

Solubility of KBr in Binary Solvents Formed by Acetone and Water in the Temperature Range between (288.15 and 313.15) K

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The solubility of potassium bromide in binary solvents formed by acetone and water was determined in the temperature range between (288.15 and 313.15) K at atmospheric pressure using an isothermal method. The reliability of the measured method used in this study was checked by comparing the experimental data with published data in the literature for the KBr–water system, and the method proved to be accurate. Experimental solubility data were correlated with Sechenov's equation.

Introduction

The investigation of phase equilibria in electrolyte systems and salt-containing systems is extremely important from either a scientific or an industrial point of view. Moreover, knowledge of solubility is very essential as a support for the design and simulation of unit operations such as crystallization and solvent selection of reaction and separation process.^{1,2} Furthermore, the solubility data can give important information about solution structures and can be used for other theoretical studies of classical thermodynamics. Solubility data, together with other properties of solvents, may also be used to correlate and predict salt solubility under different conditions.

Solubility studies on aqueous electrolyte systems have had considerable attention recently. The solubility data of various salts in aqueous electrolyte systems have been published, as evidenced in, for example, compilation books by Stephen and Stephen,^{3,4} Linke and Seidell,^{5,6} and other literature. Even the solubility of salts in organic or aqueous–organic mixed solvents is considered to be very important in the theoretical study and application of industrial processes, although data reported were not very comparable. In recent years, the investigation of the solubility of inorganic salts and of the properties of salt solutions in mixed water–organic solvents has been of great scientific interest^{7–9} because this information can be used to establish a relationship between aqueous and nonaqueous solutions of salts and to estimate a change in the properties of the solution with the properties of the solvent. As reported in ref 10, the production of KBr occurs from the reaction of bromide and potassium carbonate to make a solution of KBr. The solution requires evaporation crystallization, which costs a lot of energy. The energy cost can be reduced by antisolvent crystallization. This is a basic study for the new technology development of KBr production from KBr solution. To increase the basic data and to discover a new technology for separation of KBr from solution, we experimentally measured the solubility of KBr in the solvent formed by (CH₃)₂CO–H₂O in the temperature range of (288.15 to 313.15) K at atmospheric pressure.

Experimental Section

Materials. Distilled–deionized water was used in all experiments as a part of the solvent. All of the other chemicals were

supplied by Tianjin Chemical Reagent, China. The purity of commercial KBr is greater than 0.995 in mass fraction, and the purity of commercial acetone is said to be greater than 0.998 in mass fraction. To avoid the effect of water in the salt on the amount of water in the system, the commercial KBr was dried at $T = 393.15$ K in an oven for longer than 2 days. The purity of KBr was measured to be 0.9968 after drying, and the dried KBr was used in the experiment. The acetone was also analyzed before use in the experiments. The analyzed mass fraction of acetone was 0.9985.

Apparatus and Procedure. The solubility of potassium bromide in water–acetone solution was investigated by the isothermal method. The experiments were carried out in a thermostat. A constant temperature (± 0.05 K) of the thermostat was maintained during the experimental period. The samples were made by adding enough potassium bromide in water–acetone solvents at various concentrations according to the conditions of the experiment. The solvent and KBr solid were put in a cuvette and stirred for at least 12 h at the working temperature to ensure that the solution was in equilibrium with the potassium bromide solid. After stirring was stopped for at least 0.5 h, the clear solution was sampled with a heated syringe. The sample and syringe were weighed together before the solution was transferred to a measuring flask; then, only the syringe was weighed. The precise amount of solution was obtained. The sample solution was then dried in an oven at 333.15 K for 6 h to be sure that the free water and acetone were evaporated, and the temperature in the oven was increased to 393.15 K and was kept constant for more than 6 h. The dried potassium bromide was weighed for use in the solubility calculation. To identify the effect of sublimation on the sample analysis accuracy, the weight loss of the dried KBr was measured in the oven at 393.15 K. After the sample had been in the oven for 24 h, the weight loss was below 0.02 %. This means that the sublimation of KBr can be ignored during the sample drying. Three parallel experiments were arranged for each solubility data point, and the average value was used as the final data for the solubility. The mean deviation is within 0.2 %.

