Determination and Calculation of Phase Equilibrium for Aqueous Ternary System (NH₂)₂CO+KCl+H₂O at 283.15K

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Abstract: The solid-liquid phase equilibrium for ternary system (NH₂)₂CO+KCl+H₂O was determined by isothermal saturation method at 283.15K under atmosphere pressure. The isothermal phase diagrams was drawn in according to the measured solubility data. There are one co-saturated point and two pure solids occurred in this ternary system. The solid phases were confirmed by Schreinemaker's wet residue method and X-ray powder diffraction. Two thermodynamic models, Wilson model and NRTL model, were used to calculate the solubility data. The value of root mean-square deviation in Wilson model and NRTL model for this ternary system was 0.22 and 0.66 respectively, and the value of relative average deviation was 0.61% and 2.33% respectively, which indicated that the calculated data and the experimental results are nearly consistent.

1 Introduction

Nitrogen and potassium are the two main nutrients necessary for plant growth. Nitrogen is the greatest demand for plant growth and development[1]. Potassium can enhance the tolerance of crops to various harsh environments and the stress resistance of crops, meanwhile promote the absorption and utilization of nitrogen by plants[2]. Humans apply a large amount of chemical fertilizers containing nitrogen and potassium elements to provide a large amount of nitrogen and potassium elements needed in the process of plant growth, and to achieve the purpose of improving crop yield and quality.

As a new type of chemical fertilizer, water-soluble fertilizer has high utilization rate of effective ingredients, less environmental pollution, and can save water resources. So it is widely used on the large areas of farmland by the way of spraying, sprinkling and drip irrigation[3]. Water-soluble fertilizer obtained by chemical synthesis has better solubility and stability. Water-soluble fertilizer with stable ingredients and properties has been produced by co-crystallization technology. Therefore, the phase equilibrium data of water-soluble fertilizer has important guiding significance for the study of its production process.

Co-crystallization is the process of precipitating or crystallizing of different materials simultaneously. Usually, they had the corporate form of crystal, namely multi-component crystal, produced from vapor, solution or molten material[4]. Co-crystal is actually a mixture in the level of molecules and atoms[5]. The co-crystallization technology not only solves the problem of poor dispersibility and uniformity when the solid product is compounded, but also improves the crystal shape, fluidity, hygroscopicity and stability of the product[6]. Co-crystallization technology has been widely used in the preparation of pharmaceutical co-crystals[7-10], food additives[11], materials industry[12], energy and environment[13] and catalyst manufacturing[14].

Solid-liquid phase equilibrium is considered as fundamental content in chemical thermodynamics. Thermodynamics may be applied in the unit operations such as distillation, crystallization, extraction and purification in the chemical industry[15-16]. Multi-component solid-liquid phase equilibrium data and phase diagrams are the theoretical basis of crystallization process, so it has been a hot topic in recent years.

(NH₂)₂CO and KCl are often used to produce mixed water-soluble fertilizers, and their multi-system solid-liquid phase equilibrium is the basis of their crystallization process. In this work, the solid-liquid phase equilibrium of ternary system (NH₂)₂CO+KCl+H₂O at 283.15K were determined and its isothermal phase diagrams were plotted accordingly. Wilson model and NRTL model were used to calculate the solubility data.
2 Experimental section

2.1 Materials and apparatus

Urea (AR, Tianjin Kemiou Chemical Reagent Co., Ltd.), potassium chloride (AR, Chengdu Jinshan Chemical Reagent Co., Ltd.) were used in the experiment. The water for the experiment was deionized water with a resistivity of 18.25 MΩ cm. The main experimental apparatus includes cryogenic thermostatic bath (DC-4006, Shanghai Hengping Instrument and Meter Factory), electronic balance (HX-T100Z, Zhejiang Cixi Tianyi Weighing Apparatus Factory), magnetic stirrer (S10-3, Shanghai Sile Instrument Co., Ltd.) and X-Ray diffractometer (Bruker D8 Advance, Hebei Jixian Yaohua Glass Instrument Factory).

2.2 Experimental procedure

The solid-liquid equilibrium for ternary system \((\text{NH}_2)_2\text{CO}+\text{KCl}+\text{H}_2\text{O}\) was obtained by isothermal saturation method \([17-18]\). The experimental procedure for phase equilibrium determination have been described by the author in the author’s published article \([19]\).

