Asian Journal of Chemistry; Vol. 27, No. 3 (2015), 929-931

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.17598

Study on Phase Equilibrium of Ternary System Na^+, NH_4^+//Cl^--H_2O at 0, 10 and 60 °C

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Received: 14 March 2014; *Accepted*: 21 May 2014; *Published online*: 19 January 2015; AJC-16697

By means of laser monitoring technology, the solubility data of NaCl and NH_4Cl in water at different temperatures were obtained accurately. Solid-liquid phase equal relationship of ternary water-salt system of Na^+, NH_4^+//Cl^--H_2O was studied at 0, 10 and 60 °C using moist solid method and phase diagram was drawn. It can provide a theoretical basis for predicting dissolution, evaporation, crystallization, cooling and separation process of water-salt ternary system. The recovery of sodium chloride and ammonium chloride by thermal method were analyzed to provide reference for selecting industrial production conditions.

Keywords: Ternary water-salt system, Na^+, NH_4^+//Cl^--H_2O, Phase equilibrium, Phase diagram, Salt separation.

INTRODUCTION

The condensation of mother liquor wastewater of producing biurea by urea treatment contains a large number[1,2] of Na^+, NH_4^+ and Cl^-. To realize the separation and recycling of NaCl and NH_4Cl, reliable balance data of ternary water-salt system of Na^+, NH_4^+//Cl^--H_2O is needed to be the basis of process development[3-6]. At present, the phase diagram study of Na^+, NH_4^+//Cl^--H_2O ternary water-salt system is not sufficiently enough[7-10]. In this paper, the solid-liquid phase equal relationship of ternary water-salt system of Na^+, NH_4^+//Cl^--H_2O was studied at 0, 10 and 60 °C by using moist solid method and the relevant solubility data was also measured, the phase diagram was drawn as well. It provides a theoretical support for predicting the dissolution, evaporation, crystallization, cooling and separation processes of ternary water-salt system.

EXPERIMENTAL

Thermostatic water-circulator bath HH-501 made by Jintan Jerry Er Electric Appliance Co., Ltd.; 85-2 heat controlling magnetic stirrer made by Jiangsu Medical Instrument factory. Glass dissolution kettle with jacket self-made by Henan University. Electronic analytical balance made by Beijing Sartorius Instrument system Co. Ltd.. Microthermometer of 0-50 and 50-100 °C made by Beijing Glass factory. Semiconductor laser detection system in Laser Institute of Zhengzhou University.

Analytical reagents of sodium chloride, ammonium chloride, silver nitrate, formaldehyde, sodium hydroxide, potassium biphthalate and so on; self-made redistilled water with electrical conductivity of less than 1 μS/cm.

Experimental methods: As shown in Fig. 1, experimental apparatus consists of thermostatic water-circulator bath system and glass dissolution kettle with jacket reaction system. Add NaCl and NH_4Cl weighed accurately into dissolution kettle, add quantitative water as well, seal with a rubber plug and open the magnetic stirrer, at the same time open the circulating water system inside the jacket, control temperature with accuracy of ± 0.1 °C, taking advantage of the laser monitoring system composed of transistor laser emitter. The photoelectric conversion apparatus and signal digital display to observe the dissolution situation of solid phase, stop stirring when the solid and liquid phase come to phase equilibrium, analyze the composition at balance of supernatant and wet slag, respectively to determine the system points.

Analytical methods: The concentration of NH_4^+ and Cl^- in the solution measured respectively by formaldehyde method and Moire method[11]. The difference between the Cl^- concentration and NH_4^+ concentration is the concentration of Na^+ and the content of water is calculated by the subtraction method.

RESULTS AND DISCUSSION

Reliability testing of experimental apparatus: The experimental solubility value of NaCl and NH_4Cl in water is compared with the literature value[12] and the results are shown in Figs. 2 and 3, from which we can see that there is a good

