

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 $\text{NH}_4\text{Cl} + \text{KCl}$, $\text{NH}_4\text{Cl} + \text{NH}_4\text{NO}_3$, and $\text{KCl} + \text{KNO}_3$ 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 compiled 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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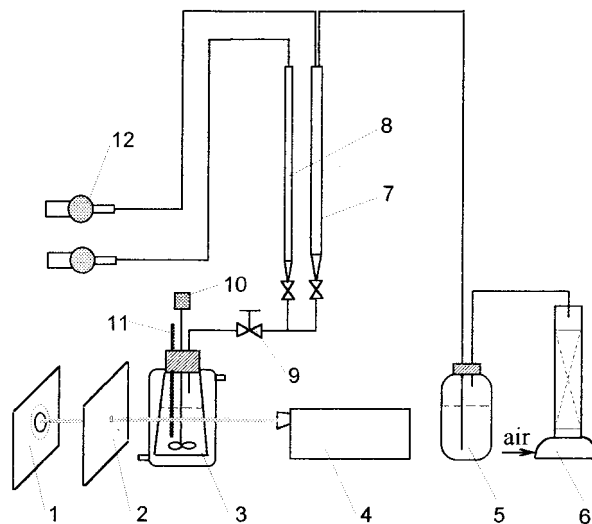


Figure 1. Schematic diagram of experiment apparatus. 1, screen; 2, light-masking plate; 3, equilibrium flask; 4, laser source; 5, water container; 6, desiccator; 7, 25 mL buret; 8, 5 mL buret; 9, cock; 10, stirrer; 11, thermometer; 12, drying tube.

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 $1.2 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1}$.

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

	$S/(\text{mol} \cdot \text{kg } (H_2O)^{-1})$					
	$T = 353.15 \text{ K}$		$T = 343.15 \text{ K}$		$T = 333.15 \text{ K}$	
	low \rightarrow high	high \rightarrow low	low \rightarrow high	high \rightarrow low	low \rightarrow high	high \rightarrow 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).

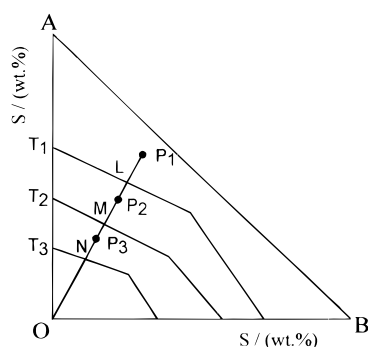
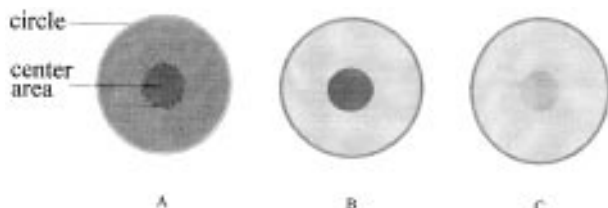
**Figure 2.** Outline of the proposed experiment approach.

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 $\pm 0.1 \text{ K}$.

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 $0.022\text{--}0.060 \text{ mol} \cdot \text{kg } H_2O^{-1}$ (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

T/K	$S/(\text{mol} \cdot \text{kg } H_2O^{-1})$	
	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.

