Measurement of Solid−Liquid Equilibria by a Flow-Cloud-Point Method

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A new apparatus utilizing the Tyndall effect to measure the solubility of salts in water was described. The solid−liquid equilibrium of salt mixtures of $NH_4Cl + KCl$, $NH_4Cl + NH_4NO_3$, and $KCl + KNO_3$ in water were determined in the temperature range of 293.15 K to 348.15 K.

Introduction

The solubility of salt in water is a fundamental property that plays an important role in industrial processes and in theoretical research. For example, optimal crystallization processes of inorganic salts from industrial aqueous solutions require reliable solubility data for various operating conditions. Although solubility data have been complied in monographs and handbooks (e.g., Linke and Seidell, 1965; Silcock, 1979), the available values are scarce for most multicomponent systems, and the data reported by different researchers may vary significantly from each other.

Considering the thermodynamics of electrolyte solutions, several models have been proposed in the literature for predicting solid−liquid equilibria (SLE) (e.g., Pitzer, 1980; Chen, 1986; Lu and Maurer, 1993). However, the applicability of these models is limited as their accuracy usually decreases with increase of temperature and solubility. There is still a need to obtain SLE experimentally, especially the data for multicomponent systems.

Several methods, such as the analytical method, the residue-volume method, the step-warming method, and the water-addition method, for measuring the solubility of solids in liquids have been described (see Nyvlt, 1977; Wyatt and Grady, 1996). Generally, the water-addition method and the step-warming method are relatively more applicable. In the step-warming method, the key point is to control the temperature-increasing rate accurately, and its drawback is that the desired data at a specific temperature cannot be obtained precisely. In the water-addition method, the temperature is kept constant and the rate of water-addition must be carefully controlled as the establishment of SLE can be time dependent. These two methods are combined in this work to improve the determination.

Experimental Section

Materials and Equipment. Potassium chloride (Guaranteed Grade, purity >99.8%, Beijing 57601 Chemical Plant, Beijing) and ammonium chloride (Guaranteed Grade, purity >99.8%, Yuling Chemical Plant, Shanghai) were

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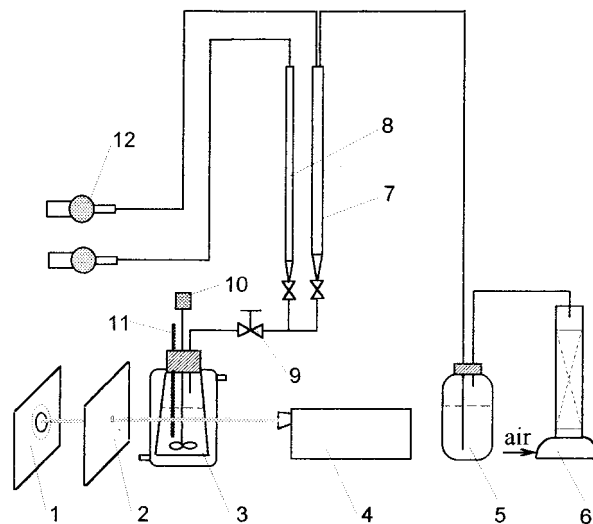
Figure 1. Schematic diagram of experiment apparatus. 1, screen; 2, light-masking plate; 3, equilibrium flask; 4, laser source; 5, water container; 6, desiccator; 7, 25 mL buret; 8, 5 mL buret; 9, cock; 10, stirrer; 11, thermometer; 12, drying tube.

dried in a vacuum desiccator at 0.01 kPa for 4 h and heated in a furnace for 4 h. Potassium nitrate (Analytical Grade, purity >99.5%, Shanghai Experimental Chemical Plant, Shanghai) and ammonium nitrate (Analytical Grade, purity greater than 99.5%, Beijing Chemical Plant, Beijing) were dried in a vacuum-dryer until a constant mass was reached. The deionized water was prepared by redistilling water in the presence of $KMnO_4$, and its electrical conductivity was less than 1.2×10^{-6} S·cm^{-1}.

A new apparatus was employed for measuring SLE. A schematic diagram of the apparatus is shown in Figure 1. It consists of an equilibrium flask, a water-addition section, and a phase-change detection setup. The equilibrium flask loaded with accurately known masses of salt and water was immersed in a thermostat. During the course of a measurement, the temperature increments were made progressively smaller as the number and size of the existing crystals decreased, and the slurry was stirred under moderate agitation in order to prevent the breaking of the crystals and the consequent supersaturation of the solution.

