ENTHALPIES OF CRYSTALLIZATION OF EQUILIBRIUM SOLID PHASES OCCURRING IN THE SYSTEM KNO$_3$–NH$_4$NO$_3$–H$_2$O AT 298.15 K

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Abstract

The concentration dependencies of the differential enthalpies of solution along several crystallization paths in the above mentioned system were measured. On this basis enthalpies of crystallization of equilibrium solid phases occurring there were calculated.

Keywords: enthalpy of crystallization, KNO$_3$–NH$_4$NO$_3$–H$_2$O system

Introduction

The physically homogeneous mixture of two or more solid substances formed mixed crystals. Each of these substances has a definite chemical formula, but the mutual molar ratio of the solid solution components is not expressed by integral numbers and can change within whole range of compositions (continuous solid solution) or within a limited range (solid solution with a gap of miscibility).

The conditions, which are necessary to form mixed crystals are known. They are: similarity of the chemical formula, similar quantity of ions, similar properties of polarization, the same type of chemical bond; the desirable but unnecessary condition is: belonging to the same type of crystallographic structure.

Solid solutions between melting salts as well as between inorganic salts in salt$_1$–salt$_2$–water systems are formed. The solid solutions formed in melting salts are more precisely investigated and elaborated [1]. In our previous papers [2, 3] the investigations of crystallization enthalpies of equilibrium solid phases occurring in the system KCl–KBr–H$_2$O (I) and K$_2$SO$_4$–(NH$_4$)$_2$SO$_4$–H$_2$O (II) were described. It was confirmed that in the system (I) the continuous solid solutions only, and in the system (II) the solid solutions with a miscibility gap were formed. Therefore, the system (I) belongs to the 3rd and the system (II) to the 5th type of solubility isotherms, according to Roozeboom's classification [4].

The literature data concerning the equilibrium solid phases of KNO$_3$–NH$_4$NO$_3$–H$_2$O system is very limited and divergent. It probably follows from the great ability to the metastable states formation. According to Chirkov data

[5] in this system two branches of mixed crystals $(K,NH_4)NO_3$ with considerable discontinuity region are formed. For that reason it belongs to the 5th type of the multicomponent systems with the discontinuity region of peritonic type. Nevertheless, the other investigators found this system more complicated: in addition there double salt $3KNO_3 \cdot NH_4NO_3$ [6] or $KNO_3 \cdot 2NH_4NO_3$ [7] exist. The existence of double salt and mixed crystals in one system causes that it is beyond the Roozeboom's classification and this fact is in agreement with Balarev data [8].

For the reasons mentioned above we have found this system as an interesting object of the crystallization enthalpies studies. It was decided to test crystallization enthalpies $\Delta_{cryst}H_m$, of mixed crystals and mixture of crystals from discontinuity region. To pinpoint these measurements were made of the concentration dependencies of the differential enthalpies of solution, $\Delta_{sol}H_2$, along several crystallization paths. This allowed calculation of the last differential enthalpies of solution, $\Delta_{sol}H_2^{sat}$, and also of the enthalpies of crystallization, according to the dependence:

$$|\Delta_{sol}H_2^{sat}| = |\Delta_{cryst}H_m| \tag{1}$$

Experimental

The experiments were carried out with a solution calorimeter of 'isoperibol' type, made in Technical University of Gdańsk [9, 10].

In order to obtain appropriate solid phases, the equilibrium data of Dejewska [1] and Dejewska and Sędzimir [7] were used. After equilibrium investigations the contents of potassium ions (by means of sodium tetraphenylborate) and ammonium ions (through the decomposition with sodium hydroxide in Parnas apparatus) in the obtained solutions and solid phases were determined.

Solid phases, after drying, were crushed in a ball vibrating grinder and then stored in desiccator over phosphorus pentoxide. The mother liquor content for every sample was determined and suitable corrections of differential enthalpies of solution were made. The quantities of dissolved crystals were constant along every crystallization paths and amounted to $1.877 \cdot 10^{-3}$ of mol.

All solutions used in calorimeter experiments were prepared by weighing. Double distilled water was used throughout the experiments. Analytical grade salts (POCH Gliwice, Poland) were used.

The calculations were performed with an IBM PC/AT microcomputer, using the program Statgraphics (Statistical Graphics System by Statistical Graphics Corporation, vers. 2.6.). The experimental data are available on request.

