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Liquid−Liquid Equilibrium, Densities, Viscosities, Refractive Indices, and Excess Properties of the Ternary System Water + 4-Hydroxy-4-methyl-2-pentanone + Benzyl Alcohol at 298.15 K

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Liquid−liquid equilibrium data are reported for the water + 4-hydroxy-4-methyl-2-pentanone + benzyl alcohol ternary system at 298.15 K. Data for the binodal curve have been determined by the cloud-point method. Tie lines were established by correlating the refractive index of the binodal curve as a function of composition and were satisfactorily correlated by the Othmer and Tobias method on a mass-fraction basis. In addition, density, viscosity, and refractive index isolines were obtained throughout the miscible region at 298.15 K. From the experimental densities and viscosities, molar excess volume and viscosity deviations from a mole fraction average were calculated for the ternary system. The extracting capability of benzyl alcohol for separating 4-hydroxy-4-methyl-2-pentanone from its aqueous solutions was investigated in terms of distribution coefficients and selectivities. It is concluded that benzyl alcohol is appropriate for this extraction process when the mass fraction of the consolute component in the extract phase is smaller than 0.22, but it is less appropriate when this concentration is greater.

Introduction

In recent years the application of (liquid + liquid) equilibria to new separation processes based on extraction has become important.

4-Hydroxy-4-methyl-2-pentanone (also called diacetone alcohol) is extensively used in the chemical industry (Kirk and Othmer, 1952), and properties of its mixtures are important. The aim of this work was to investigate the feasibility of extracting diacetone alcohol (DAA) from water (W) with benzyl alcohol (BA) at 298.15 K. The capability of benzyl alcohol for separating diacetone alcohol from its aqueous solutions was investigated in terms of phase diagram, distribution coefficients, and selectivities at 298.15 K.

Additional measurements made include densities, viscosities, and refractive indices at 298.15 K throughout the miscible region. Excess molar volumes were derived. We could not find any information about this system in the available literature.

Experimental Section

A. Chemicals. Water was bidistilled in an all-glass apparatus. Benzyl alcohol (Mallinckrodt, AR) was dried over activated CaO and fractionally distilled at reduced pressure (purity ≥ 99%, GC). Diacetone alcohol (Sintorgan, technical grade) was five times fractionally distilled over CaH_2 at reduced pressure (Hack and van Winkle, 1954) (purity ≥ 98.4%, GC). All middle organic fractions were collected and passed through a glass column packed with 4 nm molecular sieves and stored over activated molecular sieves to prevent water absorption.

The purities of the samples were checked by comparing the measured densities, viscosities, and refractive indices of the components with those reported in the literature (Riddick et al., 1986), and they are shown in Table 1.

B. Apparatus and Procedure. The binodal curve was determined by the cloud-point method. Binary mixtures of known compositions were shaken in a glass cell equipped with a magnetic stirrer and a jacket for circulating the isothermal water at (298.15 ± 0.05) K. The third component was added until the transition point was reached. The estimated error through the whole curve was less than ±0.0005 of the mass fraction, since the contents of the three components were accurately determined by mass. Tie lines were obtained by preparing mass ternary mixtures of known overall compositions lying within the two-phase region and, after being shaken thoroughly and allowed to reach equilibrium, samples were carefully taken from each phase and analyzed by refractive index in conjunction with a calibration curve (refractive index against the mass fraction of diacetone alcohol), which was prepared with solutions whose compositions were known by mass near the binodal curve.

Table 1. Densities (ϱ), Refractive Indices (n_D), and Viscosities (η) of the Pure Components at 298.15 K

	ϱ/kg·m^{-3}		n_D		η/mPa s	
compound	exptl	lit	exptl	lit	exptl	lit
water	997.1	997.1	1.3328	1.3328	0.997	0.9971
benzyl alcohol	1041.4	1041.27	1.5340	1.53837	5.737	5.687
diacetone alcohol	934.2	934.2	1.4223	1.4213	2.902	1.9[a]

[a] At 293.15 K.

