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Effect of Addition of Calcium Chloride on the Liquid−Liquid Equilibria of the Water + Propionic Acid + 1-Butanol System at 303.15 K

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The influence of the addition of $CaCl_2$ to the water + propionic acid + 1-butanol ternary system was studied at (303.15 ± 0.05) K. The quaternary system was represented projecting four sectional quaternary planes corresponding to 4.3%, 9.3%, 15.1%, and 20.3% $CaCl_2$ in aqueous solution onto the face of the tetrahedron containing the ternary system water + propionic acid + 1-butanol. Therefore, all compositions are given on a salt-free basis for the solubility curves and for tie-line data. The addition of salt always enhances significantly the distribution coefficients and selectivities, while the region of heterogeneity increases as compared to the no-salt condition. Band type curves were obtained for solubility curves above 4.3% $CaCl_2$, and no salt precipitation was observed. The experimental results show that $CaCl_2$ is not distributed in the same proportion between the phases at equilibrium and that 1-butanol appears to be a good solvent for extraction purposes. A comparison between the influence of $CaCl_2$ and NaCl on this ternary system is also made using these experimental results with earlier data. A high value of the Sestchenow's constant was obtained by a linear regression method, which is an indication that a great salting-out effect is produced by the addition of $CaCl_2$, which is more important than for NaCl.

Introduction

Mutual solubilities of partially miscible binary systems are significantly affected by the presence of a mineral salt. This phenomenon is also observed in ternary systems through changes in the sizes of the partially miscible regions with respect to the no salt condition. Depending on whether these sizes are increased or decreased, it is called the salting-out or salting-in effect. Solubilities are affected because the ionic strength of the systems are modified by the presence of an ionic salt, which modifies the activity coefficients of their components. The solvation of the ions by an ion−dipole interaction mechanism is another important factor in this property. Many papers on this subject can be found in the literature (Swabb and Mongan, 1952; Desai and Eisen, 1971; De Santis et al., 1976; Marco et al., 1988; Ting et al., 1992; Sólimo et al., 1997).

In a previous paper (Sólimo et al., 1997), we have studied the influence of the addition of NaCl to the water (W) + propionic acid (PA) + 1-butanol (B) ternary system, which exhibited a very important salting-out effect. The aim of this paper is to analyze the change caused by the substitution of the univalent sodium cation by the divalent calcium one for the same ternary system, with the result of studying the influence of the cation on that phase equilibrium and making a comparison between them. The same anion was maintained in order to analyze only the influence of the cation.

Brines approximately with 4%, 10%, 15%, and 20% mass aqueous $CaCl_2$ were prepared to obtain four quaternary planes for the system water (W or 1) + propionic acid (PA or 2) + 1-butanol (B or 3) + $CaCl_2$ (4) at 303.15 K. However, since we were only interested in obtaining information on the salting-out effect, which was achieved projecting the solubility curves located on those quaternary planes onto the face of the tetrahedron corresponding to the ternary system (W + PA + B), no systematic study of the quaternary system was made. Therefore, all compositions are given on a salt-free basis for the solubility curves and for tie-lines. The salt equilibrium compositions are also indicated in order to know the amount of salt in each phase.

The binodal curve for the proper ternary system water + 1-propionic acid + 1-butanol at 303.15 K was taken from a previous paper (Sólimo et al., 1997) for comparison.

Experimental Section

Materials. Water was bidistilled. Propionic acid (Riedel-de Haën AG), $CaCl_2$ (J. T. Baker, ACS reagent), and 1-butanol (Anedra, p.a.) with purities of at least 99.1% were used without further purification. This purity was considered as appropriate, because no abnormalities were observed on the binodal curve of the ternary system W + PA + B (Francis, 1963).

