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Equilibrium Phase Behavior of Water + Propan-1-ol or Propan-2-ol + Cesium Chloride at (298.15, 308.15, and 318.15) K

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The liquid−liquid equilibrium in the aqueous biphasic system formed by water + propan-1-ol + cesium chloride and water + propan-2-ol + cesium chloride have been determined at (298.15, 308.15, and 318.15) K. The tie lines and binodal curves as well as refractive index were measured on solutions. The LLE equilibrium experimental data were correlated using Othmer−Tobias and Bancroft correlations. The effect of temperature on the liquid−liquid equilibria was insignificantly.

Introduction

Salting out in alcohol aqueous binary systems is important for the design and simulation of unit operations such as purification, drowning-out crystallization, or liquid−liquid extractions. Zafarani-Moattar and co-workers have studied phase diagrams of $MgSO_4$ or $(NH_4)_2HPO_4$ or $NH_4H_2PO_4$ + propan-1-ol or propan-2-ol + water system.[1,2] Taboada has measured the equilibrium composition and physical properties of Li_2SO_4 + propan-1-ol + water system.[3] LLE data for the propan-1-ol or propan-2-ol + water + sodium chloride and propan-1-ol or propan-2-ol + water + potassium fluoride or sodium chloride systems were determined by Santis et al.[4] and Wang et al.,[5] respectively. Gomis et al.[6,7] have determined the solubility of lithium chloride, sodium chloride, and potassium chloride in the propan-1-ol or propan-2-ol aqueous solutions and showed the different salting out effects.

In our recent series of works, we have studied the phase diagrams of aliphatic alcohols (methanol, ethanol, propan-1-ol, and propan-2-ol) + cesium carbonate + water[8] and ethanol + cesium sulfate + water[9] systems particularly. In this present work, LLE data were obtained for the systems water + propan-1-ol or propan-2-ol + cesium chloride, which can be used to acquire the possibility of applying the salting out technique to increase the yield of cesium chloride or enrich the organic phase content in considerable reduction of the energy cost. These results can also be used to develop thermodynamic models of salt effect on liquid−liquid equilibrium.

Experimental Section

Materials. Analytic grade propan-1-ol, propan-2-ol (mass fraction purity >99.5 %, Xi'an), analytic grade cesium chloride (mass fraction purity >99.5 %, Jiangxi), and Specpure $K_2Cr_2O_7$ were used without further purification. Mercury nitrate, nitric acid, and sodium hydrate were all analytic grade. Deionized and double-distilled water was used in all experiments.

Apparatus and Procedure. The binodal curves were determined by a titration method.[10] A 25 cm^3 glass vessel was used to carry out the phase equilibrium determinations equipped with a Teflon-coated magnetic stirrer. It is provided with an external jacket in which water at constant temperature was circulated from a controlled thermostat. The temperature was controlled to within ± 0.1 K. A known mass of propan-1-ol or propan-2-ol was added to salt solution or vice versa, until the turbidity appeared. The salt solution of known concentration and density was prepared using an analytic balance (Shanghai) with a precision of $\pm 1 \times 10^{-7}$ kg. The composition for each point was calculated from the mass of propan-1-ol or propan-2-ol and the quantity of the salt solution.

For determination of the tie lines, the apparatus employed was similar to the one used previous.[9] Samples were prepared by mixing the appropriate mass of propan-1-ol or propan-2-ol, salt, and water in the vessels (about 10 cm^3). Then the sample was fixed to a carrier plate and stirred for 48 h, and the solution was allowed to settle for a further 24 h to ensure complete phase equilibrium. The thermostat was set at a desired temperature.

After equilibrium was reached, phases were withdrawn using syringes. The refractive index was measured immediately using a ZAW-J refractometer (Shanghai) with a precision of $\pm 1 \times 10^{-4}$, after the samples was withdrawn.

The concentration of the salt in the bottom phase was determined by evaporation to dryness at 150 °C. The uncertainty in the measurement of the mass fraction of the salt was estimated to be ± 0.5 %. The concentration of salt in the top phase was determined using atomic absorption spectrometry (AAS). The AAS measurements were performed using a TAS-986 (Beijing) AAS at a wavelength of 852.1 nm. The uncertainty in the measurement of the mass fraction of the salt was estimated to be ± 0.2 %. The procedure to determine the component of the solution was checked with a titration method where the chloride was titrated by mercury nitrate.

