Journal of Thermal Analysis, Vol. 45 (1995) 799-804

ENTHALPIES OF CRYSTALLISATION OF EQUILIBRIUM SOLID PHASES OCCURRING IN THE SYSTEM KCl–KBr–H_2O AT 298.15 K

A. Chmarzyński and B. Dejewska

Faculty of Chemistry, N. Copernicus University, ul. Gagarina 7, 87-100 Toruń, Poland

Abstract

The concentration dependencies of the differential enthalpies of solution were measured along several crystallization paths in the KCl–KBr–H_2O system. On this basis enthalpies of crystallization of mixed crystals occurring as a stable solid phase in the system were calculated.

Keywords: enthalpy of crystallization, KCl–KBr–H_2O system

Introduction

Extending the studies on crystallization enthalpies from binary systems to ternary of the type $salt_1$–$salt_2$–H_2O, the investigations of the system K_2SO_4–$(NH_4)_2SO_4$–H_2O were performed [1]. The obtained results confirmed the existence of region of breaking continuity in the equilibrium solid phases. Continuing investigations of the systems with mixed crystals in equilibrium solid phases we have chosen system presented in this work.

The literature data concerning the equilibrium investigations of the KCl–KBr–H_2O system are numerous [2–7] and they describe the above system well. In this system the continuous solid solutions are formed and according to Rozeboom's classification [8] it belongs to the 3rd type of the multicomponent systems with mixed crystals in solid phase.

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 and Sędzimir [11] were used. In the prepared solutions and solid phases the contents of potassium ions (by means of sodium tetraphenylborate), bromide ions (by a iodometric method after previous oxidation of Br^- to BrO_3^-) and

0368–4466/95/ $ 4.00

John Wiley & Sons, Limited
Chichester

chloride ions (from the sum of chloride and bromide ions determined by argentometry) were calculated.

Solid phases, after drying, were crushed in a ball vibrating grinder. For every sample, the mother liquor content was determined and suitable corrections in values of differential enthalpies of solution, $\Delta_{sol}H_2$, were made. The quantities of dissolved crystals were constants and amounted to $4.625 \cdot 10^{-3}$ mol.

All solutions used in calorimetric 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, the knowledge of the equilibrium data was essential, i.e. the solubility isotherm data and compositions relating to proper solid phases. Research performed earlier in our Institute [11] was therefore utilized and suitable equilibrium phases were obtained. In these experiments the time necessary for the system to reach the equilibrium state from supersaturated solutions was 24 h.

Figure 1 shows the diagram of investigated system at 298.15 K. The section KCl–KBr corresponds to the compositions of the mixed crystals of K(Cl, Br); curve A-B represents the solubility isotherm and lines I-V denote crystallization paths.

The differential enthalpies of mixed crystals solution, $\Delta_{cryst}H_{m2}$, were measured along several crystallization paths, from the binary, the appropriate salt+water systems, to the solubility isotherm. In the case of investigated system the binary solutions were KBr–H_2O (for paths I-IV) and KCl–H_2O (for path V). It means that the method 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 solvents.

The crystallization paths were described by the equation:

$$c_2 = c_2^0 + k \cdot c_1 \tag{1}$$

where c_1 and c_2 are the concentrations of KCl (in %) and KBr (in %), respectively, c_2^0 is the concentration of the binary solutions of KBr–H_2O (in %) (for path V this solution is KCl–H_2O) and k is a constant.