Procedure. The procedure for the determination of solubility and equilibrium data at (303.15 ± 0.05) K of the system W (1) + PA (2) + B (3) + $CaCl_2$ (4) was similar to that previously adopted (Sólimo et al., 1997). The salt concentrations were 4.3%, 9.3%, 15.1%, and 20.3% by mass, which are well within the saturation limit at 303.15 K. Under no circumstances was salt precipitation observed, but above 4.3% $CaCl_2$ solubility curves of band type form were obtained. Solubility curves were determined by the cloud-point method as described earlier (Sólimo et al., 1989). The temperature of the water bath was monitored by a Jumo glass thermometer with an accuracy of ±0.01 K. Since the compositions of the solubility curves were determined by mass, the error throughout these curves was

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Table 1. Solubility Data (on a Salt-free Basis) for the System Water (1) + Propionic Acid (2) + 1-Butanol (3) + Calcium Chloride (4) at 303.15 K

$w^\circ_1\%$	$w^\circ_2\%$	$w^\circ_3\%$	$w_4\%$[a]	$w^\circ_1\%$	$w^\circ_2\%$	$w^\circ_3\%$	$w_4\%$[a]	$w^\circ_1\%$	$w^\circ_2\%$	$w^\circ_3\%$	$w_4\%$[a]
4.3% by mass[b]											
93.77	0.00	6.23	4.04	43.38	38.60	18.02	1.91	15.63	42.77	41.60	0.70
90.10	4.99	4.91	3.89	40.72	41.49	17.79	1.80	14.27	38.28	47.45	0.64
84.39	10.66	4.95	3.65	33.18	47.77	19.06	1.47	12.16	33.01	54.84	0.54
76.81	16.47	6.72	3.34	29.40	50.68	19.92	1.30	11.84	25.67	62.48	0.53
70.46	20.55	9.00	3.07	27.09	51.96	20.95	1.20	11.12	21.60	67.28	0.50
64.18	24.24	11.57	2.80	22.38	51.51	26.10	1.00	11.00	15.03	73.97	0.49
60.61	26.42	12.97	2.65	19.28	50.19	30.53	0.86	10.81	6.96	82.23	0.48
53.98	30.93	15.08	2.37	16.83	47.02	36.15	0.75	10.38	0.00	89.62	0.46
50.64	33.21	16.14	2.22								
9.3% by mass[b]											
94.74	0.00	5.26	8.82	26.07	73.93	0.00	2.59	7.23	60.21	32.56	0.73
78.97	16.54	4.48	7.46	9.08	18.54	72.38	0.92	6.98	53.71	39.31	0.71
69.91	23.93	6.16	6.66	8.96	31.88	59.16	0.91	6.42	57.39	36.19	0.65
64.30	27.34	8.36	6.16	8.44	24.79	66.77	0.85	6.42	70.29	23.29	0.65
54.06	35.18	10.76	5.23	7.88	10.22	81.90	0.80	5.88	66.34	27.78	0.60
44.91	44.80	10.29	4.38	7.72	42.94	49.35	0.78	5.62	75.38	19.00	0.57
42.02	48.97	9.01	4.11	7.51	0.00	92.49	0.76	3.84	90.27	5.88	0.39
41.09	51.08	7.83	4.02	7.43	38.22	54.34	0.75	1.09	98.91	0.00	0.11
28.97	66.68	4.34	2.87								
15.1% by mass[b]											
96.07	0.00	3.93	14.59	47.67	52.33	0.00	7.82	6.20	0.00	93.80	1.09
91.36	6.26	2.38	13.98	6.99	37.38	55.63	1.23	6.02	47.19	46.79	1.06
77.89	20.34	1.77	12.17	6.56	19.68	73.75	1.15	5.74	65.95	28.31	1.01
69.99	27.28	2.73	11.07	6.55	55.85	37.60	1.15	5.22	77.37	17.41	0.92
61.98	35.79	2.23	9.93	6.27	9.99	83.73	1.10	4.31	85.35	10.34	0.76
54.48	42.01	3.51	8.83	6.20	28.54	65.25	1.09	2.02	97.98	0.00	0.36
48.77	50.53	0.70	7.98								
20.3% by mass[b]											
97.52	0.00	2.48	19.92	6.27	29.22	64.51	1.57	4.86	19.31	75.83	1.22
92.59	5.96	1.45	19.10	5.72	57.21	37.06	1.44	4.17	78.66	17.17	1.05
80.34	18.04	1.61	17.01	5.42	37.37	57.21	1.36	3.57	91.02	5.41	0.90
74.68	25.32	0.00	16.00	5.33	67.24	27.43	1.34	3.32	89.18	7.50	0.84
6.82	9.46	83.72	1.71	5.32	47.54	47.14	1.34	2.71	94.65	2.64	0.69
6.45	50.76	42.78	1.62	4.88	0.00	95.12	1.23	2.23	97.77	0.00	0.57