Table 1. Solubilities S of KCl in H_2O Obtained at Three Temperatures by Two Different Temperature-Variation Approaches

	S/(mol·kg (H_2O^{-1}))					
	$T = 353.15$ K		$T = 343.15$ K		$T = 333.15$ K	
	low → high	high → low	low → high	high → low	low → high	high → low
	6.737	6.726	6.393	6.375	6.102	6.067
	6.725	6.686	6.352	6.321	6.007	5.981
	6.805	6.736	6.400	6.395	6.102	6.032
	6.732	6.693	6.283	6.252	6.011	6.009
	6.717	6.698	6.411	6.282	6.063	5.997
ave.	6.743	6.708	6.368	6.325	6.057	6.017
std. dev.	0.036	0.022	0.052	0.060	0.047	0.033
Literature	6.883[a]		6.522[a]		6.146[b]	
	6.789[c]		6.468[d]		6.087[e]	
	6.866[b]		6.493[f]		6.115[g]	

[a] Linke (1965, Vol. 2, p 114). [b] Silcock (1979, part 2, p 371). [c] Silcock (1979, part 2, p 1141); Linke (1965,vol. 2, p 147). [d] Silcock (1979, part 2, p 1137) [e] Silcock (1979, part 3, p 647). [f] Silcock (1979, part 3, p 533) G: Silcock (1979, part 3, p 629, 638).
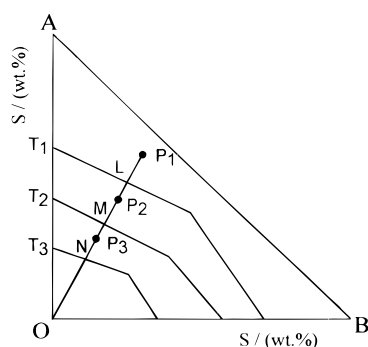
Figure 2. Outline of the proposed experiment approach.
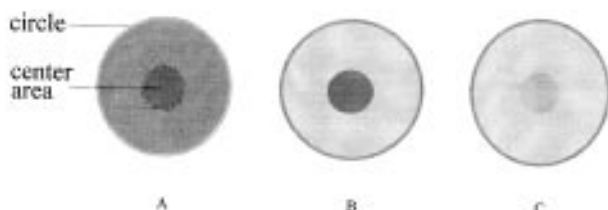
Figure 3. Screen images for three different state conditions. (A) The state of saturation solution with crystals: A circle is shown on the screen, and a light-blotch is in the center of the circle. The circle and the center area are rather dim, and the boundary of the blotch is faint. (B) Equilibrium state: The circle is shown on the screen, but the blotch is bright and the boundary is very clear. (C) Unsaturated state: There is only the circle on the screen. The center area is a faintly invisible.

The temperature was measured directly in the solution by a thermometer with an accuracy of within ±0.1 K.

Each experiment was repeated several times, and only the average values were reported. Then a series of experimental data could be measured rapidly by the method. The standard deviation of the experiments is 0.022−0.060 mol·kg H_2O^{-1} (as shown in Table 1).

Approach. The basic principle of the experimental approach to determine SLE for (salt + salt + liquid) mixtures is illustrated in Figure 2. The solubility curve is obtained by adding water drop by drop to a mixture of known overall composition of salts and water when excess salt in crystal form is in solution. A typical procedure is as follows:

Table 2. Comparison of the Experimental Solubilities S of KCl in H_2O at Different Temperatures with the Literature Values[a]

	S/(mol·kg H_2O^{-1})	
T/K	exptl	lit.
293.15	4.641	4.608 (Silcock, 1979, Vol. 3, part 2, p 1141)
303.15	5.094	5.012 (Silcock, 1979, vol. 3, part 3, p 649)
313.15	5.388	5.386 (Silcock, 1979, Vol. 3, part 2, p 1141)
318.15	5.457	5.516 (Silcock, 1979, Vol. 3, part 2, p 373)
323.15	5.726	5.749 (Silcock, 1979, Vol. 3, part 2, p 375)
328.15	5.890	
333.15	6.008	6.108 (Silcock, 1979, Vol. 3, part 2, p 1141)
338.15	6.229	6.292 (Silcock, 1979, Vol. 3, part 2, p 373)
343.15	6.397	6.464 (Silcock, 1979, Vol. 3, part 2, p 1137)
348.15	6.648	6.757 (Silcock, 1979, Vol. 3, part 2, p 375)
353.15	6.724	6.785 (Silcock, 1979, Vol. 3, part 2, p 1141)

