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Effect of Sodium Chloride on the Water–Phosphoric Acid–1-Hexanol–Cyclohexanone Liquid–Liquid Equilibria at 25 °C

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Liquid–liquid equilibria, mutual solubility, and tie-line data have been studied at 25 °C and atmospheric pressure for the quaternary system water–phosphoric acid–1-hexanol–cyclohexanone in the presence of sodium chloride at saturation with respect to both conjugated phases. The salt effect increases the distribution coefficient and selectivity for phosphoric acid in 1-hexanol and cyclohexanone and for their mixtures. Quantitative results indicate the salting-out effect due to sodium chloride in aqueous solutions, both for phosphoric acid and for the solvents.

Introduction

In the purification of wet process phosphoric acid by liquid–liquid extraction, the salt effect has a remarkable importance due to the presence of saline impurities, which are present in great quantity if the attack of phosphate rock is carried out with hydrochloric or nitric acid. There is no doubt that the impurities modify the equilibrium of extraction of water–phosphoric acid–solvents systems. The goal of most studies, mainly patents, is to remove impurities in order to obtain a good quality phosphoric acid. Information concerning equilibrium data in phosphoric acid extraction systems with salt effects is rather scarce (*1*). This paper reports the quantitative study, at 25 °C and atmospheric pressure, of the effect of sodium chloride, at saturation in the two conjugated phases, on the quaternary system water–phosphoric acid–1-hexanol–cyclohexanone. Equilibrium data for the system without the salt effect were presented in a previous paper (*2*).

The salt effect in the binary water–solvent systems, where the solvents are alcohols and ketones (*3–6*), has been explained in terms of "salting out", that is, the solubility in water of the nonelectrolyte decreases in the presence of salt. Salting out of solute was also observed for pyridine (*7*), acetic acid (*8*, *9*), benzoic acid (*10*), hydrochloric acid (*11*), and phosphoric acid (*1*) in ternary systems. A review of the salt effect for polar molecules in aqueous electrolyte solutions was performed by Treiner (*12*). The influence of sodium chloride upon the system studied in the present work is shown through distribution and selectivity curves, drawn for the systems with salt effect and for the systems in absence of it.

Table I. Solubility and Tie-Line Data on a Salt-Free Basis (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	33.98	39.93	26.09
46.81	7.78	45.41	30.55	46.40	23.05
43.75	15.29	40.96	27.10	54.48	18.42
40.31	22.96	36.73	23.81	62.41	13.78
37.22	30.37	32.41	18.87	74.13	7.00

Solubility Curve and Tie-Line Data

organic phase				aqueous phase			
X_W	X_P	X_H	X_S	X_W	X_P	X_H	X_S
3.45	0.00	96.55	0.04	99.51	0.00	0.49	26.44
6.17	3.30	90.53	0.88	87.34	12.19	0.47	21.42
6.68	7.38	85.94	1.64	76.92	22.93	0.15	17.08
7.61	12.04	80.35	2.33	67.54	32.27	0.19	13.21
8.52	17.13	74.35	2.84	59.09	40.70	0.21	9.78
9.71	23.92	66.37	3.38	49.36	50.46	0.18	6.67
10.80	29.82	59.38	3.44	42.81	56.97	0.22	4.64
12.00	37.22	50.78	3.45	35.60	64.25	0.15	3.21
11.86	45.09	43.05	3.24	29.16	70.67	0.17	2.25
13.31	57.71	28.98	2.86	20.70	79.10	0.20	1.63

Table II. Solubility and Tie-Line Data on a Salt-Free Basis (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_M	X_W	X_P	X_M
50.61	0.00	49.39	31.52	44.95	23.52
44.28	13.66	42.06	28.99	51.06	19.95
40.91	22.17	36.92	27.36	54.93	17.71
37.20	31.08	31.72	25.71	59.12	15.17
33.65	39.50	26.85	24.02	63.00	12.98

