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Solid–liquid equilibrium, crystal type, solid solubility and thermal stability studies of potassium ammonium chloride solid solution

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ABSTRACT

Solid–liquid equilibria of (KCl + NH_4Cl + H_2O) ternary system were investigated and it was found that there were five crystalline regions in the course of crystallization (respectively pure NH_4Cl, mNH_4Cl·KCl solid solution, NH_4Cl·nKCl solid solution, mixed mNH_4Cl·KCl and NH_4Cl·nKCl solid solution and pure KCl). The type of two solid solutions was determined by analysis of X-ray diffraction (XRD), Fourier transform infra-red (FTIR), lattice constant and density of solid solution crystals. It could conclude that they were limited substitutional solid solutions. Solid solubility (substitutional impurity in solvent) was measured at 25 °C and its variation was in accordance with Vergard's law. Moreover, thermal stability of two solid solutions was compared by TG-DTA. Results showed that both mNH_4Cl·KCl and NH_4Cl·nKCl shared the property of their mother phase and maintained its individual characteristics.

1. Introduction

Potassium and ammonium are important inorganic minerals, they are essential macro elements to plant growth in agriculture [1,2], but also basic chemical materials, which play an important role in electroplate, petroleum and pharmaceutical industries [3–6]. Potassium chloride (KCl) and ammonium chloride (NH_4Cl), work as the most common potassium and ammonium inorganic salts, are often used as raw materials and frequently encountered in industrial production. For instance that NH_4Cl could be used as a good eluting agent in exchanging potassium ions in zeolite when extracting potassium from seawater [7]; KCl is the basic materials for producing chloride-free potash fertilizer by reacting with $(NH_4)_2SO_4$ [8]. As for KCl and NH_4Cl mixed aqueous solution, solid solutions of mNH_4Cl·KCl (m > 1) and NH_4Cl·nKCl (n > 1) will be formed in the course of crystallization, which makes it difficult for the separation and utilization of potassium and ammonium resource. Numerous studies had been carried out to investigate this peculiar ternary system, such as phase diagram at a constant temperature [9–17], structure of KCl and NH_4Cl aqueous solutions [18,19] and methods for separation of KCl and NH_4Cl mixed aqueous solution [20–24]. However, solid–liquid equilibrium, crystal type, solid solubility and thermal property of potassium ammonium chloride solid solution are still not very clear yet, a systematic study of crystallization behavior and thermal property of solid solution is necessary.

The main purpose of this work, therefore, is to systematically investigate crystallization behavior of (KCl + NH_4Cl + H_2O) ternary system and provide basic information for the separation of two salts mixed aqueous solution. Solid–liquid equilibria of (KCl + NH_4Cl + H_2O) system were studied over a range of temperatures (from freezing point of brine to 100 °C). One liquid phase and five corresponding crystalline regions were determined and analyzed. In addition, crystal type, solid solubility, structural feature and thermal stability of mNH_4Cl·KCl and NH_4Cl·nKCl solid solutions were studied, which contributes to a further understanding of the crystallization behavior of (KCl + NH_4Cl + H_2O) ternary system and thermal characteristics of mNH_4Cl·KCl and NH_4Cl·nKCl solid solutions.

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2. Experimental

2.1. Materials

The experimental materials of KCl and NH_4Cl were of analytical grade with a purity not less than 99.5% (wt%), supplied by Tianjin Benchmark chemical reagent co., LTD (see Table 1). All chemicals were used without further purification. Water used in experiment was double distilled (conductivity <5 μS/cm).

2.2. Apparatus and procedures

Solubility data were measured in a crystallizer equipped with a magnetic stirrer and isothermal fluid water bath (oil bath over 80 °C). Saturated saline solution was made by mixing excessive salt with water. The system should be sufficiently stirred for 6 h to ensure homogeneous mixing and settled for a further 4 h [22,24]. After the equilibrium had been reached, supernatant liquid was withdrawn using syringes (maintained at a slightly elevated temperature to avoid precipitation) to determine the liquid composition, the residue of solution was then filtered off and analyzed the composition. Likewise, a certain mass percentage of KCl, NH_4Cl and water were prepared to determine solid–liquid equilibria of ($KCl + NH_4Cl + H_2O$) ternary system with the same method mentioned above. The freezing point of brine was determined in a glass tube with magnetic stirrer and alcohol cooling. KCl and NH_4Cl aqueous solution were prepared and then cooled until to the occurrence of solid phase. The uncertainty in experiments was within ±0.1 °C.

To investigate the relation among the crystal composition, density and thermal property of solid solutions, a series of $mNH_4Cl{\cdot}KCl$ and $NH_4Cl{\cdot}nKCl$ crystals were prepared by cooling crystallization according to ($KCl + NH_4Cl + H_2O$) phase diagram at 25 °C. The crystals were characterized by XRD, FTIR and SEM and the thermal stability was analyzed by TG-DTA.

