Effect of Calcium Chloride on the Ternary Liquid Equilibria of the Water–Phosphoric Acid–1-Butanol System at 35° C.

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Liquid-liquid equilibria of the ternary system 1-butanol–phosphoric acid–calcium chloride solution (2 or 5% by weight of calcium dihydrate) have been studied at 35° C. The tie-line data are determined. The solvent capacity of 1-butanol and the distribution coefficient of phosphoric acid increase with increase in calcium chloride content of the aqueous phase, indicating the salting out effect of calcium chloride on phosphoric acid.

IN THE PRECEDING paper (*4*), the liquid equilibria for the ternary system, water-phosphoric acid-1-butanol were studied at 35°C. In this investigation, the effect of calcium chloride, as an impurity, on the equilibrium of the above system at 35° C., using calcium chloride solution containing 2 and 5% by weight of calcium chloride dihydrate, has been studied.

EXPERIMENTAL

Materials. Analar grade phosphoric acid from British Drug House Co., India (B.D.H.), containing 88% by weight of phosphoric acid and not more than 0.1% impurities, is used directly. Analar grade 1-butanol from B.D.H.,

$[d_{20^\circ C.}\ 0.8098,\ n_D^{20}\ 1.3990;$ Lit. values (7) $d_{20^\circ C.}\ 0.8097,\ n_D^{20} 1.3992]$

analar grade crystalline calcium chloride from E. Merck Co. of Germany, containing a minimum of 99% by weight of crystalline calcium chloride ($CaCl_2 \cdot 2H_2O$) and not more than 0.2% impurities, reagent grade ethylene-dinitrilo-tetra-acetic acid disodium salt (EDTA) from B.D.H. of England (assay via calcium content not less than 98%), and Solochrome Black from B.D.H. of England are used directly. The refractive index is measured for sodium light with an Abbe precision refractometer calibrated to 0.001. The fourth decimal place is obtained by visual interpolation only.

Procedure. The calcium chloride solutions are prepared at the same time, immediately after opening the sample bottle. The phase boundary curve data are determined at 35° C. for these two ternary systems by the turbidity method and are given in Table I. At low concentrations of phosphoric acid, less than about 14% in the homogeneous binary mixture of 1-butanol and phosphoric acid, a small amount of white precipitate is formed which dissolves on further addition of a small amount of calcium chloride solution, for both the ternary systems. On still further addition of calcium chloride solution, turbidity is observed. At higher concentrations of phosphoric acid, more than about 14% (for runs other than 2 in Table I, for both systems), no such precipitate is observed. The precipitate, if formed, is soluble in the strong acid solution.

The tie-line data are obtained by analysis of the organic and aqueous phases for the phosphoric acid content (*3*) and are given in Table II. Both the aqueous and organic phases are tested for calcium using EDTA solution with Solochrome Black as indicator (*6*). The calcium is confined

Table I. Phase Boundary Data at 35° C.

(Data in Wt. %)

Calcium Chloride Solution	Phosphoric Acid	1-Butanol
2% by Wt., Calcium Chloride Solution–Phosphoric Acid–1-Butanol		
12.32	0.00	87.68
13.17	11.98	74.85
14.58	21.11	64.31
19.01	32.25	48.74
22.72	38.59	38.69
28.03	43.97	28.00
34.93	49.01	16.06
37.97	51.16	10.87
40.09	53.47	6.44
41.75	53.29	4.96
43.49	52.38	4.13
94.90	0.00	5.10
5% by Wt., Calcium Chloride Solution–Phosphoric Acid–1-Butanol		
10.67	0.00	89.33
14.57	10.70	74.73
15.66	21.11	63.23
17.13	30.64	52.23
20.76	39.51	39.73
26.67	45.36	27.97
34.57	49.15	16.28
39.06	50.23	10.71
45.79	48.79	5.42
95.55	0.00	4.45

Table II. Tie Line Data at 35° C.

(Data in Wt. %)

Solvent Layer			Aqueous Layer		
Water	Phosphoric acid	1-Butanol	Calcium Chloride solution	Phosphoric acid	1-Butanol
2% by Wt., Calcium Chloride Solution–Phosphoric Acid–1-Butanol					
18.2	4.80	77.0	76.60	19.35	4.05
19.1	10.70	70.2	68.40	27.56	4.04
21.4	16.42	62.18	62.50	33.49	4.01
25.3	25.52	49.18	55.40	40.69	3.91
27.2	27.80	45.00	54.00	42.04	3.96
32.2	34.60	33.2	47.40	48.65	3.95
5% by Wt., Calcium Chloride Solution–Phosphoric Acid–1-Butanol					
18.3	6.24	75.46	77.00	18.73	4.27
19.9	12.57	67.53	68.30	27.66	4.04
22.0	17.83	60.17	63.10	32.88	4.02
27.5	27.94	44.56	54.70	41.27	4.03
33.1	35.06	31.84	50.40	45.54	4.06
36.2	37.80	26.0	49.00	46.92	4.08

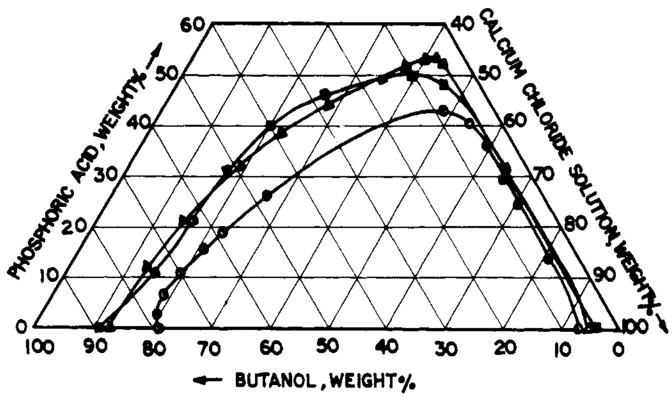

Figure 1. Phase boundary data at 35° C.