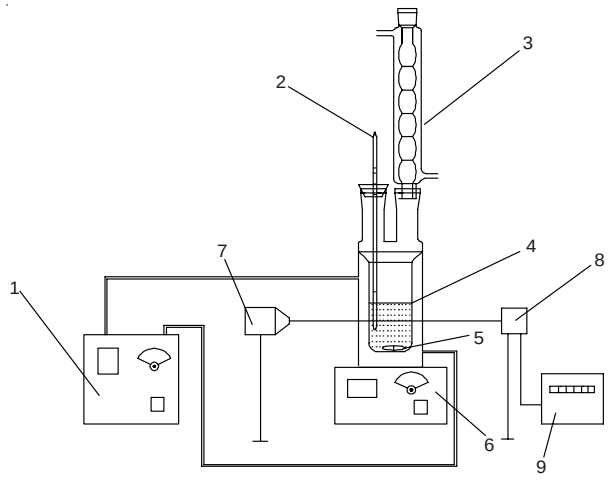

Fig. 1. Experimental setup; (1) super constant temperature water bath; (2) thermometer; (3) circulation cooling water; (4) dissolution kettle; (5) magneton; (6) magnetic stirrer; (7) laser generator; (8) photoelectric conversion apparatus; (9) signal digital display

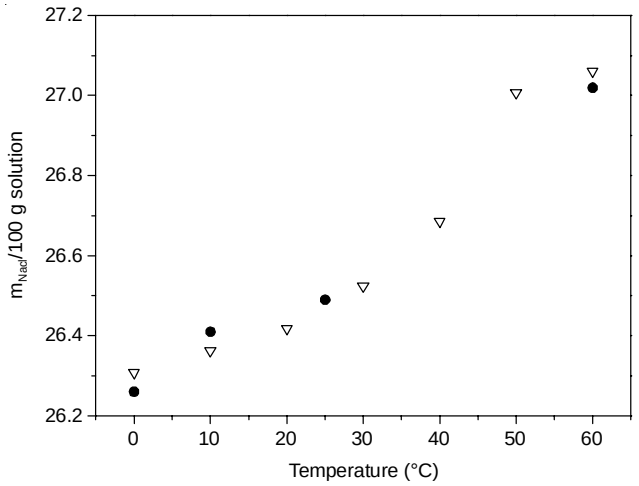

Fig. 2. NaCl-H_2O system (▽ literature values; ● experimental values)

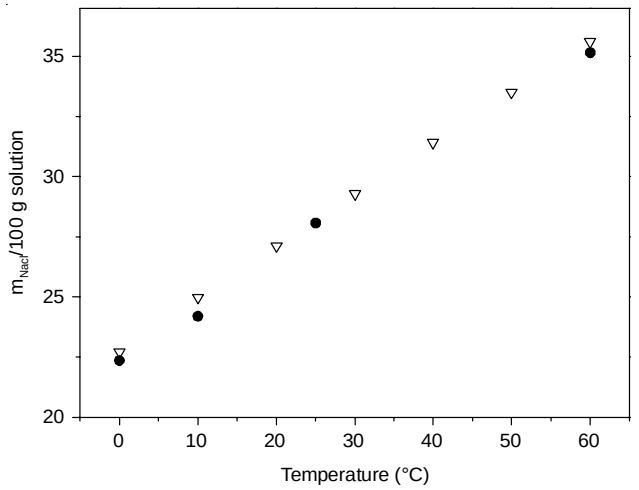

Fig. 3. NH_4Cl-H_2O system (▽ Literature values; ● experimental values)

inosculation between the measured solubility value and literature value of NaCl and NH_4Cl in water, indicating the solubility determination method is accurate and reliable.

Phase diagram of Na^+, NH_4^+//Cl^--H_2O: According to the solid-liquid equilibrium data of Na^+, NH_4^+//Cl^--H_2O ternary water-salt system, the phase diagram of Na^+, NH_4^+//Cl^--H_2O system were drawn at 0, 10 and 60 °C making use of the isosceles right triangle method (Figs. 4-6).

