Salt Effects of Lithium Chloride, Sodium Bromide, or Potassium Iodide on Liquid−Liquid Equilibrium in the System Water + 1-Butanol

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Liquid−liquid equilibrium data for the partially miscible systems of water + 1-butanol + salt were measured at 25 °C. The salts used were lithium chloride, sodium bromide, and potassium iodide. The systems were compared in terms of salting-out efficiency and solvation effects.

Introduction

Liquid−liquid equilibria in aqueous binary systems are determined by intermolecular forces, predominantly hydrogen bonding. Addition of a salt to such a system introduces ionic forces which alter the structure of the liquids in equilibrium. The water molecules that surround the ions become unavailable for the solution of the nonelectrolyte and it becomes "salted out" from the aqueous phase. The opposite process can occur if a polar organic solvent is added to an aqueous salt solution. It captures part of the water molecules that have been solvating the ions; hence, the salt crystallizes. This effect is used in a process called extractive crystallization in which salts can be recovered from concentrated aqueous solutions by the addition of a polar organic solvent, rather than by the more expensive evaporation process. On the other hand, the salting out effect is utilized for removing organic compounds from water.

Salting effects of NaCl, KCl, and KBr in partially miscible systems of 1-butanol + water and butanone + water have been studied by Li et al. (1995). For the determination of the composition of the two phases, they used the saturation density method. Ting et al. (1992) have shown that the solvent *N*,*N*-diethylmethylamine is suitable for the extraction of NaCl and Na_2SO_4 from aqueous solutions, while Brenner et al. (1992) attemped extractive crystallization of Na_2SO_4 by 1-propanol, 2-propanol, and 2-methylpropan-2-ol. Their experimental data and subsequent analysis suggested that it was preferable to choose an extractant which is partially immiscible with water in the absence of salt. The effect of sodium chloride on aqueous systems containing isomers of propanol or butanol has been extensively studied by DeSantis et al. (1976). They found that 1-butanol is one of the most favorable solvents for desalting sea water. Gomis et al. (1994) showed that the salting out effect on the system water + 1-propanol or 2-propanol is greater with NaCl than with KCl and greater for 1-propanol than for the 2-propanol. LLE data on the system 1-propanol + water + NaCl were also obtained by Cheluget et al. (1994). Gomis et al. (1993) obtained LLE data on the system water + ethyl acetate + NaCl. The salt effect is also important in biological separation processes such as purification of proteins, enzymes, nucleic acids, and others. Voros et al. (1993) have determined the LLE for the system poly(ethylene glycol) + water in the presence of ammonium sulfate or sodium carbonate at four different temperatures and for two different molecular weights of the polymer. Finally, Malinowski and Daugulis (1993, 1994) have investigated the salt effect on the improvement of recovery of alcohols in the extractive fermentation process.

In this work LLE data were obtained for the system water + 1-butanol in the presence of LiCl, NaBr, and KI. The data obtained from these and further similar experiments will serve as a base for mathematical modeling of the salt effect on liquid−liquid equilibria.

Experimental Section

Materials. Potassium bromide, lithium chloride, sodium bromide, potassiun iodide, and 1-butanol were all analytical grade reagents supplied by Ajax Chemicals. Butanol was distilled and its purity checked by gas chromatography—no impurity peaks were found. The refractive index of 1-butanol at 20 °C was 1.399; the value from the literature is 1.3993 (Dean, 1992).

Procedure. Equilibrium measurements were made by placing equal volumes of the solvent and aqueous salt solutions of concentrations ranging from 1 mass % to saturation in a thermostated vessel on a magnetic stirrer plate. The system was stirred at 25 °C at maximum speed for 2 h. The temperature was controlled to ±0.1 deg. It was left to settle for 2 h to achieve phase separation. Samples were carefully withdrawn from both phases and analyzed. The equilibration and settling time was found to be sufficient since the concentration of the phases did not change when the time was increased. Duplicates were run for each set of concentrations, and the average value was reported.