After a known mass of the third component was added to binary systems with a known constant mass fraction relation, densities, refractive indices, and viscosities of these pseudobinary mixtures were measured to obtain density, refractive index, and viscosity isolines, respectively, throughout the miscible region for the ternary system at 298.15 K and atmospheric pressure. Densities were measured with an Anton Paar electronic densimeter, DMA 45, with an accuracy of ±0.1 kg m^{-3}, using degassed pure water and dry air as calibrating substances; refractive indices were measured with a Jena Abbe refractometer with an accuracy of ±0.0001 and viscosities with

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Table 2. Experimental Binodal and Tie-Line Compositions (Mass Fraction, w_i%) for Water (1) + 4-Hydroxy-4-methyl-2-pentanone (2) + Benzyl Alcohol (3)

water rich layer			benzyl alcohol rich layer		
$100w_1$	$100w_2$	n_D[a]	$100w_1$	$100w_2$	n_D
Binodal Curve					
95.54	0.00	1.3409	47.66[b]	30.45[b]	
90.57	4.99	1.3472	44.90	31.14	1.4151
86.06	9.08	1.3528	40.99	31.98	1.4218
80.15	14.15	1.3598	36.73	32.85	1.4298
77.02	16.76	1.3645	33.44	33.29	1.4352
75.14	18.00	1.3670	29.93	33.40	1.4418
68.01	22.48	1.3772	25.49	32.52	1.4515
60.73	25.88	1.3889	21.93	30.85	1.4600
54.26	28.29	1.4000	19.11	28.41	1.4679
49.05	30.05	1.4080	16.26	24.48	1.4775
47.66[b]	30.45[b]		14.95	20.83	1.4848
			14.66	16.47	1.4924
			12.19	13.29	1.4988
			11.21	9.33	1.5049
			10.16	4.39	1.5123
			9.29	0.00	1.5188
Tie Lines					
92.5	3.1		10.7	6.8	
89.8	5.6		11.9	12.3	
85.6	9.5		14.2	18.9	
80.5	13.8		16.1	24.6	
76.5	17.1		19.5	29.3	
74.0	19.0		21.5	30.5	
67.6	22.7		25.0	33.0	

[a] n_D, refractive index at 298.15 K. [b] Estimated plait point.

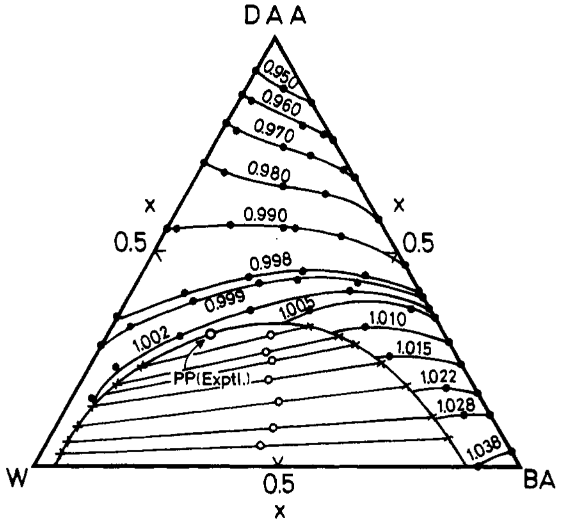

Figure 1. Binodal curve, tie lines, and density isolines for water (W) + diacetone alcohol (DAA) + benzyl alcohol (BA) at 298.15 K: ×, experimental tie lines; ●, experimental density isolines; PP, plait point; ○, overall compositions for tie lines. All compositions are expressed in mass fraction of each component.

a Schott-Gerätte AVS 400 viscosimeter with an accuracy of ±0.001 mPa s.

Results and Discussion

The experimental values for the binodal curve and tie-line data for the water + diacetone alcohol + benzyl alcohol ternary system at 298.15 K are given in Table 2.