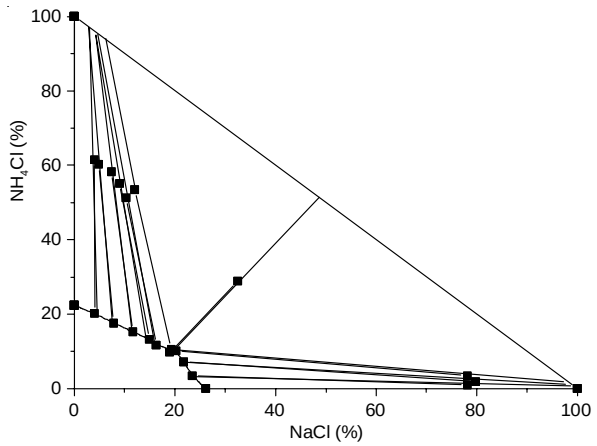

Fig. 4. Phase diagram of Na^+, NH_4^+//Cl^--H_2O at 0 °C

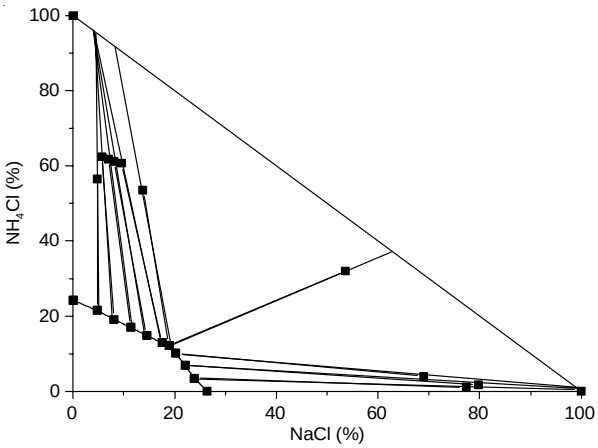

Fig. 5. Phase diagram of Na^+, NH_4^+//Cl^--H_2O at 10 °C

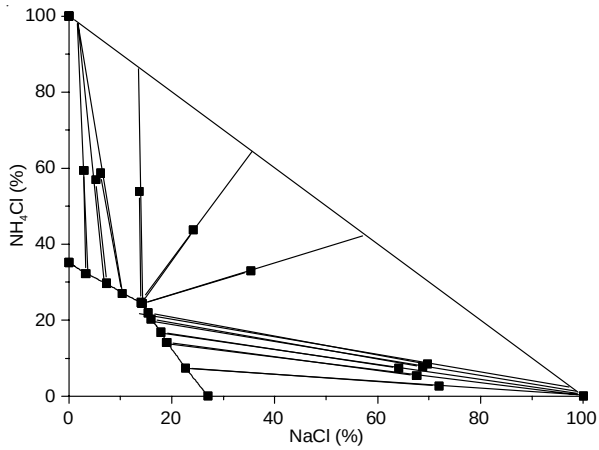

Fig. 6. Phase diagram of Na^+, NH_4^+//Cl^1-H_2O at 60 °C

Consider the phase diagram at 60 °C for example to analyze (Fig. 6), there are three reverse extension cord approximately intersect at the end close to the pure solid ammonium chloride, then the balance of solid phase is a mixture whose main part is ammonium chloride, containing a small amount of sodium chloride as well; five reverse extension cord approximately intersect at the end close to the pure solid sodium

chloride and then the balance of solid phase gives priority to with sodium chloride containing a small amount of ammonium chloride. Another three lines come to point, which is saturation point, at which the solution is the saturated solution of sodium chloride and ammonium chloride solution and the solid phase is a mixture of sodium chloride and ammonium chloride.

The phase diagrams at 0, 10 and 60 °C show that with the increase of temperature, crystallization area of solid phase all decrease due to the increase of the solubility of sodium chloride and ammonium chloride. Compare the isothermal balance line of solubility of NaCl with that of NH_4Cl at the temperature from 0 to 60 °C, as shown in Fig. 7. Fig. 7 shows that with the increase of NaCl content, the solubility isothermal balance line of NH_4Cl decline quickly, especially when pssing the liquid phase equilibrium of two kinds of solid, namely NaCl has very strong salting out effect on NH_4Cl. In addition, the solubility of NH_4Cl decreases with the decrease of temperature.