Results and discussion

For the calorimetric work a knowledge of the equilibrium data is essential, i.e. the solubility isotherm data and the compositions relating to its solid

phases. Research performed earlier in our Institute [1, 7] was therefore utilized and suitable equilibrium solid phases were obtained. The time necessary for the system to reach the equilibrium state from supersaturated solutions was 24 h. However, this time was not sufficient nearby the periotic point. In this region the equilibrium state was settled within several weeks.
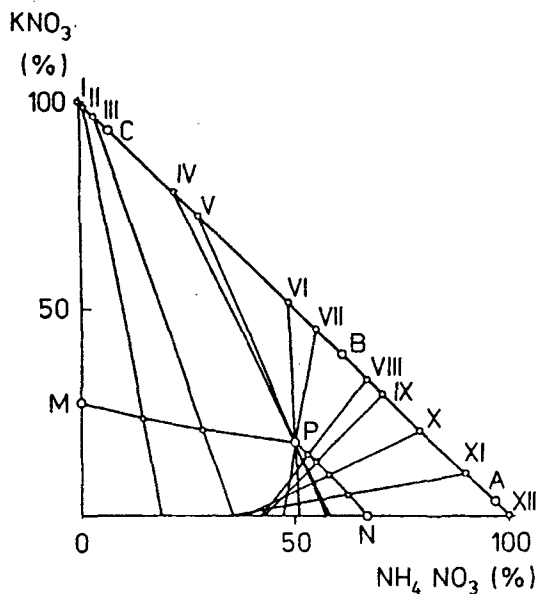

Fig. 1 The system $KNO_3–NH_4NO_3–H_2O$ at 298.15 K

Figure 1 shows the investigated systems at 298.15 K. The line M-P-N represents the solubility isotherm, point P is the peritonic point; the lines II–XI represent crystallization paths and lines I and XII binary solutions of $KNO_3–$ H_2O and $NH_4NO_3–H_2O$, respectively; the section $KNO_3–NH_4NO_3$ represents anhydrous solid phases. In the section $KNO_3–C$ there exist mixed crystals $(K,NH_4)NO_3$ formed on the base of KNO_3, in section C–B-mixture of crystals C and B, where point B represents double salt $KNO_3·2NH_4NO_3$ (the gap of miscibility occurs in the range 6.68% to 61.29% of NH_4NO_3), in the section B–A there exist mixed crystals formed on the base of crystals B or A (91.74% of NH_4NO_3) and in the section A–NH_4NO_3-mixed crystals $(NH_4,K)NO_3$ formed on the base of NH_4NO_3.

The differential enthalpies of solution, $\Delta_{sol}H_2$, were measured along the crystallization paths, from binary solutions of $NH_4NO_3–H_2O$ to the solubility isotherm. It means that the way of experiments was the same as in the case of salt–water systems, but now with binary and ternary systems instead of water and binary systems as a solvent.

The crystallization paths II, III and VIII–XI represent mixed crystals from the continuity regions; paths IV–VII – mixtures of crystals C and B; and paths I and XII – potassium and ammonium nitrates, respectively.

The paths were described by the equation:

$$c_2 = c_2^0 + kc_1 \qquad (2)$$

where c_1 and c_2 are the concentrations of KNO_3 and NH_4NO_3 (in %), respectively, c_2^0 is the concentration of the binary solutions $NH_4NO_3-H_2O$ (in %), and k is a constant.

The coefficients in Eq. (2) are given in Table 1, together with data relating to the equilibrium phases occurring along the crystallization paths.

As already mentioned, the differential enthalpies of solution were measured along the crystallization paths. As concerns both the measured $\Delta_{sol}H_2$ values and the compositions of solid phases, corrections were made for the mother liquor content, amounting to 3.5–5.5 % of the dry mass of the crystals. The obtained concentration dependencies of $\Delta_{sol}H_2$ were described by the equation:

$$\Delta_{sol}H_2 = \sum_{i=0}^{2} a_i I_m^i \qquad (3)$$

where a_i is an adjustable parameter and I_m is ionic strength of initial solutions calculated from molalities.

From those dependencies and the known compositions of the saturated solutions, the last differential enthalpies of solution were calculated and hence from Eq. (1) the molar enthalpies of crystallization of equilibrium solid phases.