[a] Average absolute deviation = 0.060. Standard deviation = 0.071.
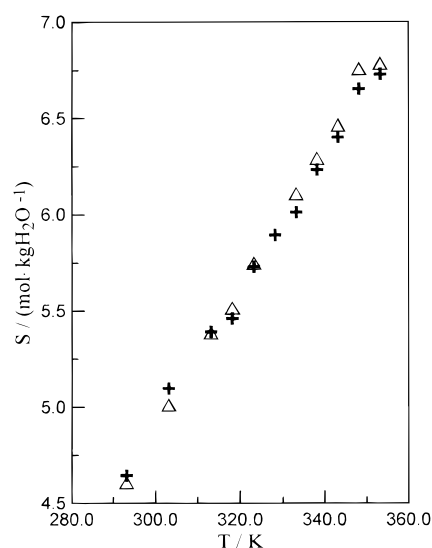
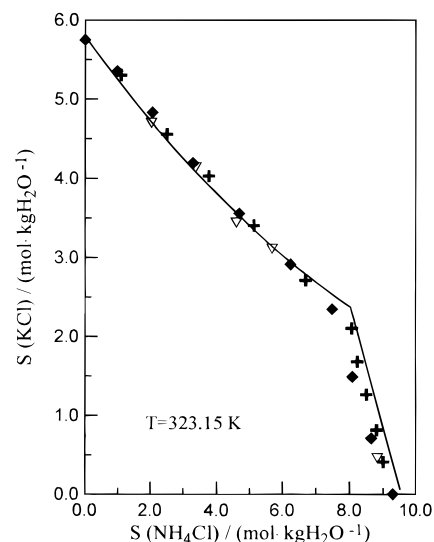**Figure 4.** Comparison of the experimental solubilities S of KCl in H_2O at different temperatures with the literature values: +, this work; △, literature values:
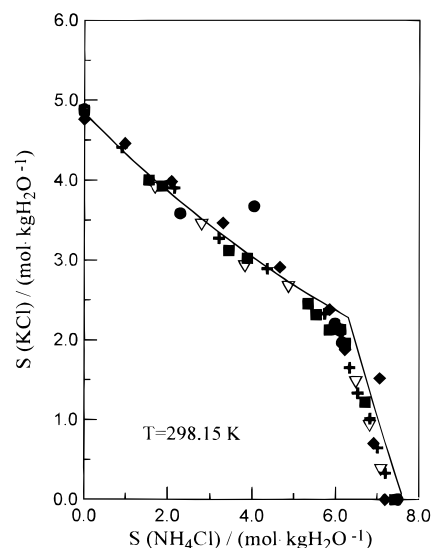
Figure 5. Comparison of the experimental solubilities S of NH_4-Cl + KCl in H_2O at 298.15 K with the literature values: +, this work 1; ◆, this work 2; ●, Linke (1965, p 144); ▽, Linke (1965, p 145); −, predicted by PHEES.

Table 3. Experimental Solubilities S (mol·kg H_2O^{-1}) of NH_4Cl + KCl in H_2O at Different Temperatures Obtained by Two Operators

