Solubility of NaCl, NaBr, and KCl in Water, Methanol, Ethanol, and Their Mixed Solvents

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The solubilities of sodium chloride, sodium bromide, and potassium bromide in the solvents water, methanol, ethanol, and methanol + ethanol as well as those of sodium bromide in water + methanol and sodium bromide and potassium chloride in water + ethanol mixed solvents were measured in the range between 298.15 and 348.15 K using an analytical gravimetric method. When possible, the reliability of the method was checked by comparing the experimental data with literature values. The method proved to be very accurate, and the solubilities are generally reproducible when compared to the data reported in the literature.

Introduction

The study of phase equilibria in salt-containing systems is very important for many industrial applications. More particularly, a knowledge of accurate solubilities is needed for the design of separation processes such as extractive crystallization[1] or for the safe operation of different processing units such as distillation columns, absorption units, and extraction plants.[2] They can also be useful for theoretical studies relating solubility to ionic radii or other possible solvation parameters[3] and for calculating the salt solubility product or the ion-pair association constants applying the Pitzer−Simonson[4] or the Clegg−Pitzer[5] equations.

Whereas for aqueous electrolyte systems solubility is generally available for many salts, namely, in the compilation books by Stephen and Stephen[6,7] or Linke and Seidell,[8,9] for organic solvents or aqueous−organic mixed solvents data is very scarce, obsolete, or not available at all.[2]

Therefore, a program for systematic measurements was implemented to measure the solubility of NaCl, NaBr, KCl, and KBr in the temperature range between 298.15 and 353.15 K in the pure solvents water, methanol, and ethanol, and their binary mixed solvents over the whole solvent composition range. Because some of the experimentally measured solubilities had already been published,[10,11] in this work the final series of measurements is presented.

Experimental Section

Chemicals. In all experiments, distilled deionized water was used. All other chemicals were supplied by Merck; salts NaCl, KCl, and NaBr with a purity higher than 99.5% and solvents methanol and ethanol with a minimum purity of 99.8% were employed with no further purification. To avoid water salt contamination, salts were dried at 393.15 K in a drying stove for more than 2 days before use.

Procedure. A detailed description of the procedure has been presented,[11] so only a brief explanation of the analytical gravimetric method used to perform the measurements is given. The method consists on the preparation of a saturated solution at constant temperature (±0.1 K). The equilibrium cell is charged with known masses (±0.1 mg) of all components, and to reach solution equilibrium conditions, stirring is carried out for at least 3 h at the working temperature. Then the solution is allowed to settle at least $^1/_2$ h before sampling with a heated syringe. The total solvent evaporation is achieved in two stages. Initially, the samples are placed on a heating plate, enhancing the formation of salt crystals, which are then completely dried in an oven at 393.15 K. The samples remain in the oven for more than 3 days and are then cooled in a drier with silica gel for 1 day. Finally, they are weighed, and the process is regularly repeated until a constant mass is achieved. Each experimental point is an average of at least three different measurements obeying one of the following criteria. If the solubility is higher than 10 (mass percent), then the quotient $\{2s\}/\{\text{solubility}\} \times 100$ should be less than 0.1, where s is the standard deviation within a set of different experimental results. If the experimental solubility is less than 10%, then this criterion is difficult to attain, and instead the standard deviation s should be less than 0.005.

Results and Discussion

Binary Systems. In Table 1, the measured solubilities of the salts in water, methanol, and ethanol at different temperatures are reported. The water + salt systems were studied in a temperature range between 298.15 and 353.15 K, whereas for systems with methanol the maximum temperature is 333.15 K. The ethanol + salt systems were studied at only three different temperatures: 298.15, 323.15, and 348.15 K because the salt solubilities are too low or the temperature dependence is not pronounced.

