Solubility of KCl and $MgCl_2$ in Binary Solvents Formed by Acetone and Water in the Temperature Range between (293.15 and 323.15) K

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The solubilities of KCl and $MgCl_2$ between (293.15 and 323.15) K in binary solvents formed by acetone and water were measured using an isothermal method. Chemical analysis was used to determine the content of chloride ions, potassium ions, and magnesium ions. The reliability of the method was checked by comparing the experimental data with literature values, and the method proved to be very accurate. The experimental data of $MgCl_2$ were correlated with an empirical equation, and this equation was found to provide an accurate mathematical representation of the experimental data.

Introduction

The study of phase equilibria in salt-containing systems is very important for many industrial applications. Moreover, knowledge of solubility 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 and absorption units.[2] They can also be useful for theoretical studies relating solubility to ionic radii or other possible solvation parameters and for calculating the salt solubility.

Solubility data are generally available for many salts in aqueous electrolyte systems, as evidenced in, for example, the compilation books by Stephen and Stephen[3,4] or Linke and Seidell.[5,6] Conversely for organic solvent or aqueous−organic mixed solvents, data ares very scarce, obsolete, or not available at all.

Therefore, a program of systematic measurements was implemented to measure the solubility of KCl and $MgCl_2$ between (293.15 and 323.15) K in the binary mixed solvents formed by acetone and water. Since an increase in the acetone concentration would cause a layering of the system into two solutions and the solubilities of the inorganic compounds in the organic layer at different temperatures would be very low therefore having little application value, the solubilities of the inorganic compounds in the aqueous layer were mainly measured in this paper. Because some of the experimentally measured solubilities had already been published, in this work the final series of measurements is presented, and the experimental data are correlated with an empirical equation.

Experimental Sections

Materials. In all experiments, distilled deionized water was used. All other chemicals were supplied by the Tianjin Chemical Reagent Co., China. Salts KCl and $MgCl_2{\cdot}6H_2O$ with a purity of " analytically pure " grade, higher than 99 %, and solvent acetone with a minimum purity of 99.5 % were employed with no further purification. To avoid water salt contamination, salts were deposited in a desiccator, and the purity was analyzed before use.

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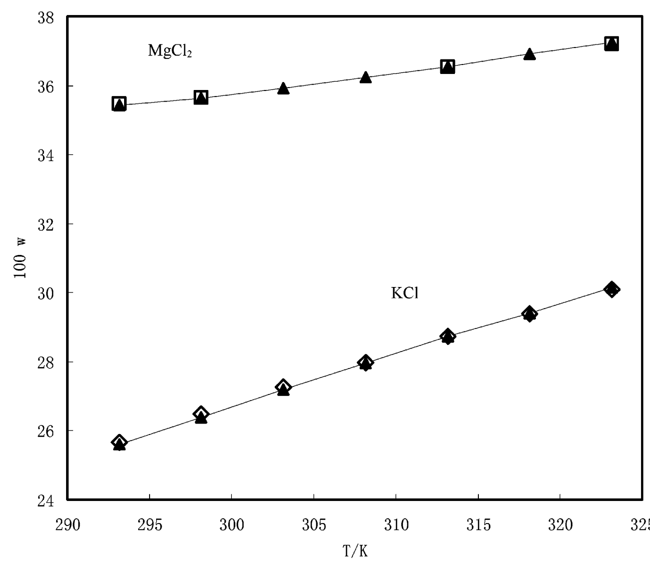

Figure 1. Comparison of the solubility of KCl and $MgCl_2$ in water at different temperatures: ◇, ref 8; □, ref 9; ▲, this work. Lines represent average curves.

