Table IV. V_2^0 and K_s^0 of 1-1 Type Electrolytes Dissolved in Water-Acetone System at 298.15 K

	V_2^0/cm^3 mol^{-1}							K_s^0/cm^3 mol^{-1} bar^{-1}						
	0[a]	10[a]	15[a]	20[a]	30[a]	40[a]	50[d]	0[a]	10[a]	15[a]	20[a]	30[a]	40[a]	50[a]
NaCl	16.7	16.7		16.8	16.6	16.3	16.7	-50.9	-45.8		-41.1	-35.0	-31.5	-25.0
KCl	26.5	26.1		26.0	26.5	27.5	27.0	-44.9	-40.5		-36.8	-32.5	-27.8	-23.2
CsCl	38.1	37.5		37.5	37.8	38.0	37.8	-37.1	-34.1		-31.0	-27.7	-23.9	-20.1
NaBr	23.4	23.1		23.8	23.7	23.5	23.8	-42.1	-37.8		-33.5	-30.0	-27.3	-24.5
KBr	33.5	33.0		32.5	33.1	33.7	32.5	-36.9	-32.9		-29.1	-25.7	-25.1	-23.1
[Ph_4P]Cl	312.2	314.3		314.7	311.2	310.0	309.2	-18.0	19.0		66.5	72.0	60.0	47.0
Na[Ph_4B]	277.2	279.3	285.0	294.6	300.1	299.9	300.1	-55.0	24.0	120.0	191.0	257.5	252.0	230.0

[a] Weight percent of acetone.

Glossary

d	density of solution g cm^{-3}
d_1	density of solvent, g cm^{-3}
m	molality, mol kg^{-1} solvent
u	ultrasonic velocity, m s^{-1}
$K_{s\phi}$	apparent molar adiabatic compressibility of solute, cm^3 (mol·bar)$^{-1}$
K_s^0	partial molar adiabatic compressibility of solute at infinite dilution, cm^3 (mol·bar)$^{-1}$
M_2	molar mass of solute, g mol^{-1}
V_ϕ	apparent molar volume of solute, cm^3 mol^{-1}
V_2^0	partial molar volume of solute at infinite dilution, cm^3 mol^{-1}
β_s	adiabatic compressibility of solution, given as 100/(u^2d), bar^{-1}
$\beta_{s,1}$	adiabatic compressibility of solvent, given as 100/(u_1^2d), bar^{-1}

Registry No. NaCl, 7647-14-5; KCl, 7447-40-7; CsCl, 7647-17-8; NaBr, 7647-15-6; KBr, 7758-02-3; [Ph_4P]Cl, 2001-45-8; Na[Ph_4B], 143-66-8; acetone, 67-64-1.

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Liquid–Liquid Equilibria for the Quaternary System Water–Phosphoric Acid–1-Hexanol–Cyclohexanone at 25 °C

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Mutual solubility and tie-line data at 25 °C and atmospheric pressure were obtained for the quaternary system water–phosphoric acid–1-hexanol–cyclohexanone, using an analytical method. In the liquid–liquid extraction of wet process phosphoric acid, no advantage is observed in the use of the mixed solvent, 1-hexanol and cyclohexanone, as an extractant solvent instead of the pure solvents.

Introduction

Solvent extraction of phosphoric acid from aqueous solutions has been widely studies in recent years, mainly with alcohols, ethers, ketones, and amines, and a very complete review was done by Blumberg (*1*). Other solvents used were trialkyl phosphates (*2*) and trialkylphosphine oxides (*3*).

The present work reports experimental equilibrium data for the system water–phosphoric acid–1-hexanol–cyclohexanone at 25 °C and atmospheric pressure. The system contains two pairs of partly miscible compounds, water–1-hexanol and water–cyclohexanone; two type 1 systems in the Treybal's classification (*4*), water–phosphoric acid–1-hexanol and water–phosphoric acid–cyclohexanone; one type 2 ternary system in the same classification, 1-hexanol–water–cyclohexanone; and one ternary system with complete miscibility, 1-hexanol–phosphoric acid–cyclohexanone.

Experimental Section

Chemicals. All chemicals were supplied by Merck. Organic solvents (Analytical Reagent Grade) contained less than 0.5% of volatile impurities, confirmed by chromatographic analysis, and the phosphoric acid (CP Grade) content was 85 wt % and less than 0.1% of impurities. Deionized water was used with subsequent treatment in Millipore filters to remove organic residuals and to reduce conductivity. Chromatographic analysis of water did not show any presence of detectable impurities.