operator 1			operator 2		
S			S		
NH_4Cl	KCl	precipitate	NH_4Cl	KCl	precipitate
		$T = 298.15$ K			
7.204	0.331	NH_4Cl	7.198	0.000	NH_4Cl
7.013	0.650	NH_4Cl	6.914	0.706	NH_4Cl
6.824	1.016	NH_4Cl	7.062	1.519	NH_4Cl
6.526	1.335	NH_4Cl	6.222	1.877	NH_4Cl
6.332	1.652	NH_4Cl	5.851	2.379	NH_4Cl
5.734	2.326	KCl	4.660	2.911	KCl
4.352	2.894	KCl	3.299	3.464	KCl
3.201	3.273	KCl	2.080	3.986	KCl
2.145	3.901	KCl	0.984	4.459	KCl
0.908	4.411	KCl	0.000	4.762	KCl
		$T = 313.15$ K			
8.333	0.380	NH_4Cl	8.545	0.000	NH_4Cl
8.047	0.745	NH_4Cl	7.231	1.808	NH_4Cl
7.785	1.159	NH_4Cl	6.629	2.331	NH_4Cl
7.566	1.548	NH_4Cl	4.442	2.964	KCl
7.364	1.921	NH_4Cl	2.770	4.158	KCl
6.235	2.529	KCl	1.207	4.834	KCl
4.732	3.146	KCl	0.000	5.400	KCl
3.557	3.703	KCl			
2.324	4.227	KCl			
1.002	4.865	KCl			
		$T = 323.15$ K			
9.001	0.410	NH_4Cl	9.291	0.000	NH_4Cl
8.795	0.815	NH_4Cl	8.639	0.711	NH_4Cl
8.494	1.265	NH_4Cl	8.078	1.490	NH_4Cl
8.226	1.682	NH_4Cl	7.478	2.345	KCl
8.061	2.103	NH_4Cl	6.232	2.911	KCl
6.687	2.712	KCl	4.674	3.557	KCl
5.119	3.404	KCl	3.283	4.192	KCl
3.759	4.030	KCl	2.062	4.833	KCl
2.506	4.558	KCl	0.977	5.354	KCl
1.092	5.304	KCl	0.000	5.749	KCl
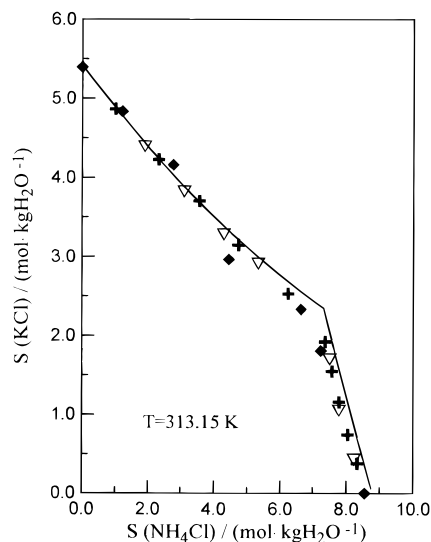
Figure 6. Comparison of the experimental solubilities S of NH_4-Cl + KCl in H_2O at 313.15 K with the literature values: +, this work 1; ◆, this work 2; ▽, Silcock (1979, p 370); —, predicted by PHEES.

A certain quantity of solid−liquid saturated solution with crystals was prepared at temperature T_1 (point P_1). The temperature was maintained constant, and the solvent (water) was added processively. The crystals in the solution dissolved gradually, and the solution at P_1 moved toward the point O along the line P_1O in the diagram.

Figure 7. Comparison of the experimental solubilities S of NH_4-Cl + KCl in H_2O at 323.15 K with the literature values: +, this work 1; ◆ this work 2; ▽ Silcock (1979, p 375); —, predicted by PHEES.

Table 4. Experimental Solubilities S (mol·kg H_2O^{-1}) of NH_4Cl + KCl in H_2O at Different Temperatures

S			S		
NH_4Cl	KCl	precipitate	NH_4Cl	KCl	precipitate
		$T = 303.15$ K			
7.502	0.342	NH_4Cl	5.930	2.406	KCl
7.381	0.684	NH_4Cl	4.526	3.009	KCl
7.119	1.060	NH_4Cl	3.327	3.463	KCl
6.857	1.402	NH_4Cl	2.203	4.007	KCl
6.644	1.734	NH_4Cl	0.938	4.556	KCl
		$T = 308.15$ K			
7.956	0.362	NH_4Cl	6.024	2.443	KCl
7.700	0.713	NH_4Cl	4.593	3.054	KCl
7.476	1.111	NH_4Cl	3.453	3.595	KCl
7.257	1.484	NH_4Cl	2.262	4.117	KCl
6.990	1.835	NH_4Cl	0.971	4.716	KCl
		$T = 318.15$ K			
8.682	0.396	NH_4Cl	6.408	2.599	KCl
8.437	0.781	NH_4Cl	4.923	3.274	KCl
8.138	1.212	NH_4Cl	3.693	3.845	KCl
7.877	1.611	NH_4Cl	2.414	4.390	KCl
7.688	2.006	NH_4Cl	1.039	5.046	KCl
		$T = 328.15$ K			
9.443	0.430	NH_4Cl	6.935	2.813	KCl
9.180	0.850	NH_4Cl	5.298	3.523	KCl
8.873	1.321	NH_4Cl	3.926	4.087	KCl
8.671	1.774	NH_4Cl	2.538	4.616	KCl
8.430	2.200	NH_4Cl	1.116	5.418	KCl
		$T = 333.15$ K			
9.899	0.451	NH_4Cl	7.316	2.968	KCl
9.576	0.887	NH_4Cl	5.451	3.625	KCl
9.279	1.382	NH_4Cl	4.008	4.172	KCl
9.031	1.847	NH_4Cl	2.623	4.769	KCl
8.741	2.281	NH_4Cl	1.139	5.534	KCl