The amount of the propan-1-ol or propan-2-ol was determined using the oxidation process, and the $K_2Cr_2O_7$ was used as oxidant.[11,12] The reproducibility of the determination of the propan-1-ol or propan-2-ol mass fraction was less than ± 0.5 %. The solid phase in equilibrium was filtered carefully and analyzed using TGA (performed on a TA-SDT Q600 thermal analyzer in air atmosphere with a heating rate of 10 °C /min).

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Table 1. Binodal Curve Data as Mass Fraction of the Water (1) + Propan-1-ol or Propan-2-ol (2) + Cesium Chloride (3) System at (298.15, 308.15, and 318.15) K

$100w_2$	$100w_3$	$100w_2$	$100w_3$	$100w_2$	$100w_3$
H_2O (1) + $CH_3CH_2CH_2OH$ (2) + CsCl (3) at 298.15 K					
78.42	3.28	32.75	15.59	16.91	22.46
63.24	5.89	29.48	16.77	15.08	24.12
56.83	7.42	27.08	17.35	9.78	28.34
44.40	11.02	25.28	18.20	7.66	34.82
38.23	13.12	23.70	19.08	6.06	39.41
34.35	14.40	21.23	20.38	2.75	49.67
H_2O (1) + $CH_3CH_2CH_2OH$ (2) + CsCl(3) at 308.15 K					
65.35	5.55	33.17	14.84	17.67	21.79
58.06	8.07	36.30	15.26	17.02	22.67
45.23	11.03	32.03	15.85	14.20	26.10
39.80	13.02	23.42	19.28	7.67	35.15
40.91	13.41	19.17	21.23		
H_2O (1) + $CH_3CH_2CH_2OH$ (2) + CsCl (3) at 318.15 K					
60.97	6.69	28.08	16.86	15.31	23.33
48.36	9.54	26.35	17.17	9.43	30.07
46.11	10.24	23.85	18.67	6.43	34.96
39.34	12.74	23.81	18.77		
29.80	16.48	19.30	20.90		
H_2O (1) + CH_3-CH(OH)CH_3 (2) + CsCl (3) at 298.15 K					
71.83	6.41	36.41	19.21	11.45	35.01
63.55	8.72	29.98	22.76	8.98	37.36
54.96	10.89	22.15	27.05	4.10	49.20
47.39	14.38	18.04	29.34		
44.03	16.10	14.19	32.41		
H_2O (1) + CH_3-CH(OH)CH_3 (2) + CsCl (3) at 308.15 K					
70.81	5.93	37.47	18.18	15.77	34.19
62.51	7.61	32.35	20.54	13.64	38.44
56.88	9.48	28.72	23.34	8.91	43.84
47.74	13.45	24.20	26.34		
43.79	15.36	19.55	30.82		
H_2O (1) + CH_3-CH(OH)CH_3 (2) + CsCl (3) at 318.15 K					
83.09	1.67	50.94	11.43	18.48	29.33
80.71	2.23	46.50	13.00	17.27	33.09
73.74	3.90	40.47	15.85	11.85	34.28
71.52	4.50	32.95	20.22	9.01	39.53
62.27	7.25	28.12	22.89	7.00	43.10
56.14	8.04	21.80	26.82	6.53	47.54

Table 2. Values of the Parameters of Equation 1

t/K	A	B	C	D	E	$100\delta^a$
H_2O + $CH_3CH_2CH_2OH$ + CsCl						
298.15	0.606	−6.436	11.13	−47.96	56.32	0.67
308.15	0.023	−2.786	6.872	−60.62	95.27	1.21
318.15	−0.171	1.046	−8.825	−2.491	3.324	0.64
H_2O + CH_3-CH(OH)CH_3 + CsCl						
298.15	1.955	−16.19	32.40	−66.62	53.11	0.51
308.15	1.015	−8.657	14.37	−32.87	28.45	0.60
318.15	0.01929	−1.290	−1.821	−4.778	−1.256	1.17

[a] $\delta = \sum((w_2^{\text{cal}} - w_2^{\text{exp}})^2/N)^{0.5}$ where N is the number of binodal data.