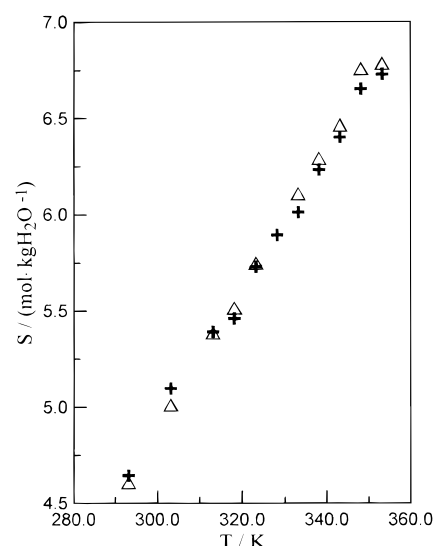
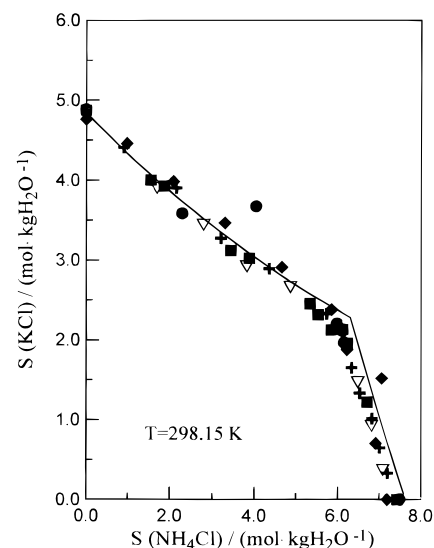
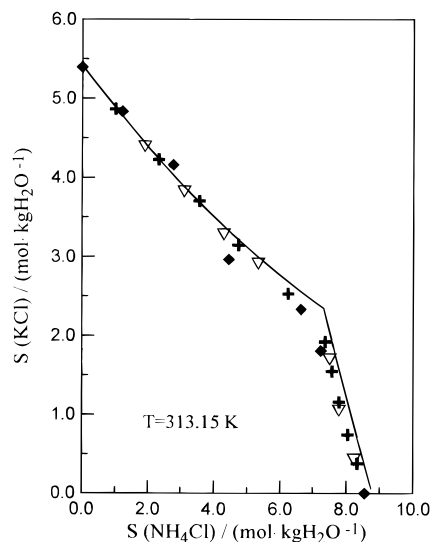
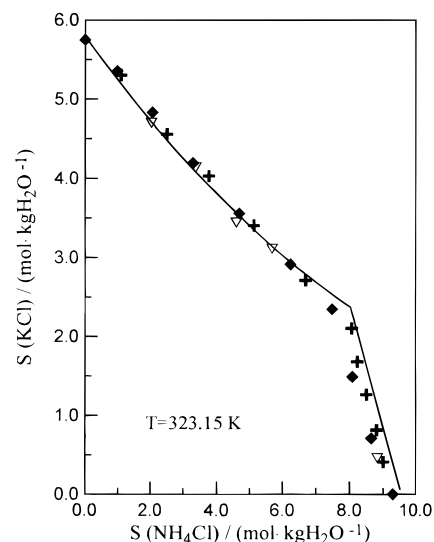
**Figure 4.** Comparison of the experimental solubilities S of KCl in H_2O at different temperatures with the literature values: +, this work; Δ , literature values:**Figure 5.** Comparison of the experimental solubilities S of $NH_4Cl + KCl$ in H_2O at 298.15 K with the literature values: +, this work 1; \blacklozenge , this work 2; \bullet , Linke (1965, p 144); ∇ , Linke (1965, p 145); —, predicted by PHEES.

Table 3. Experimental Solubilities S (mol·kg H₂O⁻¹) of NH₄Cl + KCl in H₂O at Different Temperatures Obtained by Two Operators

operator 1			operator 2		
S			S		
NH ₄ Cl	KCl	precipitate	NH ₄ Cl	KCl	precipitate
$T = 298.15$ K					
7.204	0.331	NH ₄ Cl	7.198	0.000	NH ₄ Cl
7.013	0.650	NH ₄ Cl	6.914	0.706	NH ₄ Cl
6.824	1.016	NH ₄ Cl	7.062	1.519	NH ₄ Cl
6.526	1.335	NH ₄ Cl	6.222	1.877	NH ₄ Cl
6.332	1.652	NH ₄ Cl	5.851	2.379	NH ₄ Cl
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 ₄ Cl	8.545	0.000	NH ₄ Cl
8.047	0.745	NH ₄ Cl	7.231	1.808	NH ₄ Cl
7.785	1.159	NH ₄ Cl	6.629	2.331	NH ₄ Cl
7.566	1.548	NH ₄ Cl	4.442	2.964	KCl
7.364	1.921	NH ₄ Cl	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 ₄ Cl	9.291	0.000	NH ₄ Cl
8.795	0.815	NH ₄ Cl	8.639	0.711	NH ₄ Cl
8.494	1.265	NH ₄ Cl	8.078	1.490	NH ₄ Cl
8.226	1.682	NH ₄ Cl	7.478	2.345	KCl
8.061	2.103	NH ₄ Cl	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 NH₄Cl + KCl in H₂O 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 P₁). The temperature was maintained constant, and the solvent (water) was added processively. The crystals in the solution dissolved gradually, and the solution at P₁ moved toward the point O along the line P₁O in the diagram.