2.3. Analytical methods

Titration was used to detect the concentration of ion: chloride concentration was measured by titration with silver nitrate; ammonium concentration was determined by the formaldehyde method [25], and the relative accuracy of both measurements was within ±0.2%. Potassium concentration was calculated by subtracting ammonium concentration from the total anion. Finally, water content was obtained using mass-balance equation [22–24,26]. The equilibrium solid phase was analyzed by means of wet dregs method with the help of X-ray diffraction (XRD) and scanning electron microscope (SEM), at ambient temperature and atmospheric pressure.

Chemical characteristics, morphology and thermal property of solid solution crystals were characterized by XRD, FTIR, SEM and TG-DTA. The operating parameter was as follows: XRD patterns were determined on a Bruker D8 FOCUS X-ray diffractometer with Cu Kα radiation (λ = 0.15406 nm), the scan mode with a scanning range of 10–80° (2-theta) and a speed of 8°/min; Fourier transform infra-red (FTIR) spectra were collected using a Bruker VECTOR22 FTIR with a wavelength coverage of 400–4000 cm^{-1} and a distinguishability of 4 cm^{-1}; Scanning electron microscopy (SEM) micrographs were recorded using a Shimadzu SS-550 with a magnification of 70–300 times and a resolution of 3.5 nm; Differential thermal analysis (DTA) was performed on DuPont SDT/Q600 under the protection of N_2 with a heating rate of 10 °C/min, which can provides DTA and TG curves.

Moreover, the crystal Miller indices and crystal system of two solid solutions were determined by indexing the X-ray diffraction data using Powder X software [27], from which the crystal cell parameters were obtained. The density of solid solution was measured by the method of pycnometer, which could be calculated by the Eq. (1).

$$\rho = m/(V - v) \tag{1}$$

where ρ represents density, m is the mass of crystals, v is volume of acetone in pycnometer, V is the new scale reading after the adding of crystals.

3. Results and discussion

3.1. Solubility and phase diagram at different temperatures

Solubility and solid–liquid equilibrium data for ($KCl + NH_4Cl + H_2O$) ternary system at different temperatures are given in appendix, and the corresponding phase diagram is plotted in Fig. 1. In the diagram A, B and H respectively represent NH_4Cl, KCl and H_2O; W, E_1 and E_2 are freezing points of H_2O, NH_4Cl and KCl aqueous solutions; E_1E_1' and E_2E_2' are solubility curves of NH_4Cl and KCl in water; EE_3 is coexistence curve of saturated NH_4Cl and KCl solution; CC′ and DD′ are solid solubility curves, representing KCl concentration in $mNH_4Cl{\cdot}KCl$ solid solution and NH_4Cl concentration in $NH_4Cl{\cdot}nKCl$ solid solution respectively.

Obviously, the diagram consists of six fields, one liquid phase and five crystalline regions (respectively pure NH_4Cl, $mNH_4Cl{\cdot}KCl$ solid solution, $NH_4Cl{\cdot}nKCl$ solid solution, mixed $mNH_4Cl{\cdot}KCl$ and $NH_4Cl{\cdot}nKCl$ solid solution and pure KCl). With the increase of temperature, the area of saturated liquid phase becomes larger. It is due to that the solubility of both salts in water increases as the temperature rises [22,24]. However, coexistence curve (EE_3), mixed $mNH_4Cl{\cdot}KCl$ and $NH_4Cl{\cdot}nKCl$ crystalline region boundaries (CE_3 and DE_3) and solid solubility curves (CC′ and DD′) slightly shift to the direction of NH_4Cl with ascending of temperature. It can be explained by the fact that the increasing solubility rate of NH_4Cl with temperature is higher than that of KCl [24]. Characteristics of solid solution crystalline felids ($mNH_4Cl{\cdot}KCl$ solid solution, $NH_4Cl{\cdot}nKCl$ solid solution and two solid solutions mixed area) will be discussed from the analysis of solid solution type, solid solubility, crystal structure and thermal stability in the following part.

3.2. Determination of solid solution type

3.2.1. XRD and FTIR data

XRD spectrums of solid solution crystals are shown in Fig. 2 (a, b, c and d respectively for $mNH_4Cl{\cdot}KCl$ solid solution, $NH_4Cl{\cdot}nKCl$ solid solution, mixed crystal and enlarged view of 26°–34° in c). It is found that the XRD spectrums of two solid solutions are neither

Table 1
Chemical sample description.

Chemical name	Source	Initial mass fraction purity	Purification method	Final mass fraction purity	Analysis method
KCl	Benchmark chemical reagent co., LTD (Tianjin, China)	0.995	None	–	
NH_4Cl	Benchmark chemical reagent co., LTD (Tianjin, China)	0.995	None	–	