Results and Discussion

The experimental data for the binodal curves of water + propan-1-ol + cesium chloride and water + propan-2-ol + cesium chloride systems at (298.15, 308.15, and 318.15) K are showed in Table 1. The mean deviations for each data are listed in Table 2. The binodal curves of two ternary systems are illustrated in Figure 1, which shows that the effect of the temperature on the two-phase area is insignificant. Additionally, the effect of polarity of propan-2-ol as compared with that of propan-1-ol is visible from the shift in binodal curves, as can been seen in Figure 1. These trends are in agreement with the experimental results obtained by Zafarani-Moattar and Salabat[1] for aliphatic alcohols + magnesium sulfate systems.

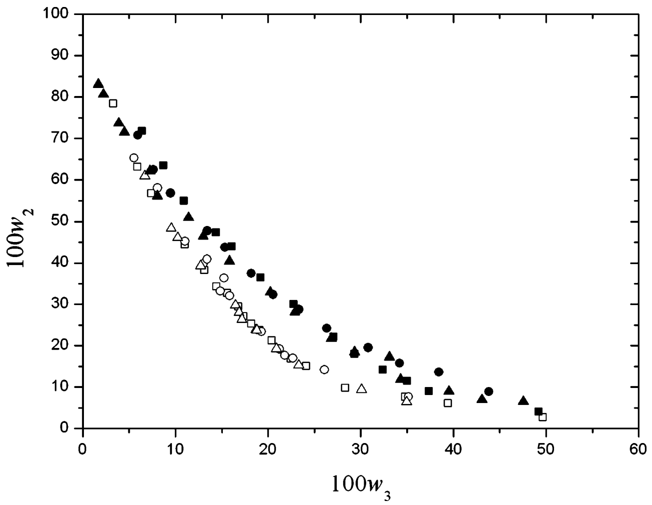

Figure 1. Binodol curves of water (1) + propan-1-ol (2) + cesium chloride (3) and water (1) + propan-2-ol (2) + cesium chloride (3) systems: □, 298.15 K propan-1-ol; ○, 308.15 K propan-1-ol; △, 318.15 K propan-1-ol; ■, 298.15 K propan-2-ol; ●, 308.15 K propan-2-ol; ▲, 318.15 K propan-2-ol.

The binodal curves were also filled to the following nonlinear expression we have described in the former work:[9]

$$\ln w_2 = A + Bw_3^{0.5} + Cw_3 + Dw_3^{2} + Ew_3^{3} \qquad (1)$$

where w_2 and w_3 represented the mass fraction of propan-1-ol or propan-2-ol and cesium chloride, respectively. The coefficients of eq 1 along with the corresponding standard deviations for the investigated systems are given in Table 2. The standard deviations between experimental and calculated values are below 1.2 %. On the basis of the standard deviations, we conclude that eq 1 can be satisfactorily used to correlate the binodal curves of the investigated systems.

The compositions of the tie lines are given in Table 3. In this table, it can be observed that the index of refractive was higher in the bottom phase because of the influence of the higher salt concentration. The same result was obtained at all systems investigated.The binodal curves and tie lines of water + propan-1-ol + cesium chloride and water + propan-2-ol + cesium chloride systems at 298.15 K are presented in Figure 2 and Figure 3.

The reliability of the measured tie line compositions was ascertained by the correlation equations given by Othmer—Tobias (eq 2) and Bancroft (eq 3):[13,14]

$$\frac{1 - w_2^{\text{t}}}{w_2^{\text{t}}} = k_1\left(\frac{1 - w_3^{\text{b}}}{w_3^{\text{b}}}\right)^n \qquad (2)$$

$$\frac{w_1^{\text{b}}}{w_3^{\text{b}}} = k_2\left(\frac{w_1^{\text{t}}}{w_2^{\text{t}}}\right)^r \qquad (3)$$

where w_2^{t} is the mass fraction of propan-1-ol or propan-2-ol in the top phase; w_3^{b} is the mass fraction of cesium chloride in the bottom phase; and w_1^{b} and w_1^{t} are the mass fraction of water in the bottom and top phase, respectively. k_1, k_2, n, and r represent fit parameters. The values of the parameters are given in Table 4. A linear dependency of the plots $\log((1 - w_2^{\text{t}})/w_2^{\text{t}})$ against $\log((1 - w_3^{\text{b}})/w_3^{\text{b}})$ and $\log(w_1^{\text{b}}/w_3^{\text{b}})$ against $\log(w_1^{\text{t}}/w_2^{\text{t}})$ indicates an acceptable consistency of the results. The corresponding correlation coef-

