Solubilities of Salts in Mixed Solvents

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A simple and accurate apparatus for the measurement of salt solubilities in mixed solvents by an analytical method is presented. Salt solubility data have been measured at 298.15, 323.15, and 348.15 K for the following ternary systems: water + ethanol + KCl, water + 1,2-ethanediol + KCl, water + 2-methoxyethanol + KCl, water + 2-ethoxyethanol + KCl, water + 1-methoxy-2-propanol + KCl, water + 2-isopropoxyethanol + KCl, water + 2-methoxyethanol + KBr, and water + 2-butoxyethanol + KBr. The solubility of the salt was observed to decrease with rising temperature for solvent mixtures with a high concentration of glycol ether and to increase with temperature for low glycol ether contents. Liquid–liquid equilibria of some of the salt-saturated solutions have also been determined.

Introduction

The experimental study of the solubilities of salts in mixed solvents provides valuable information for scientific and industrial applications (*1*). Furthermore, liquid extraction using salt has become a useful separation process technique that has, for example, been applied to the purification of enzymes (*2*).

The existing salt solubility data in mixed solvents have been examined on the basis of two handbooks (*3, 4*) and a Chemical Abstracts computer search. The review shows inconsistencies, e.g., water + ethanol + potassium chloride ternary data sets in the handbooks can differ by up to 20%. More reliable and accurate data are, therefore, required. Furthermore, only a few systems are reported at different temperatures, and thus the solubility dependence on temperature cannot be evaluated.

In this work we have designed an experimental setup based on an analytical method (*5*) to perform the desired solubility measurements. We have defined a series of systems to be measured in order to create a base for future modeling work.

Experimental Section

Materials. Double-distilled water has been used. The supplier purities of the other components are listed in Table I. For organic solvents the water content has been measured by a coulometric Karl-Fischer titration (*6*). These water determinations are used to correct the directly calculated solvent mixture compositions.

Apparatus and Procedures. Figure 1 shows the apparatus for the measurement of the solubilities of salts in mixed solvents.

The jacketed glass cell (110 cm³) is charged with dried salt and with a solvent (about 80 cm³) of gravimetrically prepared composition, with a precision of 0.1 mg. The amount of salt is to be in small excess relative to the highest estimated solubility in the chosen amount of solvent. The cell is closed during the measurements, and care is taken to ensure a sufficient liquid:vapor ratio so that the solvent composition is not changed due to evaporation.

The temperature of the cell is controlled by circulating thermostated water in the jacket, and it is considered to be accurate within ±0.1 K. In order to avoid formation of microcrystals, the solubilities are determined on a cooling cycle. Normally, the temperature is first set at 353 K, and then the solubilities are measured at 348.15, 323.15, and 298.15 K. At each temperature, the mixture is stirred for $1^1/_2$ h and then allowed to settle for $^1/_2$ h before sampling.
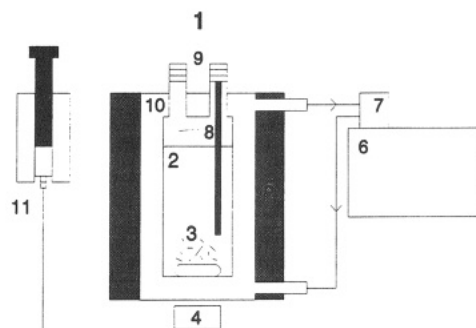

Figure 1. Apparatus for solubility measurements: 1, jacketed glass cell; 2, solution; 3, excess of salt; 4, magnetic stirrer; 5, insulation; 6, insulated bath; 7, thermostat and pump; 8, thermometer; 9, caps and septa; 10, jacket; 11, thermostated syringe.

