Ternary Liquid Equilibria of the Water–Phosphoric Acid–1-Butanol, Butyl Acetate, or Methyl Ethyl Ketone Systems at 35° C.

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Liquid-liquid equilibria of the three ternary systems water–phosphoric acid–1-butanol or butyl acetate or methyl ethyl ketone have been studied at 35° C. The tie-line data and the plait points are determined. 1-Butanol is a good solvent for phosphoric acid.

LIQUID-LIQUID equilibrium studies on the ternary systems containing water, phosphoric acid, and a polar organic solvent are very useful in the solvent extraction of phosphoric acid from an aqueous solution obtained in the wet process of treating rock phosphate with hydrochloric acid.

Baniel and others (*1*, *2*, *3*) and Seaton and Geankoplis (*6*) have reported the use of an organic solvent such as 1-butanol, isoamyl alcohol, or a hydrocarbon solvent in the above-mentioned process, but equilibrium data have not been reported so far for such systems. The authors studied the equilibria for the ternary systems, water–phosphoric acid–a polar organic solvent such as 1-butanol, butyl acetate, or methyl ethyl ketone at 35° C. in this investigation.

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% impurties is

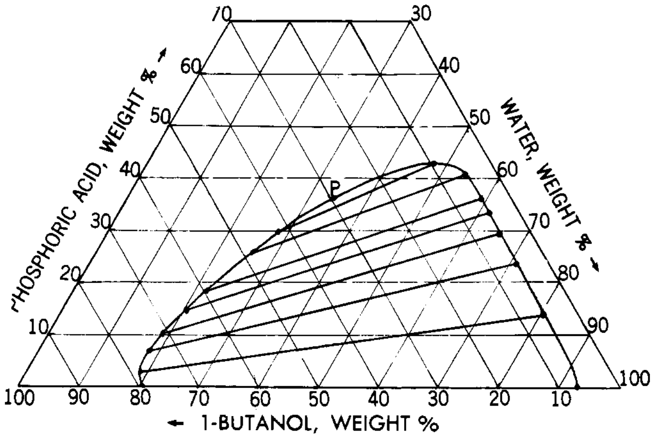

Figure 2. Equilibria of the system 1-butanol–water–phosphoric acid at 35° C.

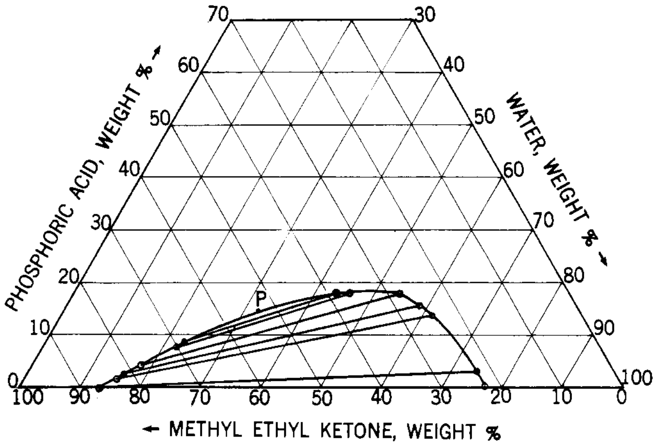

Figure 1. Equilibria of the system methyl ethyl ketone–water–phosphoric acid at 35° C.

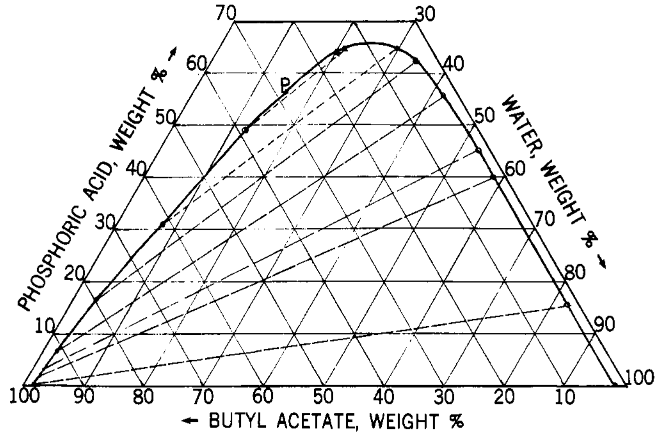

Figure 3. Equilibria of the system butyl acetate–water–phosphoric acid at 35° C.