2.3 Analysis

The content of KCl in equilibrium liquid phase and that of wet solid were determined by \(\text{NH}_4\text{Fe(SO}_4\text{)}_2\cdot12\text{H}_2\text{O}\) indicator method. The content of urea was determined with UV spectrophotometry \([20-21]\). Solid phase were confirmed by Schreinemaker’s method and X-ray powder diffraction \([22-24]\).

2.4 Results and discussion

The solubility data in mass fraction and the phase diagram for the ternary system of \((\text{NH}_2)_2\text{CO}+\text{KCl}+\text{H}_2\text{O}\) are shown in Table 1 and Figure 1.

| NO. | Liquid phase | Wilson | NRTL | Moist solid phase | solid phase |
|-----|--------------|--------|------|-------------------|-------------|
|     | 100w<sub>1</sub> | 100w<sub>2</sub> | 100w<sub>1</sub> | 100w<sub>2</sub> | 100w<sub>1</sub> | 100w<sub>2</sub> | 100w<sub>1</sub> | 100w<sub>2</sub> | 100w<sub>1</sub> | 100w<sub>2</sub> |
| 1   | 0            | 23.69  | --   | 23.73            | --          | 23.43          | --          | --          | KCl          |
| 2   | 6.63         | 22.39  | --   | 22.53            | --          | 21.80          | 1.44        | 79.84       | KCl          |
| 3   | 12           | 20.48  | --   | 20.23            | --          | 21.71          | 2.99        | 76.43       | KCl          |
| 4   | 19.36        | 19.65  | --   | 19.84            | --          | 18.95          | 6.85        | 72.40       | KCl          |
| 5   | 21.56        | 18.43  | --   | 18.20            | --          | 19.41          | 6.88        | 69.89       | KCl          |
| 6   | 28.76        | 17.55  | --   | 17.71            | --          | 16.91          | 10.00       | 69.56       | KCl          |
| 7   | 35.41        | 15.81  | --   | 15.78            | --          | 15.76          | 10.05       | 76.61       | KCl          |
| 8   | 37.84        | 15.33  | --   | 15.33            | --          | 15.18          | 11.52       | 72.79       | KCl          |
| 9   | 40.41        | 14.68  | 40.70 | --                | 39.73       | --            | 20.83       | 58.81       | KCl+(NH<sub>2</sub>)<sub>2</sub>CO |
| 10  | 40.51        | 14.01  | 40.72 | --                | 39.69       | --            | 77.21       | 5.63        | (NH<sub>2</sub>)<sub>2</sub>CO |
| 11  | 41.85        | 9.92   | 41.86 | --                | 41.68       | --            | 77.26       | 3.77        | (NH<sub>2</sub>)<sub>2</sub>CO |
| 12  | 44.58        | 5.20   | 44.67 | --                | 44.03       | --            | 66.84       | 3.47        | (NH<sub>2</sub>)<sub>2</sub>CO |
| 13  | 45.66        | 0      | 45.12 | --                | 45.03       | --            | --          | --          | (NH<sub>2</sub>)<sub>2</sub>CO |
| 100RAD | 0.61   |        | 2.33  |                  |              |               |             |             |              |
| RMSD | 0.22        |        | 0.66  |                  |              |               |             |             |              |

w<sub>1</sub>: mass fraction of \((\text{NH}_2)_2\text{CO}\), w<sub>2</sub>: mass fraction of KCl
Figure 1 the phase diagram for ternary system of $\text{(NH}_2\text{)}_2\text{CO}+\text{KCl}+\text{H}_2\text{O}$ at 283.15K.

In Figure 1, the points A, B, and C stand for the pure water, potassium chloride and urea respectively. $a_1$ and $b_1$ represent the mass fraction solubility of urea and potassium chloride in water at 283.15K respectively. $e_1$ is invariant point, at which urea and potassium chloride were saturate with a liquid phase. $a_1e_1$ and $b_1e_1$ are crystalline curves of pure urea and potassium chloride, respectively. The phase diagram is divided into four regions by two crystalline curves: $A_1a_1e_1b_1$ is an unsaturated region, $C_1a_1e_1$ is the crystallization zone of urea, $B_1b_1e_1$ is the crystallization zone of Potassium chloride, $C_1e_1B_1$ is the crystallization region of mixture solids of urea and Potassium chloride.