When the amount of water added reached a certain quantity, all the crystals in the solution were just dissolved completely. According to the quantity of water added and the initial composition of the solution, the SLE point L at temperature T_1 was now determined. Subsequently, a small amount of water was added to the solution to make it subsaturated, and simultaneously the temperature of the solution was decreased to make saturation solution with crystals at temperature T_2 (point P_2). The water addition procedure was repeated until the SLE point M at T_2 was

Table 5. Experimental Solubilities S (mol·kg H_2O^{-1}) of NH_4Cl + NH_4NO_3 in H_2O at Different Temperatures

T = 293.15 K

NH_4Cl	NH_4NO_3	precipitate
6.897	0.000	NH_4Cl
6.855	0.513	NH_4Cl
6.718	1.062	NH_4Cl
6.579	2.311	NH_4Cl
6.510	2.727	NH_4Cl
6.317	4.259	NH_4Cl
6.123	6.110	NH_4Cl
5.781	9.513	NH_4Cl
5.518	14.320	NH_4Cl
4.728	21.102	NH_4NO_3
0.000	22.840	NH_4NO_3

T = 298.15 K

NH_4Cl	NH_4NO_3	precipitate
7.271	0.000	NH_4Cl
7.249	0.543	NH_4Cl
7.096	1.122	NH_4Cl
6.955	2.444	NH_4Cl
6.880	2.882	NH_4Cl
6.576	4.433	NH_4Cl
6.467	6.453	NH_4Cl
6.123	10.074	NH_4Cl
5.804	15.065	NH_4Cl
5.270	23.522	NH_4Cl
0.000	25.212	NH_4NO_3

T = 303.15 K

NH_4Cl	NH_4NO_3	precipitate
7.639	0.000	NH_4Cl
7.618	0.570	NH_4Cl
7.466	1.181	NH_4Cl
7.295	2.563	NH_4Cl
7.222	3.025	NH_4Cl
7.022	4.734	NH_4Cl
6.821	6.806	NH_4Cl
6.472	10.648	NH_4Cl
6.176	16.031	NH_4Cl
5.866	26.180	NH_4NO_3
0.000	27.854	NH_4NO_3

T = 308.15 K

NH_4Cl	NH_4NO_3	precipitate
8.021	0.000	NH_4Cl
7.946	0.595	NH_4Cl
7.806	1.234	NH_4Cl
7.668	2.694	NH_4Cl
7.622	3.193	NH_4Cl
7.417	5.001	NH_4Cl
7.194	7.179	NH_4Cl
6.777	11.151	NH_4Cl
6.588	17.098	NH_4Cl
6.307	28.151	NH_4Cl
0.000	30.460	NH_4NO_3

T = 313.15 K

NH_4Cl	NH_4NO_3	precipitate
8.399	0.000	NH_4Cl
8.352	0.625	NH_4Cl
8.268	1.308	NH_4Cl
8.077	2.838	NH_4Cl
7.999	3.351	NH_4Cl
7.742	5.220	NH_4Cl
7.563	7.547	NH_4Cl
7.230	11.896	NH_4Cl
6.982	18.122	NH_4Cl
6.822	30.447	NH_4Cl
0.000	33.959	NH_4NO_3

T = 318.15 K

NH_4Cl	NH_4NO_3	precipitate
8.829	0.000	NH_4Cl
8.754	0.655	NH_4Cl
8.659	1.369	NH_4Cl
8.452	2.969	NH_4Cl
8.374	3.508	NH_4Cl
8.181	5.516	NH_4Cl
7.953	7.937	NH_4Cl
7.639	12.569	NH_4Cl
7.355	19.088	NH_4Cl
0.000	37.155	NH_4NO_3

T = 323.15 K

NH_4Cl	NH_4NO_3	precipitate
9.188	0.000	NH_4Cl
9.138	0.684	NH_4Cl
9.059	1.433	NH_4Cl
8.892	3.124	NH_4Cl
8.788	3.681	NH_4Cl
8.494	5.769	NH_4Cl
8.593	5.793	NH_4Cl
8.364	8.347	NH_4Cl
7.935	13.057	NH_4Cl
7.812	20.274	NH_4Cl
7.742	34.554	NH_4NO_3
0.000	40.453	NH_4NO_3

