



A Water–Urea–Ammonium Sulfamate system: Experimental investigation and thermodynamic modelling

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ABSTRACT

The Water–Urea–Ammonium Sulfamate ternary system was investigated by means of experimental methods and thermodynamic modelling. Experimental part of the work includes (i) DSC measurements of liquidus and solidus of the Urea–Ammonium Sulfamate, the Water–Ammonium Sulfamate subsystems with the estimation of eutectic point position and a set of experiments on the phase boundaries in the ternary system; (ii) vapor pressure measurements in the binary Water–Ammonium Sulfamate and ternary Water–Ammonium Sulfamate–Urea systems at 298.15 K in a wide concentration range. Excess Gibbs energies of the Water–Ammonium Sulfamate–Urea system and its binary subsystems were described by the Pitzer–Simonson–Clegg model which is reduced to polynomial formalism in case of nonelectrolyte systems. Results of the Water–Urea subsystem reassessment are given.

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1. Introduction

Urea ($(\text{NH}_2)_2\text{CO}$ or Ur) is one of the most popular nitrogen fertilizers and an ecologically benign component of de-icers. Addition of salts containing sulfur and other elements to solid urea or its solutions allows developing new complex fertilizers and de-icers. In this work we investigate ammonium sulfamate ($\text{NH}_4\text{SO}_3\text{NH}_2$ or ASM) as possible urea additive. This substance is highly soluble in water [1–4], decomposes to common salts over time and can be used for developing new mixtures stable in a wide range of temperatures and compositions. Due to herbicide action of ASM in mixtures with a high content of salt its solutions can be used as a double-action reagents to decrease the freezing point of de-icers and to remove vegetation near airport runways. The product of ASM degradation is ammonium sulfate [5] which is environmentally benign.

Critical review and thermodynamic modelling of the water–urea binary subsystem was made by Voskov et al. [6]. However, it uses only experimental data about solid–liquid equilibrium (SLE) in the binary system; thermodynamic properties of solution were not used for model parameterization. Therefore, the reassessment of

the $\text{H}_2\text{O}-(\text{NH}_2)_2\text{CO}$ system is desirable to obtain more reliable thermodynamic model of the liquid phase; it was one of the purposes of present investigation. Water solubility of ammonium sulfamate was investigated by Ushida et al. [1], Ricci et al. [2,3] and Deiter et al. [4]. Nevertheless, the part of the fusibility diagram of the water–ammonium sulfamate system near the solvent angle hasn't been researched previously. Solidus temperature and the eutectic composition of the water–ammonium sulfamate system are unknown. Information about phase equilibria and thermodynamic properties of solutions in the $(\text{NH}_2)_2\text{CO}-\text{NH}_4\text{SO}_3\text{NH}_2$ binary and $\text{H}_2\text{O}-\text{NH}_4\text{SO}_3\text{NH}_2-(\text{NH}_2)_2\text{CO}$ ternary systems is not available in literature.

The aim of the present work was to study thermodynamic properties and phase diagrams of the $\text{H}_2\text{O}-\text{NH}_4\text{SO}_3\text{NH}_2-(\text{NH}_2)_2\text{CO}$ ternary system and constituent binary subsystems. Experiments and thermodynamic modelling were used to investigate them. We applied the following algorithm to solve the problem: at the first step the experimental data for the binary systems were obtained and used to determine the binary model parameters, then the possibility of ternary system description with only this set of parameters was tested, and finally ternary interaction parameters were updated by fitting a vapor pressure measurements in the ternary system.

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2. Experimental section

2.1. Reagents

Commercial reagents of urea (analytical grade, 99%) and ammonium sulfamate (analytical grade, 99%) were recrystallized from distilled water. Substances were dried under pressure of 13 Pa using an oil pump. Purified reagents were characterized by means of DSC (ASTM E 928) and XRD method. According to ASTM E 928 it is possible to determine total molar content of the impurities in the sample by means of DSC. As a result purity after recrystallization of the Ur and ASM is expressed in mole percent in Table 1. In the present study, distilled water was used to prepare aqueous solutions.

2.2. Methods

X-ray powder diffraction data were obtained on a diffractometer STOE STADI-P (Ge-monochromator, radiation $\text{CuK}\alpha 1.1 = 1.54056 \text{ \AA}$, linear PSD) in transmission geometry. Angle 2θ was varied in the range from 10 to 80° in steps of 0.02° ; the exposure time was 10 s per point. Samples of recrystallized urea and ammonium sulfamate were identified by comparing theoretical and experimental diffractograms, by means of computer programs WinXPOW [7].