The solid of invariant point was collected and analyzed by X-ray diffraction from $10^\circ$ to $90^\circ$ at a scan speed of $8^\circ\cdot\text{min}^{-1}$. The pattern of XRD diagram is shown in Figure 2, it can be determined that the solid phase at the invariant point is mixture solid of urea and Potassium chloride.

Figure 2 XRD pattern of invariant points.
(a) the standard card of urea;(b) the standard card of Potassium chloride;(c) the XRD pattern of invariant point
2.5 Solid-liquid phase equilibrium correlation and calculation

In this paper, Wilson model [25] and NRTL model [26] were used to correlate the solid-liquid phase equilibrium data of the ternary system (NH$_2$)$_2$CO+KCl+H$_2$O at 283.15K.

Wilson model was showed in Equation (1).

$$\ln(y_i) = 1 - \ln(\sum_{j=1}^{N} A_{ij}x_j) - \sum_{k=1}^{N} \frac{\Lambda_{ij}x_k}{\sum_{j=1}^{N} A_{ij}x_j}$$

(1)

where, $A_{ij}$ are the Wilson parameters, which is related to the molar volume of pure substance and interaction energy of molecules, can be expressed as Equation (2).

$$\Lambda_{ij} = \frac{V_i}{V_j} \exp\left(-\frac{(g_{ij} - g_{jj})}{RT}\right) = \frac{V_i}{V_j} \exp\left(-\frac{E_{ij}}{RT}\right)$$

(2)

$v_i$ and $v_j$ are the molar volume of pure substances $i$ and $j$ respectively, which can be calculated from the molar mass and density. $E_{ij}$ is the adjustable interaction energy parameter (J mol$^{-1}$), which is less affected by temperature and can be regarded as a constant in a not too wide temperature range.

NRTL model and the computational formula of relative parameters was showed in Equation (3)-(6).

$$\ln\gamma_i = \sum_{j=1}^{N} x_j \frac{G_{ij}}{G_{jj}} + \sum_{j=1}^{N} x_j x_i \frac{\tau_{ij}}{G_{jj}}$$

(3)

$$G_{ij} = \exp\left(-\alpha_{ij} \tau_{ij}\right)$$

(4)

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT}$$

(5)

$$\alpha_{ij} = \alpha_{ji}$$

(6)

$\alpha$ is a nonrandom parameter and usually varies in the range from 0.2 to 0.47. In this paper, it is taken as 0.3.

The relative average deviation (RAD) and root mean-square deviation (RMSD) was used to evaluate the applicability and accuracy of the two models (Equation (7) and (8)).

$$\text{RAD} = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{w_i - w_i^{cal}}{w_i}\right|$$

(7)

$$\text{RMSD} = \left[ \frac{1}{N} \sum_{i=1}^{N} \left( w_i^{e} - w_i^{cal}\right)^2 \right]^{1/2}$$

(8)

where $N$ was the number of all experimental data; the $w^e$ and $w^{cal}$ represent experimental value and calculated value in mass fraction, respectively.

During the regression process, the density of urea, the melting temperature $T_m$ and fusion enthalpy $\Delta_f$H, the density and melting temperature of potassium chloride, the fusion enthalpy $\Delta_f$H for potassium chloride were cited from in the References [27-30]. The interaction energy parameter $\Delta_{g_{ij}}$ for binary systems of (NH$_2$)$_2$CO+H$_2$O, KCl+H$_2$O were obtained on the basis of the solubility data by the nonlinear regression method through 1stopt software [31-32]. For the two binary systems, the root mean-square deviation were no more than 0.3% in the Wilson model, and that were no more than 0.4% in the NRTL model. Based on the interaction energy parameters of binary system of (NH$_2$)$_2$CO+H$_2$O and KCl+H$_2$O, the binary interaction energy parameters of (NH$_2$)$_2$CO+KCl was acquired and showed in Table 2.