Table I. Physical Properties of Materials (9)

	Normal Boiling Point, °C.		Density at 35° C.		Refractive Index at 35° C.	
	Exptl.	Lit.	Exptl.	Lit.	Exptl.	Lit.
1-Butanol	117.6	117.7	0.8098[a]	0.8097[a]	1.3990[a]	1.3992[a]
Butyl acetate	126.7	126.5	0.8666	0.8665[b]	1.3875	1.3873[b]
Methyl ethyl ketone	79.5	79.6	0.7892	0.7889[b]	1.3740	1.3737[b]

[a] At 20° C. only. [b] Obtained by using temperature correction.

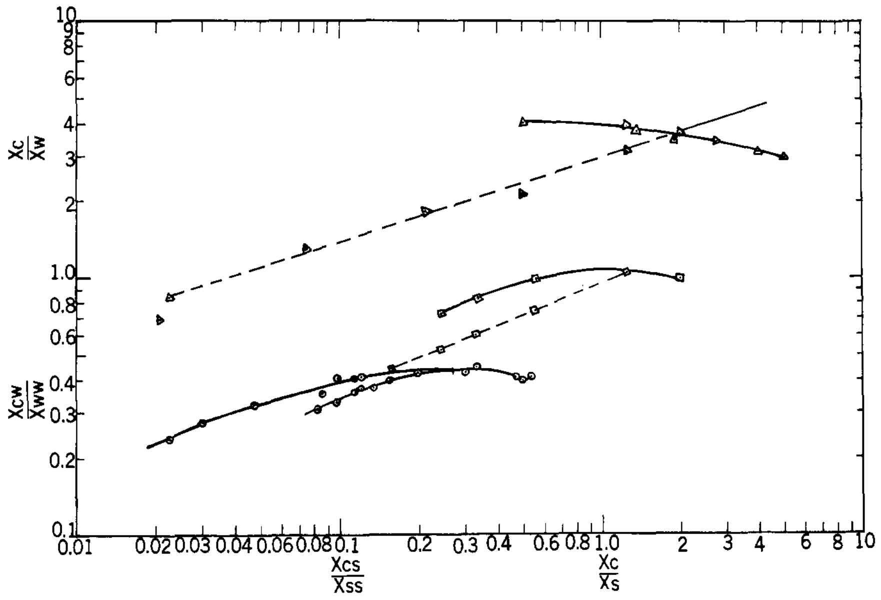

Figure 4. Plait point determination using Hand's coordinates

⊙ Metnyl ethyl ketone–water–phosphoric acid

▣ 1-Butanol–water–phosphoric acid

△ Butyl acetate–water–phosphoric acid

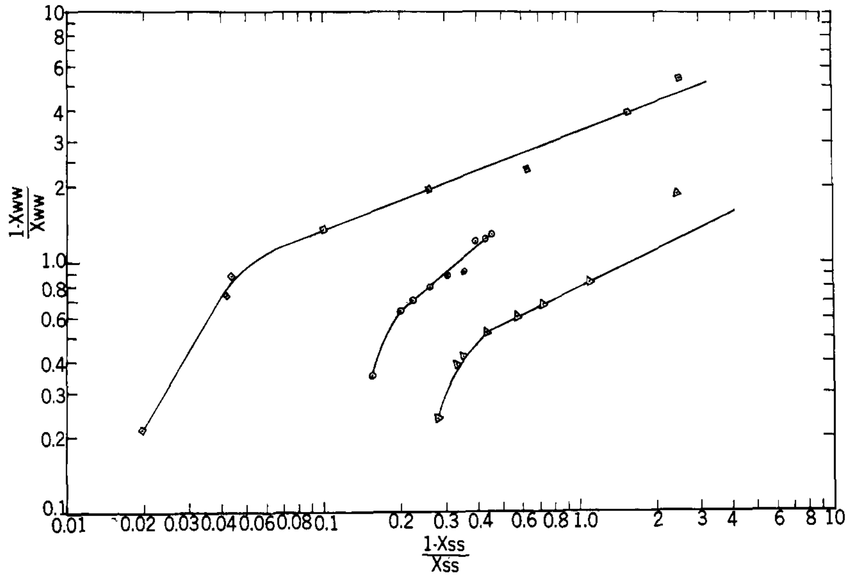

Figure 5. Equilibrium data on Othmer-Tobias coordinates at 35° C.