Liquidus and solidus of the Ur–ASM, H_2O –ASM and H_2O –ASM–Ur systems were received by a NETZSCH DSC 204 F1 in a stream of dry Ar (40 ml min^{-1}) with heating (HR) and cooling (CR) rates 0.5 – 10 K min^{-1} . Maximum temperature range of DSC-experiments was 123.15 – 423.15 K . NETZSCH DSC 204 F1 was calibrated directly prior to measurements at 0.5 , 2 , 5 , 10 K min^{-1} heating rates by temperatures of standard substances (C_6H_{12} , Hg, H_2O , Ga, benzoic acid, KNO_3 , In; Sn; Bi, Pb, Zn purity 99.999%) according to ASTM E 967; systematic uncertainty of calibration were 0.1 K . The number of statistically independent experimental points was at least three. All measured values are characterized by a t -distribution with 95% confidence interval.

Thermogravimetry measurements (TGA) were processed using NETZSCH TG 209 F1 in the temperature range 303.15 – 423.15 K for the estimation of the thermal stability of solid components and their mixtures at elevated temperatures. The conditions of experiments and preparation of samples were conducted similarly to DSC measurements. Calibration technique of apparatus was the same as described by Grishenko et al. [8].

Samples for DSC and TGA experiments were weighed on an analytical balance A&D GH-202 with an accuracy of 0.01 mg . Specimens ($m = 3$ – 7 mg) were tested in standard aluminium crucibles ($V = 56 \text{ mm}^3$, $d = 6 \text{ mm}$). Crucibles were closed to prevent evaporation of water when the aqueous solutions were investigated by DSC.

DSC and TGA curves were processed using NETZSCH Proteus Analysis. According to Hohne [9] and Zhao [10], solidus temperatures were determined by onset temperatures (T_{onset}) of the first DSC peaks and liquidus temperatures were obtained by the extremum temperatures of last DSC peaks (T_{peak}). Additional temperature corrections on thermal resistance [9] of experimental DSC signals were conducted for the accurate determination of liquidus temperatures. The sample of fresh distilled water was used as a

standard substance in case of water–ASM and ternary system investigation; the sample of benzoic acid (purity 99.999%) was used as a standard substance in case of Ur–ASM system investigation.

Vapor-liquid equilibria data for the H_2O –ASM and H_2O –ASM–Ur systems were obtained by the static method at 298.15 K . A detailed description of the apparatus and the measurement technique was given previously by Kovalenko et al. [11]. The vapor pressure apparatus consists of two parts: the degassing block and the pressure measuring system. The main task of the degassing block is to remove all dissolved gases from the solution under investigation. The pressure measurement system includes the flask with solution, magnetic stirrer, thermometer and pressure transducer. The flask was immersed in the constant-temperature double-walled bath. Temperature inside the bath was maintained by circulating water from a liquid thermostat. As compared with previous version of the apparatus, a few improvements were introduced to the pressure measuring system. At first, the glass body of the apparatus was replaced by stainless steel elements and vacuum valves. Secondly, for vapor pressure measurements vacuum pressure transducer Setra 764 with integral heated sensor was used. Maintaining an internal constant temperature (temperature controlled to 318.15 K) leads to decreasing the error of the measurement, the accuracy of the transducer is $\pm 0.15\%$ of reading. Thirdly, Pt-100 resistance thermometer with an accuracy of 0.02 K was used for temperature measurements. Finally, the pressure measuring system was placed in the air thermostat. The air thermostat temperature was kept 1 – 2 K higher than the bath temperature; thereby the condensation of the vapor on the wall of the pipeline was prevented. In addition, the usage of the air thermostat led to decreasing of the temperature fluctuations in the bath. The uncertainties of the vapor pressure measurements were estimated by comparison of measured values $p(\text{H}_2\text{O})$ and recommended by Dykij et al. [12] in the temperature range of 277.15 – 311.15 K ; a relative error does not exceed 0.5% . Components of solutions for vapor pressure measurements were weighted on an AXIS AG300 balance with an accuracy of 0.001 g . Mass of samples were 20 – 30 g .

3. Thermodynamic models

3.1. Stability parameters

The Gibbs energy of melting of pure components was described assuming that $\Delta_m C_p = \text{const}$ because of narrow temperature interval and lack of experimental data about C_p temperature dependence for liquid Ur and ASM:

$$\begin{aligned} \Delta_m G(T) &= \Delta_m H(T) - T \Delta_m S(T) \\ &= \Delta_m H(T_m) + \Delta_m C_p (T - T_m) - T \left(\frac{\Delta_m H(T_m)}{T_m} \right. \\ &\quad \left. + \Delta_m C_p \ln \frac{T}{T_m} \right), \end{aligned} \quad (1)$$

where T_m is the melting temperature, $\Delta_m H(T_m)$ is the enthalpy of melting at T_m . For all components $\Delta_m C_p$ was estimated for T_m . Thermodynamic properties required for the calculation of stability parameters ($\Delta_m G(T)$) are given in Table 2.

Table 1
Purities and sources of chemicals.

Chemical name	CAS number	Source	Initial purity (weight percent)	Purification method	Final purity (mole percent)
$(\text{NH}_2)_2\text{CO}$	57-13-6	«Reahim»	99.0	recrystallization	99.97
$\text{NH}_4\text{SO}_3\text{NH}_2$	7773-06-0	«Reahim»	99.0	recrystallization	99.95

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