Solubility Curve and Tie-Line Data

organic phase					aqueous phase				
X_W	X_P	X_H	X_K	X_S	X_W	X_P	X_H	X_K	X_S
4.50	0.00	76.39	19.11	0.04	99.42	0.00	0.58	0.00	26.45
6.78	6.87	68.90	17.45	1.33	79.49	20.01	0.50	0.00	18.17
8.78	12.43	63.40	15.39	2.07	69.24	30.36	0.22	0.18	13.70
10.23	19.09	57.53	13.15	2.66	58.48	40.82	0.16	0.54	9.48
11.54	25.10	52.02	11.34	2.98	49.33	49.96	0.16	0.55	6.81
12.48	30.81	47.02	9.69	3.13	44.39	54.76	0.17	0.68	5.00
12.95	36.50	42.14	8.41	3.10	38.71	60.26	0.22	0.81	3.75
14.79	40.73	37.03	7.45	3.07	35.21	63.75	0.22	0.81	3.11
14.50	45.08	33.97	6.45	2.96	31.77	66.82	0.33	1.08	2.61
15.21	49.03	30.34	5.42	2.85	28.86	69.73	0.36	1.05	2.29

Table III. Solubility and Tie-Line Data on a Salt-Free Basis (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_M	X_W	X_P	X_M
50.32	0.00	49.68	34.76	35.84	29.40
47.10	6.95	45.95	32.78	40.90	26.32
44.25	13.70	42.05	30.93	45.08	23.99
39.56	25.02	35.42	29.56	48.51	21.93
37.63	29.41	32.96	28.16	51.65	20.19

Solubility Curve and Tie-Line Data

organic phase					aqueous phase				
X_W	X_P	X_H	X_K	X_S	X_W	X_P	X_H	X_K	X_S
4.66	0.00	57.26	38.08	0.03	99.25	0.00	0.24	0.51	26.40
5.57	2.85	55.56	36.02	0.65	88.04	11.17	0.35	0.44	23.47
7.17	7.09	52.52	33.22	1.26	79.33	20.03	0.16	0.48	18.26
9.61	15.85	47.73	28.81	2.19	65.00	33.88	0.13	0.99	12.07
11.28	19.12	42.94	26.66	2.43	60.73	38.05	0.12	1.10	10.39
12.17	24.59	40.30	22.94	2.77	53.40	45.14	0.14	1.32	7.80
15.64	29.87	34.35	20.14	2.93	47.62	50.71	0.16	1.51	6.04
15.82	34.26	31.81	18.11	2.99	43.70	54.58	0.17	1.55	4.87
16.74	38.13	28.90	16.23	2.96	40.27	57.73	0.22	1.78	4.10
17.24	40.89	27.36	14.51	2.91	37.34	60.43	0.26	1.97	3.46

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Table IV. Solubility and Tie-Line Data on a Salt-Free Basis (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_M	X_W	X_P	X_M
50.18	0.00	49.82	38.57	27.08	34.35
47.62	5.95	46.43	36.49	32.33	31.18
45.35	11.27	43.38	34.74	35.39	29.87
42.60	17.42	39.98	33.50	37.89	28.61
40.27	22.88	36.85	32.12	42.18	25.70

Solubility Curve and Tie-Line Data

organic phase					aqueous phase				
X_W	X_P	X_H	X_K	X_S	X_W	X_P	X_H	X_K	X_S
4.01	0.00	38.40	57.59	0.01	99.10	0.00	0.20	0.70	26.40
4.92	2.02	37.78	55.28	0.45	89.20	9.74	0.22	0.84	22.77
6.58	5.26	36.02	52.14	0.88	81.89	16.99	0.15	0.97	19.58
8.28	9.96	33.41	48.35	1.37	73.73	24.64	0.31	1.32	16.02
10.00	14.33	30.86	44.81	1.82	67.86	30.51	0.11	1.52	13.37
12.24	18.20	28.82	40.74	2.17	62.75	35.33	0.13	1.79	11.31
14.05	23.52	26.51	35.92	2.56	56.97	40.85	0.13	2.05	8.91
15.15	26.70	24.94	33.21	2.73	53.60	44.03	0.15	2.22	7.32
17.86	30.59	22.56	28.99	2.94	49.55	47.66	0.18	2.61	6.54
18.35	34.41	20.84	26.40	3.00	46.48	50.57	0.20	2.75	5.56

Table V. Solubility and Tie-Line Data on a Salt-Free Basis (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_M	X_W	X_P	X_M
50.35	0.00	49.65	40.27	23.11	36.62
47.60	5.71	46.69	38.78	26.25	34.97
45.09	11.68	43.23	37.89	28.64	33.47
43.32	15.92	40.76	36.90	31.29	31.81
41.94	19.10	38.96	36.00	33.05	30.95
			33.80	38.11	28.09