Those data and also the coefficients in Eq. (3) are listed in Table 2, together with the number of experimental points used in each fit.

The obtained results permit calculation of the excess enthalpies of crystallization, $\Delta_{cryst}H_m^E$, which were taken as the measure of interactions between the components of equilibrium solid phases. Those values were determined as the difference between the enthalpy of crystallization, $\Delta_{cryst}H_m$, per mole of solid phase and the sum of crystallization enthalpies of a molar mixture of KNO_3 and NH_4NO_3, corresponding to the mole of solid phase, according to the following equation:

$$\Delta_{cryst}H_m^E = \Delta_{cryst}H_m - [x_1 \cdot \Delta_{cryst}H_{m(1)} + x_2 \cdot \Delta_{cryst}H_{m(2)}] \qquad (4)$$

where $\Delta_{cryst}H_{m(1)}$ and $\Delta_{cryst}H_{m(2)}$ are the crystallization enthalpies of KNO_3 and NH_4NO_3, respectively; and x_1 and x_2 are the molar fractions of KNO_3 and NH_4NO_3 in the solid phases, respectively.

Table 1 Coefficients of Eq. (2) and compositons of equilibrium solid phases along the crystallization paths; M_{cr} denotes the molar mass of equilibrium solid phases

Crystallization path	Coefficients of Eq. (2)		Satur. solns	Equilibrium solid phases		
	c_2^0 /%	K	C_1^{sat} /%	KNO_3/%	KNO_3 /mol %	M_{cr} /g·mol^{-1}
II	18.87	-0.1811	23.96	99.07	98.83	100.86
III	35.68	-0.3348	21.63	96.69	95.85	100.24
IV	58.63	-0.4671	17.67	77.62	73.30	95.48
V	57.64	-0.4107	17.67	71.89	66.94	94.12
VI	51.45	-0.0606	17.67	51.68	45.85	89.69
VII	47.33	0.1725	17.67	44.92	39.24	88.30
VIII	42.90	0.7092	14.67	33.41	28.43	86.03
IX	42.02	0.9535	13.55	29.68	25.04	85.32
X	37.57	1.9972	10.26	20.83	17.24	83.68
XI	35.17	5.2968	5.18	10.20	8.25	81.78

Table 2 Coefficients of Eq. (3) and values of crystallization enthalpies of equilibrium solid phases; N-number of experimental points used in each fit, R-correlation coefficient

Crystallization path	N	a_0 / $J \cdot mol^{-1}$	a_1 / $J \cdot kg \cdot mol^{-2}$	a_2 / $J \cdot kg^2 \cdot mol^{-3}$	R	$-\Delta_{cryst}H_m$ / $J \cdot mol^{-1}$
II	34	3.22695 E4	−3.10804E3	1.39045E2	0.9901	17558±98
III	34	3.12223 E4	−2.31342E3	7.70020E1	0.9533	14856±101
IV	28	1.79947 E4	−5.38154E2	8.59385E0	0.9781	9894±69
V	26	2.61987 E4	−1.37671E3	2.91599E1	0.9015	10021±156
VI	21	2.04994 E4	−8.29490E2	1.66889E1	0.9745	10194±122
VII	20	1.89845 E4	−6.29259E2	1.14034E1	0.9863	10370±125
VIII	25	1.85038 E4	−6.02017E2	1.10082E1	0.9972	10312±71
IX	24	1.83195 E4	−5.82581E2	1.03998E1	0.9891	10201±106
X	27	1.72134 E4	−4.87086E2	8.31418E0	0.9813	10164±193
XI	35	1.80248 E4	−6.01635E2	1.14724E1	0.9969	10138±98

The value of $\Delta_{cryst}H_{m(1)}$ used in Eq. (4) was calculated from Parker's data [11] and amounts to -22572 ± 126 J·mol^{-1}, for $m_1^{sat}=3.7515$ mol·kg^{-1} [7]. However, the value of $\Delta_{cryst}H_{m(2)}$ was calculated from complied data of Parker (in the molality range 0–20 mol·kg^{-1}) and our measurements of $\Delta_{sol}H_2$ (in the molality range 20.0–24.5 mol·kg^{-1}) and amounts to -12292 ± 307 J·mol^{-1}, for $m_2^{sat}=25.4812$ mol·kg^{-1} [7].