**Figure 7.** Comparison of the experimental solubilities S of NH₄Cl + KCl in H₂O 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 H₂O⁻¹) of NH₄Cl + KCl in H₂O at Different Temperatures**

S			S		
NH ₄ Cl	KCl	precipitate	NH ₄ Cl	KCl	precipitate
$T = 303.15$ K					
7.502	0.342	NH ₄ Cl	5.930	2.406	KCl
7.381	0.684	NH ₄ Cl	4.526	3.009	KCl
7.119	1.060	NH ₄ Cl	3.327	3.463	KCl
6.857	1.402	NH ₄ Cl	2.203	4.007	KCl
6.644	1.734	NH ₄ Cl	0.938	4.556	KCl
$T = 308.15$ K					
7.956	0.362	NH ₄ Cl	6.024	2.443	KCl
7.700	0.713	NH ₄ Cl	4.593	3.054	KCl
7.476	1.111	NH ₄ Cl	3.453	3.595	KCl
7.257	1.484	NH ₄ Cl	2.262	4.117	KCl
6.990	1.835	NH ₄ Cl	0.971	4.716	KCl
$T = 318.15$ K					
8.682	0.396	NH ₄ Cl	6.408	2.599	KCl
8.437	0.781	NH ₄ Cl	4.923	3.274	KCl
8.138	1.212	NH ₄ Cl	3.693	3.845	KCl
7.877	1.611	NH ₄ Cl	2.414	4.390	KCl
7.688	2.006	NH ₄ Cl	1.039	5.046	KCl
$T = 328.15$ K					
9.443	0.430	NH ₄ Cl	6.935	2.813	KCl
9.180	0.850	NH ₄ Cl	5.298	3.523	KCl
8.873	1.321	NH ₄ Cl	3.926	4.087	KCl
8.671	1.774	NH ₄ Cl	2.538	4.616	KCl
8.430	2.200	NH ₄ Cl	1.116	5.418	KCl
$T = 333.15$ K					
9.899	0.451	NH ₄ Cl	7.316	2.968	KCl
9.576	0.887	NH ₄ Cl	5.451	3.625	KCl
9.279	1.382	NH ₄ Cl	4.008	4.172	KCl
9.031	1.847	NH ₄ Cl	2.623	4.769	KCl
8.741	2.281	NH ₄ Cl	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 P₂). 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 $\text{NH}_4\text{Cl} + \text{NH}_4\text{NO}_3$ in H_2O at Different Temperatures