Ternary Equilibrium Data Determination. Binodal curves and tie-line data were obtained simultaneously by means of an analytical method (*5*) in ternary systems. Heterogeneous mixtures of known overall composition were stirred for 12 h in a thermostated bath at 25 ± 0.1 °C, and they settled for at least 12 h before proceeding to the analysis of each component in each of the equilibrium phases.

Water and organic solvents were determined by chromatographic analysis, using a Hewlett-Packard 5840-A chromatograph equipped with electronic integrator. A good separation

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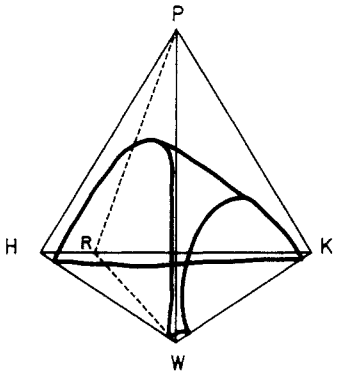

Figure 1. Experimental plan to obtain the quaternary solubility surface of the system water (W)–phosphoric acid (P)–1-hexanol (H)–cyclohexanone (K).

Table I. Ternary Solubility and Tie-Line Data (weight percent) for Water (W)–Phosphoric Acid (P)–1-Hexanol (H) at 25 °C

Initial Mixture					
X_W	X_P	X_H	X_W	X_P	X_H
49.77	0.00	50.23	33.60	39.82	26.58
46.17	8.31	45.52	29.42	47.03	23.55
43.21	16.05	40.74	26.09	55.51	18.40
39.84	24.02	36.14	22.83	64.20	12.97
36.45	30.93	32.62	18.04	74.33	7.63

Solubility Curve and Tie-Line Data					
organic phase			aqueous phase		
X_W	X_P	X_H	X_W	X_P	X_H
7.55	0.00	92.45	99.08	0.00	0.92
7.86	0.82	91.32	84.01	15.39	0.60
8.28	2.47	89.25	72.15	27.45	0.40
7.82	5.80	86.38	62.66	36.98	0.36
9.21	10.98	79.81	55.34	44.35	0.31
10.33	20.08	69.59	46.86	52.84	0.30
12.63	28.27	59.10	40.46	59.19	0.35
14.79	38.27	46.94	33.77	65.94	0.29
15.38	49.50	35.12	26.86	72.81	0.33
15.86	62.73	21.41	18.36	78.64	3.00

was obtained on a 2 m × $^1/_8$ in. column, packed with Porapak P 50/80. The column temperature was 190 °C, with helium as gas carrier at a flow rate of 25 mL/min, and the detection was carried out by thermal conductivity with a detector current of 100 mA.

The analysis of phosphoric acid contents was done by potentiometric titration of weighted samples with NaOH, in a Radiometer PHM62-Titrator TTT60 pH meter, using a glass electrode and a calomel saturated of KCl as reference electrode, until the first pH jump in the value 4.6, obtaining the concentration of phosphoric acid. The relative ratios of water and organic solvents obtained by chromatographic analysis and the material balance enabled us to find the compositions of phases.

Quaternary Solubility Surface Determination. The study of quaternary solubility surface and tie-line data was carried out for systems made up of water, phosphoric acid, and mixtures of 1-hexanol and cyclohexanone in the ratios 4/1, 3/2, 2/3, and 1/4 (pseudoternary systems) with the same analytical method used for ternary equilibrium; Figure 1 shows the method schematically, where R is the ratio of the solvents.

Reliability Test. Three tie lines per ternary or pseudoternary system were repeated as a reproducibility test, which was found to be 0.5% for each component.

Results and Discussion

Mutual solubility and tie-line data for the two ternary and four pseudoternary type 1 systems measured in this research are

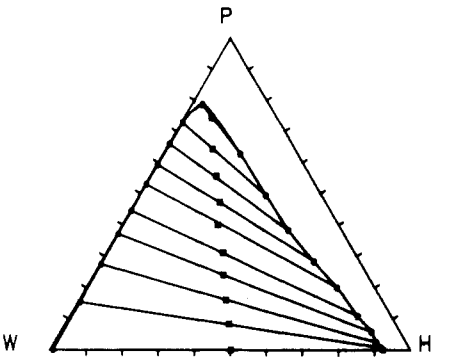

Figure 2. Phase equilibria for the system water (W)–phosphoric acid (P)–1-hexanol (H) at 25 °C.