Table I. Sources and Purities of the Used Compounds

substance	supplier	purity/ (mass %)	measd water content/(mass %)
ethanol	Merck	min 99.8	0.026
1,2-ethanediol	Merck	min 99.5	0.012
2-methoxyethanol	Merck	min 99.5	0.029
2-ethoxyethanol	Aldrich	99+	0.044
1-methoxy-2-propanol	Aldrich	98	0.025
2-isopropoxyethanol	Aldrich	99	0.045
2-butoxyethanol	Merck	>99	0.022
potassium chloride	Merck	min 99.5	
potassium bromide	Merck	min 99.5	

The salt solubility is determined by evaporating the solvent blandly from a sample of saturated solution (3–5 cm³) and weighing the precipitated salt. The sample is withdrawn from the cell with a thermostated metal syringe at a temperature 5 K above the equilibrium temperature. This procedure was found to be safe, so that no sample stratification has been detected. Each salt solubility is an average of two repeated measurements with a reproducibility of less than 0.1 mass %. In the case of liquid–liquid equilibria this reproducibility of the salt solubilities may not be quite obtained, because the total concentration of the solvent mixture is slightly changed when the samples of the two different liquid phases are withdrawn.

The apparatus can also be used to measure liquid–liquid equilibrium data of salt-saturated solutions. It should be emphasized that more settling time is required for a complete phase split. From each of the liquid phases two samples are withdrawn for each measurement. One sample is used for

Table II. Solubilities of Salts in Various Mass Fractions of Water (w_1')

100w_1' [a]	100w_3 [b]		
	298.15 K	323.15 K	348.15 K
Water (1) + Ethanol (2) + Potassium Chloride (3)			
0.026	0.024	0.032	0.051
8.003	0.109	0.159	0.238
18.947	0.588		
20.098		1.034	1.407
55.808	7.801	10.942	13.520
89.064	20.935	24.726	28.044
100.000	26.387	29.966	33.092
Water (1) + 1,2-Ethanediol (2) + Potassium Chloride (3)			
0.012	4.983	5.686	6.372
5.896	5.365	6.415	7.288
14.419	6.527	7.778	9.016
34.497	10.001	12.064	14.096
55.683	14.753	17.614	20.300
77.948	20.436	23.928	26.872
Water (1) + 2-Methoxyethanol (2) + Potassium Chloride (3)			
0.029	0.429	0.349	0.240
4.674	0.761	0.676	0.630
10.385	1.283	1.325	1.386
18.556	2.258	2.516	2.916
31.630	4.432	5.481	6.511
52.256	9.544	11.922	14.158
Water (1) + 2-Ethoxyethanol (2) + Potassium Chloride (3)			
0.044	0.084	0.059	0.039
3.963	0.162	0.156	0.133
9.921	0.392	0.442	0.501
15.025	0.797	0.930	1.163
26.133	2.246	3.040	3.770
51.431	8.055	10.970	13.406
Water (1) + 1-Methoxy-2-propanol (2) + Potassium Chloride (3)			
0.025	0.031	0.023	0.019
3.765	0.079	0.066	0.062
8.884	0.226	0.270	0.280
16.586	0.796	1.034	1.258
28.298	2.481	3.336	4.258
50.530	7.820	10.436	12.888
Water (1) + 2-Isopropoxyethanol (2) + Potassium Chloride (3)			
0.045	0.022	0.020	0.016
2.862	0.044	0.042	0.040
8.180	0.173	0.194	0.216
15.029	0.629	0.840[c]	1.050[c]
33.628	4.090		
65.252	13.484		
Water (1) + 2-Methoxyethanol (2) + Potassium Bromide (3)			
0.029	3.926	3.065	2.369
3.482	4.898	4.312	3.764
9.616	6.738	6.679	6.564
19.294	9.889	10.664	11.417
32.685	14.669	16.793	18.633
54.185	22.636	26.411	29.571
100.000	40.665	44.946	48.394
Water (1) + 2-Butoxyethanol (2) + Potassium Bromide (3)			
0.022	0.158	0.124	0.090
3.065	0.398	0.375	0.334
6.606	1.071	1.151	1.194
9.201	1.858[c]	2.113[c]	2.290[c]

[a] w_1' = water mass fraction in salt-free solvent mixture. [b] w_3 = solubility of salt in mass fraction. [c] Data follow in Table III for liquid-liquid equilibria.

the determination of salt solubility and one for the determination of water content in the solvent mixture by means of a coulometric Karl-Fischer titration (6).