The salt content in both phases was measured by carefully evaporating the samples to dryness. In the case of very low salt concentrations flame photometric analysis had to be used for the measurement of the salt content, as was the case with lithium chloride in the organic phase. The concentration of water and butanol was determined by gas chromatography on a 2 m × $^1/_4$ in. Porapak Q 100−120 mesh packed column using a Chrompack CP 9001 gas chromatograph. The column temperature was 240 °C, and the detection was carried out by thermal conductivity with helium at a flow rate of 20 mL/min. The analysis of the organic phase was done by using an external standard. Since the concentration of 1-butanol in the aqueous phase was low relative to water, it was determined by using ethanol as an internal standard. From standard solutions

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Table 1. Solubility of Salts in Single Solvents at 298 K

salt	solubility in water, mass % (from literature)	solubility in water, mass %, (experimental)	solubility in 1-butanol, mass %, (experimental)
KBr	40.44^a	40.70	0.017
LiCl	45.85^b	44.89	11.36
NaBr	48.61^b	48.53	0.33
KI	59.67^a	59.84	0.47

^{a} Rennard (1965). ^{b} Siedell (1940).

Table 2. LLE Data as Mass Fraction *w* for the System Water (1) + 1-Butanol (2) + KBr (3) at 25 °C

organic phase			aqueous phase		
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$
20.72	79.28	0	92.69	7.31	0
19.45	80.49	0.059	91.24	6.62	2.14
18.34	81.49	0.17	89.07	5.69	5.25
16.60	83.09	0.31	85.37	4.49	10.14
15.50	84.12	0.38	82.02	3.65	14.33
14.31	85.22	0.47	78.51	2.94	18.55
13.18	86.28	0.54	75.12	2.28	22.60
12.31	87.09	0.60	72.24	1.83	25.93
11.49	87.89	0.62	69.21	1.47	29.32
10.60	88.75	0.65	65.91	1.19	32.96
9.11^a	90.20	0.69	59.55	0.62	39.83

^{a} Saturation conditions.

the calibration factor was calculated as

$$\mathrm{CF} = \frac{\text{mass \% PrOH}}{\text{mass \% BuOH}} \times \frac{\text{area \% BuOH}}{\text{area \% PrOH}}$$

This method was adopted from Ting et al. (1992). A known mass of ethanol was added to the sample. To obtain well-defined and repeatable peaks, an injection volume of 2 μL was chosen. From the measured area ratio, the amount of internal standard, and the calibration factor, the concentration of 1-butanol was calculated. To obtain the same detector response, the composition of the calibration mixture was adjusted to resemble closely the composition of the sample. In all cases the injections were repeated at least 3−4 times and the average result reported. The salt deposition caused broadening of peaks, but that could easily be remedied by regularly changing the glass−wool lining in the injector port. The relative accuracy of the concentration measurements is approximately 0.1 mass %.

Results and Discussion

The solubilities of salts in water and pure solvent are given in Table 1. To verify the accuracy of the experimental procedure and the analysis, the LLE data for the system water + 1-butanol + KBr were measured, as shown in Table 2 and in Figures 1 and 2. They are in good agreement with the data from Li et al. (1995). The LLE data for the systems water + 1-butanol + LiCl, water + 1-butanol + NaBr, and water + 1-butanol + KI are given in Tables 3−5, respectively.

For all systems, the concentration of water in the aqueous phase decreases with increasing salt concentration. However, in the organic phase the concentration of 1-butanol increases sharply with the increasing NaBr or KBr concentration, goes through a slight minimum in the system containing KI, and exhibits a prominent maximum just below 2 mass % of salt in the case of LiCl. This change of concentration is evident in Figure 3. The water concentration changes accordingly. It drops sharply with increasing NaBr or KBr concentration and decreases gradually with KI, while in the case of LiCl it decreases sharply to about 2 mass % of salt. Thereafter, its concentration stays relatively constant, as shown in Figure 4. Such behavior can be linked to different solvation effects for the four salts. In aqueous solutions of organic solvents, ions solvate with both water and cosolvent but usually water is the preferred

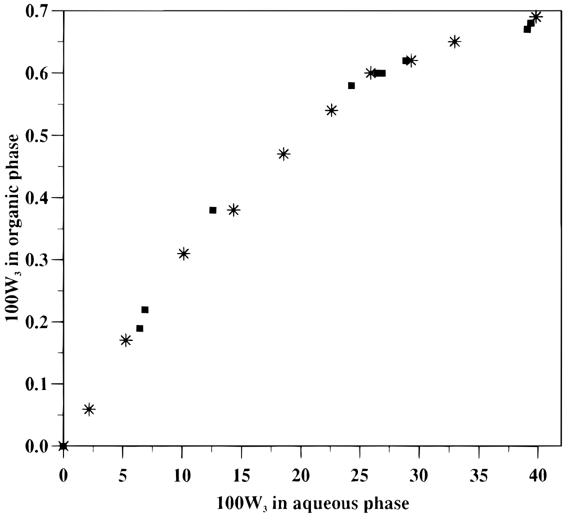

Figure 1. Distribution of KBr between water and 1-butanol at 25 °C. Comparison of this work with data from literature: (*) this work; (■) Li et al. (1995).

