Solubility of Magnesium Chloride Hexammoniate in Ethylene Glycol Solution Saturated by Ammonia Gas

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The white and regular octahedral crystals of magnesium chloride hexammoniate are prepared by reaction crystallization between magnesium chloride and ammonia gas in ethylene glycol solution. The solubility of magnesium chloride hexammoniate in ethylene glycol solution saturated by ammonia gas has been determined by use of the ethylenediaminetetraacetic acid disodium salt (EDTA) titration method in the temperature range from (5 to 37.5) °C.

Introduction

Magnesium chloride hexammoniate ($MgCl_2 \cdot 6NH_3$) is the significant intermediate of high-purity anhydrous magnesium chloride ($MgCl_2$) which is a primary feed material in the production of magnesium metal by electrolytic methods.[1−3] Furthermore, it also can be used as a solid high-density ammonia/hydrogen storage carrier.[4]

One of the primary approaches to preparation of $MgCl_2 \cdot 6NH_3$ is that magnesium chloride reacts with ammonia gas in organic solvent (methanol, ethanol, glycol, or their blending solvents) by reaction crystallization. This crystallization process is also a key step in the process of producing anhydrous magnesium chloride from magnesite ($MgCO_3$), hydrated magnesium chloride, or other Mg-containing minerals.[1−3] The temperature of the considered reaction crystallization process must be kept below 60 °C; otherwise, the byproducts (the biglycollate biammoniate magnesium chloride ($MgCl_2 \cdot 2C_2H_6O_2 \cdot 2NH_3$) or other chelate complexes) will be formed in the crystallization process.[5] The reaction crystallization temperature is commonly controlled at (10 to 20) °C.

Solubility data are significant to kinetics investigation, process design, and operation of the crystallization process. However, few data are available on the solubility and temperature dependence of solubility of $MgCl_2 \cdot 6NH_3$. The objective of this paper is to explore the solubility of $MgCl_2 \cdot 6NH_3$ in ethylene glycol solution saturated by ammonia gas in the temperature range from (5 to 37.5) °C.

Experimental Section

The solubility data of $MgCl_2 \cdot 6NH_3$ in ethylene glycol solution saturated by ammonia gas have been determined by measuring the Mg^{2+} concentration in ethylene glycol solution when the reaction crystallization is completely performed by use of the EDTA titration method in the temperature range from (5 to 37.5) °C.[6]

Materials. Magnesite ($MgCO_3$, purity > 98 %) was provided by the Pailou Magnesite Company of Haicheng, China. Ethylenediaminetetraacetic acid disodium salt (EDTA) (CAS: 139-33-3, AR, purity > 99 %), ammonium chloride (CAS: 12125-02-9, AR, purity > 99.5 %), ethylene glycol (CAS: 107-21-1, AR), ethanol (CAS: 64-17-5, AR, purity > 99.8 %), triethanolamine (CAS: 102-71-6, AR), ammonia solution (CAS: 1336-21-6, AR), eriochrome black T (CAS: 1787-61-7, AR), methyl red (CAS: 493-52-7, AR), thymolphthalein (CAS: 125-20-2, AR), and one-component Karl Fischer reagent (AR) were purchased from the Beijing Chemical Reagent Company, China. Ammonia gas (CAS: 7664-41-7, purity > 99.999 %) was purchased from the Institute of Special Gas, Beijing, China. The water was distilled and deionized.

Procedures. A 0.1 $mol \cdot L^{-1}$ EDTA standard solution was prepared by dissolving 33.621 g of EDTA in 1000 mL of distilled water. The indicator was obtained by dissolving 0.7 g of eriochrome black T, 0.1 g of methyl red, and 0.1 g of thymolphthalein in 100 mL of ethanol. The buffering solvent was prepared by dissolving 17 g of ammonium chloride in 100 mL of ammonia solution. A 50 % (V/V) triethanolamine/ethanol solution was used as the shielding solvent.

The process of preparing $MgCl_2 \cdot 6NH_3$ from magnesite consisted of:[2,3] (1) selective calcination of magnesite into high activity magnesia for 2 h in a muffle furnace at (750 ± 2) °C; (2) selective leaching between high activity magnesia and ammonium chloride in ethylene glycol solution at (140 ± 1) °C; (3) separation of insoluble impurities (for example, SiO_2 and $CaCO_3$, etc.) by the vacuum filtration method; (4) removing water by a vacumm distillation operation in a packed column (the internal diameter and the height are (30 and 1200) mm, respectively) until the water percentage in solution is less than 0.1 % (measured by Karl Fischer method[7]); (5) cooling the solution to room temperature; (6) precipitation of $MgCl_2 \cdot 6NH_3$ by injecting ammonia gas into the solution at a given temperature and at the atmospheric pressure; and (7) filtration of the precipitate and washing in ethanol saturated by ammonia gas. The crystal properties, including purities, structures, and crystal size distribution, etc., were obtained by analyzing the solid products. The solubility data of $MgCl_2 \cdot 6NH_3$ were determined by measuring the Mg^{2+} concentration in the liquid phase of this reaction crystallization system. The densities of the liquid phase at the different temperatures were measured by the densimeter.