The quality of the measured data may be investigated by comparing it with literature values reported in the compilation books[6−9] and in the open literature; for the water + salt binary systems, the comparisons can be easily done because of the extensive amount of published data. In some cases, the amount of consistent data presented in the compilation books is enough to make an average curve fit for a better graphical comparison with the more recently

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Table 1. Solubility (Mass Fraction, w) in Pure Solvents at Different Temperatures

T/K	100w		
	NaCl	NaBr	KCl
	Water		
298.15	26.483	48.620	26.476
303.15	26.550	49.583	27.257
313.15	26.701	51.571	28.728
318.15		52.673	
323.15	26.889	53.838	30.094
328.15		54.015	
333.15	27.106	54.087	31.366
343.15	27.338	54.281	32.582
348.15	27.478	54.369	33.146
353.15	27.602	54.495	33.709
	Methanol		
298.15	1.375[a]	14.938	0.539[a]
303.15	1.360	14.754	0.554
313.15	1.310	14.461	0.593
323.15	1.235[a]	14.196	0.630[a]
333.15	1.220	13.941	0.670
	Ethanol		
298.15	0.055[a]	2.496	0.034
323.15	0.065[a]	2.416	0.039
348.15	0.077[a]	2.297	0.049

[a] Reference 10.

published data. That is shown in Figure 1 for the systems water + NaCl and water + KCl. From Figure 1, it is possible to observe the good agreement of the data, even if the solubilities measured in this work are systematically higher (around 0.05 g of NaCl per 100 g of solution) when compared with the values of Farelo et al.[12] Although the data reported by Farelo and collaborators are clearly in better accordance with the average curve, they have used the polythermal synthetic method, which is not the most adequate because the temperature exhibits little influence on the NaCl solubility.[13] It seems that this is the main reason for the unexpected irregular trend shown by their experimental data at low temperatures because the solubility is almost constant until 300 K.

Comparing the solubilities measured here and the ones reported by Farelo et al.[12] for the system water + KCl at different temperatures, it is possible to observe in Figure 1 a better agreement than for the previous system. Now, the systematically higher deviations do not occur. At lower temperatures, the solubility measured in this work is only slightly superior, whereas at higher temperatures it is slightly inferior. The solubilities measured by Zhang et al.[14] with a new method combining the polythermal and isothermal synthetic methods are also displayed, showing higher deviations from the average curve.

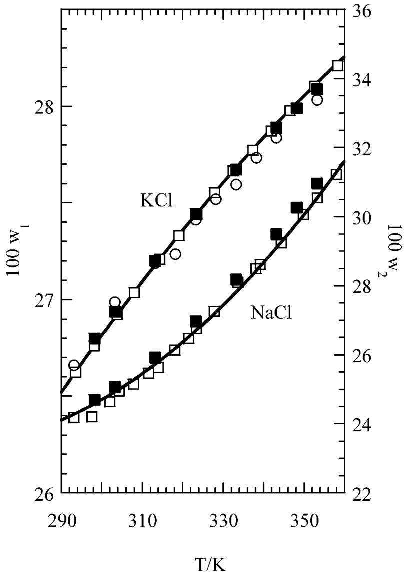

Figure 1. Comparison of the solubility of NaCl (1) and KCl (2) in water at different temperatures: □, Farelo et al.;[12] ○, Zhang et al.;[14] ■, this work. Lines represent average curves.

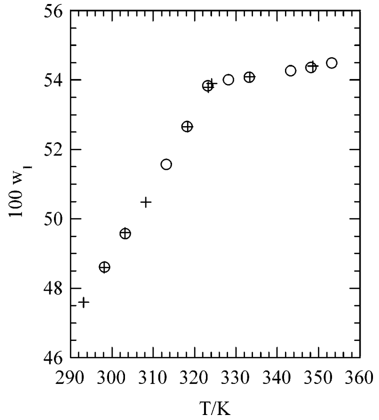

Figure 2. Comparison of the solubility of NaBr (1) in water at different temperatures: +, Linke and Seidell;[8] ○, this work.

As can be observed from Figure 2 for the NaBr + water system, it was also possible to find good agreement of the data measured in this work with the values compiled by Linke an Seidell.[8] The solubility change with temperature is very different from that of the precedent systems; up to 323.15 K, the solubility increase is very evident, but beyond that value, it is almost constant. The observed breaking behavior corresponds to a solid-phase transition. According to Rard and Archer,[15] the transition occurs at 323.98 K; below this temperature, the solid phase is $NaBr{\cdot}2H_2O$, and above it, the solid phase is NaBr.