[a] Equilibrium percent mass fraction of salt. [b] Salt concentration in the initial saline solution.

estimated within ±0.0005 mass fraction (taking into account that cloud-point determinations involve uncertainties due to visual perception), while for tie-lines it was estimated within ±0.001. Samples of each phase for tie-line determinations were drawn with hypodermic syringes after equilibrium was reached. The analysis for the determination of the concentration of propionic acid, water, and $CaCl_2$ in the two equilibrium layers was done as previously described (Sólimo et al., 1997).

Results and Discussion

Tables 1 and 2 show the solubility data and tie-line data (both on a salt-free basis), respectively, for the system W (1) + PA (2) + B (3) + $CaCl_2$ (4) with $CaCl_2$ concentrations of 4.3%, 9.3%, 15.1%, and 20.3 mass %. The equilibrium compositions of salt were also included in both tables. The four solubility curves for the sectional quaternary planes are plotted in Figure 1, in which the tie-lines do not appear because it is not possible to show them since they do not lie in these planes and their ends do not lie on the solubility curves. These quaternary planes only contain the solubility curves and global initial mixtures for tie-lines.

As can be observed in this plot, the region of heterogeneity increases with the salt concentration adopting a band type form above 4.3% $CaCl_2$.

The effect of aqueous PA concentration on the PA distribution coefficients, m, defined as the ratio of the PA mass fraction in the organic phase to that in the aqueous phase, and on solvent selectivity, β ($= m\ w_{11}/w_{13}$, where w_{11} and w_{13} are the mass fractions of water in the raffinate and extract phases, respectively), are important factors in solvent selection. Figures 2 and 3 show the dependence of these extraction properties with the PA percent mass fraction in the extract phase on a salt-free basis $w^\circ_{23}\%$). As can be seen in Figure 2, all distribution coefficients are far greater rather than unity because PA always prefers the organic phase rather than the aqueous one. This indicates that there is a significant transfer of PA from the aqueous layer to the 1-butanol layer, which is important in extraction processes. These curves pass through maxima, increasing their values when the initial salt concentration is increased. Selectivity curves have a similar behavior (see Figure 3) with the highest value corresponding to the system with 20.3 mass % $CaCl_2$.

The distribution coefficients and selectivities trends are as follows:

$$m''' > m'' > m' > m$$

$$\beta''' > \beta'' > \beta' > \beta$$

where m, m', m'', and m''' are the experimental PA distribution coefficients for the system with 4.3%, 9.3%, 15.1%, and 20.3 mass % $CaCl_2$ on a salt-free basis and β, β', β'', and β''' are their corresponding selectivities.