Results and Discussion

To prove the accuracy of the experimental method used in this study, we measured the solubility of KBr in the pure water

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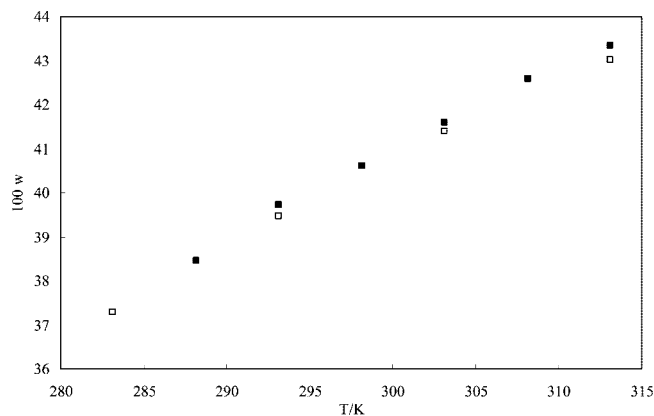


Figure 1. Comparison of the KBr solubility (mass fraction, w) in water at different temperatures: \square , data from ref 10; \blacksquare , this work.

Table 1. Solubility of KBr (Mass Fraction, w) in (Water + Acetone) Solvents from $T = (288.15$ to $313.15)$ K

100 w_2	288.15 K			293.15 K			relative error (%)
	100 w_{exptl}	100 w_{calcd}	relative error (%)	100 w_2	100 w_{exptl}	100 w_{calcd}	
0.00	38.50	38.50	0.00	0.00	39.70	39.70	0.00
3.00	38.07	37.41	-1.81	3.00	38.62	38.56	-0.15
6.00	36.90	36.36	-1.62	6.00	37.40	37.45	0.13
9.00	35.56	35.33	-0.87	9.00	36.10	36.37	0.74
12.00	34.53	34.34	-0.87	12.00	35.09	35.32	0.67
14.00	33.60	33.69	-0.10	14.00	34.10	34.64	1.58
16.00	32.50	33.05	1.28	16.00	33.29	33.97	2.03
19.00	31.48	32.12	1.55	19.00	32.20	32.99	2.45
22.00	30.52	31.21	1.68	22.00	31.20	32.04	2.69
25.00	29.31	30.33	2.81	25.00	30.30	31.12	2.69
298.15 K							
0.00	40.61	40.60	-0.01	0.00	41.58	41.60	0.04
3.00	39.75	39.44	-0.78	3.00	40.65	40.42	-0.59
6.00	38.67	38.31	-0.95	6.00	39.49	39.26	-0.58
9.00	37.57	37.21	-0.96	9.00	38.26	38.14	-0.31
12.00	36.42	36.14	-0.76	12.00	37.32	37.05	-0.72
14.00	35.20	35.45	0.70	14.00	36.34	36.35	0.03
16.00	34.20	34.77	1.66	16.00	35.49	35.65	0.47
19.00	33.60	33.77	0.51	19.00	34.28	34.64	1.05
22.00	32.60	32.80	0.62	22.00	33.22	33.65	1.31
25.00	31.50	31.86	1.15	25.00	31.82	32.69	2.72
303.15 K							
0.00	42.59	42.60	0.03	0.00	43.33	43.30	-0.08
3.00	41.29	41.39	0.24	3.00	42.16	42.08	-0.18
6.00	40.37	40.22	-0.38	6.00	41.04	40.89	-0.36
9.00	38.99	39.08	0.22	9.00	39.85	39.74	-0.28
12.00	37.92	37.98	0.12	12.00	38.73	38.62	-0.28
14.00	37.23	37.25	0.05	14.00	37.91	37.89	-0.06
16.00	36.21	36.54	0.91	16.00	37.09	37.17	0.23
19.00	35.10	35.50	1.16	19.00	35.86	36.12	0.74
22.00	33.62	34.50	2.60	22.00	34.56	35.10	1.58
25.00	32.46	33.52	3.26	25.00	33.12	34.11	3.00
308.15 K							
0.00	42.59	42.60	0.03	0.00	43.33	43.30	-0.08
3.00	41.29	41.39	0.24	3.00	42.16	42.08	-0.18
6.00	40.37	40.22	-0.38	6.00	41.04	40.89	-0.36
9.00	38.99	39.08	0.22	9.00	39.85	39.74	-0.28
12.00	37.92	37.98	0.12	12.00	38.73	38.62	-0.28
14.00	37.23	37.25	0.05	14.00	37.91	37.89	-0.06
16.00	36.21	36.54	0.91	16.00	37.09	37.17	0.23
19.00	35.10	35.50	1.16	19.00	35.86	36.12	0.74
22.00	33.62	34.50	2.60	22.00	34.56	35.10	1.58
25.00	32.46	33.52	3.26	25.00	33.12	34.11	3.00
313.15 K							
0.00	42.59	42.60	0.03	0.00	43.33	43.30	-0.08
3.00	41.29	41.39	0.24	3.00	42.16	42.08	-0.18
6.00	40.37	40.22	-0.38	6.00	41.04	40.89	-0.36
9.00	38.99	39.08	0.22	9.00	39.85	39.74	-0.28
12.00	37.92	37.98	0.12	12.00	38.73	38.62	-0.28
14.00	37.23	37.25	0.05	14.00	37.91	37.89	-0.06
16.00	36.21	36.54	0.91	16.00	37.09	37.17	0.23
19.00	35.10	35.50	1.16	19.00	35.86	36.12	0.74
22.00	33.62	34.50	2.60	22.00	34.56	35.10	1.58
25.00	32.46	33.52	3.26	25.00	33.12	34.11	3.00