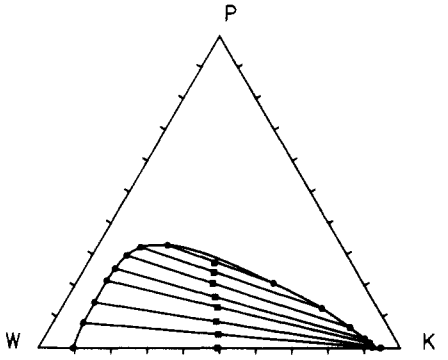

Figure 3. Phase equilibria for the system water (W)–phosphoric acid (P)–cyclohexanone (K) at 25 °C.

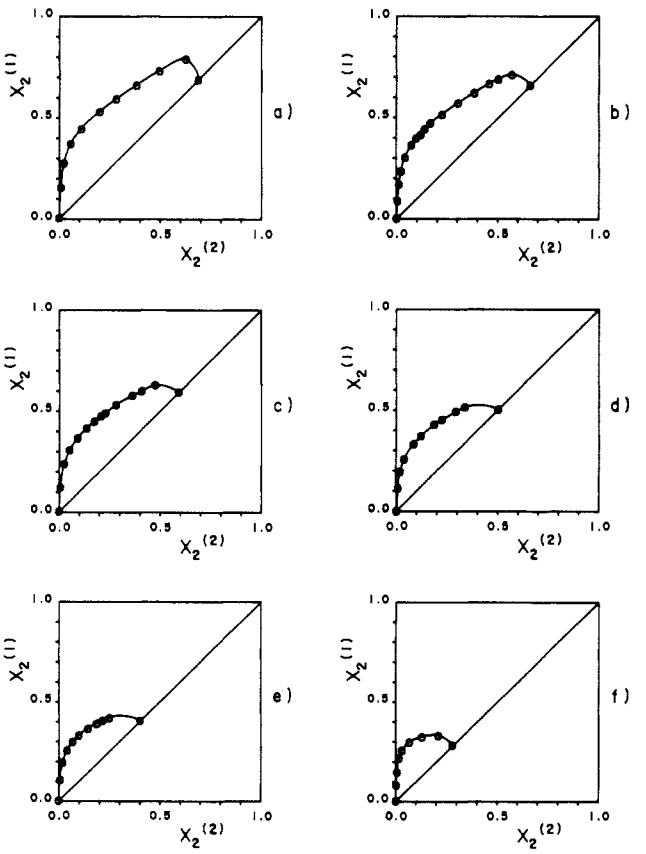

Figure 4. Distribution of phosphoric acid between solvents and water. Solvents: (a) 1-hexanol, (b) 1-hexanol/cyclohexanone (4/1), (c) 1-hexanol/cyclohexanone (3/2), (d) 1-hexanol/cyclohexanone (2/3), (e) 1-hexanol/cyclohexanone (1/4), (f) cyclohexanone.

Table II. Quaternary Solubility and Tie-Line Data (weight percent) for Water (W)–Phosphoric Acid (P)–1-Hexanol (H)–Cyclohexanone (K) at 25 °C (Ratio of Solvents 4/1)

Initial Mixture

X_W	X_P	X_H/X_K (4/1)	X_W	X_P	X_H/X_K (4/1)
50.80	0.00	49.20	36.53	32.00	31.47
48.05	4.97	46.98	35.06	35.28	29.66
45.13	9.71	45.16	33.11	40.03	26.86
44.30	13.89	41.81	30.44	46.71	22.85
42.18	19.02	38.80	27.99	52.12	19.89
39.71	24.33	35.96	25.42	57.89	16.69
38.65	27.60	33.75	24.21	61.05	14.74
37.61	29.38	33.01	22.70	64.56	12.74