Results and Discussion

The experimental solubility results are reported in Tables II and III.

Measured and Literature Data. Measurements for the two systems, with ethanol (3, 4) and 1,2-ethanediol (7), have

Table III. Liquid-Liquid Equilibria and Salt Solubility Measurements

T/K	upper phase		lower phase	
	100w_1' [a]	100w_3 [b]	100w_1' [a]	100w_3 [b]
Water (1) + 2-Isopropoxyethanol (2) + Potassium Chloride (3)				
312.55[c]	61.080	14.498		
312.55[c]	60.902	14.475		
313.15	49.191	10.853	70.088	17.597
313.15	51.388	11.320	68.719	17.182
323.15	27.809	3.770	91.580	25.488
323.15	28.603	3.782	92.496	25.613
348.15	18.534	1.892	96.392	30.786
348.15	18.774	1.885	96.553	30.732
358.15	17.705	1.664	98.062	32.214
Water (1) + 2-Butoxyethanol (2) + Potassium Bromide (3)				
280.45[c]	73.648	27.342		
280.85	60.517	22.927	87.886	32.330
280.85	60.752	22.855	88.214	32.352
298.15	21.408	7.746	97.316	39.806
298.15	21.671	7.721	97.294	39.314
323.15	13.014	4.028	98.826	44.099
323.15	13.243	4.138	98.533	44.267
348.15	9.689	3.001	98.904	47.859
348.15			98.621	48.028

[a] w_1' = water mass fraction in salt-free solvent mixture. [b] w_3 = solubility of salt in mass fraction. [c] Lower critical solution temperature, only one phase.
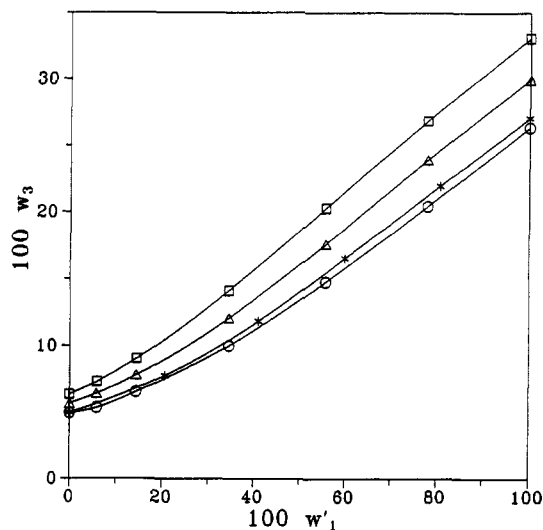

Figure 2. Salt solubility diagram for water (1) + 1,2-ethanediol (2) + potassium chloride (3): w_3, solubility of salt in mass fraction; w_1', water mass fraction in salt-free solvent mixture; O, 298.15; *, 303 (7); △, 323.15; and □, 348.15 K.

been presented in the literature by other researchers. Figure 2 shows the agreement between the only isotherm at 303 K given in the literature (7) and our measured data for 1,2-ethanediol.

It is important to point out that deviations of less than 0.5% from the published (3, 4, 8) salt solubilities in pure water for the three temperatures have been found.

Temperature Dependence of Salt Solubility. For all the systems with glycol ethers with a high concentration of glycol ether the salt solubility decreases with rising temperature. Figure 3 illustrates this behavior and also shows that the effect is more pronounced for potassium bromide than for potassium chloride. To emphasize the differences in the solubilities and the solvent compositions, the figures have been drawn using units of either mass percent or mole fraction, depending on which will give the best visual representation.

