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Academician G. G. URAZOV, A. K. KIRAKOSYAN, and R. S. MKHITARYAN

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Abstract

Full Text

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STUDY OF THE INTERACTION BETWEEN AMMONIA AND ZINC CHLORIDE IN AQUEOUS MEDIUM

A study of the interaction between zinc chloride and ammonia in aqueous medium over the entire concentration range of the latter in solution at different temperatures has not been carried out. Existing studies are devoted to the synthesis of zinc chloride ammines and their thermal stability.

Anhydrous hexamminozinc chloride was obtained by passing gaseous ammonia through anhydrous zinc chloride ^(1,4). The dissociation pressure of hexamminozinc chloride and of the products of its decomposition was determined ^(2,4). Monoaquopentamminozinc chloride was obtained by cooling a saturated ammoniacal solution of zinc chloride ⁽¹¹⁾. Tetramminozinc chloride with varying water content was obtained by cooling an ammoniacal solution of zinc chloride ^(3,5,7). The decomposition temperature was determined ⁽³⁾. Diamminozinc chloride, both containing water of crystallization and anhydrous, was obtained by various methods: by dissolving zinc oxide in solutions of ammonium chloride ⁽⁹⁾, by passing gaseous ammonia through a solution of zinc chloride ^(5,8), by thermal decomposition of higher zinc chloride ammines ^(5,6), etc. The dissociation temperatures and the onset of decomposition of diamminozinc chloride were determined ^(1,3). Monoamminozinc chloride is the final product of the thermal decomposition of higher ammines; it can be sublimed without decomposition ⁽⁵⁾. The formation of ammonia-containing basic salts was indicated by André ⁽⁸⁾ and Allan ⁽¹⁰⁾. They obtained ammonia-containing basic salts by dissolving anhydrous zinc chloride in concentrated aqueous ammonia solutions.

Experimental Part

The study of the interaction between zinc chloride and ammonia in aqueous medium was carried out by the method of isothermal solubility. The interaction between ammonia and zinc chloride in aqueous medium proceeds in two stages: at low ammonia contents in the equilibrium liquid phase, ammonia-containing basic salts crystallize, while at its high concentration—zinc chloride ammines crystallize.

The crystallization region of the ammines was considered as a ternary system composed of zinc chloride, ammonia, and water, and was studied at two temper-

atures—0 and 25°, in order to determine the change in the solubility of ZnCl_2 in aqueous-ammonia solutions and the compositions of the crystallizing phases as a function of temperature. The crystallization region of the basic salts was studied only at 25°.

In the crystallization region of the basic salts, aqueous ammonia solutions of various concentrations were taken, and crystalline zinc chloride was added to them until precipitates of basic salts appeared. To study the crystallization region of the amines, zinc chloride solutions of various concentrations were taken, and gaseous ammonia was passed through them until a crystalline precipitate appeared.

Prepared mixtures from the crystallization region of the amines were kept in closed vessels in a thermostat with stirring for 6-8 hours, while for mixtures from the crystallization region of the basic salts, 20-25 days were required for equilibrium to be established between the liquid and solid phases.

The liquid and solid phases from both regions of the system were analyzed for the content of Zn^{2+} by precipitation with disubstituted ammonium phosphate, for Cl^- by titration with a solution of silver nitrate, and for OH^- and NH_3 both in the solid and in the liquid phases by direct titration with sulfuric acid.

Discussion of Results

Crystallization of ammonia-containing basic salts is completed at contents of 9.04 wt.% ammonia and 18.92 wt.% zinc chloride in the equilibrium liquid phase. The content of zinc chloride increases with increasing ammonia concentration and is directly proportional to its content in the liquid phase (Fig. 2).

Fig. 1

Fig. 1

Fig. 2

Fig. 2

Crystallization of ammonia-containing basic salts of zinc chloride is the result of the partial occurrence of an exchange reaction between ammonium hydroxide and zinc chloride. With increasing concentration of ammonia in the liquid phase, exchange between the indicated substances decreases according to a parabolic dependence (Fig. 1).

The solid phases of the crystallization region of basic zinc chloride salts are formations of variable composition. Without exception they all contain ammonia and have the composition $\text{ZnCl}_2 \cdot n\text{Zn}(\text{OH})_2 \cdot s\text{NH}_3 \cdot x\text{H}_2\text{O}$, where the coefficients n , s , and x have various values, both integral and fractional.

The ammonia content in the solid phases depends on its concentration in the liquid phases. The more ammonia there is in the liquid phase, the more of it enters into the composition of the solid phase, while the content of zinc hydroxide correspondingly decreases.

Fig. 3

Figure 1: Fig. 3

Fig. 4

Figure 2: Fig. 4

Ammonia-containing basic salts of zinc chloride, despite their different chemical compositions, possess identical properties (thermal, crystallo-optical, etc.). The Debye grams of the indicated salts are completely similar to one another. The coincidence of certain properties, as well as of the crystal lattice of the ammonia-containing basic salts, is probably connected with isomorphous substitution of groups entering into the composition of these substances, most likely OH^- and NH_3 and, possibly, H_2O and NH_3 .