The experimental results measured in this work can be used to estimate the transition temperature by making two linear fits, one with the experimental results until 323.15 K and the other with the results obtained at temperatures higher than this one. The intersection of these two lines should give the transition temperature. Using the data presented in Table 1, the calculated value for that temperature is 324.00 K, which in comparison with the value given by Rard and Archer[15] is good support for the quality of the data measured in this work.

Concerning the salt + alcohol systems, it is worthwhile first to notice the inverse salt solubility temperature dependence—the salt solubility decreases with rising temperature for salts NaCl in methanol and NaBr in methanol and ethanol. This unusual effect of the temperature on the solubility, although unforeseen for a given system, may be explained both by Debye–Hückel and ion association Bjerrum theories[16] because at such low ionic concentrations the electrostatic interactions are more pronounced and association is favored by the lower dielectric constant. This effect and the change in the association constant with temperature influence the salt solubility in organic solvents.

It has already been mentioned that solubility data of salts in alcohols at different temperatures are scarce. Thus, the same kind of comparison as for aqueous systems was possible only for the system methanol + NaBr. As can be seen from Figure 3, the measured solubilities of NaBr in methanol reported by Stephen and Stephen[6] present values that are somewhat different from those obtained in this work.

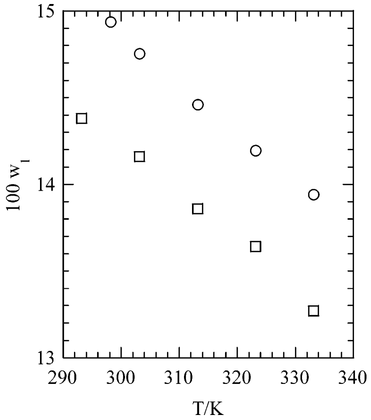

Figure 3. Comparison of the solubility of NaBr (1) in methanol at different temperatures: □, Stephen and Stephen;[6] ○, this work.

Table 2. Solubility (Mass Fraction, *w*) in Water + Methanol and Methanol + Ethanol Mixed Solvents

	100*w*	
$100w_1$[a]	298.15 K	323.15 K
	Water (1) + Methanol (2) + NaBr (3)	
10.00	18.772	18.532
20.00	23.524	23.465
30.00	28.258	28.326
40.00	32.634	32.829
49.98	35.862	36.931
59.98	38.339	40.793
69.99	41.070	44.306
79.99	43.716	47.686
89.99	46.245	50.910
	Methanol (1) + Ethanol (2) + NaCl (3)	
20.01	0.139	0.140
40.18	0.331	0.288
59.77	0.548	0.517
80.01	0.885	0.818
	Methanol (1) + Ethanol (2) + NaBr (3)	
10.07	3.406	3.264
19.87	4.497	4.287
30.01	5.835	5.522
40.13	6.985	6.636
50.03	8.266	7.873
59.96	9.579	9.110
70.00	11.033	10.438
79.97	12.226	11.603
89.99	13.568	12.918
	Methanol (1) + Ethanol (2) + KCl (3)	
20.01	0.065	0.078
39.95	0.117	0.138
60.11	0.204	0.259
80.15	0.352	0.424

[a] w_1 mass fraction of component 1 on a salt-free basis.

Unfortunately, no reliable or more recent data were found for that system in order to carry out a better data evaluation. In this way, a comparison for the solubilities values at 298.15 K was done; in the compilation books,[6,7] that solubility was found to be between 14.79 and 15.888 g of NaBr in 100 g of saturated solution, which includes our measured value. This procedure was repeated for all other salt + alcohol systems for which it was possible to find a much higher consistency.

Ternary Systems. In Table 2, the measured solubilities at 298.15 and 323.15 K for NaBr in water + methanol and for NaCl, NaBr, and KCl in methanol + ethanol solvents are presented.

For the methanol + ethanol solvent mixtures, the only data set found for comparison was for NaBr at 298.15 K. However, the values showed high inconsistency for the pure solvents' solubility, and no comparison is presented. Therefore, only for the water + methanol + NaBr system at 298.15 K is it possible to analyze the data agreement with other sources. In Figure 4, it is possible to observe the good agreement between our data and that compiled by Stephen and Stephen.[7] Additionally, for that set the reported solubility value in pure methanol is, at 298.15 K, 14.8 g of NaBr in 100 g of saturated solution, which is good support for our measured data for the solubility of NaBr in pure methanol.