Table 2. The regressed binary interaction energy parameter of (NH$_2$)$_2$CO(1)+KCl(2)+H$_2$O(3).

| i-j | Wilson | NRTL |
|-----|--------|------|
|     | $\Delta g_{ij}$ | $\Delta g_{ij}$ | $\Delta g_{ij}$ | $\Delta g_{ij}$ |
| 1-2 | 2317.90 | -4738.41 | 12950.01 | 54970.00 |
| 1-3 | -2111.43 | 1045.28 | -4223.09 | 7634.08 |
| 2-3 | -6720.84 | -2791.38 | -5549.50 | -5009.95 |

The solubility were calculated based on the obtained interaction energy parameters, and the calculated results were presented in Table 1. The value of RMSD and RAD of Wilson model and NRTL model for the ternary system (NH$_2$)$_2$CO+KCl+H$_2$O are listed in Table 1. The value of root mean-square deviation in Wilson model and NRTL model for this ternary system was 0.22 and 0.66 respectively, and the value of relative average deviation was 0.61% and 2.33% respectively, which indicated that the calculated data and the experimental results are nearly consistent.

3 Conclusion

The solid-liquid equilibrium for ternary system (NH$_2$)$_2$CO+KCl+H$_2$O was determined by isothermal saturation method at 283.15 K under atmosphere pressure and their isothermal dissolution phase diagrams were constructed. This ternary system belongs to a simple eutectic type with an invariant point and neither solid solutions nor double salts are found.

The solid-liquid phase equilibrium data were correlated by using the Wilson model and NRTL model. The largest value of RMSD for the ternary system (NH$_2$)$_2$CO+KCl+H$_2$O were 0.66, and that of RAD were
2.33%. So the calculated solubility via the two models provided good agreement with the experimental values. Furthermore, the Wilson model provided a better correlation results than NRTL model for this system.