Solubility Curve and Tie-Line Data

organic phase					aqueous phase				
X_W	X_P	X_H	X_K	X_S	X_W	X_P	X_H	X_K	X_S
3.80	0.00	19.23	76.97	<0.01	98.68	0.00	0.12	1.20	26.41
6.74	1.34	18.77	73.15	0.30	88.66	9.94	0.13	1.27	23.09
6.62	4.73	18.32	70.33	0.75	80.05	18.29	0.16	1.50	19.06
7.66	8.04	17.27	67.03	1.11	75.14	23.07	0.08	1.71	16.73
9.23	11.30	16.51	62.96	1.40	71.06	26.83	0.00	2.11	14.89
10.80	15.25	15.53	58.42	1.79	66.98	30.56	0.09	2.37	13.01
13.41	18.68	14.40	53.51	2.11	62.98	34.11	0.10	2.81	11.50
14.94	21.15	13.72	50.19	2.28	60.51	36.35	0.10	3.04	10.46
16.35	24.04	12.91	46.70	2.51	57.78	39.09	0.10	3.03	9.36
17.44	26.10	12.39	44.07	2.67	55.68	40.86	0.11	3.35	8.66
22.26	32.50	10.02	35.22	2.95	49.04	44.99	0.20	5.76	7.52

Experimental Section

Chemicals. Organic solvents (Analytical Reagent grade) containing less than 0.5% of volatile impurities, as confirmed by chromatographic analysis, phosphoric acid (CP grade) containing 85 wt % and less than 0.1% of impurities, and sodium chloride (Suprapur), all of them supplied by Merck, were used. Deionized water was used, with subsequent treatment in Millipore filters in order to remove organic residuals and to reduce its conductivity. Chromatographic analysis of the water did not show the presence of detectable impurities.

Procedures. Ternary or quaternary heterogeneous mixtures of known overall composition were prepared. Sodium chloride was added. The heterogeneous mixtures were stirred 12 h in a thermostated bath at 25 ± 0.1 °C. They settled for at least 12 h prior to the analysis of each component in each of the equilibrium phases.

Table VI. Solubility and Tie-Line Data on a Salt-Free Basis (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	41.71	19.60	38.69
48.31	3.72	47.97	40.25	22.96	36.79
46.75	8.00	45.25	38.57	27.39	34.04
45.03	11.74	43.23	37.01	30.20	32.79
43.63	15.32	41.05	35.76	33.69	30.55

Solubility Curve and Tie-Line Data

organic phase				aqueous phase			
X_W	X_P	X_K	X_S	X_W	X_P	X_K	X_S
2.87	0.00	97.13	<0.01	98.34	0.00	1.66	26.42
3.09	0.23	96.68	0.03	91.19	7.26	1.55	23.22
3.71	0.96	95.33	0.11	83.29	14.37	2.34	20.52
4.99	2.48	92.53	0.27	77.85	19.66	2.49	18.44
7.14	5.46	87.40	0.62	73.35	23.84	2.81	16.42
9.73	10.72	79.55	1.06	69.45	27.58	2.97	14.78
12.04	14.84	73.12	1.60	65.89	30.62	3.49	13.16
16.17	21.15	62.68	2.27	61.81	34.19	4.00	11.38
19.20	24.99	55.81	2.44	58.63	36.45	4.92	10.61
24.90	30.63	44.47	2.73	54.80	39.12	6.08	9.76

Table VII. Solubility and Tie-Line Data on a Salt-Free Basis (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	50.69	31.13
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_S	X_H	X_W	X_K	X_S
96.55	3.45	0.00	0.04	0.49	99.51	0.00	26.44
84.27	3.62	12.11	0.04	0.41	99.59	0.00	26.39
71.20	4.56	24.24	0.04	0.30	99.50	0.20	26.41
60.74	5.16	34.10	0.03	0.26	99.36	0.38	26.39
48.07	4.27	47.66	0.02	0.20	99.24	0.56	26.40
35.59	4.07	60.34	0.01	0.21	98.88	0.91	26.40
25.20	3.96	70.84	<0.01	0.21	98.77	1.02	26.40
12.23	3.58	84.19	<0.01	0.00	98.92	1.08	26.41
0.00	2.87	97.13	<0.01	0.00	98.34	1.66	26.42

Binodal curve and tie-line data were obtained simultaneously by means of an analytical method in the ternary systems. Water and organic solvents were determined by chromatographic analysis, using a Hewlett-Packard 5840-A chromatograph equipped with an electronic integrator. A good separation 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 carrier gas at a flow rate of 25 mL/min. Detection was carried out by thermal conductivity with a detector current of 100 mA.