T = 328.15 K

NH_4Cl	NH_4NO_3	precipitate
9.655	0.000	NH_4Cl
9.559	0.716	NH_4Cl
9.515	1.505	NH_4Cl
9.304	3.269	NH_4Cl
9.239	3.870	NH_4Cl
8.930	6.065	NH_4Cl
8.984	6.057	NH_4Cl
8.791	8.773	NH_4Cl
8.508	12.692	NH_4Cl
8.508	14.000	NH_4Cl
8.320	21.594	NH_4Cl
8.301	23.018	NH_4Cl
8.507	37.968	NH_4Cl
6.777	46.623	NH_4NO_3
0.000	44.951	NH_4NO_3

T = 333.15 K

NH_4Cl	NH_4NO_3	precipitate
10.090	0.000	NH_4Cl
10.023	0.750	NH_4Cl
9.938	1.572	NH_4Cl
9.762	3.430	NH_4Cl
9.649	4.042	NH_4Cl
9.385	6.374	NH_4Cl
9.246	9.227	NH_4Cl
8.976	13.39	NH_4Cl
8.976	14.770	NH_4Cl
8.821	22.895	NH_4Cl
8.850	24.541	NH_4Cl
7.618	52.410	NH_4NO_3
0.000	48.780	NH_4NO_3

T = 338.15 K

NH_4Cl	NH_4NO_3	precipitate
10.477	0.000	NH_4Cl
10.441	0.782	NH_4Cl
10.362	1.639	NH_4Cl
10.250	3.601	NH_4Cl
10.104	4.232	NH_4Cl
9.853	6.692	NH_4Cl
9.759	9.738	NH_4Cl
9.438	14.080	NH_4Cl
9.468	26.255	NH_4Cl
8.541	58.761	NH_4NO_3
0.000	54.216	NH_4NO_3

T = 343.15 K

NH_4Cl	NH_4NO_3	precipitate
10.996	0.000	NH_4Cl
10.933	0.819	NH_4Cl
10.820	1.711	NH_4Cl
10.689	3.755	NH_4Cl
10.572	4.428	NH_4Cl
10.320	6.994	NH_4Cl
10.212	10.191	NH_4Cl
9.906	14.778	NH_4Cl
10.099	28.005	NH_4Cl
9.592	65.989	NH_4NO_3
0.000	60.075	NH_4NO_3

T = 348.15 K

NH_4Cl	NH_4NO_3	precipitate
11.396	0.000	NH_4Cl
11.440	0.857	NH_4Cl
11.287	1.785	NH_4Cl
11.184	3.928	NH_4Cl
11.067	4.636	NH_4Cl
10.848	7.368	NH_4Cl
10.761	10.739	NH_4Cl
10.548	15.737	NH_4Cl
10.828	30.026	NH_4Cl
10.916	75.100	NH_4NO_3
0.000	67.556	NH_4NO_3

obtained. A series of equilibrium points (L, M, N, etc.) were obtained in this manner. Connecting those points at the same temperature yielded the desired SLE diagram.

To observe the disappearance of solid phase clearly, a beam of single-colored laser was used as a light source to pass through the solution. Due to the Tyndall effect (Fridrihsberg, 1986), the projected images vary with the states of the solution. The three states of the solution (saturation solution with crystals, equilibrium, and subsaturation) were determined on the basis of the distinct pattern and the contrast of the images observed on the screen as shown in Figure 3. Because these image changes reflect the phase changes of the system almost instantly, determination of SLE is made accurately and conveniently.

Results and Discussion

Testing the Apparatus. When the solubility values were measured from a higher temperature to a lower temperature, it was assumed that the equilibrium was reached when the last crystal was dissolved. When the measurements were carried out from a lower temperature to a higher temperature, it was assumed that the equilibrium was reached when the first crystal appeared. It was found that the values obtained from these two approaches were somewhat different. The results obtained for the solubility of KCl in H_2O are presented in Table 1. The maximum difference is 0.043 mol·kgH_2O^{-1}. The difference is caused by the effect of supersaturation, but a comparison with the literature values indicates that the deviations are of the same magnitude as those between literature values.