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References

1. Yao X, Xinghua M. Progress on Effect of Nitrogen Form on Plant Growth. Journal of Agricultural Science and Technology | J Agric Sci Tech China. 2015;17(2):109-17.
2. Derong Z, Jing W, Hongxia, Yue W, Ming H, Ruman Z. The role of potassium fertilizer in plant growth and its effect on maize production in Wuan City. Modern Agricultural Science and Technology. 2011-04-10(07):313-7.
3. Jiaming W. Water soluble fertilizer development status and market prospects. Shanghai Chemical Industry. 2011;36(12):27-31.
4. Gagnière E, Mangin D, Puel F, et al. Formation of co-crystals: Kinetic and thermodynamic aspects. J CRYST GROWTH. 2009;311(9):2689-95.
5. Jayasankar A, Somwangthanaroj A, Shao ZJ, Rodriguez-Hornedo N. Cocrystal Formation during Cogrinding and Storage is Mediated by Amorphous Phase. PHARM RES-DORDR. 2006 2006-10-04;23(10):2381-92.
6. Shan N, Toda F, Jones W. Mechanochemistry and co-crystal formation: effect of solvent on reaction. CHEM COMMUN. 2002 2002-10-11(20):2372-3.
7. Walsh RDB, Bradner MW, Fleischman S, et al. Crystal engineering of the composition of pharmaceutical phases. CHEM COMMUN. 2003 2003-01-07(2):186-7.
8. Ghosh S, Bag PP, Reddy CM. Co-Crystals of Sulfamethazine with Some Carboxylic Acids and Amides: Co-Former Assisted Tautomeration in an Active Pharmaceutical Ingredient and Hydrogen Bond Competition Study. CRYST GROWTH DES. 2011 2011-01-01;11(8):3489-503.
9. Hickey MB, Peterson ML, Scoppettuolo LA, et al. Performance comparison of a co-crystal of carbamazepine with marketed product. EUR J PHARM BIOPHARM. 2007;67(1):112-9.
10. Rodriguez-Hornedo N, Nehm SJ, Seefeldt KF, Pagan-Torres Y, Falkiewicz CJ. Reaction Crystallization of Pharmaceutical Molecular Complexes. MOL PHARMACEUT. 2006;3(3):362-7.
11. Umesh Hebbar H, Rastogi NK, Subramanian R. Properties of Dried and Intermediate Moisture Honey Products: A Review. INT J FOOD PROP. 2008 2008-01-01;11(4):804-19.
12. Yancheng Z, Zhi P, Tao L, Chunming W. Preparation and organization of Al(Cr)2O3-Cr(Mo) ceramic matrix composites. Acta Materiae Compositae Sinica. 2006 2006-04-30(02):104-9.
13. Zongwei Y, Yanli Z, Hongzhen L, et al. Preparation, Structure and Properties of CL-20/TNT Cocrystal. Chinese Journal of Energetic Materials. 2012;20(6):674-9.
14. Longya X, Jianbiao P, Sujuan X, Qingxia W, Zhihua W; ZSM-35/MCM-22 co-crystallized molecular sieve and preparation method thereof. 2002 2002-11-29.
15. Guo L, Hu Y, Wang Y, Wu L. A quasi-ternary wet residue method applied to solid-liquid equilibrium systems. FLUID PHASE EQUILIBR. 2018;456:161-7.
16. Jakob A, Joh R, Rose C, Gmehling J. Solid-liquid equilibria in binary mixtures of organic compounds. 1995;113(1):117-26.
17. Nyl'nt J. Solid-liquid phase equilibria. Prague: Publishing House of the Czechoslovak; 1977.
18. He T, Sun J, Shen W, Ren Y. Solid-liquid phase equilibria of quaternary system NH4+/Cl-/SO4^2-/H2PO4^-H2O and its subsystems NH4+/Cl-/SO4^2-/H2O, NH4+/Cl-/H2PO4^-H2O at 313.15 K. The Journal of Chemical Thermodynamics. 2017;112:31-42.
19. Xue H, Jing Z, Ruizhe W, Hongguo L. Research on phase equilibrium of ternary system of (NH2)2CO-NH4H2PO4-H2O at 10°C. Inorganic Chemicals Industry. 2019;51(5):41-4.
20. Yao G, Wang L, Sun Y, Yi J, Meng L, Zhao H. Ternary Phase Diagram for Systems of Succinic Acid + Urea + Water, Glutaric Acid + Urea + Water, and Adipic Acid + Urea + Water at (288.15 and 303.15). K. Journal of Chemical & Engineering Data. 2014 2014-12-11;59(12):4081-9.
21. Li Y, Li C, Han S, Zhao H. Binary and ternary solid-liquid phase equilibrium for the systems formed by succinic acid, urea and diethylene glycol: Determination and modelling. The Journal of Chemical Thermodynamics. 2017;108:97-104.
22. SCHOTT H. A Mathematical Extrapolation for The Method of Wet Residues. Journal of Chemical & Engineering Data. 1961 1961-01-01;6(3):324.
23. Schreinemakers FAH. Graphical deductions from the solution isotherms of a double salt and its components. Z. Phys. Chem. 1893;6:53-109.
24. Du CB, Han S, Zhong YH, Yao GB, Wang J, Zhao H. Determination and prediction of solid-liquid phase equilibrium for quaternary system of terephthalic acid+sophthalic acid+phthalic acid+N-methyl-2-pyrrolidone at 303.15K and 313.15K. FLUID PHASE EQUILIBR. 2015;397:103-10.
25. Wilson GM. A New Expression for the Excess Free
26. Renon H, Prausnitz JM. Estimation of Parameters for the NRTL Equation for Excess Gibbs Energies of Strongly Nonideal Liquid Mixtures. Industrial & Engineering Chemistry Process Design and Development. 1969;8(3):413-9.

27. Guangqi L, Liangxiang M, Jie L. Chemical and chemical property data sheet organic volume. First edition*ed. Beijing: Chemical Industry Press; 2002.

28. Gatta GD, Ferro D. Enthalpies of fusion and solid-to-solid transition, entropies of fusion for urea and twelve alkylureas. THERMOCHIM ACTA. 1987;122(1):143-52.

29. Guangqi L, Liangxiang M, Jie L. Chemical and chemical properties data sheet inorganic volume. First edition*ed. Beijing: Chemical Industry Press; 2002.

30. Dean JA. Lange's Handbook of Chemistry. Beijing: Science Press; 1991.

31. Louis S, Sunier AA. The solubility of urea in water. J.phys.chem. 1932;36(4):1232-40.

32. Sunier AA, Baumbach J. The solubility of potassium chloride in ordinary and heavy water. Journal of Chemical & Engineering Data. 1976 1976-01-01;21(3):335-6.