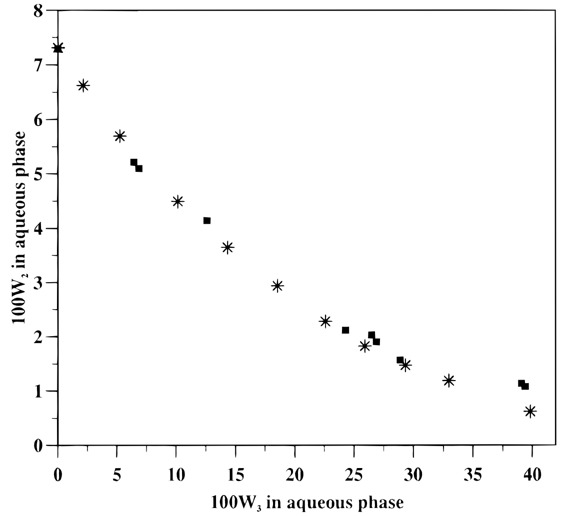

Figure 2. Salting out of 1-butanol from water by KBr at 25 °C. Comparison of this work with data from literature: (*), this work; (■) Li et al. (1995).

Table 3. LLE Data as Mass Fraction *w* for the System Water (1) + 1-Butanol (2) + LiCl (3) at 25 °C

organic phase			aqueous phase		
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$
20.72	79.28	0.00	92.69	7.31	0.00
20.09	79.90	0.007	92.75	7.01	0.24
19.61	80.37	0.019	92.58	6.86	0.56
18.79	81.16	0.044	92.29	6.60	1.11
18.45	81.49	0.066	92.11	6.26	1.63
17.85	82.07	0.083	91.78	5.99	2.23
15.53	84.20	0.27	90.25	4.64	5.11
13.05	86.43	0.52	86.86	3.38	9.76
11.62	87.41	0.97	83.59	2.25	14.16
10.76	87.44	1.80	80.07	1.69	18.24
10.87	86.15	2.98	76.99	1.30	21.71
11.07	84.30	4.63	73.95	0.97	25.08
11.38	82.46	6.16	71.58	0.77	27.65
11.43	80.59	7.98	68.37	0.57	31.04
11.26	79.51	9.23	65.72	0.42	33.86
10.93	78.52	10.56	62.71	0.30	36.99
10.38	77.88	11.76	59.70	0.20	40.11

Table 4. LLE Data as Mass Fraction *w* for the System Water (1) + 1-Butanol (2) + NaBr (3) at 25 °C

organic phase			aqueous phase		
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$
20.72	79.28	0.00	92.69	7.31	0.00
20.12	79.84	0.04	91.86	7.07	1.05
19.52	80.40	0.08	91.31	6.58	2.11
18.56	81.26	0.18	89.18	5.75	5.07
16.76	82.91	0.33	85.99	4.36	9.65
15.25	84.30	0.45	82.62	3.36	14.02
14.48	84.96	0.56	79.48	2.61	17.91
13.18	86.16	0.66	76.30	2.03	21.67
12.06	87.18	0.76	72.88	1.75	25.37
11.14	88.01	0.85	69.88	1.33	28.79
10.33	88.42	0.95	67.21	1.02	31.77
9.63	89.32	1.05	64.85	0.79	34.36
8.87	89.90	1.23	62.15	0.60	37.25
8.14	90.53	1.33	59.82	0.46	39.72
7.60	90.90	1.50	57.18	0.37	42.45
6.71	91.57	1.66	55.51	0.32	44.17
6.71	91.37	1.92	53.11	0.22	46.67
6.23[a]	91.61	2.16	51.34	0.19	48.47

[a] Saturation conditions.