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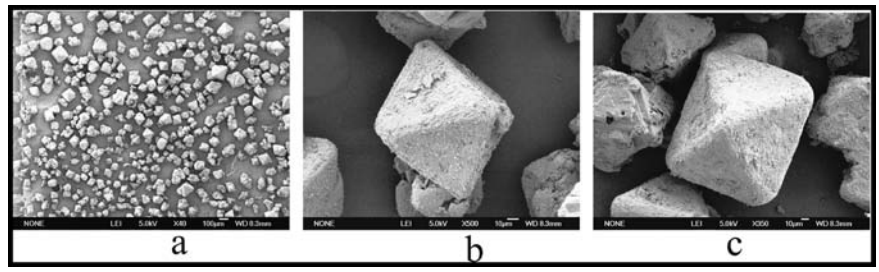

Figure 1. SEM microphotography of $MgCl_2 \cdot 6NH_3$: (a) whole view; (b) side view; and (c) top view.

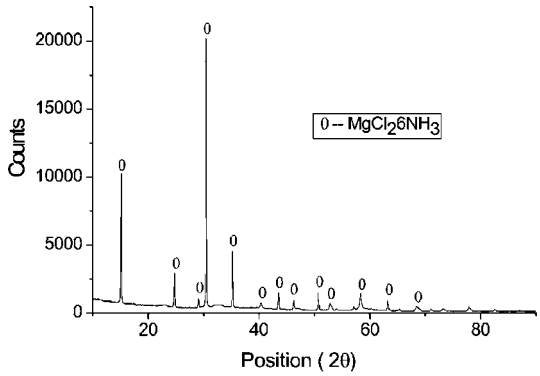

Figure 2. XRD pattern of $MgCl_2 \cdot 6NH_3$ obtained from this work.

The reaction crystallization experiments were performed in 200 mL reactors at (5, 8, 15, 22.5, 30, and 37.5) °C, respectively. The temperature was controlled by thermostat baths, and the temperature in reaction solution was validated by a mercury thermometer (± 0.01 °C). After complete reaction between magnesium chloride and ammonia gas, the reaction conditions were fixed for a long time to reach equilibrium. The reaction equilibrium is established when the Mg^{2+} concentration in the liquid phase remains unchanged.

The titration process was operated according to the steps as follows: (1) centrifugal separation of 10 mL of mother liquor to remove microliters; (2) mixing between 2 mL clear mother liquor and 50 mL distilled water; (3) regulating pH (= 10) by inputting ammonia solution and buffering solvent; (4) eliminating the effect of ferric ions by use of 5 mL of shielding solvent; (5) adding 5 drops of indicator; and (6) titrating by EDTA standard solution. The purple solution becomes blue at the titration end point.

Results and Discussion

The crystals of $MgCl_2 \cdot 6NH_3$ prepared at 15 °C in this work are shown in Figure 1, in which (a) is the whole view, (b) the side view, and (c) the top view. The crystals are not like the block-shaped products of the size range of several centimeters obtained by Zhu et al.;[8] the $MgCl_2 \cdot 6NH_3$ obtained in this work are white and regular octahedral crystals of average size 0.1 mm. In addition, the product emanates pungent ammonia for a long time although being fully washed and dispersed by use of ethanol, which indicates that $MgCl_2 \cdot 6NH_3$ is unstable when it is exposed in the atmosphere.

The XRD pattern and data of $MgCl_2 \cdot 6NH_3$ prepared at 15 °C in the experiment are shown in Figure 2 and Table 1, respectively. XRD analysis reveals that the positions of the diffraction peaks are almost consistent with the literature, and just the relative intensities are somewhat different from those of previous work.[1,7] Furthermore, impurities (SiO_2 and $CaCO_3$, etc.) contained in magnesite are thoroughly separated in the process of preparing $MgCl_2 \cdot 6NH_3$; otherwise, $CaCl_2 \cdot 8NH_3$ would be found in the XRD pattern.[9] It can be concluded that the products obtained in the experiments are $MgCl_2 \cdot 6NH_3$.