Table 3. Tie Line Data as Mass Fraction of the Water (1) + Propan-1-ol or Propan-2-ol (2) + Cesium Chloride (3) System at (298.15, 308.15, and 318.15) K

top phase			bottom phase			solid phase
$100w_2$	$100w_3$	n_D	$100w_2$	$100w_3$	n_D	
H_2O (1) + $CH_3CH_2CH_2OH$ (2) + CsCl (3) at 298.15 K						
86.79	1.85	1.3827	1.67	64.09	1.4170	CsCl
86.50	1.89	1.3827	1.88	63.81	1.4170	
85.04	2.15	1.3820	2.03	59.70	1.3879	
82.02	3.10	1.3821	4.61	45.36	1.3865	
80.08	3.41	1.3783	5.92	40.85	1.3855	
H_2O (1) + $CH_3CH_2CH_2OH$ (2) + CsCl (3) at 308.15 K						
90.47	1.84	1.3790	1.44	65.47	1.4194	CsCl
84.06	2.60	1.3756	4.95	52.49	1.3855	
80.42	2.75	1.3682	6.37	50.00	1.3812	
80.46	2.79	1.3675	7.53	48.49	1.3755	
75.06	3.05	1.3660	8.78	43.39	1.3705	
H_2O (1) + $CH_3CH_2CH_2OH$ (2) + CsCl (3) at 318.15 K						
89.81	2.16	1.3770	1.04	65.80	1.4195	CsCl
82.31	2.68	1.3770	2.78	52.96	1.3940	
82.40	2.75	1.3765	2.90	50.25	1.3921	
80.42	3.34	1.3759	3.00	47.88	1.3867	
72.48	3.63	1.3749	5.30	38.37	1.3751	
H_2O (1) + CH_3-$CH(OH)CH_3$ (2) + CsCl (3) at 298.15 K						
90.09	1.96	1.3766	1.02	63.21	1.4163	CsCl
89.80	1.97	1.3764	1.68	63.07	1.4166	
86.94	2.51	1.3764	3.51	58.00	1.4066	
78.99	5.98	1.3766	7.33	43.39	1.3869	
74.88	7.10	1.3766	10.04	39.32	1.3841	
H_2O (1) + CH_3-$CH(OH)CH_3$ (2) + CsCl (3) at 308.15 K						
91.61	1.70	1.3730	1.22	64.52	1.4182	CsCl
84.86	2.59	1.3739	4.52	56.71	1.4028	
81.68	3.59	1.3733	5.92	50.54	1.3945	
75.70	5.13	1.3730	7.83	44.31	1.3860	
70.62	7.01	1.3735	11.42	39.43	1.3815	
H_2O (1) + CH_3-$CH(OH)CH_3$ (2) + CsCl (3) at 318.15 K						
91.28	1.76	1.3690	1.11	66.41	1.4190	CsCl
89.81	2.92	1.3690	2.50	63.47	1.4140	
80.10	3.35	1.3685	4.29	54.46	1.4015	
76.00	3.88	1.3694	5.06	50.44	1.3950	
73.06	5.08	1.3697	9.64	44.40	1.3845	

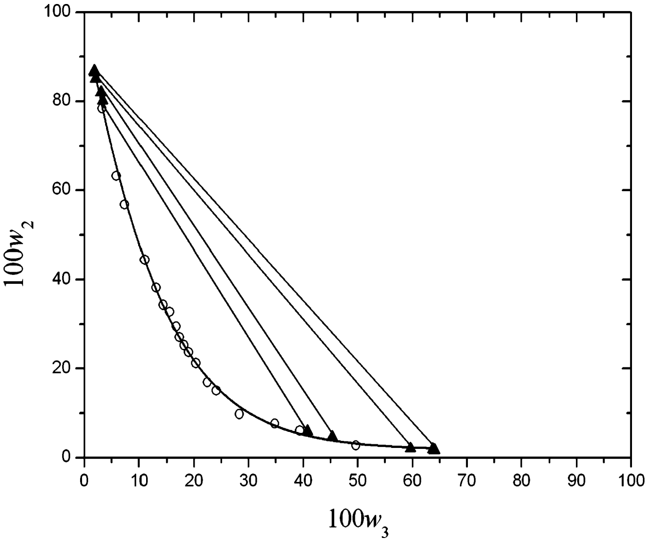

Figure 2. Binodal curve and tie lines for water (1) + propan-1-ol (2) + cesium chloride (3) at 298.15 K: ○, binodal curve data; ▲, tie line data.

ficient values (R_1 and R_2) are also given in Table 4. All correlation coefficients for these equations exceed 0.98. Furthermore, on the basis of the standard deviations (δ_2 and δ_3) given in Table 4, we conclude that eq 2 and eq 3 can be used to correlate the tie line data of the investigated systems.