Table 1. Experimental Solubilities (Mass Fraction, *w*) in Pure Water in the Temperature Range from (293.15 to 328.15) K

T	100 *w*		*T*	100 *w*	
K	KCl	$MgCl_2$	K	KCl	$MgCl_2$
293.15	25.603	35.428	313.15	28.735	36.546
298.15	26.375	35.632	318.15	29.398	36.912
303.15	27.196	35.924	323.15	30.149	37.251
308.15	27.957	36.237			

Apparatus and Procedure. The solubilities of KCl and $MgCl_2$ in binary solvents formed by acetone and water were investigated by an isothermal method. The method consists of the preparation of a saturated solution at constant temperature (± 0.05 K). The equilibrium cell was charged with known masses (± 0.1 mg) of all components, and to reach solution equilibrium conditions, stirring was carried out for at least 6 h at the working temperature. The solution was then allowed to settle for at least 0.5 h before sampling with a heated syringe. Weighed liquid specimens were then transferred into measuring flasks, the volume of the solution was brought to 100 mL, and the

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Table 2. Experimental Solubilities (Mass Fraction, *w*) of KCl in Binary Acetone + Water Solvent Mixtures in the Temperature Range from (293.15 and 313.15) K

293.15 K		313.15 K	
100 w_1[a]	100 w	100 w_1[a]	100 w
0.000	25.603	0.000	28.735
3.772	23.512	3.622	26.684
7.551	21.589	7.259	24.811
15.945	17.591	15.380	20.814
25.130	13.680	25.524	16.090

[a] w_1 is mass fraction of acetone in the KCl + acetone + water system.

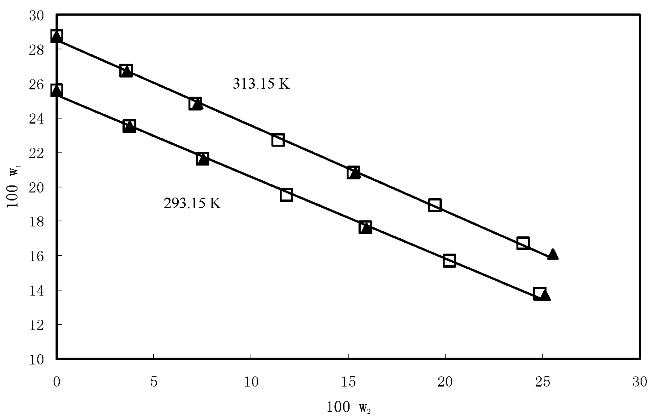

Figure 2. Comparison of the solubility of KCl (1) in acetone (2) + water (3) solvent mixtures at different temperatures: □, ref 10; ▲, this work. Lines represent average curves.

specimens were analyzed. Chloride ions, potassium ions, and magnesium ions were all analyzed so as to get accurate results. Chloride ions were determined by an argentometric titration, potassium ions were determined by a sodium tetraphenylboron−quaterary ammonium salt titration, and magnesium ions were determined by an EDTA titration.[7] Each experimental point is an average of at least three different measurements, and the uncertainty of the experimental solubility values is about 0.2 %.

Results and Discussion

Binary Systems. In Table 1, the measured solubilities of KCl or $MgCl_2$ in water in the range between (293.15 and 323.15) K are reported. The quality of the measured data may be investigated by comparing them with literature values reported 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 published data. Such comparison is shown in Figure 1, and it is possible to observe the good agreement of the data.

Ternary Systems. In Table 2, the measured solubilities for KCl in the aqueous layer of the KCl + water + acetone system at a temperature range of (293.15 to 313.15) K are presented. Our data are compared with those published by Bondarenko et al.[10] The comparison is shown in Figure 2. Good agreement is obtained at the different temperatures.