⊙ Water–phosphoric acid–1-butanol (*4*)

△ Calcium chloride solution (2% by wt.)–phosphoric acid–1-butanol

⊡ Calcium chloride solution (5% by wt.)–phosphoric acid–1-butanol

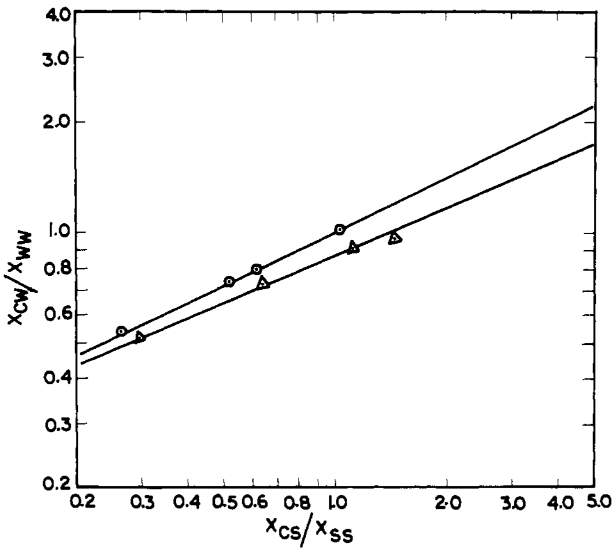

Figure 2. Equilibrium data on Hand's coordinates at 35° C.

⊙ Calcium chloride solution (2% by wt.)–phosphoric acid–1-butanol

△ Calcium chloride solution (5% by wt.)–phosphoric acid–1-butanol

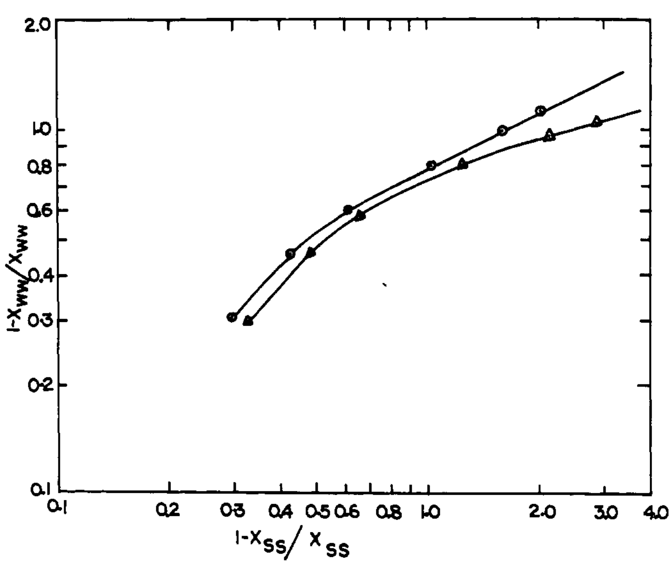

Figure 3. Equilibrium data on Othmer-Tobias coordinates at 35° C.

⊙ Calcium chloride solution (2% by wt.)–phosphoric acid–1-butanol

△ Calcium chloride solution (5% by wt.)–phosphoric acid–1-butanol

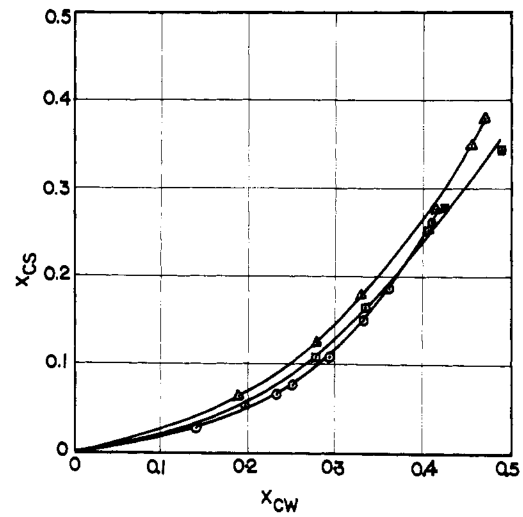

Figure 4. Distribution of phosphoric acid between 1-butanol and calcium chloride solution at 35° C.

⊙ Water

⊡ 2% by wt. calcium chloride solution

△ 5% by wt. calcium chloride solution

to the aqueous layer. The complete equilibrium compositions of the aqueous and organic phases are obtained from the phase boundary curve data for the calcium chloride solution–phosphoric acid–1-butanol system and the water–phosphoric acid–1-butanol system (*4*), respectively. The titration of phosphoric acid is an even more accurate method (*1*), and this composition must lie on the phase boundary curve. Two independent analyses are not necessary in this case. The tie-line data are plotted on Hand's (*2*) and Othmer-Tobias (*5*) coordinates in Figures 2 and 3. These data were taken at 35° ± 0.01° C. The distribution diagram is given in Figure 4. The accuracy of the data is within ±0.5%. Figures 1 and 4 show that the solvent capacity of 1-butanol and the distribution coefficient of phosphoric acid increase with an increase in the calcium chloride content of the aqueous phase.

NOMENCLATURE

X_{cw} = weight fraction of solute in water-rich phase
X_{ww} = weight fraction of water in water-rich phase
X_{cs} = weight fraction of solute in solvent-rich phase
X_{ss} = weight fraction of solvent in solvent-rich phase
X_c = weight fraction of solute
X_w = weight fraction of water
X_s = weight fraction of solvent

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