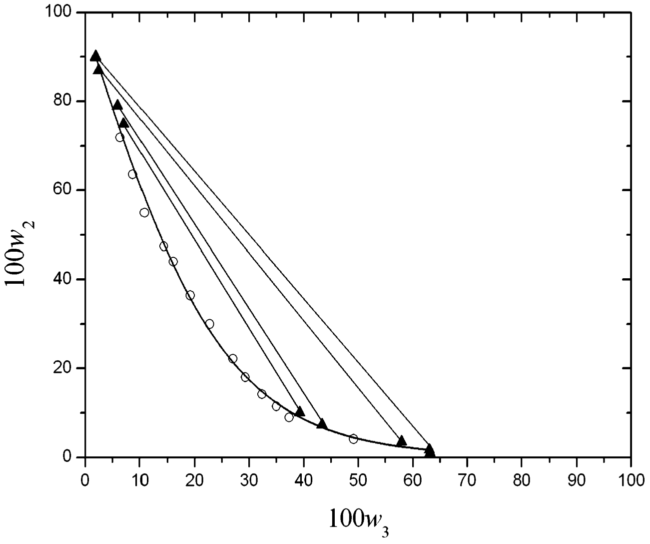

Figure 3. Binodal curve and tie lines for water (1) + propan-2-ol (2) + cesium chloride (3) at 298.15 K: ○, binodal curve data; ▲, tie line data.

Table 4. Values of the Parameters of Equations 2 and 3

t/K	k_1	n	k_2	r	R_1	R_2	$100\delta_2$	$100\delta_3$
H_2O + $CH_3CH_2CH_2OH$ + CsCl								
298.15	0.2054	0.4814	37.79	2.113	0.994	0.991	0.21	0.77
308.15	0.2312	1.260	2.392	0.6216	0.993	0.991	0.46	0.62
318.15	0.2275	1.055	3.678	0.8241	0.995	0.992	0.42	0.67
H_2O + CH_3-$CH(OH)CH_3$ + CsCl								
298.15	0.2049	1.099	4.630	0.8835	0.998	0.990	0.26	0.44
308.15	0.2326	1.428	2.390	0.5959	0.992	0.981	0.55	0.79
318.15	0.2942	1.609	1.772	0.5036	0.984	0.989	1.20	1.06

[a] $$\sigma_j = \left\{\frac{1}{2L}\sum_{i=1}^{L}[(w^{t}_{i,j,\mathrm{cal}} - w^{t}_{i,j,\mathrm{exp}})^2 + (w^{b}_{i,j,\mathrm{cal}} - w^{b}_{i,j,\mathrm{exp}})^2]\right\}^{0.5}$$

where L is the number of tie lines, and j = 2 and 3. δ_2 and δ_3 represent the mass standard deviation (%) for propan-1-ol or propan-2-ol and cesium chloride, respectively.

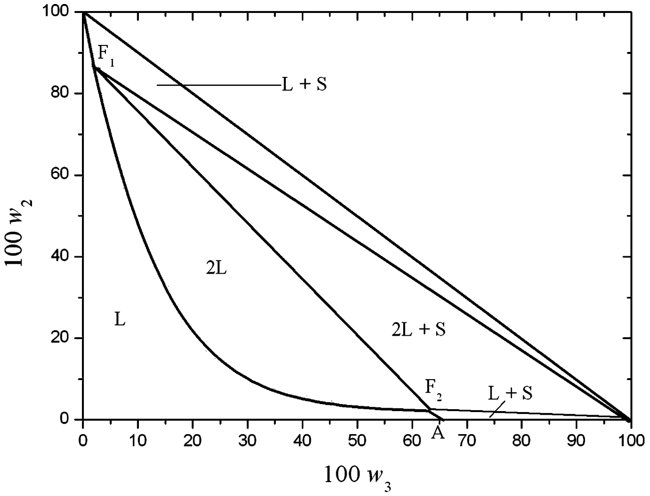

Figure 4. Phase diagram of the water + propan-1-ol + cesium chloride system at 198.15 K: A, the solubility point of the salt in pure water; F_1 and F_2, two eutectics.