Figure 1 shows the experimental liquid−liquid equilibrium (LLE) diagram and density isolines in the miscible region of the ternary system at 298.15 K. All smoothing curves connecting the experimental data points are hand-drawn; no attempt to fit the data by an empirical equation was made.

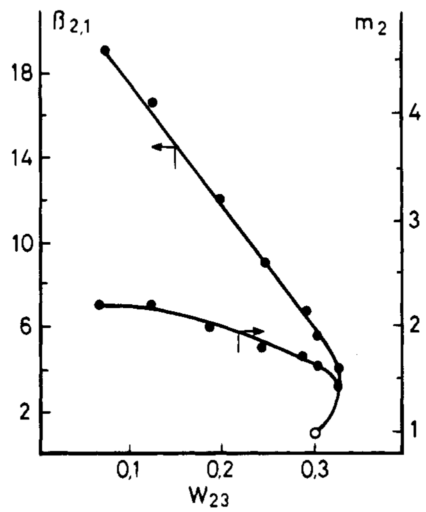

Figure 2. Selectivity ($\beta_{2,1}$) and distribution coefficient (m_2) for water (W) + diacetone alcohol (DAA) + benzyl alcohol (BA) at 298.15 K. w_{23} is the mass fraction of diacetone alcohol in the extract phase.

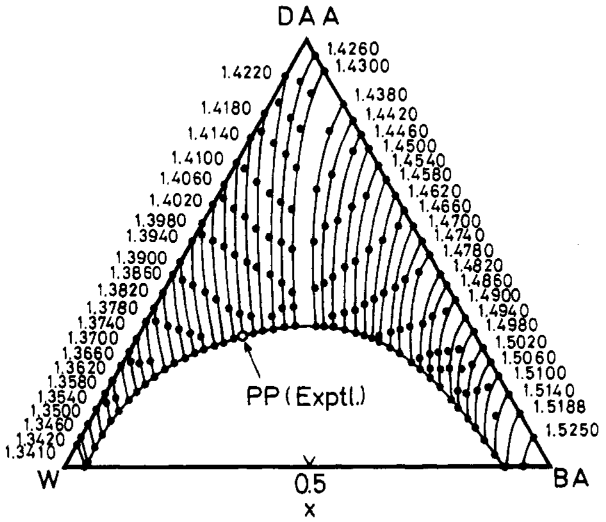

Figure 3. Refractive index isolines and binodal curve for water (W) + diacetone alcohol (DAA) + benzyl alcohol (BA) at 298.15 K: PP, plait point. All compositions are expressed in mass fraction of each component.

The tie-line data are satisfactorily correlated by the method of Othmer and Tobias (1942), where an empirical equation:

$$\log[(1 - w_1)/w_1] = m \log[(1 - w_3)/w_3] + b \qquad (1)$$

can represent all tie-line data with adequate precision, w_1 being the mass fraction of water in the water rich layer and w_3 the mass fraction of benzyl alcohol in the solvent rich layer. The best values of the parameters of eq 1 are $m = 0.9342$ and $b = -0.4750$ with a linear correlation coefficient equal to 0.9964.

The capability of a given solvent as an extractive agent can be determined through the evaluation of the selectivity ($\beta_{2,1}$), and the distribution coefficient (m_2) for the consolute component. Hence, we have calculated these quantities for this system.

The diacetone alcohol distribution coefficient (m_2), defined as the ratio of the diacetone alcohol mass fraction in organic phase (w_{23}) to that in the aqueous phase (w_{21}), is greater than 1 since the extract phase is richer in diacetone alcohol than the raffinate phase, while the selectivity