system at $T = 298.15$ K with the method introduced above and compared it with published data,¹¹ as shown in Figure 1. Good agreement is shown between the solubility data obtained in this work and those reported by Karyakin for the KBr–water system. The mean relative error for this study is 0.6 %. As mentioned above, the experimental mean deviation of the measurement is within 0.2 %.

The measured solubility data of KBr in the water–acetone binary solvent at temperatures of 288.15 K, 293.15 K, 298.15 K, 303.15 K, 308.15 K, and 313.15 K are given in Table 1. It clearly shows that the solubility of potassium bromide decreases with an increase in acetone concentration in the solvent at all temperatures, and the solubility increases with increasing temperature for a constant solvent composition.

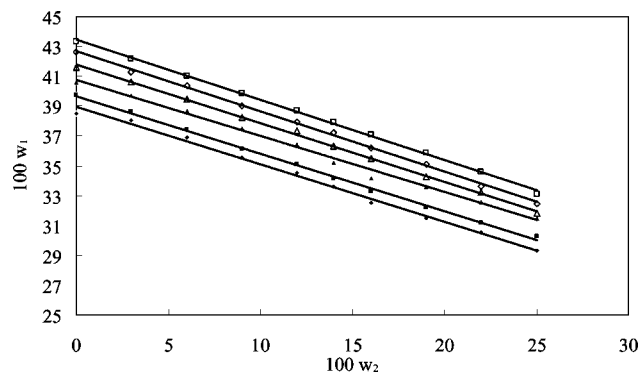


Figure 2. Solubility of KBr (1) in acetone (2) + water (3) solvent mixtures at different temperatures: \blacklozenge , $T = 288.15$ K; \blacksquare , $T = 293.15$ K; \blacktriangle , $T = 298.15$ K; \triangle , $T = 303.15$ K; \diamond , $T = 308.15$ K; \square , $T = 313.15$ K. w_1 is mass fraction of KBr, which was calculated by the mass of KBr in the solution divided by the total mass of the solution (KBr + water + acetone). w_2 is mass fraction of acetone in the solvent, which was calculated by the mass of acetone divided by the total mass of the solvent (water + acetone).

As reported, the solubilities of salts in mixed solvents can be correlated by the equation proposed by Sechenov as a function of solvent composition and temperature.^{12,13} Sechenov's equation is generally expressed as

$$\log S = \log S_0 - c(a - bT) \quad (1)$$

where S and S_0 are the solubilities of the solute in the mixed solvent and in water, respectively, c is the composition of an organic solvent (mass of organic solvent/total mass of the solution %), and a and b are the constants that do not vary with temperature.

The experimental solubility data were correlated with eq 1. The following equation was obtained for presenting the solubility of KBr in water + acetone at different temperatures with a mean relative error of 0.93 %

$$\log S_{\text{KBr}} = \log S_{\text{KBr},0} - c(0.005529 - 0.000044T) \quad (2)$$

where S_{KBr} and $S_{\text{KBr},0}$ are the solubilities of KBr in the mixed solvent and in water, respectively, and c is the composition of acetone in the solvent (mass %).