Figure 4 illustrates the effect of the addition of $CaCl_2$ on the distribution ratio of propionic acid between water and 1-butanol. At the highest investigated $CaCl_2$ concentration, increments of more than 100% were observed. Similar conclusion can be obtained from Figures 2 and 3. It is evident from these plots that the salting-out effect

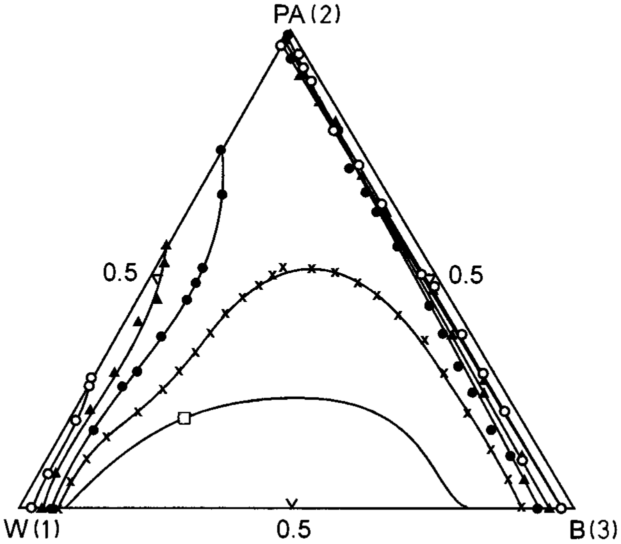

Figure 1. Projection of the solubility curves onto the face of the tetrahedron containing the ternary system water + propionic acid + 1-butanol at 303.15 K, corresponding to ×, 4.3%; ●, 9.3%; ▲, 15.1%; ○, 20.3 mass % $CaCl_2$. □, Plait point situated on the binodal curve of the ternary W + PA + B system. All solid lines are splines.

Table 2. Tie-line Data (on a Salt-free Basis) for the System Water (1) + Propionic Acid (2) + 1-Butanol (3) + Calcium Chloride (4) at 303.15 K

aqueous phase (R)			organic phase (E)		
w°_{11}%	w°_{21}%	w_{41}%	w°_{13}%	w°_{23}%	w_{43}%
		4.3 mass % $CaCl_2$			
92.1	3.4	6.0	17.5	15.4	0.2
89.8	2.7	5.3	17.1	8.4	0.3
88.6	4.9	5.3	21.1	20.7	0.2
84.7	8.0	5.7	21.2	27.7	0.3
84.1	8.9	6.1	24.6	32.1	0.3
78.4	15.4	5.4	34.1	36.7	0.9
75.6	20.0	4.9	35.8	39.7	1.2
		9.3 mass % $CaCl_2$			
93.5	1.3	9.8	17.4	8.8	0.3
91.5	2.9	10.1	15.2	16.5	0.3
90.3	5.4	10.7	18.4	27.8	0.4
86.1	8.5	11.0	21.5	37.0	0.6
81.0	14.0	11.0	29.5	46.3	1.1
79.1	16.7	9.1	33.3	45.3	1.6
		15.1 mass % $CaCl_2$			
96.9	1.5	16.5	11.3	9.9	0.3
92.0	2.8	16.3	11.8	20.3	0.3
91.4	7.4	12.7	15.2	48.7	0.7
90.7	2.4	16.4	12.2	19.5	0.3
90.3	4.8	17.4	13.8	33.9	0.6
90.3	6.6	18.0	15.1	43.4	0.4
87.0	10.7	17.2	16.6	57.6	0.9
83.9	15.3	16.1	25.4	60.9	2.0
		20.3 mass % $CaCl_2$			
97.1	0.9	21.6	9.1	11.1	0.4
94.0	4.7	21.0	11.9	39.1	0.3
91.6	7.4	21.4	13.7	52.7	0.6
90.7	9.4	22.0	18.9	60.5	0.8
89.9	7.0	21.9	13.3	51.8	0.6
87.2	2.7	22.0	9.7	24.4	0.4

occurs at all the salt concentrations investigated here, and that is very pronounced for this system.