The values of $\Delta_{cryst}H_m^E$, calculated this way, as a function of equilibrium solid phase composition (expressed in mol%), are presented in Fig. 2.
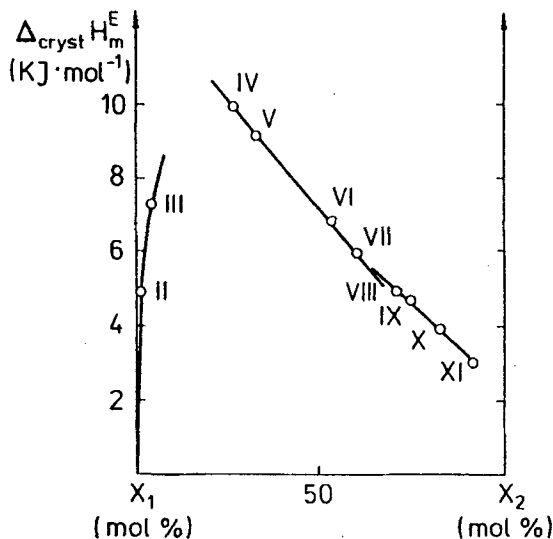

Fig. 2 The excess molar enthalpies of crystallization of equilibrium solid phases, $\Delta_{cryst}H_m^E$, as a function of their contents; x_1 and x_2 are the molar fractions of KNO_3 and NH_4NO_3, respectively

It can be seen from the graph that there exist three separated curves corresponding to the two series of mixed crystals (points II, III and VIII–XI) and to the discontinuity region (points IV–VII). That fact confirms the existence of those regions. But it also can be seen that there is a lack of data concerning the region 93.35–100.00 mol% of NH_4NO_3 (section A–NH_4NO_3, Fig. 1). It follows from uncertainty what kind of equilibrium solid phase exists in that region. Recent equilibrium works [12, 13] suggest that starting from ammonium nitrate there exist mixed crystals $(NH_4,K)NO_3$ formed on the base of crystals NH_4NO_3 (IV). In point A (91.74% NH_4NO_3) the change of modification of NH_4NO_3 (IV) to NH_4NO_3 (III) takes place. Nevertheless that supposition requires further equilibrium investigations.

In Fig. 3 there are presented the crystallization enthalpies values of the mixture of the crystals B and C (discontinuity region, points IV–VII) as a function
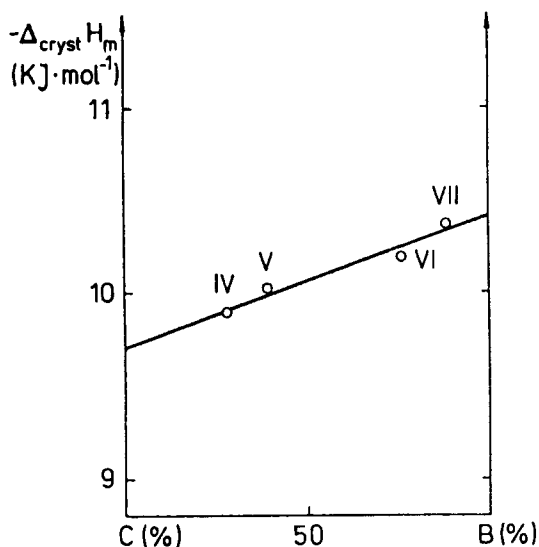
Fig. 3 The crystallization enthalpies, $\Delta_{cryst}H_m$ of mixture of crystals B and C in the region of discontinuity as a function of their contents

of their contents (in %). As it can be seen from the graphs those points lie on a straight line, which is described by the equation:

$$-\Delta_{cryst}H_m = 9709.3 + 7.0508 \cdot B, \quad (RSQ = 0.9345)$$

where B means a content of crystal B in the mixture of crystals (in %). It allowed the calculation of the $\Delta_{cryst}H_m$ values for double salt $KNO_3 \cdot 2NH_4NO_3$ (crystal B) which amount to -10414 ± 53 J·mol^{-1} and -9709 ± 67 J·mol^{-1} for crystal C.

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Zusammenfassung — Es wurde die Konzentrationsabhängigkeit der differentiellen Lösungsenthalpien des Titelsystemes auf verschiedenen Kristallisationswegen gemessen. Ausgehend hiervon wurden die Kristallisationsenthalpien der darin vorkommenden festen Gleichgewichtsphasen berechnet.