Solubility Curve and Tie-Line Data

organic phase				aqueous phase			
X_W	X_P	X_H	X_K	X_W	X_P	X_H	X_K
8.17	0.00	73.50	18.33	97.09	0.00	0.81	2.10
7.18	0.53	75.22	17.07	89.04	9.14	0.81	1.01
7.13	1.21	74.86	16.80	81.22	17.23	0.46	1.09
7.52	2.32	73.76	16.40	74.89	23.81	0.39	0.91
7.84	4.31	72.01	15.84	68.45	30.58	0.33	0.64
8.47	7.47	68.90	15.16	62.17	36.62	0.32	0.89
8.91	9.77	66.53	14.79	58.83	39.95	0.31	0.91
9.32	12.07	64.68	13.93	56.99	41.83	0.32	0.86
10.46	14.04	62.08	13.42	54.23	44.61	0.32	0.84
10.42	16.80	59.95	12.83	51.43	47.42	0.39	0.76
11.84	22.68	53.39	12.09	46.81	51.80	0.44	0.95
13.78	30.44	45.95	9.83	41.47	57.39	0.35	0.79
15.51	38.39	38.29	7.81	36.14	62.44	0.36	1.06
16.51	45.77	31.56	6.16	31.77	66.87	0.36	1.00
17.59	50.29	26.99	5.13	29.49	69.14	0.45	0.92
17.50	57.00	21.66	3.84	27.38	71.34	0.53	0.75

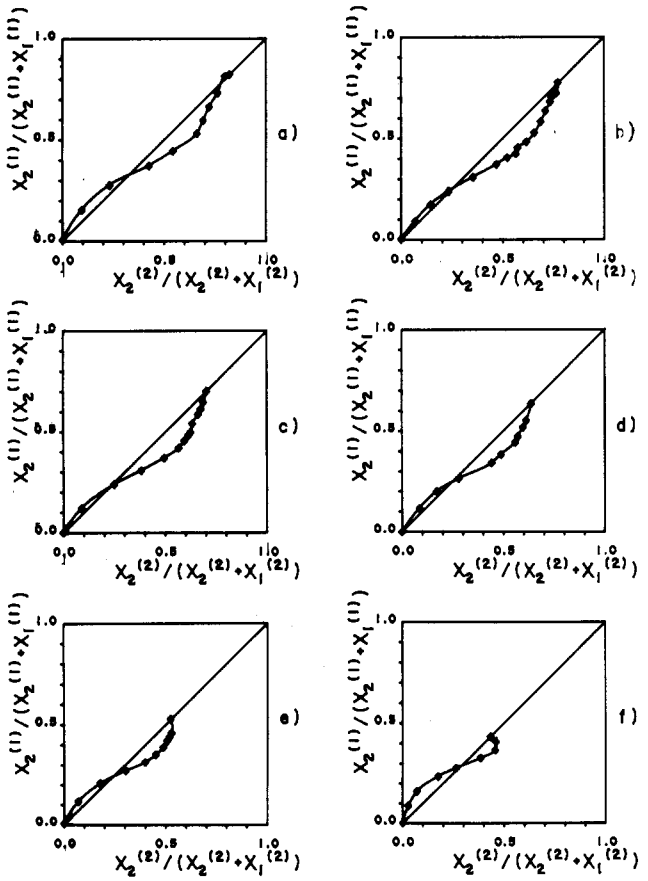

Figure 5. Selectivity diagrams for the system water (W)–phosphoric acid (P)–solvents. Solvents: (a) 1-hexanol, (b) 1-hexanol/cyclohexanone (4/1), (c) 1-hexanol/cyclohexanone (3/2), (d) 1-hexanol/cyclohexanone (2/3), (e) 1-hexanol/cyclohexanone (1/4), (f) cyclohexanone.

Table III. Quaternary Solubility and Tie-Line Data (weight percent) for Water (W)–Phosphoric Acid (P)–1-Hexanol (H)–Cyclohexanone (K) at 25 °C (Ratio of Solvents 3/2)

Initial Mixture

X_W	X_P	X_H/X_K (3/2)	X_W	X_P	X_H/X_K (3/2)
50.45	0.00	49.55	34.80	36.14	29.06
47.52	6.41	46.07	33.95	37.97	28.08
44.17	13.95	41.88	32.24	41.80	25.96
41.69	19.32	38.99	29.99	47.26	22.75
39.55	25.06	35.39	28.78	51.32	19.90
37.88	29.01	33.11	27.11	53.27	19.62
35.93	33.19	30.88			