The predicted solubilities and calculated solubilities with eq 2 for different experimental data along with the relative error are listed in Table 1. From Table 1, it can be seen that the maximum relative error is 3.26 %, and the minimum relative error is zero. The points with relative large errors may come from occasional experimental error. However, these points are few. This indicates that this model can present the experimental data well and can be used for the prediction of the solubility of KBr in the water and acetone solvent system.

From Figure 2, it can be clearly seen that the composition of acetone in the solvent has a greater effect on the solubility of KBr than does the temperature. This means that the use of the antisolvent crystallization method will be more efficient than a decrease in temperature for the separation of KBr from solution.

Conclusions

The solubility of KBr in water–acetone solvent was obtained experimentally. The solubility of KBr in water and acetone solvent increases with an increase in temperature and with a decrease in the concentration of acetone. The concentration of acetone in the solvent has greater effect on the solubility of KBr than does the temperature.

The model to predict the solubility of KBr in water and acetone was based on the Sechenov empirical equation. The relative error of the model-predicted solubility is about 0.93 %.

Literature Cited

- (1) Bader, M. S. H. Precipitation and separation of chloride and sulfate ions from aqueous solutions: basic experimental performance and modeling. *Environ. Prog.* **1998**, *17*, 126–135.
- (2) Grant, D. J. W.; Higuchi, T. *Solubility Behavior of Organic Compounds*; Techniques of Chemistry, Vol. 21; Wiley: New York, 1990.
- (3) Stephen, H.; Stephen, T. *Binary Systems*; Solubilities of Inorganic and Organic Compounds, Vol. 1; Pergamon Press: Oxford, 1963.
- (4) Stephen, H.; Stephen, T. *Ternary Systems*; Solubilities of Inorganic and Organic Compounds, Vol. 2, Part 1; Pergamon Press: Oxford, 1964.
- (5) Linke, W. F.; Seidell, A. *Solubilities: Inorganic and Metal-Organic Compounds: A Compilation of Solubility Data from the Periodical Literature*, 4th ed.; American Chemical Society: Washington, 1958; Vol. 1.
- (6) Linke, W. F.; Seidell, A. *Solubilities: Inorganic and Metal-Organic Compounds: A Compilation of Solubility Data from the Periodical Literature*, 4th ed.; American Chemical Society: Washington, 1965; Vol. 2.
- (7) Weidong, Y.; Rui, Z.; Shijun, H. Thermodynamic properties of the ternary system potassium bromide + lithium bromide + water at 25 °C. *J. Solution Chem.* **2001**, *30*, 193–200.
- (8) Santiago, I.; Pereyra, C.; Ariza, M. R.; Martínez de la Ossa, E. Ethanol + 2-methyl-1-butanol + calcium chloride system: vapor–liquid equilibrium data and correlation using the NRTL electrolyte model. *J. Chem. Eng. Data* **2007**, *52*, 458–462.
- (9) Pinhoa, S. P.; Macedo, E. A. Experimental measurement and modelling of KBr solubility in water, methanol, ethanol, and its binary mixed solvents at different temperatures. *J. Chem. Thermodyn.* **2002**, *34*, 337–360.
- (10) *Kirk–Othmer Encyclopedia of Chemical Technology*, 4th ed.; Kroschwitz, J. I.; Howe-Grant, M., Eds.; Wiley: New York, 1995; Vol. 19.
- (11) Karyakin, Y. V.; Angelo, I. I. *Inorganic Chemistry Reagent Handbook*; National Chemical Press: Moscow, 1955.
- (12) Krizhazfnnovskii, A. V.; Nenno, E. S. The NaCl-(CH₃)₂CO-H₂O system. *Russ. J. Inorg. Chem.* **1971**, *16*, 746–749.
- (13) Li, J.-T.; Wang, J.-K.; Wang, Y.-L. Solubility of KCl and MgCl₂ in binary solvents formed by acetone and water in the temperature range between (293.15 and 323.15) K. *J. Chem. Eng. Data* **2007**, *52*, 1069–1071.

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