In distributed systems to which an electrolyte is added, the effect was first correlated empirically by Sestchenow (Sestchenow, 1889) by means of the following equation

$$\ln w^\circ_{21}/w^*_{21} = kw_s \qquad (1)$$

where w^*_{21} and w°_{21} are, respectively, the aqueous phase PA mass fractions with salt and, on a salt-free basis, in equilibrium with the same solvent phase solute concentrations, w_s, is the aqueous phase salt concentration, and k is the salting-out parameter or the Sestchenow constant. The $\ln w^\circ_{21}/w^*_{21}$, plotted against the mass fraction of the aqueous salt concentration, w_s, is presented in Figure 5. The experimental value of the Sestchenow constant obtained by least squares is 1.103, with a linear correlation coefficient $r^2 = 0.9970$.

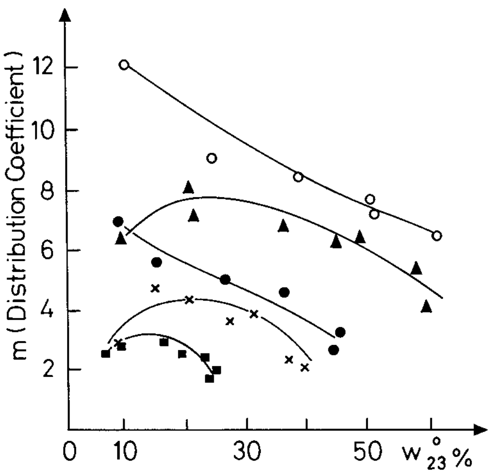

Figure 2. Distribution coefficient (m) against percent mass fraction of propionic acid in the extract phase (w°_{23}%) on a salt-free basis for the system water + propionic acid + 1-butanol with ×, 4.3%; ●, 9.3%; ▲, 15.1%; ○, 20.3 mass % $CaCl_2$. ■, no salt condition at 303.15 K. All solid lines are splines.

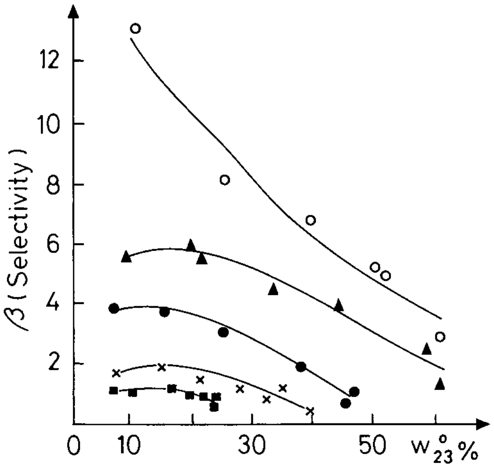

Figure 3. Selectivity (β) against percent mass fraction of propionic acid in the extract phase (w°_{23}%) on a salt-free basis for the system water + propionic acid + 1-butanol with ×, 4.3%; ●, 9.3%; ▲, 15.1%; ○, 20.3% of $CaCl_2$. ■, no salt condition at 303.15 K. All solid lines are splines.

From these experimental results we can conclude that there are some similitudes and some differences between this system and that previously studied (Sólimo et al., 1997): (i) no salt precipitation was observed at any concentration of $CaCl_2$ studied here, while for the system with NaCl this situation appears above 5% of NaCl; (ii) above 4.3% of $CaCl_2$, solubility curves are band type curves, while for the system with NaCl they are open curves interrupted by salt precipitation; (iii) up to 4.3% salt, solubility curves are closed for both systems; (iv) both systems present high values of the Sestchenow's constant, which is an indication of a great salting-out effect, but this value for the $CaCl_2$ system ($k = 1.103$) is higher than for the NaCl one ($k = 1.087$); (vi) both systems have high