Split into Two Liquid Phases. Liquid-liquid equilibrium data of salt-saturated solutions have been measured for
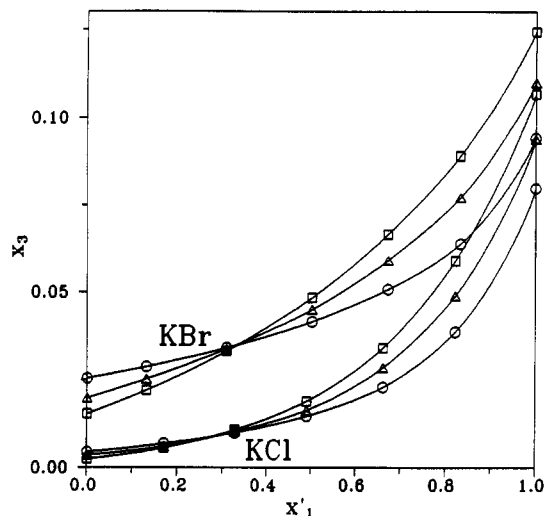
Figure 3. Salt solubility diagram for water (1) + 2-methoxyethanol (2) + potassium chloride (3) and potassium bromide (3): x_3, mole fraction of salt; x_1', water mole fraction in salt-free solvent mixture; O, 298.15; △, 323.15; and □, 348.15 K.
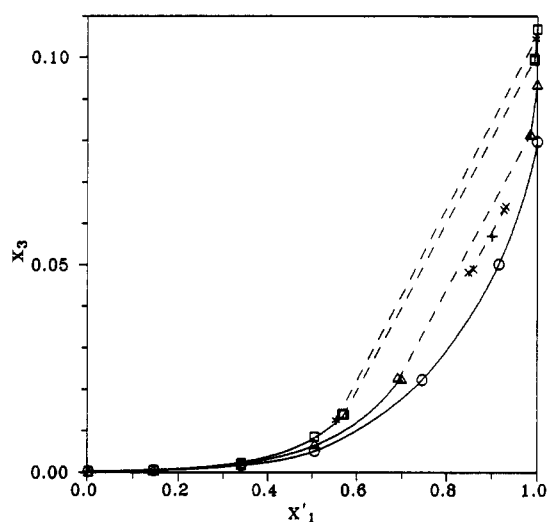

Figure 4. Solubility diagram for water (1) + 2-isopropoxyethanol (2) + potassium chloride (3): x_3, mole fraction of salt; x_1', water mole fraction in salt-free solvent mixture; O, 298.15; +, 312.55; ×, 313.15; △, 323.15; □, 348.15; and *, 358.15 K.

the systems with 2-isopropoxyethanol and 2-butoxyethanol, and the results are shown in Table III. It is interesting to observe that the binary water + 2-isopropoxyethanol is completely miscible. However, by adding a third component,
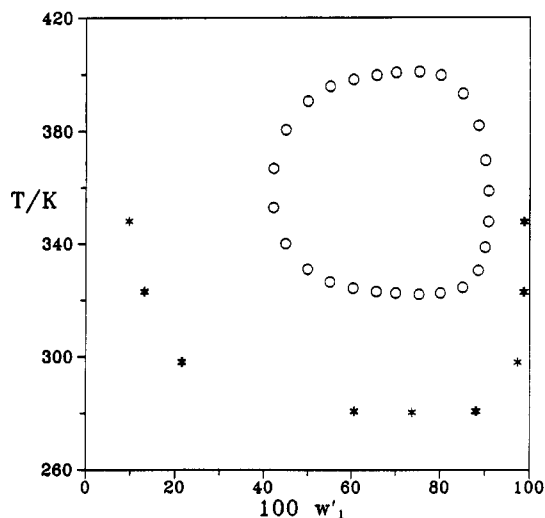

Figure 5. Temperature–composition diagram for water (1) + 2-butoxyethanol (2) + potassium bromide (3): *, concentration of salt-saturated solutions; and O, binary data for water (1) + 2-butoxyethanol (2) from ref 9.

potassium chloride, we get a two-liquid-phase region beginning at 312.55 K as is shown in Figure 4. Solutions whose temperatures are very close to or at the critical temperature showed a formation of a light blue color. A temperature–composition plot, Figure 5 compares literature liquid–liquid equilibrium data (9) for the binary water + 2-butoxyethanol system with the measured concentrations of the salt-saturated solutions. It is clear that the addition of potassium bromide increases the immiscibility gap.

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