0.0042	0.4549	0.0099
0.100 03	92.1	0.4553	0.0058	0.1748	0.0124
0.100 02	93.2	0.4919	0.0052	0.2019	0.0114
0.099 90	95.3	0.5483	0.0066	0.2443	0.0118
0.099 91	96.7	0.5920	0.0070	0.2800	0.0159
0.099 95	98.9	0.6414	0.0067	0.3396	0.0137
0.100 77	101.6	0.7066	0.0109	0.4064	0.0298
0.100 77	102.5	0.7382	0.0087	0.4487	0.0258
0.100 93	92.2	0.4433	0.0148	0.1699	0.0217
0.100 86	91.6	0.4239	0.0101	0.1591	0.0205
0.100 81	83.0	0.1175	0.4970	0.0443	0.4722
0.100 77	83.6	0.0838	0.6680	0.0451	0.5158
0.100 69	84.3	0.0663	0.7595	0.0547	0.5480
0.100 85	89.1	0.4292	0.4505	0.1745	0.5628
0.100 81	90.9	0.4793	0.3620	0.2127	0.5471
0.100 77	89.8	0.4871	0.3096	0.1859	0.4933
0.100 09	82.0	0.0800	0.3994	0.0312	0.4049
0.099 86	82.6	0.1281	0.3809	0.0481	0.4157
0.100 59	84.2	0.1389	0.4080	0.0726	0.4214
0.100 55	85.9	0.2387	0.3406	0.1079	0.4311
0.100 51	87.4	0.3963	0.2783	0.1364	0.4544
0.100 86	90.0	0.5244	0.2369	0.1930	0.4772
0.100 82	91.4	0.5887	0.2045	0.2260	0.4636
0.100 82	92.4	0.6276	0.1802	0.2413	0.4581
0.100 79	93.6	0.6261	0.1880	0.2817	0.4416
0.100 75	92.5	0.6207	0.2304	0.2545	0.5188
0.100 83	82.7	0.1240	0.1187	0.0414	0.1753
0.100 81	81.9	0.1320	0.1664	0.0339	0.2710
0.100 79	81.6	0.1124	0.3114	0.0301	0.3536
0.100 70	86.8	0.1741	0.6421	0.1241	0.5914
0.099 41	86.8	0.2135	0.6201	0.1205	0.5916
0.100 51	88.1	0.2118	0.6472	0.1639	0.6342
0.100 02	85.2	0.0188	0.9169	0.0666	0.5655
0.099 95	85.9	0.0320	0.9061	0.0925	0.5843
0.100 06	93.4	0.5270	0.0260	0.2215	0.0753
0.100 05	94.5	0.5575	0.0269	0.2467	0.0722
0.099 99	95.9	0.5924	0.0248	0.2811	0.0683
0.099 95	94.2	0.5040	0.0097	0.2281	0.0111
0.100 09	94.6	0.5326	0.0119	0.2408	0.0272
0.100 07	95.6	0.5679	0.0120	0.2645	0.0256
0.100 06	96.6	0.6007	0.0101	0.2939	0.0261
0.100 03	98.4	0.6512	0.0083	0.3447	0.0209
0.099 90	94.1	0.5141	0.0069	0.2201	0.0132
0.099 86	95.5	0.5422	0.0055	0.2772	0.0153
0.099 90	96.8	0.5873	0.0073	0.2914	0.0130
0.099 93	98.4	0.6353	0.0054	0.3244	0.0124
0.100 59	91.7	0.4502	0.5163	0.2471	0.7043

Table 4. Liquid *x* and Vapor *y* Mole Fractions for Two-Phase Systems at Ambient Pressure for 1-Butanol (1) + Water (2) + 2-Propanol (3)

p/MPa	t/°C	x_1	x_2	y_1	y_2
0.100 33	90.5	0.2314	0.7240	0.2276	0.6847
0.100 39	90.6	0.2180	0.7450	0.2320	0.6813
0.100 49	90.7	0.1763	0.7965	0.2103	0.7118
0.100 55	90.8	0.1569	0.8184	0.2161	0.7100
0.100 97	90.8	0.1872	0.7854	0.2094	0.7172
0.100 99	90.9	0.1921	0.7811	0.2150	0.7189
0.100 99	90.0	0.1263	0.8356	0.1921	0.6878
0.100 99	90.4	0.1226	0.8474	0.2075	0.6882
0.101 03	91.6	0.3692	0.6060	0.2491	0.7101
0.101 01	91.4	0.2827	0.6962	0.2384	0.7192
0.100 94	91.4	0.2745	0.7074	0.2362	0.7217
0.100 86	91.4	0.3100	0.6677	0.2359	0.7223
0.100 83	91.5	0.2891	0.6919	0.2479	0.7129
0.100 58	91.5	0.2815	0.6991	0.2375	0.7231
0.100 50	91.5	0.2079	0.7777	0.2326	0.7336
0.100 42	91.6	0.1548	0.8367	0.2383	0.7352

In Table 3 the vapor–liquid equilibrium data for the ternary system 1-butanol + water + 2-propanol in the one-phase state are listed. The first column gives the pressure (MPa), the second gives the boiling temperature (°C), the next two give the composition of the liquid phase in mole fraction, and the last two give the composition of the vapor, again in mole fraction. The data for the two-phase state are given in Table 4. The columns are in the same order as those in Table 3. The liquid compositions are overall compositions of the two liquid phases.

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