A comparison of the experimental solubility of KCl in H_2O with the literature values is presented in Table 2 and depicted in Figure 4. It is observed that the experimental values are as consistent as the literature values. The standard deviation is 0.071 mol·kgH_2O^{-1} and the average absolute deviation 0.060 mol·kgH_2O^{-1}. The solid−liquid equilibria of a typical ternary system (KCl + NH_4Cl + H_2O) at 298.15 K, 313.15 K, and 323.15 K were also determined by two operators to check the possible personal errors involved in the proposed method of determination. The

Table 6. Experimental Solubilities S (mol·kg H_2O^{-1}) of KCl + KNO_3 in H_2O at Different Temperatures

$T = 293.15$ K

KNO_3	KCl	precipitate	KNO_3	KCl	precipitate
0.000	4.497	KCl	2.217	1.930	KNO_3
0.393	4.538	KCl	2.389	1.469	KNO_3
1.014	4.484	KCl	2.613	0.864	KNO_3
1.329	4.435	KCl	2.827	0.438	KNO_3
1.874	3.940	KNO_3	3.081	0.000	KNO_3
2.099	2.777	KNO_3			

$T = 298.15$ K

KNO_3	KCl	precipitate	KNO_3	KCl	precipitate
0.000	4.749	KCl	2.684	2.335	KNO_3
0.410	4.728	KCl	2.859	1.753	KNO_3
1.047	4.630	KCl	2.927	1.298	KNO_3
1.381	4.610	KCl	3.041	1.005	KNO_3
2.177	4.578	KCl	3.380	0.523	KNO_3
2.424	3.207	KNO_3	3.664	0.000	KNO_3

$T = 303.15$ K

KNO_3	KCl	precipitate	KNO_3	KCl	precipitate
0.000	4.935	KCl	3.041	2.646	KNO_3
0.425	4.903	KCl	3.305	2.032	KNO_3
1.079	4.773	KCl	3.428	1.521	KNO_3
1.436	4.795	KCl	3.669	1.212	KNO_3
2.250	4.733	KCl	4.051	0.627	KNO_3
2.812	3.720	KNO_3	4.288	0.000	KNO_3

$T = 308.15$ K

KNO_3	KCl	precipitate	KNO_3	KCl	precipitate
0.000	5.052	KCl	3.566	3.103	KNO_3
0.442	5.095	KCl	3.845	2.364	KNO_3
1.131	5.004	KCl	3.981	1.766	KNO_3
1.491	4.979	KCl	4.278	1.414	KNO_3
2.318	4.875	KCl	4.736	0.733	KNO_3
3.193	4.225	KNO_3	5.264	0.000	KNO_3

$T = 313.15$ K

KNO_3	KCl	precipitate	KNO_3	KCl	precipitate
0.000	5.301	KCl	4.059	3.532	KNO_3
0.457	5.276	KCl	4.428	2.723	KNO_3
1.166	5.158	KCl	4.556	2.021	KNO_3
1.537	5.130	KCl	4.950	1.636	KNO_3
2.383	5.013	KCl	5.452	0.844	KNO_3
3.722	4.924	KCl	6.072	0.000	KNO_3

$T = 318.15$ K

KNO_3	KCl	precipitate	KNO_3	KCl	precipitate
0.000	5.364	KCl	4.606	4.008	KNO_3
0.470	5.419	KCl	4.931	3.032	KNO_3
1.205	5.328	KCl	5.363	2.379	KNO_3
1.574	5.256	KCl	5.658	1.869	KNO_3
2.458	5.168	KCl	6.409	0.992	KNO_3
3.852	5.096	KCl	7.189	0.000	KNO_3
4.330	5.011	KCl			

$T = 323.15$ K

KNO_3	KCl	precipitate	KNO_3	KCl	precipitate
0.000	5.567	KCl	5.751	3.536	KNO_3
0.486	5.611	KCl	5.869	3.265	KNO_3
1.248	5.517	KCl	6.116	2.713	KNO_3
1.628	5.435	KCl	6.328	2.604	KNO_3
3.907	5.026	KCl	6.500	2.148	KNO_3
3.972	5.255	KCl	7.202	1.115	KNO_3
4.401	5.094	KCl	7.250	1.070	KNO_3
5.234	4.555	KNO_3	8.085	0.000	KNO_3
5.451	4.151	KNO_3			

$T = 328.15$ K

KNO_3	KCl	precipitate	KNO_3	KCl	precipitate
0.000	5.732	KCl	6.190	4.714	KNO_3
0.501	5.783	KCl	6.634	3.690	KNO_3
1.284	5.679	KCl	7.009	2.885	KNO_3
1.689	5.637	KCl	7.390	2.442	KNO_3
2.638	5.548	KCl	8.175	1.207	KNO_3
4.559	5.276	KCl	9.643	0.000	KNO_3