The solubilities of $MgCl_2$ in the aqueous layer of the $MgCl_2$ + water + acetone system between (293.15 and 323.15) K are measured and listed in Table 3. The solubility is described by Sechenov's equation:[11]

$$\log S = \log S_o - cK \tag{1}$$

where S and S_o are the solubilities of $MgCl_2$ in water + acetone and in water, respectively; c is the concentration of acetone (mass %); and K is a constant for the system that varies with temperature:

$$K = a - bT \tag{2}$$

The general form of the equation for calculating the solubility of $MgCl_2$ in water + acetone solvent can then be represented as

$$\log S = \log S_o - c(a - bT) \tag{3}$$

An analysis of the equation that describes the solubility shows an increase in solubility. Such an increase is due on one hand

Table 3. Experimental Solubilities (Mass Fraction, *w*) of $MgCl_2$ in Binary Acetone + Water Solvent Mixtures in the Temperature Range from (293.15 to 323.15) K

100 w_1[a]	100 w^{exptl}	100 w^{calcd}	relative error (%)	100 w_1[a]	100 w^{exptl}	100 w^{calcd}	relative error (%)	100 w_1[a]	100 w^{exptl}	100 w^{calcd}	relative error (%)
293.15 K				303.15 K				313.15 K			
0.000	35.428	35.428	0.00000	0.000	35.924	35.924	0.0000	0.000	36.540	36.540	0.0000
3.645	34.738	34.728	0.0288	3.499	35.249	35.257	−0.0227	3.337	35.916	35.907	0.0251
5.244	34.413	34.423	−0.0291	4.942	35.023	34.983	0.1142	4.689	35.634	35.652	−0.0505
7.485	34.043	33.998	0.1322	7.168	34.538	34.563	−0.0724	6.840	35.223	35.248	−0.0710
9.952	33.513	33.533	−0.0597	9.503	34.469	34.125	0.9980	9.126	34.814	34.821	−0.0201
12.087	33.189	33.133	0.1687	11.772	33.740	33.702	0.1126	11.294	34.456	34.419	0.1074
14.268	32.700	32.726	−0.0795	13.925	33.312	33.303	0.0270	13.563	34.044	34.000	0.1292
16.910	32.172	32.238	−0.2051	16.150	32.937	32.893	0.1336	15.345	33.800	33.672	0.3787
20.154	31.605	31.643	−0.1202	19.253	32.338	32.326	0.0371	18.404	33.039	33.114	−0.2270
24.387	30.830	30.876	−0.1492	23.379	31.544	31.579	−0.1110	22.470	32.345	32.379	−0.1051
318.15 K				323.15 K							
0.000	36.912	36.912	0.0000	0.000	37.251	37.251	0.0000				
3.216	36.293	36.304	−0.0303	3.153	36.598	36.656	−0.1585				
4.426	36.076	36.076	0.0000	4.251	36.476	36.450	0.0713				
6.678	35.664	35.654	0.0280	6.501	36.027	36.030	−0.0083				
9.014	35.208	35.218	−0.0284	8.742	35.666	35.613	0.1486				
10.820	34.897	34.883	0.0401	10.472	35.320	35.292	0.0793				
13.290	34.427	34.427	0.0000	13.006	34.903	34.825	0.2235				
14.743	34.207	34.161	0.1345	14.000	34.603	34.643	−0.1156				
18.145	33.533	33.539	−0.0179	17.857	33.972	33.939	0.0971				
21.682	32.931	32.900	0.0941	21.003	33.427	33.371	0.1675				

[a] w_1 is mass fraction of acetone in the KCl + acetone + water system.

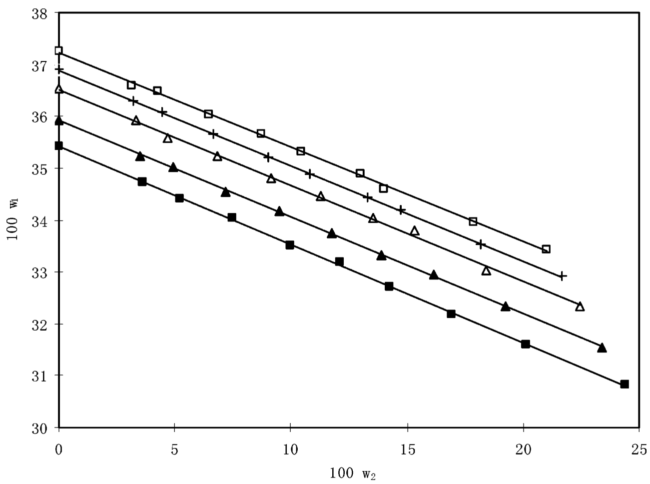

Figure 3. Solubility of $MgCl_2$ (1) in acetone (2) + water (3) solvent mixtures at different temperatures: ■, T = 293.15 K; ▲, T = 303.15 K; △, T = 313.15 K; +, T = 318.15 K; □, T = 323.15 K.