▣ Butyl acetate–water–phosphoric acid

⊙ Methyl ethyl ketone–water–phosphoric acid

△ 1-Butanol–water–phosphoric acid

used directly. Analar grade (B.D.H.) 1-butanol, reagent grade (B.D.H.) methyl ethyl ketone, and reagent grade butyl acetate are distilled at atmospheric pressure in a laboratory fractionating column. The physical properties of these materials are compared with the literature values in Table I. The refractive index is measured for sodium light with an Abbé precision refractometer calibrated to 0.001. The fourth decimal place is obtained by visual interpolation only

The binodal curve is determined at 35° C. for these three systems by the turbidity method and plotted in Figures 1, 2, and 3. The tie-line data are obtained by analyzing the organic and aqueous phases for phosphoric acid content (*5*) and plotted on Hand's and Othmer-Tobias coordinates in Figures 4 and 5. The plait point is determined by an empirical treatment of the tie-line data (*8*). All these data are taken at 35° ± 0.01° C. The distribution and the selectivity diagrams for these three systems are given in Figures 6 and 7.

The standard deviations for the binodal data and the tie-line data are calculated on the basis of phosphoric acid content (Table II).

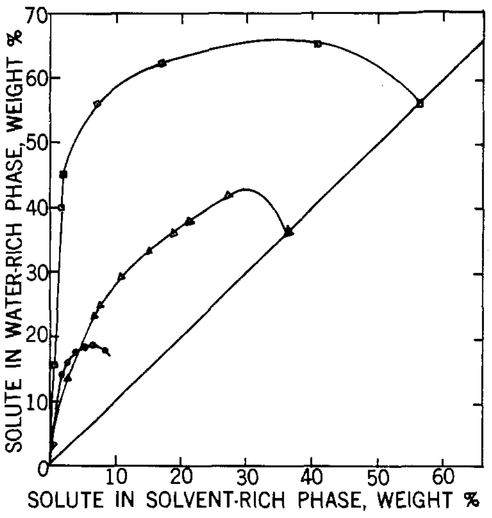

Figure 6. Distribution of phosphoric acid between water and solvent

⊙ Methyl ethyl ketone as solvent

△ 1-Butanol as solvent

▣ Butyl acetate as solvent

DISCUSSION

The tie-line data for the system with methyl ethyl ketone as a solvent, plotted on Hand's coordinates, do not fall

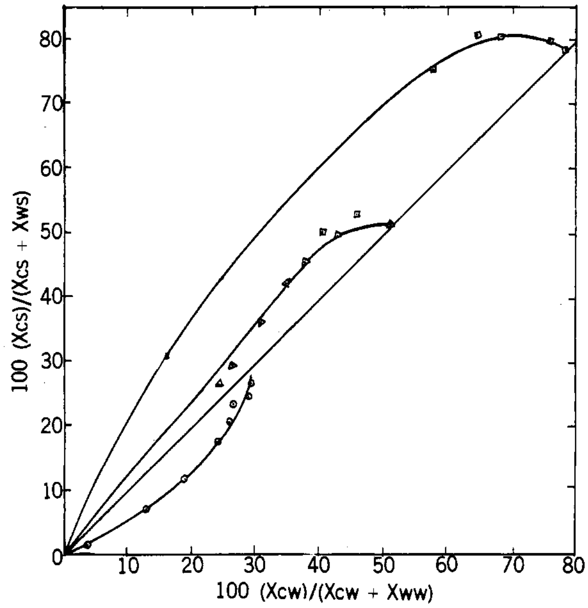

Figure 7. Selectivity diagrams

Methyl ethyl ketone as solvent
1-Butanol as solvent
Butyl acetate as solvent

Table II. Standard Deviation

	Binodal Data	Tie-line Data	
		Aqueous phase	Organic phase
Standard deviation	0.007	0.08	0.18
Standard deviation % of mean value	0.02	0.20	0.60