S			S			S			S		
NH ₄ Cl	NH ₄ NO ₃	precipitate	NH ₄ Cl	NH ₄ NO ₃	precipitate	NH ₄ Cl	NH ₄ NO ₃	precipitate	NH ₄ Cl	NH ₄ NO ₃	precipitate
T= 293.15 K											
6.897	0.000	NH ₄ Cl	6.123	6.110	NH ₄ Cl	9.188	0.000	NH ₄ Cl	8.593	5.793	NH ₄ Cl
6.855	0.513	NH ₄ Cl	5.781	9.513	NH ₄ Cl	9.138	0.684	NH ₄ Cl	8.364	8.347	NH ₄ Cl
6.718	1.062	NH ₄ Cl	5.518	14.320	NH ₄ Cl	9.059	1.433	NH ₄ Cl	7.935	13.057	NH ₄ Cl
6.579	2.311	NH ₄ Cl	4.728	21.102	NH ₄ NO ₃	8.892	3.124	NH ₄ Cl	7.812	20.274	NH ₄ Cl
6.510	2.727	NH ₄ Cl	0.000	22.840	NH ₄ NO ₃	8.788	3.681	NH ₄ Cl	7.742	34.554	NH ₄ NO ₃
6.317	4.259	NH ₄ Cl				8.494	5.769	NH ₄ Cl	0.000	40.453	NH ₄ NO ₃
T= 298.15 K											
7.271	0.000	NH ₄ Cl	6.467	6.453	NH ₄ Cl	9.655	0.000	NH ₄ Cl	8.508	12.692	NH ₄ Cl
7.249	0.543	NH ₄ Cl	6.123	10.074	NH ₄ Cl	9.559	0.716	NH ₄ Cl	8.508	14.000	NH ₄ Cl
7.096	1.122	NH ₄ Cl	5.804	15.065	NH ₄ Cl	9.515	1.505	NH ₄ Cl	8.320	21.594	NH ₄ Cl
6.955	2.444	NH ₄ Cl	5.270	23.522	NH ₄ Cl	9.304	3.269	NH ₄ Cl	8.301	23.018	NH ₄ Cl
6.880	2.882	NH ₄ Cl	0.000	25.212	NH ₄ NO ₃	9.239	3.870	NH ₄ Cl	8.507	37.968	NH ₄ Cl
6.576	4.433	NH ₄ Cl				8.930	6.065	NH ₄ Cl	6.777	46.623	NH ₄ NO ₃
T= 303.15 K											
7.639	0.000	NH ₄ Cl	6.821	6.806	NH ₄ Cl	8.984	6.057	NH ₄ Cl	0.000	44.951	NH ₄ NO ₃
7.618	0.570	NH ₄ Cl	6.472	10.648	NH ₄ Cl	8.791	8.773	NH ₄ Cl			
7.466	1.181	NH ₄ Cl	6.176	16.031	NH ₄ Cl	10.090	0.000	NH ₄ Cl	8.976	13.39	NH ₄ Cl
7.295	2.563	NH ₄ Cl	5.866	26.180	NH ₄ NO ₃	10.023	0.750	NH ₄ Cl	8.976	14.770	NH ₄ Cl
7.222	3.025	NH ₄ Cl	0.000	27.854	NH ₄ NO ₃	9.938	1.572	NH ₄ Cl	8.821	22.895	NH ₄ Cl
7.022	4.734	NH ₄ Cl				9.762	3.430	NH ₄ Cl	8.850	24.541	NH ₄ Cl
T= 308.15 K											
8.021	0.000	NH ₄ Cl	7.194	7.179	NH ₄ Cl	9.649	4.042	NH ₄ Cl	7.618	52.410	NH ₄ NO ₃
7.946	0.595	NH ₄ Cl	6.777	11.151	NH ₄ Cl	9.385	6.374	NH ₄ Cl	0.000	48.780	NH ₄ NO ₃
7.806	1.234	NH ₄ Cl	6.588	17.098	NH ₄ Cl	9.246	9.227	NH ₄ Cl			
7.668	2.694	NH ₄ Cl	6.307	28.151	NH ₄ Cl	10.477	0.000	NH ₄ Cl	9.759	9.738	NH ₄ Cl
7.622	3.193	NH ₄ Cl	0.000	30.460	NH ₄ NO ₃	10.441	0.782	NH ₄ Cl	9.438	14.080	NH ₄ Cl
7.417	5.001	NH ₄ Cl				10.362	1.639	NH ₄ Cl	9.468	26.255	NH ₄ Cl
T= 313.15 K											
8.399	0.000	NH ₄ Cl	7.563	7.547	NH ₄ Cl	10.250	3.601	NH ₄ Cl	8.541	58.761	NH ₄ NO ₃
8.352	0.625	NH ₄ Cl	7.230	11.896	NH ₄ Cl	10.104	4.232	NH ₄ Cl	0.000	54.216	NH ₄ NO ₃
8.268	1.308	NH ₄ Cl	6.982	18.122	NH ₄ Cl	9.853	6.692	NH ₄ Cl			
8.077	2.838	NH ₄ Cl	6.822	30.447	NH ₄ Cl	T= 333.15 K					
7.999	3.351	NH ₄ Cl	0.000	33.959	NH ₄ NO ₃	10.996	0.000	NH ₄ Cl	10.212	10.191	NH ₄ Cl
7.742	5.220	NH ₄ Cl				10.933	0.819	NH ₄ Cl	9.906	14.778	NH ₄ Cl
T= 318.15 K											
8.829	0.000	NH ₄ Cl	7.953	7.937	NH ₄ Cl	10.820	1.711	NH ₄ Cl	10.099	28.005	NH ₄ Cl
8.754	0.655	NH ₄ Cl	7.639	12.569	NH ₄ Cl	10.689	3.755	NH ₄ Cl	9.592	65.989	NH ₄ NO ₃
8.659	1.369	NH ₄ Cl	7.355	19.088	NH ₄ Cl	10.572	4.428	NH ₄ Cl	0.000	60.075	NH ₄ NO ₃
8.452	2.969	NH ₄ Cl	0.000	37.155	NH ₄ NO ₃	10.320	6.994	NH ₄ Cl			
8.374	3.508	NH ₄ Cl				T= 343.15 K					
8.181	5.516	NH ₄ Cl				11.396	0.000	NH ₄ Cl	10.761	10.739	NH ₄ Cl
						11.440	0.857	NH ₄ Cl	10.548	15.737	NH ₄ Cl
						11.287	1.785	NH ₄ Cl	10.828	30.026	NH ₄ Cl
						11.184	3.928	NH ₄ Cl	10.916	75.100	NH ₄ NO ₃
						11.067	4.636	NH ₄ Cl	0.000	67.556	NH ₄ NO ₃
						10.848	7.368	NH ₄ Cl			