The analysis of phosphoric acid and sodium chloride contents were done by potentiometric titration of weighted samples in a Radiometer PHM62–Titrator TTT60 pH meter. Phosphoric acid was titrated with NaOH by using a glass electrode and a saturated calomel reference electrode. Titration of sodium chloride was carried out with silver nitrate, using a silver/silver chloride electrode and a mercury/mercury(I) sulfate saturated with potassium sulfate electrode. The concentrations of phosphoric acid and sodium chloride, as well as the relative ratios of water and organic solvents were obtained from the

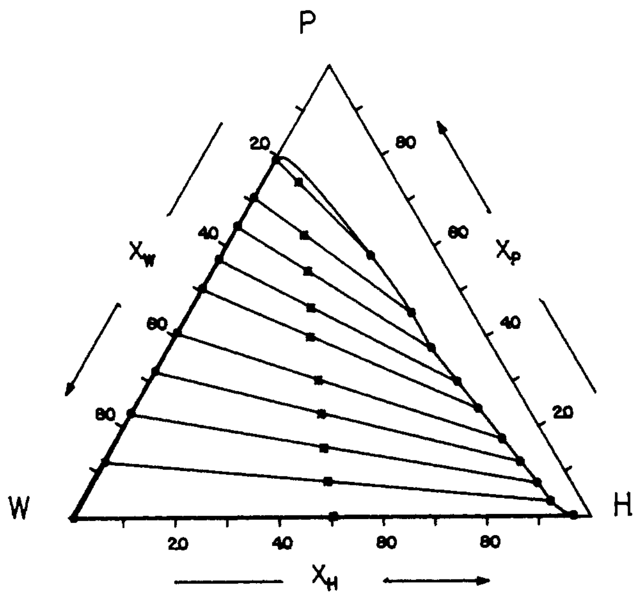

Figure 1. Phase equilibria on a salt-free basis for the water (W)-phosphoric acid (P)-1-hexanol (H) system saturated with NaCl at 25 °C.

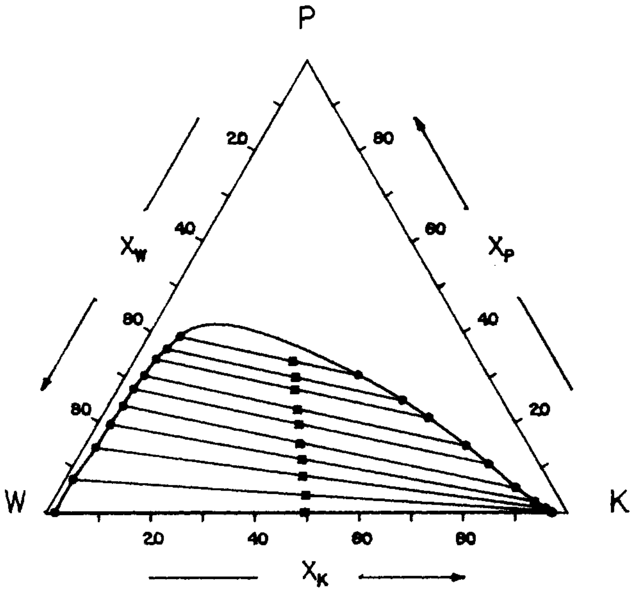

Figure 2. Phase equilibria on a salt-free basis for the water (W)-phosphoric acid (P)-cyclohexanone (K) system saturated with NaCl at 25 °C.

analytical methods. The material balance enabled us to find the composition of each phases.

The study of quaternary solubility surface and tie-line data was carried out for the systems made up of water, phosphoric acid and mixtures of 1-hexanol and cyclohexanone in the weight ratios 4/1, 3/2, 2/3, and 1/4 (pseudoternary systems) with the same analytical method used for ternary equilibrium.

Reliability Test. The relative accuracy of weight fraction measurements was 0.5% for water and organic solvents and 0.1% for phosphoric acid and sodium chloride. Three tie lines per ternary or pseudoternary system were repeated as a study of reproducibility, which was found to be 0.5% for each component.