Solubility Curve and Tie-Line Data

organic phase				aqueous phase			
X_W	X_P	X_H	X_K	X_W	X_P	X_H	X_K
8.35	0.00	55.02	36.63	95.39	0.00	0.69	3.92
8.24	0.80	55.66	35.30	83.95	11.87	1.05	3.13
8.18	2.70	54.85	34.27	73.88	23.32	0.46	2.35
8.49	5.26	53.87	32.38	67.16	30.25	0.39	2.20
9.29	9.08	51.32	30.31	61.07	36.16	0.52	2.25
10.41	13.53	48.05	28.01	56.58	41.07	0.33	2.02
11.87	17.39	44.95	25.79	52.84	44.60	0.34	2.22
13.00	20.65	42.27	24.08	50.24	47.19	0.33	2.24
13.79	22.92	40.45	22.84	48.67	48.71	0.35	2.27
16.29	28.08	36.10	19.53	44.44	52.82	0.38	2.36
18.48	36.17	29.64	15.71	39.96	57.38	0.42	2.24
19.62	40.84	25.70	13.84	37.33	59.71	0.57	2.39
21.55	47.60	20.03	10.82	33.90	62.59	0.80	2.71

Table IV. Quaternary Solubility and Tie-Line Data (weight percent) for Water (W)–Phosphoric Acid (P)–1-Hexanol (H)–Cyclohexanone (K) at 25 °C (Ratio of Solvents 2/3)

Initial Mixture

X_W	X_P	X_H/X_H (2/3)	X_W	X_P	X_H/X_H (2/3)
50.38	0.00	49.62	38.86	26.45	34.69
47.62	5.95	46.43	36.74	32.12	31.14
45.68	11.27	43.05	35.44	35.96	28.60
44.41	15.84	39.75	33.25	39.71	27.04
40.93	22.17	36.90	31.78	43.30	24.92

Solubility Curve and Tie-Line Data

organic phase				aqueous phase			
X_W	X_P	X_H	X_K	X_W	X_P	X_H	X_K
8.10	0.00	36.73	55.17	94.14	0.00	0.62	5.24
10.05	0.94	37.43	51.58	84.72	11.49	0.30	3.49
9.95	2.05	37.53	50.47	76.76	19.50	0.31	3.42
10.16	3.94	36.77	49.13	70.87	25.57	0.26	3.31
10.73	8.51	34.52	46.24	63.13	33.13	0.27	3.47
12.65	12.12	32.69	42.54	58.79	37.09	0.30	3.82
14.78	18.71	29.30	37.21	52.90	42.79	0.33	3.98
16.87	22.54	27.26	33.33	50.16	45.20	0.38	4.2
19.88	29.49	23.11	27.52	45.31	49.28	0.51	4.90
21.36	33.85	20.56	24.23	41.50	51.61	2.90	3.99

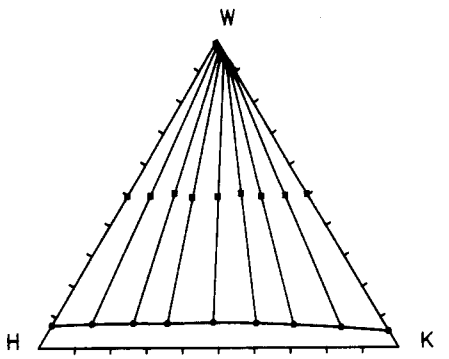

Figure 6. Phase equilibria for the system 1-hexanol (H)–water (W)–cyclohexanone (K) at 25 °C.

Table V. Quaternary Solubility and Tie-Line Data (weight percent) for Water (W)–Phosphoric Acid (P)–1-Hexanol (H)–Cyclohexanone (K) at 25 °C (Ratio of Solvents 1/4)

Initial Mixture					
X_W	X_P	X_H/X_K (1/4)	X_W	X_P	X_H/X_K (1/4)
50.27	0.00	49.73	40.33	23.02	36.65
47.60	5.83	46.57	38.71	26.63	34.66
45.41	11.45	43.14	37.40	29.46	33.14
43.34	16.07	40.59	36.98	31.12	31.90
41.65	19.79	38.56	36.00	33.26	30.74