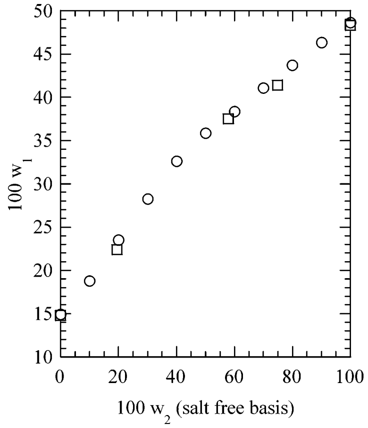

Figure 4. Comparison of the solubility of NaBr (1) in water (2) + methanol (3) solvent mixtures at 298.15 K: □, Stephen and Stephen;[7] ○, this work.

Table 3. Solubility (Mass Fraction, *w*) in Water + Ethanol Mixed Solvents

	100*w*			100*w*
$100w_1$[a]	298.15 K	323.15 K	$100w_1$[a]	348.15 K
	Water (1) + Ethanol (2) + NaBr (3)			
10.00	8.527	8.840	10.00	9.051
20.00	13.648	16.277	20.00	16.491
30.00	19.808	23.009	30.00	23.299
40.00	25.124	28.905	40.00	29.328
50.00	29.119	34.121	50.00	34.637
60.00	34.007	38.689	60.00	39.224
70.00	37.928	42.876	70.00	43.501
80.00	41.662	46.706	79.99	47.266
90.00	45.162	50.276	89.99	50.892
	Water (1) + Ethanol (2) + KCl (3)			
10.00	0.164	0.254	10.00	0.344
20.00	0.685	1.064	20.00	1.458
30.00	1.874	2.834	29.99	3.796
40.04	3.759	5.544	40.00	7.206
50.00	6.198	8.828	50.00	11.189
60.00	9.123	12.519	60.00	15.415
70.00	12.544	16.436	70.00	19.666
80.00	16.589	20.666	79.44	23.745
89.98	21.352	25.225	89.81	28.452

[a] w_1 mass fraction of component 1 on a salt-free basis.

In Table 3, the measured solubilities at 298.15, 323.15, and 348.15 K for KCl and NaBr in water + ethanol solvents are shown. Although for NaBr it was not possible to find any data for comparison, in Figure 5 our data is compared with that published by Chiavone-Filho and Rasmussen[17] at 298.15 K and 348.15 K and by Delesalle and Heubel[18] and Galleguillos et al.[19] at 298.15 K for the water + ethanol + KCl system. A good resemblance is obtained at the different temperatures over the entire solvent composition range.

Conclusions

The simple apparatus designed for the measurement of salt solubilities in mixed solvents using an analytical

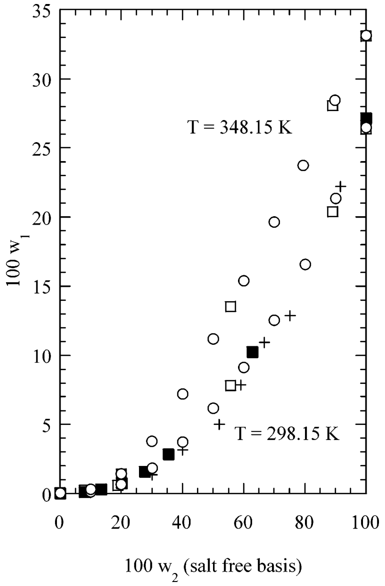

Figure 5. Comparison of the solubility of KCl (1) in water (2) + ethanol (3) solvent mixtures at different temperatures: □, Chiavone-Filho and Rasmussen;[17] ■, Delesalle and Heubel;[18] +, Galleguillos et al.;[19] ○, this work.

method proved to be very successful; high precision and accurate results were obtained, and the solubilities are generally reproducible when compared to the values reported in the literature.

The systematized experimental study implemented is an important contribution to the fulfillment of the great demand for salt solubility in nonaqueous and mixed solvent systems; a high number of new experimental solubilities have been measured for the salts NaCl, KCl, and NaBr in the pure solvents water, methanol, ethanol and in the mixed solvents water + methanol, water + ethanol, and methanol + ethanol at different temperatures.

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