Figure 4 shows the complete phase diagram of water + propan-1-ol + cesium chloride system at 298.15 K. The letters L and S denote the liquid phase and the solid phase, respectively. The solid phase is anhydrous cesium chloride, and the solubility of salt in pure water is determined experimentally as mass fraction (A = 65.6 %). The complete phase diagram of the investigated systems is similar to the one we have reported for ethanol + cesium sulfate + water system at 30 °C.[9] There are also five phase regions in the complete diagram: L, 2L, L + S (two), and 2L + S.

Literature Cited

(1) Zafarani-Moattar, M. T.; Salabat, A. Phase diagrams of aliphatic + magnesium sulfate + water. *J. Chem. Eng. Data* **1997**, *42*, 1241−1243.

(2) Zafarani-Moattar, M. T.; Gasemi, J. Phase diagrams of some aliphatic alcohols + ammonium dihydrogen phosphate or dimmonium hydrogen phosphate + water. *J. Chem. Eng. Data* **2002**, *47*, 525−528.

(3) Taboada, M. E. Liquid−liquid and liquid−solid equilibrium of the 1-propanol + lithium sulfate + water system at 25, 35 and 45 °C. *Fluid Phase Equilib.* **2003**, *204*, 155−165.

(4) Santis, R. D.; Marrelli, L.; Muscetta, P. N. Liquid−liquid equilibria in water−aliphatic alcohol systems in the presence of sodium chloride. *J. Chem. Eng. Data* **1976**, *11*, 207−214.

(5) Wang, J. G.; Zhang, Y. M.; Wang, Y. R. Liquid−liquid equilibria for 1-propanol (or 2-propanol)−water systems containing potassium fluoride. *J. Chem. Eng. Data* **2002**, *47*, 110−112.

(6) Gomis, V.; Ruiz, F.; de Vera, G.; Lopez, E.; Saquete, M. D. Liquid−liquid−solid equilibria for the ternary systems water−sodium chloride or potassium chloride−1-propanol or 2-propanol. *Fluid Phase Equilib.* **1994**, *98*, 141−147.

(7) Gomis, V.; Ruiz, F.; Asensi, J. C.; Cayvela, P. Liquid−liquid−solid equilibria for the ternary systems water−lithium chloride−1-propanol or 2-propanol at 25 °C . *Fluid Phase Equilib*. **1996**, *119*, 191−195.

(8) Hu, M. C.; Jin, L. H.; Zhai, Q. G.; Li, S. N.; Liu, Z. H. Liquid−liquid equilibria for some aliphatic alcohols + cesium carbonate + water systems. *Fluid Phase Equilib.* **2005**, *232*, 23−27.

(9) Hu, M. C.; Zhai, Q. G.; Liu, Z. H.; Xia, S. P. Liquid−liquid and solid−liquid equilibrium of the ternary system ethanol + cesium sulfate + water at (10, 30, and 50) °C . *J. Chem. Eng. Data* **2003**, *48*, 1561−1564.

(10) Othmer, D. F.; White, R. E.; Trueger, E. Liquid−liquid extraction data. *Ind. Eng. Chem*. **1941**, *33*, 1240−1248.

(11) Barahard, J. A.; Karayanmls, N. The determination of some aliphatic alcohols and aldehydes by oxidation with acid potassium dichromate. *Anal. Chem. Acta* **1962**, *26*, 253−258.

(12) Xia, S. P.; Wang, G. F. The determination of ethanol by oxidation with acid potassium dichromate. *J. Salt Lake Res*. **1987**, *1*, 14−17.

(13) Othmer, D. F.; Tobias, P. E. Toluene and acetaldehyde systems: tie line correlation; partial pressures of ternary liquid systems and the prediction of tie lines. *Ind. Eng. Chem.* **1942**, *34*, 690−700.

(14) Bancroft, W. D. Ternary mixtures, III. *J. Phys. Chem.* **1897**, *1* (7), 403−410.

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