Table 1. XRD Spectrum of $MgCl_2 \cdot 6NH_3$ from This Work and Reference 1

this work		ref 1	
d (Å)	intensity (%)	*d* (Å)	intensity (%)
5.866	51.65	5.9	95
--	--	5.1	3
3.599	12.91	3.6	48
3.074	3.52	3.07	5.5
2.939	100	2.94	100
2.548	26.82	2.55	34
2.278	2.36	2.27	1.3
2.081	8.72	2.08	8.4
1.962	5.83	1.96	5.7
1.803	10.41	1.8	11.6
1.724	4.41	1.72	3.3
--	--	1.7	1.4
1.611	8.19	1.61	4.5
1.471	5.37	1.47	3.5
1.362	2.86	1.36	3

The solution densities at (5, 8, 15, 22.5, 30, and 37.5) °C are (1.0620, 1.0601, 1.0552, 1.0496, 1.0449, and 1.0400) $kg \cdot L^{-1}$, respectively. Because of being saturated by ammonia gas, the solution density is obviously lower than pure ethylene glycol despite having the same temperature.

The solubility data of $MgCl_2 \cdot 6NH_3$ in ethylene glycol solution saturated by ammonia gas at the temperature range from (5 to 37.5) °C and at atmospheric pressure are presented in Table 2. The expression of the influence of temperature on solubility is commonly fitted with a second-order polynomial.[10]

$$c = A + Bt + Ct^2 \quad (1)$$

where t is the temperature; c is the solubility; and A, B, and C are constants. For $MgCl_2 \cdot 6NH_3$, the values of the parameters A, B, and C and the root-mean-square deviation (rmsd) are 1.053, 0.3855, 0.0126, and 0.3345, respectively. For comparison with each of the experimental points, the average values of the experimental solubility data and the fitting curve of $MgCl_2 \cdot 6NH_3$ in ethylene glycol solution saturated by ammonia gas are presented in Figure 3.

From Table 2 and Figure 3, the solubility of $MgCl_2 \cdot 6NH_3$ in ethylene glycol solution saturated by ammonia gas is a function of temperature and increases with an increase of temperature. In fact, the reaction crystallization temperature of $MgCl_2 \cdot 6NH_3$ is commonly controlled below 20 °C to avoid the formation of some byproducts (biglycollate biammoniate magnesium chloride or other chelate complexes). Therefore, the solubility data in the temperature range (5 and 20) °C are more practical to a kinetics investigation, process design, and the operation of the reaction crystallization process of $MgCl_2 \cdot 6NH_3$.

Table 2. Solubility of $MgCl_2 \cdot 6NH_3$ in Ethylene Glycol Solution Saturated by Ammonia Gas Between (5 and 37.5) °C

	three measured values and the average value ($g \cdot L^{-1}$) [$g \cdot kg^{-1}$]			
t/°C	1	2	3	average value
5	3.3063 [3.1133]	3.4050 [3.2062]	3.3557 [3.1598]	3.3557 [3.1598]
8	4.9348 [4.6550]	4.9842 [4.7016]	5.0829 [4.7947]	5.0006 [4.7171]
15	9.9190 [9.4001]	9.8697 [9.3534]	9.7710 [9.2598]	9.8532 [9.3378]
22.5	14.7749 [14.0767]	14.8539 [14.1520]	14.9033 [14.1990]	14.8440 [14.1425]
30	25.4638 [24.3696]	25.6120 [24.5114]	25.5132 [24.4169]	25.5297 [24.4327]
37.5	32.5700 [31.3173]	32.6687 [31.4122]	32.8661 [31.6020]	32.7016 [31.4438]

Conclusions

The white and regular octahedral crystals of magnesium chloride hexammoniate are prepared by reaction crystallization between magnesium chloride and ammonia gas in ethylene glycol solution. The solubility data of $MgCl_2 \cdot 6NH_3$ in ethylene glycol solution saturated by ammonia gas at (5, 8, 15, 22.5, 30, and 37.5) °C have been determined by measuring the Mg^{2+} concentration in ethylene glycol solution when the reaction crystallization is completely performed. The expression of the influence of temperature on solubility in the temperature range from (5 to 37.5) °C can be fitted as $c = 1.053 + 0.3855t + 0.0126t^2$.

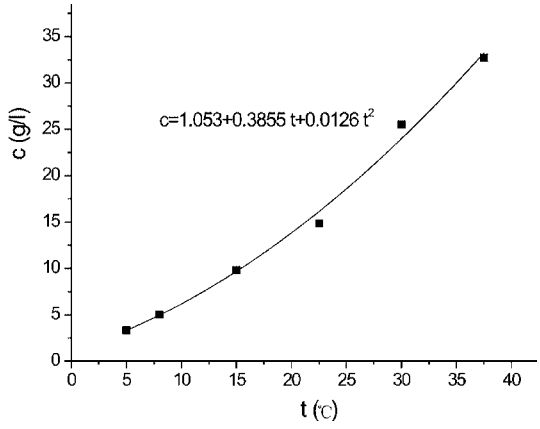

Figure 3. Solubility and the fitting curve of $MgCl_2 \cdot 6NH_3$ between (5 and 37.5) °C.

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