$T = 333.15$ K

KNO_3	KCl	precipitate	KNO_3	KCl	precipitate
0.000	5.898	KCl	6.972	5.309	KNO_3
0.515	5.937	KCl	7.335	4.081	KNO_3
1.327	5.867	KCl	7.949	3.271	KNO_3
1.735	5.793	KCl	8.290	2.739	KNO_3
2.698	5.673	KCl	9.303	1.374	KNO_3
4.682	5.419	KCl	10.700	0.000	KNO_3
6.769	5.155	KCl			

$T = 338.15$ K

KNO_3	KCl	precipitate	KNO_3	KCl	precipitate
0.000	6.029	KCl	6.972	5.309	KCl
0.530	6.111	KCl	8.173	4.547	KNO_3
1.356	5.996	KCl	8.878	3.654	KNO_3
1.774	5.924	KCl	9.227	3.049	KNO_3
2.778	5.842	KCl	10.351	1.528	KNO_3
4.824	5.583	KCl	11.912	0.000	KNO_3

$T = 343.15$ K

KNO_3	KCl	precipitate	KNO_3	KCl	precipitate
0.000	6.274	KCl	4.960	5.740	KCl
0.546	6.293	KCl	7.178	5.466	KCl
1.398	6.185	KCl	9.124	5.076	KNO_3
1.814	6.056	KCl	9.942	4.092	KNO_3
2.841	5.974	KCl	10.294	3.402	KNO_3
4.340	5.582	KCl	11.528	1.702	KNO_3
4.960	5.740	KCl	13.629	0.000	KNO_3
7.178	5.466	KCl			

$T = 348.15$ K

KNO_3	KCl	precipitate	KNO_3	KCl	precipitate
0.569	6.565	KCl	5.090	5.891	KCl
1.436	6.353	KCl	7.375	5.617	KCl
1.864	6.222	KCl	9.583	5.331	KCl
2.922	6.145	KCl	11.340	3.747	KNO_3
4.436	5.707	KCl	12.379	1.917	KNO_3
5.090	5.891	KCl	12.771	1.886	KNO_3
7.375	5.617	KCl	14.965	0.000	KNO_3

results are reported in Table 3. As depicted in Figures 5−7, the experimental values obtained by the two operators closely overlap. Furthermore, it is shown in Figures 4−7 that the solubilities of experiment in this work agree well with those of literature. The values predicted by the computer program PHEES (phase equilibrium of electrolyte solution), software based on the model recently proposed by Lu and Maurer (1993) and established in our laboratory (Zhang et al., 1995), are also included in the figures for comparison. It appears that the proposed method for determining the solid−liquid equilibria is acceptable. It should be mentioned that in all the experimental determinations of SLE for (salt + salt + water) mixtures, the solubility values were measured by the approach from a higher temperature to a low temperature.

SLE Measurement of Three Ternary Systems at Different Temperatures. Following the testing of the apparatus, the solid−liquid equilibrium data of the three ternary systems NH_4Cl + KCl + H_2O, NH_4Cl + NH_4NO_3 + H_2O, and KCl + KNO_3 + H_2O were determined over the temperature range from 293.15 K to 348.15 K. In addition to Table 3, the additional experimental SLE results for the system NH_4Cl + KCl + H_2O are presented in Table 4. The results for the systems NH_4Cl + NH_4NO_3 + H_2O and KCl + KNO_3 + H_2O are presented in Tables 5 and 6, respectively. The uncertainty of the experimental values is usually 0.04−0.10 mol·kgH_2O^{-1} except very few points at higher temperatures. A survey of the literature indicates that solubilities of these salt mixtures in water are lacking at higher temperatures, especially for the NH_4Cl + NH_4NO_3 + H_2O and KCl + KNO_3 + H_2O systems, whose equilibrium values have not been reported at the temperatures 308.15 K, 318.15 K, 328.15 K, 338.15 K, and 343.15 K.

Conclusions

A new experimental approach and a new apparatus for measuring solid−liquid equilibria (SLE) continuously and conveniently were established successfully. A comparison of the experimental results obtained for (KCl + H$_2$O) and (NH$_4$Cl + KCl + H$_2$O) mixtures with those reported in the literature indicated that the experimental values were reliable and the proposed method was effective. Experimental SLE values for three (salt + salt + water) systems over wider ranges of temperatures were reported.

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