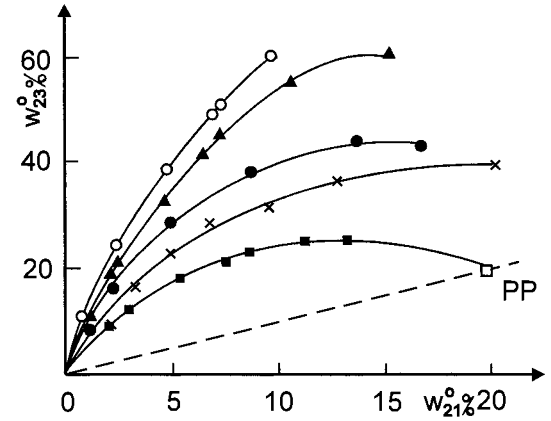

Figure 4. Distribution of propionic acid between 1-butanol and water on a salt-free basis for the system water + propionic acid + 1-butanol with ×, 4.3%; ●, 9.3%; ▲, 15.1%; ○, 20.3% $CaCl_2$. ■, no salt condition at 303.15 K. □, Plait point of the ternary system. Broken line: 45° diagonal. All solid lines are splines.

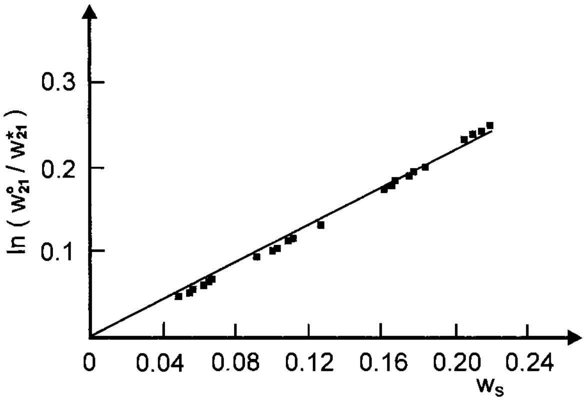

Figure 5. Sestchenow's correlation for the system water + propionic acid + 1-butanol with calcium chloride at 303.15 K. Solid line: $\ln w^\circ_{21}/w^*_{21} = 1.103 \times w_s$, from eq 1.

values of their distribution coefficients and selectivities, which is an indication that 1-butanol is a potential solvent for extraction processes.

Since the only change introduced in this study with respect to the previous one (Sólimo et al., 1997) was the substitution of the cation in the salt, all discrepancies between the two systems could be attributed to this fact. However, the nature of both salts, taken as an entity, could play an important role because the $CaCl_2$ presents a dihydrate at 303.15 K and has a solubility in water that is significantly greater than NaCl that does not have any hydrate. On the other hand, preliminary experiments carried out in our laboratory (not included in this paper) show the possibility of the presence of binary compounds between $CaCl_2$ and B and between $CaCl_2$ and PA. This is probably the reason the solubility of $CaCl_2$ in B and in PA has unusually high values. In addition, it is known that $CaCl_2$ forms ternary compounds (Bogardus and Lynch, 1943) with water and some organic chemicals, which surely modify the solid−liquid equilibrium surface in the quaternary system with respect to that for NaCl. The presence of band type solubility curves could be a consequence of these facts, which were not investigated extensively here.

Conclusions

The influence of the addition of $CaCl_2$ to the ternary system W + PA + B was analyzed at 303.15 K, projecting four sectional quaternary planes (4.3%, 9.3%, 15.1%, and 20.3% $CaCl_2$ aqueous solutions) onto the face of the tetrahedron corresponding to that ternary system. An increasing of the heterogeneous zone was observed for all quaternary planes (see Figure 1). The addition of $CaCl_2$ improves propionic acid extraction by butanol. This improvement results from the salt effect, which modifies the phase equilibria of the ternary system changing the ionic strength of the system, increasing the distribution coefficients of PA and the selectivities of butanol as the amount of salt increases.

A comparison with the effect produced by the addition of NaCl to the same ternary system was also made. The Sestchenow's constant or salting-out parameter was calculated from the experimental data giving a higher value for $CaCl_2$ than for NaCl, which is an indication that the effect of the salt is enhanced by the presence of a divalent cation and also by the special characteristics of $CaCl_2$ taken as an entity when compared with NaCl.

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