Table 3. Experimental Densities (ϱ), Viscosities (η), Refractive Indices (n_D), Excess Molar Volumes (V^E), and Viscosity Deviations ($\Delta\eta$) for Water (1) + Diacetone Alcohol (2) + Benzyl Alcohol (3) at 298.15 K

x_1/x_2	x_1	ϱ/Kg·m^{-3}	η/mPa s	n_D	V^E/cm^3·mol^{-1}	$\Delta\eta$/mPa s
5.329	0.9609	1001.8	1.679	1.3624	−0.270	0.739
5.329	0.9667	1000.5	1.586	1.3572	−0.269	0.657
2.994	0.9346	1002.4	2.255	1.3757	−0.430	1.282
2.994	0.9412	1001.6	2.149	1.3710	−0.442	1.188
1.877	0.9012	1000.4	2.943	1.3883	−0.561	1.925
1.877	0.9123	999.3	2.811	1.3820	−0.592	1.815
1.877	0.8881	1001.7	3.152	1.3959	−0.529	2.109
1.204	0.8740	996.1	3.654	1.3922	−0.789	2.611
1.204	0.8306	1000.5	3.926	1.4122	−0.666	2.791
1.204	0.8467	998.9	3.807	1.4059	−0.708	2.707
1.204	0.8606	997.5	3.742	1.3996	−0.749	2.671
0.780	0.8028	992.0	4.566	1.4102	−0.920	3.413
0.780	0.7495	998.9	4.572	1.4297	−0.775	3.289
0.780	0.7866	994.8	4.545	1.4168	−0.873	3.354
0.780	0.7681	996.9	4.547	1.4234	−0.823	3.311
0.780	0.8193	991.0	4.568	1.4034	−0.974	3.452
0.780	0.7272	1001.3	4.549	1.4368	−0.725	3.208
0.537	0.7445	988.6	5.196	1.4164	−1.128	3.958
0.537	0.7280	990.7	5.116	1.4220	−1.076	3.835
0.537	0.6903	995.3	4.968	1.4342	−0.965	3.584
0.537	0.7044	993.7	5.047	1.4295	−1.008	3.702
0.537	0.7605	986.3	5.293	1.4102	−1.175	4.095
0.382	0.6812	982.3	5.713	1.4208	−1.229	4.377
0.382	0.6615	985.2	5.521	1.4270	−1.166	4.127
0.382	0.6962	979.8	5.759	1.4159	−1.271	4.465
0.382	0.6446	987.5	5.410	1.4322	−1.108	3.965
0.239	0.5905	971.2	6.032	1.4219	−1.324	4.561
0.239	0.5755	973.8	5.917	1.3264	−1.262	4.394
0.239	0.5564	977.2	5.750	1.4321	−1.198	4.158
0.144	0.4456	967.1	5.538	1.4320	−1.154	3.731
0.144	0.4584	964.1	5.620	1.4277	−1.192	3.872
0.144	0.4705	961.3	5.688	1.4241	−1.232	3.995
0.053	0.2504	945.6	4.174	1.4249	−0.655	1.988
0.053	0.2448	948.0	4.174	1.4272	−0.655	1.941
6.698	0.1656	1028.1	5.110	1.5182	−0.261	1.178
6.698	0.4278	1027.4	4.727	1.5028	−0.304	2.262
6.698	0.2556	1027.9	4.999	1.5120	−0.276	1.649
4.025	0.4150	1022.2	4.797	1.4973	−0.433	2.340
4.025	0.2527	1021.9	5.068	1.5063	−0.406	1.812
2.874	0.4611	1017.6	4.913	1.4874	−0.522	2.692
2.874	0.2710	1016.8	5.046	1.4981	−0.512	1.980
2.360	0.4032	1014.5	5.002	1.4892	−0.607	2.589
2.360	0.5210	1015.1	4.780	1.4800	−0.585	2.798
2.360	0.2326	1013.0	5.058	1.4983	−0.563	1.850
1.616	0.5828	1010.6	4.801	1.4672	−0.736	3.055
1.616	0.2858	1006.9	5.036	1.4856	−0.780	2.216
1.616	0.4595	1009.1	4.980	1.4771	−0.781	2.850
1.083	0.6900	1005.4	4.709	1.4471	−0.744	3.270
1.083	0.4834	1001.3	5.113	1.4570	−0.870	3.132
1.083	0.6073	1003.8	4.937	1.4561	−0.816	3.302
1.083	0.3321	996.8	4.981	1.4745	−0.738	2.477
0.715	0.8137	1002.5	4.151	1.4194	−0.645	2.978
0.715	0.3556	989.2	5.201	1.4614	−0.934	2.894
0.715	0.7699	1001.8	4.478	1.4282	−0.746	3.227
0.715	0.7055	1000.0	4.842	1.4376	−0.849	3.466
0.715	0.5930	996.5	5.267	1.4488	−0.955	3.642
0.464	0.6215	990.9	5.353	1.4394	−1.061	3.836
0.464	0.2468	976.7	4.876	1.4544	−0.903	2.304
0.464	0.5040	986.1	5.444	1.4464	−1.104	3.654
0.295	0.4018	974.4	5.384	1.4418	−1.133	3.392
0.295	0.5478	981.4	5.773	1.4367	−1.204	4.137
0.295	0.2484	968.0	4.676	1.4450	−0.917	2.228
0.191	0.4301	968.7	5.280	1.4356	−1.108	3.414
0.191	0.2572	960.5	4.406	1.4385	−0.813	2.071