Crystallization of the ammines, both at 0° and at 25° , begins at contents of 11.0 wt.% ammonia and 28.0 wt.% zinc chloride in the equilibrium solution. Between the beginning of crystallization of the ammines and the completion of crystallization of the ammonia-containing basic salts there is

there is a certain interval (from 9.0 to 11 wt. % ammonia in the solution) in which, owing to the high solubility of the newly formed compound, crystallization of the solid phase does not occur. The system consists only of a homogeneous liquid phase. In the region of crystallization of the ammoniates at 0° , two compounds crystallize: $\text{ZnCl}_2 \cdot 2.2\text{NH}_3 \cdot 0.5\text{H}_2\text{O}$ and $\text{ZnCl}_2 \cdot 5.75\text{NH}_3 \cdot 0.75\text{H}_2\text{O}$. The results of experiments on the solubility of zinc chloride in aqueous-ammonia solutions in the region of crystallization of the ammoniates at 0° are presented in Fig. 3, and at 25° in Fig. 4. At 25° in the system $\text{ZnCl}_2\text{—NH}_3\text{—H}_2\text{O}$, in the region of crystallization of the ammoniates, two compounds also crystallize: $\text{ZnCl}_2 \cdot 2.2\text{NH}_3 \cdot 0.5\text{H}_2\text{O}$ and $\text{ZnCl}_2 \cdot 5.33\text{NH}_3 \cdot 0.35\text{H}_2\text{O}$. The compositions of the above substances were established by the residue method and by chemical analysis.

Fig. 3

Crystallization of $\text{ZnCl}_2 \cdot 2.2\text{NH}_3 \cdot 0.5\text{H}_2\text{O}$, both at 0° and at 25° , begins at an ammonia content of 11 wt. % and ends at 24.64 wt. % ammonia in the equilibrium solution.

The solubility of the latter compound increases with the concentration of ammonia in the solution and does not depend on temperature. Therefore, the solubility value of zinc chloride at 25° fully coincides with the value at 0° . The point of joint crystallization of $\text{ZnCl}_2 \cdot 2.2\text{NH}_3 \cdot 0.5\text{H}_2\text{O}$ and $\text{ZnCl}_2 \cdot 5.75\text{NH}_3 \cdot 0.75\text{H}_2\text{O}$ at 0° ; $\text{ZnCl}_2 \cdot 2.2\text{NH}_3 \cdot 0.5\text{H}_2\text{O}$ and $\text{ZnCl}_2 \cdot 5.33\text{NH}_3 \cdot 0.35\text{H}_2\text{O}$ at 25° corresponds to solutions of composition NH_3 24.14 wt. %, ZnCl_2 48.38 wt. %, and H_2O 26.98 wt. %.

Fig. 4

The salting-out of the higher ammoniates $\text{ZnCl}_2 \cdot 5.75\text{NH}_3 \cdot 0.75\text{H}_2\text{O}$ and $\text{ZnCl}_2 \cdot 5.33\text{NH}_3 \cdot 0.33\text{H}_2\text{O}$ at the beginning of their crystallization proceeds several times faster than at the completion of crystallization; this is especially clearly seen at 0° . Lowering the temperature promotes

crystallization of substances rich in ammonia and crystallization water.

The zinc chloride amines listed are well-crystallizing substances. In air they all decompose without exception. $\text{ZnCl}_2 \cdot 2.2\text{NH}_3 \cdot 0.5\text{H}_2\text{O}$ in air, after 2.5–3 hours, passes into anhydrous diamminozinc chloride, $\text{ZnCl}_2 \cdot 2\text{NH}_3$. The substances $\text{ZnCl}_2 \cdot 5.75\text{NH}_3 \cdot 0.75\text{H}_2\text{O}$ and $\text{ZnCl}_2 \cdot 5.33\text{NH}_3 \cdot 0.33\text{H}_2\text{O}$, both in air and over 96% sulfuric acid, after 5–6 hours likewise pass into anhydrous diamminozinc chloride.

On the heating curve of $\text{ZnCl}_2 \cdot 2.2\text{NH}_3 \cdot 0.5\text{H}_2\text{O}$ there are three endothermic effects. During the first two thermal effects, at 65° and at 125° , 0.2 mol of ammonia is removed, and the crystallization water is removed completely. During the third effect, at $230\text{--}245^\circ$, the remaining anhydrous diamminozinc chloride melts and its decomposition begins. Further heating of diamminozinc chloride is not accompanied by thermal effects. With the aid of heating curves in this case it is impossible to establish the decomposition temperature of diamminozinc chloride to monoamminozinc chloride. At high temperatures—above 400° —monoamminozinc chloride partially sublimates. On the heating curve of $\text{ZnCl}_2 \cdot 5.75\text{NH}_3 \cdot 0.75\text{H}_2\text{O}$ there are two endothermic effects. During the first effect, at $75\text{--}100^\circ$, water and ammonia are removed simultaneously up to anhydrous diamminozinc chloride. The second—at $230\text{--}245^\circ$ —corresponds to the melting and the beginning of decomposition of $\text{ZnCl}_2 \cdot 2\text{NH}_3$. Thus, zinc chloride amines containing more than two molecules of ammonia are unstable compounds that readily give off ammonia and water both on heating and at room temperature.

Institute of General and Inorganic Chemistry
named after N. S. Kurnakov

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