Solubility Curve and Tie-Line Data							
organic phase				aqueous phase			
X_W	X_P	X_H	X_K	X_W	X_P	X_H	X_K
7.72	0.00	18.49	73.79	91.96	0.00	0.38	7.66
8.22	0.62	19.91	71.25	82.71	10.61	0.55	6.13
8.73	1.89	19.79	69.59	75.05	19.25	0.27	5.43
9.50	4.14	19.13	67.23	68.98	25.19	0.25	5.58
10.30	6.80	18.62	64.28	65.42	29.41	0.23	4.94
12.10	9.91	17.77	60.22	61.48	32.73	0.24	5.55
15.03	14.29	16.33	54.35	57.91	36.12	0.27	5.70
18.18	18.71	14.69	48.42	54.32	38.76	0.35	6.62
20.12	21.51	13.79	44.58	52.88	40.18	0.37	6.57
22.26	24.86	12.55	40.33	50.02	41.72	0.53	7.73

Table VI. Ternary Solubility and Tie-Line Data (weight percent) for Water (W)–Phosphoric Acid (P)–Cyclohexanone (K) at 25 °C

Initial Mixture					
X_W	X_P	X_K	X_W	X_P	X_K
50.37	0.00	49.63	42.86	16.33	40.81
47.93	4.33	47.74	41.38	20.63	37.99
46.51	8.44	45.05	39.37	24.14	36.49
44.02	12.99	42.99	37.69	27.23	35.08

Solubility Curve and Tie-Line Data					
organic phase			aqueous phase		
X_W	X_P	X_K	X_W	X_P	X_K
5.45	0.00	94.55	90.34	0.00	9.66
7.58	0.22	92.20	83.58	8.08	8.34
7.74	0.58	91.68	77.18	14.65	8.17
7.57	1.60	90.83	70.36	21.59	8.05
8.38	2.99	88.63	66.18	25.39	8.43
10.65	6.61	82.74	60.83	29.61	9.56
15.23	12.77	72.00	55.66	32.28	12.06
24.60	20.85	54.55	47.77	32.94	19.29

presented in Tables I–VI. Figures 2 and 3 show the triangular ternary diagrams for the two type 1 systems; figures for pseudoternary systems are similar. Distribution and selectivity curves for ternary and pseudoternary type 1 systems are shown in Figures 4 and 5. Table VII and Figure 6 stand for the type 2 ternary system.

Both solvents and their mixtures show distribution coefficients less than unity for any concentration of phosphoric acid. Likewise, selectivity diagrams for the two solvents and their mixtures show inversion of selectivity from values less than unity, for low and middle phosphoric acid concentrations, to values higher than unity for elevated concentrations of phosphoric acid in the ternary diagram.

Table VII. Ternary Solubility and Tie-Line Data (weight percent) for 1-Hexanol (H)–Water (W)–Cyclohexanone (K) at 25 °C

Initial Mixture					
X_H	X_W	X_K	X_H	X_W	X_K
50.23	49.77	0.00	18.18	50.59	31.23
43.76	49.86	6.38	13.02	49.76	37.22
36.74	50.64	12.62	6.17	50.00	43.83
32.44	49.37	18.19	0.00	50.37	49.63
25.17	49.68	25.15			

Solubility Curve and Tie-Line Data					
organic phase			aqueous phase		
X_H	X_W	X_K	X_H	X_W	X_K
92.45	7.55	0.00	0.92	99.08	0.00
81.04	8.03	10.93	0.86	98.21	0.93
69.47	8.20	22.33	0.76	97.16	2.08
60.03	8.17	31.80	0.71	96.27	3.02
47.14	8.45	44.41	0.64	95.08	4.28
35.32	8.18	56.50	0.56	94.00	5.44
25.25	7.66	67.09	0.45	92.98	6.57
12.50	6.75	80.75	0.30	91.84	7.87
0.00	5.45	94.55	0.00	90.34	9.66

The variation of selectivity with mixtures of both solvents is of little significance, with 1-hexanol appearing as the better extractant solvent on account of the wide heterogeneous zone in the solubility diagram. The use of mixed solvents to improve the extraction of phosphoric acid will only be advisable when both solvents show some favorable properties, such as distribution coefficient and/or selectivity, in order to take advantage of the synergistic effect of the mixture.

Glossary

H	1-hexanol
K	cyclohexanone
P	phosphoric acid
W	water
$X_i^{(1)}$	weight percentage of component i in the aqueous phase
$X_i^{(2)}$	weight percentage of component i in the organic phase

Registry No. H_3PO_4, 7664-38-2; 1-hexanol, 111-27-3; cyclohexanone, 108-94-1.

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