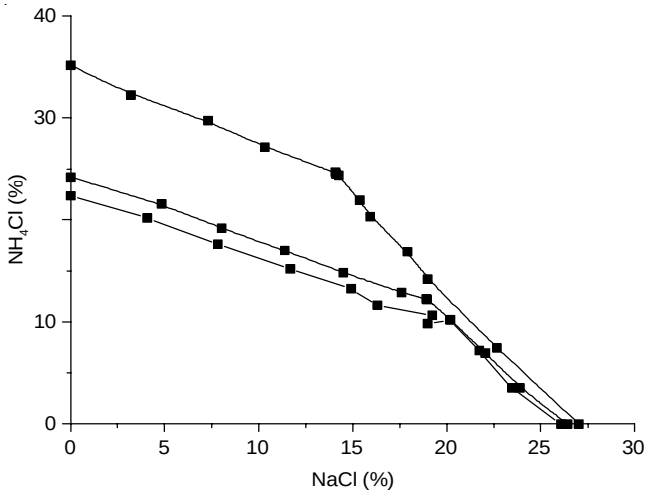

Fig. 7. Solubility isothermal equilibrium line of NaCl and NH_4Cl from 0 to 60 °C

Salt separation analysis of industrial waste water: According to the experimental data, the phase diagram of Na^+, NH_4^+//Cl^--H_2O ternary water-salt system at 0 and 60 °C were drawn, as shown in Fig. 8, of which $a_1c_1b_1$ and $a_2c_2b_2$ are, respectively the solubility curves at 0 and 60 °C, c_1 and c_2 are, respectively saturation points of sodium chloride and ammonium chloride, $Oa_1c_1b_1$ and $Oa_2c_2b_2$ are single-phase areas, Ac_1a_1 and Ac_2a_2 are, respectively two phase regions of solid ammonium chloride and Na^+, NH_4^+//Cl^--H_2O system double saturated liquid, Ac_1B and Ac_2B is the three-phase region of solid sodium chloride, ammonium chloride and double saturated liquid of Na^+, NH_4^+//Cl^--H_2O system.

In an industrial wastewater whose contents of NaCl and NH_4Cl are, respectively about 15.40 and 5.57 %, which stands for point D in the phase diagram. System point moves along the isothermal evaporation ray OF if evaporated at constant temperature of 60 °C and NaCl begin to precipitate when it reaches to the point of n on the b_2c_2. With the water evaporation and the crystallization of sodium chloride, liquid phase point moves along b_2c_2 line from n to c_2. When being evaporated to E point on the line of Bc_2, the amount of sodium chloride

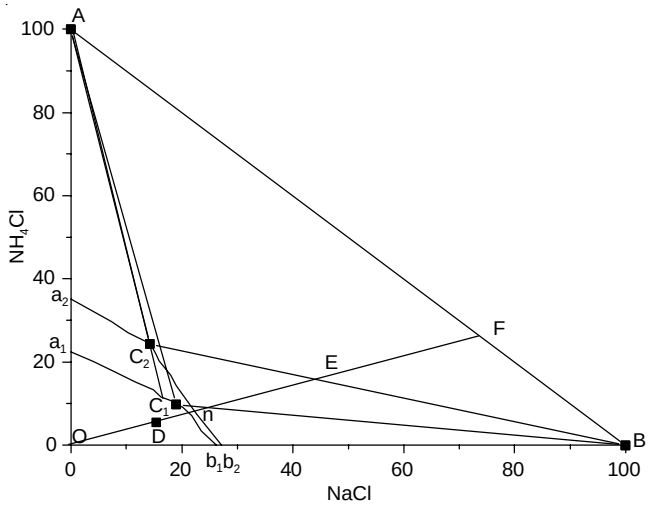

Fig. 8. Phase diagram analysis on separation of NaCl and NH_4Cl

precipitated at pure state reaches to the maximum, after which ammonium chloride precipitate as well, when system point come to point E, stop evaporating and, filter the sodium chloride crystals. Cooling the mother liquor after filtering sodium chloride to 0 °C and solid ammonium chloride be precipitated.

Conclusions

• Solid-liquid phase equal relationship of ternary water-salt system of Na^+, NH_4^+//Cl^--H_2O was studied at 0, 10 and 60 °C by using moist solid method and the solubility data of NaCl and NH_4Cl in water at different temperatures were obtained accurately, the phase diagram was drawn as well.

• The solubility isothermal equilibrium lines of NaCl and NH_4Cl in water at 0, 10 and 60 °C were analyzed, which provides a theoretical support for predicting the dissolution, crystallization, evaporation, cooling and separation processes of ternary water-salt system. While the separation process of actual industrial wastewater was analyzed to provide theoretical guidance for its industrial application.

ACKNOWLEDGEMENTS

The support from the Ministry of Education of Henan Province (No. 122102310500).

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