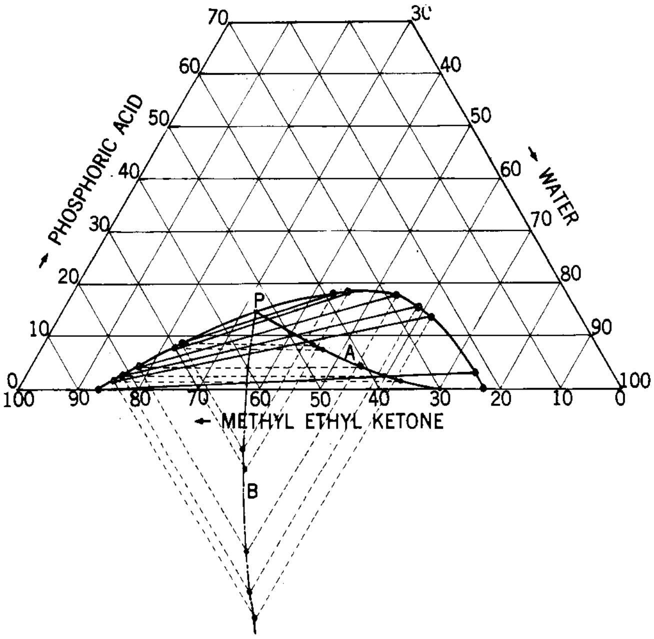

Figure 8. Graphic interpolation of tie lines for system methyl ethyl ketone–water–phosphoric acid at 35° C. by Sherwood's and Coolidge's methods

A. Sherwood's method (7)
B. Coolidge's method (4)

Table III. Liquid-Liquid Equilibrium Data at 35° C.

(Data in wt. %)

Methyl Ethyl Ketone–Water–Phosphoric Acid

Solvent Layer			Water Layer		
Solvent	Water	Phosphoric acid	Solvent	Water	Phosphoric acid
87.0	13.0	0.0	22.8	77.2	0.0
86.6	13.2	0.2	22.7	74.3	3.0
83.2	14.9	1.9	24.7	61.0	14.3
82.0	15.5	2.5	25.8	58.2	16.0
79.3	17.0	3.7	27.2	55.2	17.6
78.0	17.7	4.3	27.9	54.1	18.0
76.6	18.4	5.0	28.6	53.0	18.4
73.9	19.9	6.2	29.0	52.3	18.7
72.0	21.0	7.0	36.0	45.4	18.6
70.0	22.0	8.0	36.5	45.3	18.2
69.0	22.6	8.4	38.5	43.5	18.0

Plait Point. 15% phosphoric acid
32% water
53% methyl ethyl ketone

1-Butanol–Water–Phosphoric Acid

79.0	21.0	0.0	6.8	93.2	0.0
78.2	19.0	2.8	5.4	81.0	13.6
75.0	18.3	6.7	5.0	71.8	23.2
74.0	18.4	7.6	5.0	70.8	24.2
69.9	19.2	10.9	5.1	65.6	29.3
63.7	21.0	15.3	4.6	62.2	33.2
58.4	22.7	18.9	4.6	59.4	36.0
47.5	26.3	26.2	5.0	54.2	40.8
29.4	34.5	36.1	29.4	34.5	36.1

Plait Point. 36.1% phosphoric acid
34.5% water
29.4% 1-butanol

Butyl Acetate–Water–Phosphoric Acid

98.7	1.3	0.00	1.5	98.5	0.0
98.0	1.4	0.6	1.6	82.6	15.8
96.0	2.0	2.0	1.8	58.2	40.0
95.8	2.0	2.2	1.9	53.1	45.0
91.0	2.2	6.8	2.3	42.0	55.7
79.4	2.9	16.7	3.7	34.0	62.3
61.5	7.5	3.1	5.3	29.9	64.8
38.8	12.2	49.0	15.5	20.3	64.2
28.2	15.4	56.4	28.2	15.4	56.4