Results and Discussion

Tables I-VI show experimental solubility and tie-line data on a salt-free basis, as well as the absolute percentage of sodium chloride in each phase, for the two ternary and four pseudoternary type 1 systems characterized in the present research. Triangular ternary diagrams for the two type 1 ternary systems are shown in Figures 1 and 2; figures for pseudoternary systems are similar. The data for the type 2 ternary 1-hexanol-water-cyclohexanone system are presented in Table VII and

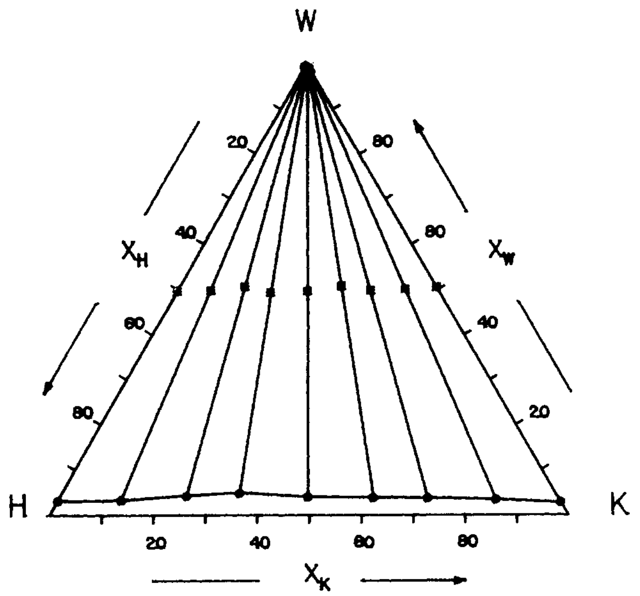

Figure 3. Phase equilibria on a salt-free basis for the 1-hexanol (H)-water (W)-cyclohexanone (K) system saturated with NaCl at 25 °C.

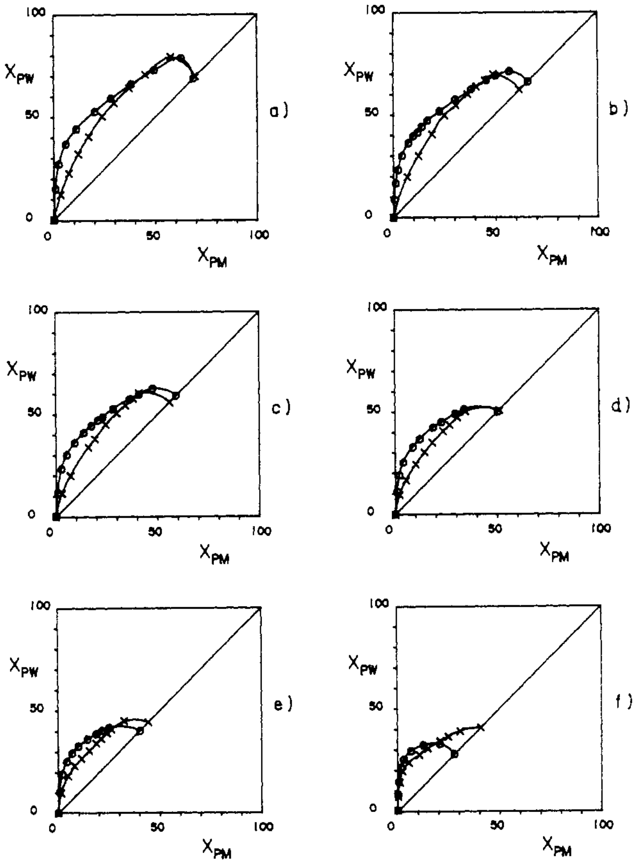

Figure 4. Distribution of phosphoric acid between solvents and water: (O) no salt present, (X) NaCl at saturation. Solvents: (a) 1-hexanol, (b) 1-hexanol/cyclohexanone (4/1), (c) 1-hexanol/cyclohexanone (3/2), (d) 1-hexanol/cyclohexanone (2/3), (e) 1-hexanol/cyclohexanone (1/4), (f) cyclohexanone.