Table 5. LLE Data as Mass Fraction *w* for the System Water (1) + 1-Butanol (2) + KI (3) at 25 °C

organic phase			aqueous phase		
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$
20.72	79.28	0	92.69	7.31	0
20.34	79.61	0.05	91.76	7.18	1.06
19.92	79.94	0.15	91.02	6.84	2.15
19.58	80.00	0.42	88.32	6.39	5.30
19.27	79.80	0.95	84.67	5.47	9.86
18.69	79.85	1.46	81.36	4.85	13.79
18.47	79.40	2.13	77.74	4.27	17.99
17.80	78.87	3.33	71.51	3.26	25.23
16.89	78.59	4.52	65.75	2.39	31.86
15.66	78.78	5.57	60.52	1.75	37.73
14.61	78.94	6.45	55.75	1.25	43.00
13.41	79.31	7.28	50.51	0.83	48.66
11.88	80.45	7.68	46.81	0.59	52.60
10.71	81.25	8.04	43.10	0.42	56.48
9.74[a]	82.04	8.22	40.54	0.31	59.15

[a] LLS equilibrium.

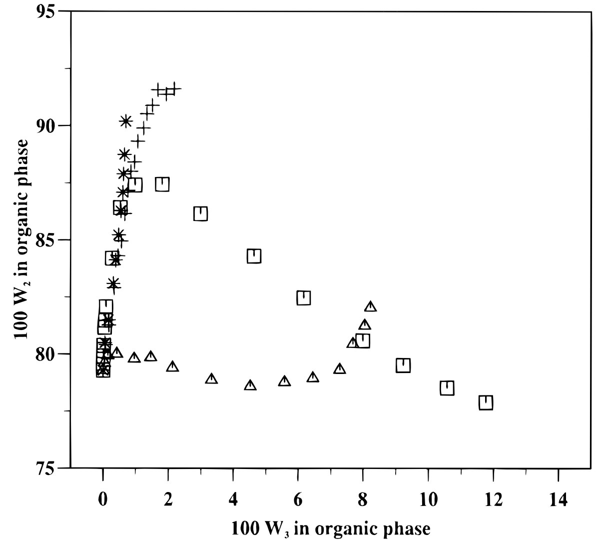

Figure 3. Change of 1-butanol concentration in the organic phase for water + 1-butanol with different salts at 25 °C: (□) LiCl; (+) NaBr; (Δ) KI; (*) KBr.

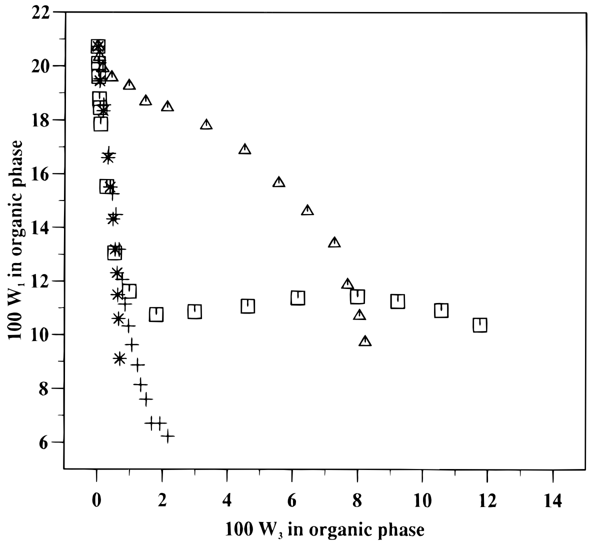

Figure 4. Change of water concentration in the organic phase for water + 1-butanol with different salts at 25 °C: (□), LiCl; (+), NaBr; (Δ) KI; (*) KBr.

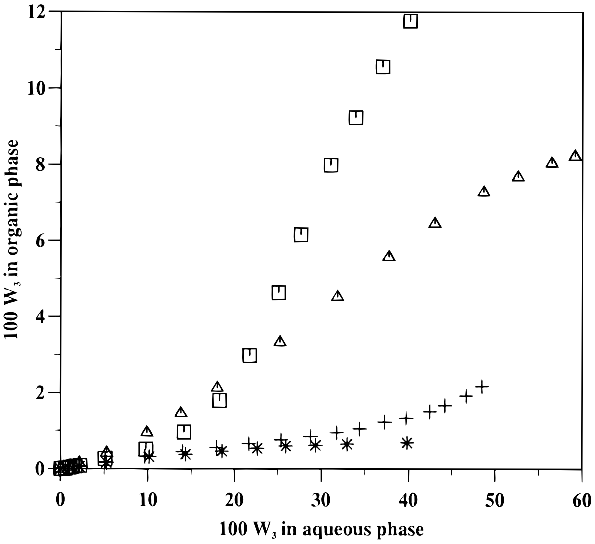

Figure 5. Distribution of salt between organic and aqueous phase for water + 1-butanol at 25 °C: (□), LiCl; (+), NaBr; (Δ), KI; (*) KBr.