Plait Point. 56.4% phosphoric acid
15.4% water
28.2% butyl acetate

on a straight line. But a curve is obtained which meets the binodal curve, indicating the plait point to be 13.4% by weight of phosphoric acid, 30.6% by weight of water, and 56% by weight of methyl ethyl ketone. So in order to test the correctness of this value, the plait point is also determined by the methods suggested by Coolidge (*4*) and Sherwood (*7*), as in Figure 8, and found to be 15% by weight of phosphoric acid, 32% by weight of water, and 53% by weight of methyl ethyl ketone. Therefore, the value of the plait point obtained from Hand's plot agrees well with that obtained by the other two methods.

Figure 7 shows that methyl ethyl ketone has a very low selectivity for the solute. The distribution coefficient of phosphoric acid between the solvent and the water is also small compared with the other two solvents. The mutual solubility of methyl ethyl ketone and water is high and the plait point for this system indicates that the capacity of the solvent for the solute is low. Hence, these disadvantages curtail the usefulness of this solvent.

In the case of 1-butanol and butyl acetate, butyl acetate has a greater selectivity towards the solute than 1-butanol. However, a study of Figure 6 indicates that 1-butanol is a better solvent than butyl acetate because of its high distribution coefficients.

NOMENCLATURE

Xcw = weight fraction of solute in water-rich phase
Xww = weight fraction of water in water-rich phase
Xcs = weight fraction of solute in solvent-rich phase
Xss = weight fraction of solvent in solvent-rich phase
Xc = weight fraction of solute
Xw = weight fraction of water
Xs = weight fraction of solvent

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Isothermal Vapor-Liquid Equilibrium Data for the Systems Heptane–1-Propanol at 75° C. and Decane–1-Butanol at 100° C.

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Isothermal equilibrium vapor and liquid composition measurements have been made for the heptane–1-propanol system at 75° C. and the decane–1-butanol system at 100° C. Liquid phase activity coefficients were calculated from the equilibrium data and checked for both internal and over-all thermodynamic consistency. Composition-molar volume data were also obtained for both systems at 20° C.

BOTH isothermal and isobaric vapor-liquid equilibrium data for a number of paraffin-alcohol systems have been published (*1*, *9*), but the available information is still far from complete. A thorough literature search indicates that isothermal equilibrium data are lacking on the heptane–1-propanol system in the vicinity of 75° C. and the decane–1-butanol system in the vicinity of 100° C. Data for these systems have been obtained and their thermodynamic consistencies have been checked. Composition–molar volume data at 20° C. have also been obtained for the two systems.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

A detailed description of the experimental equipment, calibrations, procedures, and methods has been given by Lodl and Scheller (*6*).

Briefly, a modification of the vapor recirculation type equilibrium still described by Hipkin and Myers (*3*) was used in this work. Pressure in the still was controlled by a Cartesian manostat of the type described by Gilmont (*2*) and was measured with a mercury manometer to ±0.1 mm. Temperature was measured with an iron-constantan thermocouple and a Leeds and Northrup Type K-2 potentiometer to ±0.1° C. Compositions of equilibrium samples were obtained from molar volume measurements made with the aid of calibrated pycnometers of the type described by Lipkin *et al.* (*5*). The over-all precision of these composition analyses is about ±0.2 mole % (*4*). Molar volume–composition data for each of the systems at 20° C. are contained in Table I.

Table I. Composition–Molar Volume Measurements at 20° C

Mole Fraction, Heptane	Molar Volume, Cc./G.-Mole
HEPTANE–1-PROPANOL SYSTEM	
0.000	74.7
0.084	80.7
0.201	90.1
0.265	95.3
0.314	98.4
0.356	101.4
0.520	113.5
0.654	122.3
0.756	129.9
0.887	138.7
1.000	146.5
Mole Fraction, Decane	
DECANE –1-BUTANOL SYSTEM	
0.000	91.5
0.053	97.2
0.181	110.5
0.330	126.1
0.383	131.6
0.648	159.3
0.720	166.3
0.758	170.3
0.823	176.9
1.000	194.9