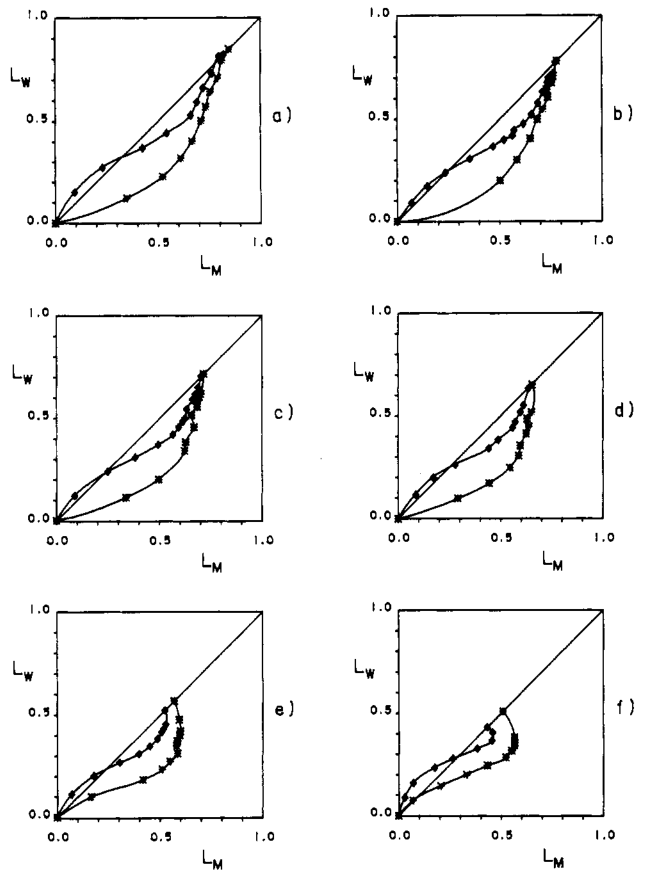

Figure 5. Selectivity diagrams for water (W)-phosphoric acid (P)-solvent systems: (◆) no salt present, (*) NaCl at saturation. Solvents: (a) 1-hexanol, (b) 1-hexanol/cyclohexanone (4/1), (c) 1-hexanol/cyclohexanone (3/2), (d) 1-hexanol/cyclohexanone (2/3), (e) 1-hexanol/cyclohexanone (1/4), (f) cyclohexanone.

Figure 3. In Tables II–V the subscript M represents 1-hexanol–cyclohexanone mixtures.

Figures 4 and 5 represent, respectively, the distribution and selectivity curves for each type 1 ternary and pseudoternary system. The diagrams present the equilibria obtained in the presence and absence of salt. Subscript M refers to the organic phase. Figure 4 shows that the distribution coefficients of phosphoric acid between pure solvents and water, as well as between mixtures of solvents and water, are always higher in the presence of salt than in the absence of it. The diagrams of the Figure 5 show that selectivity, in the absence of the salt effect, suffers an inversion from values less than the unity for low concentrations of phosphoric acid to values greater than the unity for higher concentrations. The salt effect increases the selectivity to values greater than unity for any concentration of phosphoric acid for all the ternary and pseudoternary type 1 systems.

In conclusion, the addition of sodium chloride improves phosphoric acid extraction by means of 1-hexanol, cyclohexanone, and their mixtures. This improvement results from the salt effect which modifies the phase equilibria of the water–phosphoric acid–1-hexanol–cyclohexanone system, increasing the distribution coefficient for phosphoric acid and the selectivity of the solvents.

Glossary

H	1-hexanol
K	cyclohexanone
P	phosphoric acid
W	water
S	sodium chloride
M	1-hexanol–cyclohexanone mixture
X	weight percentage
X_{PW}	weight percentage of phosphoric acid in the aqueous phase on a salt-free basis
X_{PM}	weight percentage of phosphoric acid in the organic phase on a salt-free basis
X_{WW}	weight percentage of water in the aqueous phase on a salt-free basis
X_{WM}	weight percentage of water in the organic phase on a salt-free basis
L_W	ordinate of selectivity diagram defined as $L_W = X_{PW}/(X_{PW} + X_{WW})$
L_M	abscissa of selectivity diagram defined as $L_M = X_{PM}/(X_{PM} + X_{WM})$

Registry No. NaCl, 7647-14-5; phosphoric acid, 7664-38-2; 1-hexanol, 111-27-3; cyclohexanone, 108-94-1.

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