component for solvation (Zerres and Prausnitz, 1994). In our case, it seems that NaBr and KBr are solvated entirely by water while with LiCl and KI the solvation equilibrium changes with the changing salt concentration, with both water and cosolvent taking part in the solvation of ions. Such behavior could be seen as additional support to the thesis that hydration phenomena must be treated as an equilibrium of various stages of hydration, as outlined by Stokes and Robinson (1973).

The solubilities of these four salts in the organic phase are shown in Figure 5. LiCl reaches the highest concentration with 11.76 mass % at saturation. The maximum concentration of KI is 8.22 mass %, while NaBr and KBr reach only 2.16 and 0.69 mass %, respectively. The solubility of NaCl in the butanol phase, measured by DeSantis et al. (1976), is 0.167 mass %. It appears that in this case the size of the ionic radii has no major influence on the solution of these salts in 1-butanol.

The concentration of 1-butanol in the aqueous phase decreases to below 1 mass % at saturation for any one of the salts studied. Over the salt concentration range the salting out efficiency decreases in the following order: LiCl > NaBr > KBr > KI, as shown in Figure 6. Gomis et al. (1994) observed that the salting out effect, in the systems water + NaCl or KCl + 1-propanol or 2-propanol, is greater

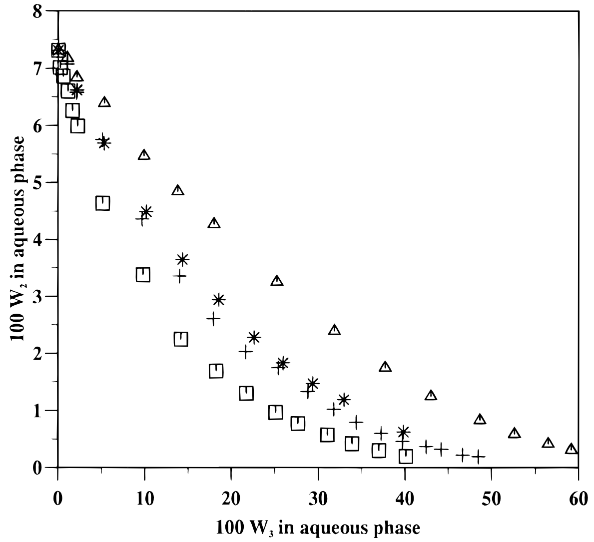

Figure 6. Comparison of salting out efficiency for water + 1-butanol with different salts at 25 °C: (□), LiCl; (+), NaBr; (Δ), KI; (*) KBr.

with NaCl than with KCl. Similarly, Eisen and Joffe (1966) found that the salting out decreased in the order LiCl > NaCl > KCl in the system water + benzene + carboxylic acid. This can be explained qualitatively (Gomis et al., 1994) using the hydration theory. Each salt ion binds a constant number of water molecules in the form of a shell of oriented water dipoles surrounding it. This "bound" water is then unavailable as solvent to the non-electrolyte. The Na^+ ion binds more molecules of water than K^+ (this is indicated by the greater decrease in the vapor pressure of aqueous solutions when adding sodium salts compared to potassium salts). Consequently, salting out is thought to be greater with NaCl than with KCl. However, contrary to the above findings, Li et al. (1995) observed that in the system water + 1-butanol + salt, KCl has a somewhat higher salting out efficiency than NaCl, with KBr being the least effective. Such results suggest that the hydration of both cation and anion, as well as the type of solvent to be salted out, play an important role in the efficiency of the salt.

Conclusion

LLE data for the system water + 1-butanol in the presence of either LiCl, NaBr or KI at 25 °C have been reported. The solvation process in the organic phase is different for all three salts; the solvation of NaBr seems to be affected by water alone, while with LiCl and KI there are mixed solvation effects. All three salts show a strong salting out effect for 1-butanol from the aqueous phase, the efficiency decreases in the order LiCl > NaBr > KI.

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