defined as $\beta_{2,1} = m_2 w_{11}/w_{13}$ (where w_{11} and w_{13} are the mass fractions of water in the raffinate and extract phases, respectively) shows high values when the mass fraction of the consolute component in the extract phase is smaller than 0.22. These quantities are not constant over the whole two-phase region and depend on the concentration of the consolute component (DAA). The selectivity and the diacetone alcohol distribution coefficient have a tendency to decrease when the diacetone alcohol concentration is increased, as can be seen in Figure 2.

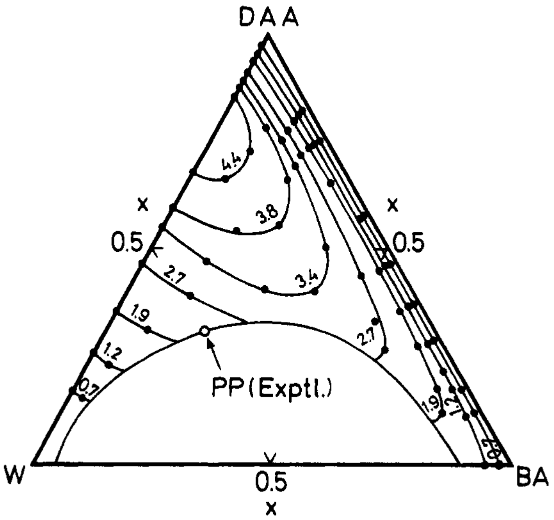

Figure 4. Viscosity isolines and binodal curve for water (W) + diacetone alcohol (DAA) + benzyl alcohol (BA) at 298.15 K: PP, plait point. All compositions are expressed in mass fraction of each component.

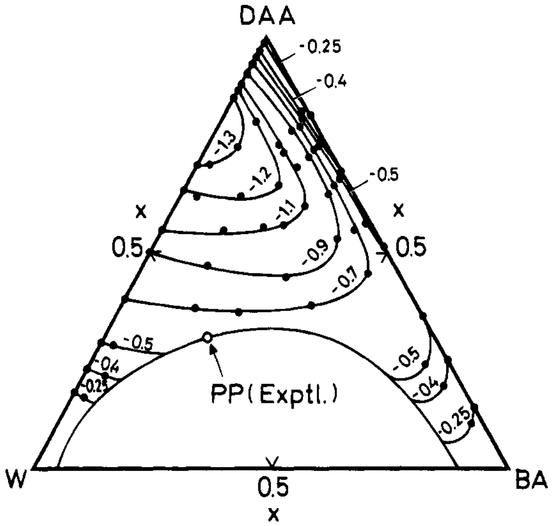

Figure 5. Excess molar volume isolines and binodal curve for water (W) + diacetone alcohol (DAA) + benzyl alcohol (BA) at 298.15 K: PP, plait point. All compositions are expressed in mass fraction of each component.