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 sub-saturation) 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 $0.043 \text{ mol}\cdot\text{kgH}_2\text{O}^{-1}$. 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 $0.071 \text{ mol}\cdot\text{kgH}_2\text{O}^{-1}$ and the average absolute deviation $0.060 \text{ mol}\cdot\text{kgH}_2\text{O}^{-1}$. The solid-liquid equilibria of a typical ternary system ($\text{KCl} + \text{NH}_4\text{Cl} + \text{H}_2\text{O}$) 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 H₂O⁻¹) of KCl + KNO₃ in H₂O at Different Temperatures

S			S			S			S		
KNO ₃	KCl	precipitate	KNO ₃	KCl	precipitate	KNO ₃	KCl	precipitate	KNO ₃	KCl	precipitate
$T = 293.15$ K						$T = 323.15$ K					
0.000	4.497	KCl	2.217	1.930	KNO ₃	0.000	5.567	KCl	5.751	3.536	KNO ₃
0.393	4.538	KCl	2.389	1.469	KNO ₃	0.486	5.611	KCl	5.869	3.265	KNO ₃
1.014	4.484	KCl	2.613	0.864	KNO ₃	1.248	5.517	KCl	6.116	2.713	KNO ₃
1.329	4.435	KCl	2.827	0.438	KNO ₃	1.628	5.435	KCl	6.328	2.604	KNO ₃
1.874	3.940	KNO ₃	3.081	0.000	KNO ₃	3.907	5.026	KCl	6.500	2.148	KNO ₃
2.099	2.777	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			
$T = 298.15$ K						$T = 328.15$ K					
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	0.000	5.732	KCl	6.190	4.714	KNO ₃
2.177	4.578	KCl	3.380	0.523	KNO ₃	0.501	5.783	KCl	6.634	3.690	KNO ₃
2.424	3.207	KNO ₃	3.664	0.000	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
$T = 303.15$ K						$T = 333.15$ K					
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	0.000	5.898	KCl	6.972	5.309	KNO ₃
2.250	4.733	KCl	4.051	0.627	KNO ₃	0.515	5.937	KCl	7.335	4.081	KNO ₃
2.812	3.720	KNO ₃	4.288	0.000	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			
$T = 308.15$ K						$T = 338.15$ K					
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	0.000	6.029	KCl	6.972	5.309	KCl
3.193	4.225	KNO ₃	5.264	0.000	KNO ₃	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
$T = 313.15$ K						$T = 343.15$ K					
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	0.000	6.274	KCl	4.960	5.740	KCl
3.722	4.924	KCl	6.072	0.000	KNO ₃	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			
$T = 318.15$ K						$T = 348.15$ K					
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				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 NH₄Cl + KCl + H₂O, NH₄Cl + NH₄NO₃ + H₂O, and KCl + KNO₃ + H₂O 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 NH₄Cl + KCl + H₂O are presented in Table 4. The results for the systems NH₄Cl + NH₄NO₃ + H₂O and KCl + KNO₃ + H₂O are presented in Tables 5 and 6, respectively. The uncertainty of the experimental values is usually 0.04–0.10 mol·kgH₂O⁻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 NH₄Cl + NH₄NO₃ + H₂O and KCl + KNO₃ + H₂O 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 + H₂O) and (NH₄Cl + KCl + H₂O) 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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