to an increase in the solubility of $MgCl_2$ in water and to an increase in temperature and on the other hand to a decrease in the effect of the concentration of acetone on the solubility of $MgCl_2$. Investigation shows that for maximal decrease in the solubility of $MgCl_2$ in this system there must be a simultaneous increase in the acetone concentration and a reduction in temperature.

The experimental solubility data correlated with eq 3 and the calculated solubilities together with relative errors are listed in Table 3. The general form of the equation for calculating the solubility of $MgCl_2$ in water + acetone solvent can be represented as

$$\log S = \log S_o - c(0.50986 - 0.00049T) \qquad (4)$$

In comparison with each of the experimental points, the values of the solubilities of $MgCl_2$ in binary acetone + water solvent mixtures in the temperature range from (293.15 to 323.15) K are presented in Figure 3.

From Tables 2 and 3 and Figures 2 and 3, we can draw the following conclusions:

(i) The isothermal and chemical analytical methods conducted for measurement of salt solubilities in mixed solvents proved to be very successful. Accurate results were obtained.

(ii) The solubilities of KCl or $MgCl_2$ in the aqueous layer of the system are a function of temperature and the concentration of acetone. The solubilities increase with an increase of temprature or a decrease in the concentration of acetone.

(iii) The calculated solubilities of $MgCl_2$ show good agreement with the experimental values.

Literature Cited

(1) Bader, M. S. H. Precipitation and separation of chloride and sulfate ions from aqueous slutions: basic experimental performance and modelling. *Environ. Prog.* **1998**, *17*, 126−135.

(2) Wagner, K.; Friese, T.; Schulz, S.; Ulbig, P. Solubilities of sodium chloride in organic and aqueous−organic solvent mixtures. *J. Chem. Data* **1998**, *43*, 871−875.

(3) Stephen, H.; Stephen, T. *Solubilities of Inorganic and Organic Compounds: Binary Systems*; Pergamon Press: Oxford, England, 1963.

(4) Stephen, H.; Stephen, T. *Solubilities of Inorganic and Organic Compounds: Ternary Systems*; Pergamon Press: Oxford, England, 1964.

(5) Linke, W. F.; Seidell, A. *Solubilities of Inorganic and Metal−Organic Compounds*, 4th ed.; American Chemical Society: Washington, DC, 1958.

(6) Linke, W. F.; Seidell, A. *Solubilities of Inorganic and Metal−Organic Compounds*, 4th ed.; American Chemical Society: Washington, DC, 1965.

(7) Qinghai Institute of Salt Lakes, The Chinese Academy of Sciences. *Analysis of Brine and Salt*; Science and Technology Press: Beijing, 1988.

(8) Farelo, F.;von Brachel, G.; Offermann, H. Solid−liquid equilibria in the ternary system NaCl−KCl−H_2O. *J. Chem. Eng.* **1993**, *71*, 141−146.

(9) Howard L. Silcock. *Solubilities of Inorganic and Organic Compounds: Ternary and Multicomponent Systems of Inorganic Substances*; Pergamon Press: Oxford, 1979.

(10) Bondarenko, K. A.; Dzyuba, N. K.; Krizhanovskii, A. V.; Kugai, V. V.;Koval'chuk, S. S. The KCl−$(CH_3)_2CO$−H_2O system. *Russ. J. Inorg. Chem.* **1986**, *31* (4), 601−602.

(11) Krizhanovskii, A. V.; Nenno, E. S. The NaCl−$(CH_3)_2CO$−H_2O system. *Russ. J. Inorg. Chem.* **1971**, *16* (5), 746−749.

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