Zane Egan et al. (1988) conclude that solvents with experimental distribution coefficients greater than 0.15 and selectivities greater than 10 are potential candidates for extraction processes. From analysis of Figure 2, we can conclude that these extraction properties are only reached by benzyl alcohol at low diacetone alcohol concentration. Then, benzyl alcohol is not so appropriate for the diacetone alcohol extraction process from aqueous solutions at high diacetone alcohol concentration. This could be a consequence of the high mutual solubility between the two nonconsolute components (see Table 2).

The molar volumes V of mixtures were calculated as usual from the expression

$$V = \sum x_i M_i / \varrho \tag{2}$$

where x_i is the mole fraction of component i in the mixture, M_i its molecular weight, and ϱ the measured density of the mixture. Molar excess volumes were calculated with the equation

$$V^E = V - \sum x_i V_i \tag{3}$$

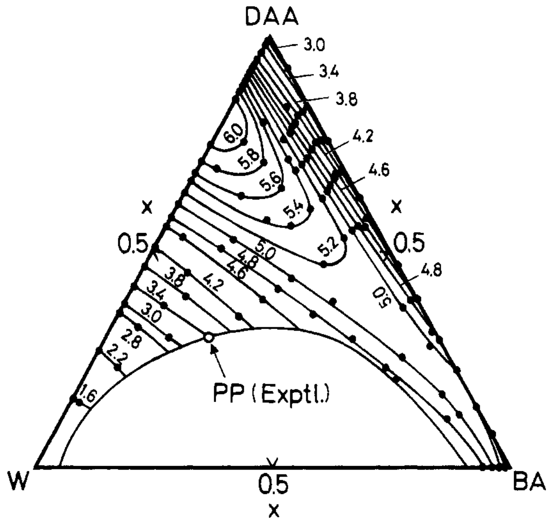

Figure 6. Viscosity deviation isolines and binodal curve for water (W) + diacetone alcohol (DAA) + benzyl alcohol (BA) at 298.15 K: PP, plait point. All compositions are expressed in mass fraction of each component.

where V_i is the molar volume of pure component i. The viscosity deviation from mole fraction average is defined by the equation

$$\Delta\eta = \eta - \exp \sum x_i \ln \eta_i \qquad (4)$$

where η and η_i are the viscosities of the mixture and the pure components, respectively. The uncertainty in excess molar volume and viscosity deviation were estimated within $\pm 1 \times 10^{-9}$ m^3 mol^{-1} and 0.001 mPa s, respectively. Table 3 lists the experimental values of densities, refractive indices, viscosities, excess molar volumes, and viscosity deviations for the ternary system at 298.15 K.

Figures 3, 4, 5, and 6 show n_D, η, V^E, and $\Delta\eta$ isolines in the miscible region of the ternary system, respectively, together with the binodal curve at 298.15 K.

Conclusions

LLE data for the ternary system water + diacetone alcohol + benzyl alcohol were determined. In addition, density, viscosity, refractive index, excess molar volume, and viscosity deviation isolines were also obtained at 298.15 K.

From the experimental results it is evident that benzyl alcohol could be used for extract diacetone alcohol from diluted aqueous solutions, since its extractive properties reach those fixed by Zane Egan et al. (1988), but it is less appropriate for concentrated aqueous solutions. Density isolines for the ternary system show a little curvature and become more pronounced at lower diacetone alcohol concentration. On the other hand, viscosity isolines show the greatest curvature toward the benzyl alcohol edge of the composition diagram (see Figure 4), while refractive index isolines are straight lines with a little curvature toward the side of the binary diacetone alcohol + benzyl alcohol (see Figure 3).

Over the whole concentration range, the excess volumes are negative and the excess viscosities are positive for the ternary system. This is an indication that association forces are dominant in this system.

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