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

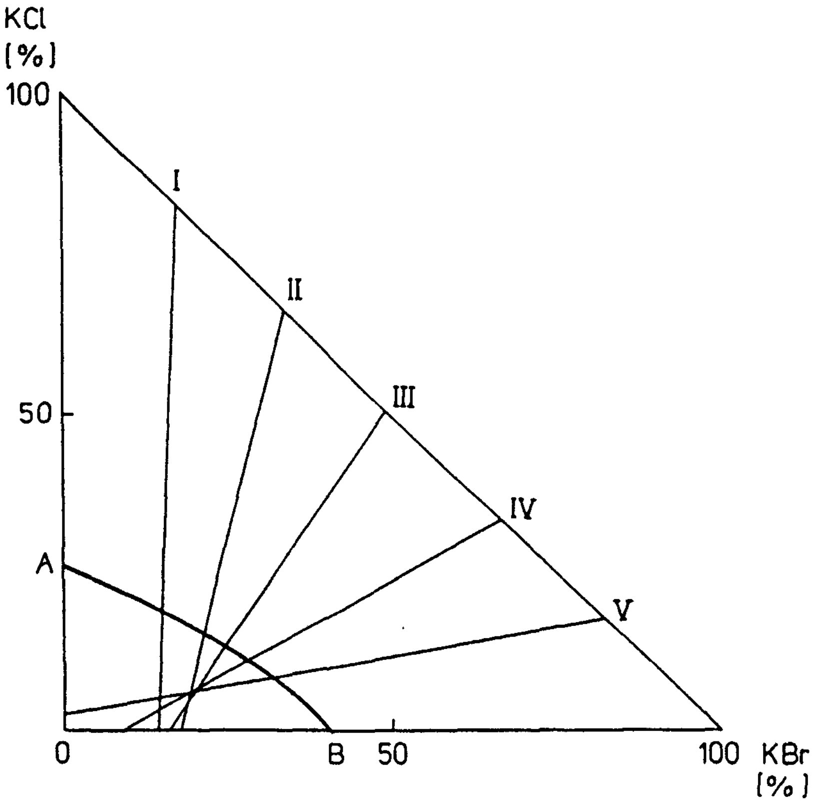

Fig. 1 The system KCl–KBr–H_2O at 298.15 K

The obtained concentration dependencies of differential solution enthalpies of mixed crystals along crystallization paths were described by the equation:

$$\Delta_{sol}H_2 = \sum_{i=0}^{2} a_i I_m^i \tag{2}$$

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

From these dependencies and the known compositions of saturated solutions, the last differential enthalpies of solution, $\Delta_{sol}H_2^{sat}$, were calculated. Then, using well known dependence:

$$|\Delta_{sol}H_2^{sat}| = |\Delta_{cryst}H_m| \tag{3}$$

the molar enthalpies of crystallization, $\Delta_{cryst}H_m$, of mixed crystals were determined.

Those data and also the coefficients in Eq. (2) 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, $\Delta_{cryst}H^E_m$, which were takes as the measure of interactions between the components of mixed crystals these values were determined as the difference between the enthalpy of crystallization, $\Delta_{cryst}H_m$, per mole of mixed crystals K(Cl, Br) and the sum of the enthalpies of crystallization of molar mixture of KCl and KBr, corresponding to the mol of appropriate mixed crystals, according to the following equation:

$$\Delta_{cryst}H^E_m = \Delta_{cryst}H_m - (x_1\cdot\Delta_{cryst}H_{m(1)} + x_2\cdot\Delta_{cryst}H_{m(2)}) \tag{4}$$

where $\Delta_{cryst}H_{m(1)}$ and $\Delta_{cryst}H_{m(2)}$ are the crystallization enthalpies of KCl and KBr, respectively; x_1 and x_2 are the molar fractions of KCl and KBr in mixed crystals, respectively.

Table 1 Coefficients of Eq. (1) and compositions of mixed crystals along the crystallization paths; M_{cr} denotes the molar mass of mixed crystals

Crystallization path	Coeffiicient of Eq. (1)		Sat. soln.	Mixed crystals		
	c_2^0 / %	k	c_1^{sat} / %	KCl / %	KCl mol %	M_{cr} / g·mol^{-1}
I	14.21	0.0449	18.66	82.10	87.98	79.90
II	17.70	0.2458	15.24	66.06	75.65	85.38
III	15.94	0.6609	12.95	50.61	62.06	91.42
IV	9.05	1.7346	10.98	33.26	44.30	99.32
V	–14.29	5.4289	8.45	17.78	25.66	107.60

Table 2 Coefficients of Eq. (2) and values of crystallization enthalpies of mixed crystals; N – number of experimental points used in each fit, R – correlation coefficient

Cryst. path	N	a_0 / J·mol^{-1}	a_1 / J·kg·mol^{-2}	a_2 / J·kg^2·mol^{-3}	R	$-\Delta_{cryst}H_m$ / J·mol^{-1}
I	28	1.69772 E4	–1.31362 E3	9.42906 E1	0.9933	12557 ± 75
II	26	1.68503 E4	–1.31677 E3	9.15312 E1	0.9932	12228 ± 70
III	27	1.70091 E4	–1.33027 E3	8.85165 E1	0.9914	12196 ±100
IV	30	1.81247 E4	–1.58344 E3	1.06613 E2	0.9962	12382 ±111
V	38	1.91288 E4	–1.77437 E3	1.16334 E2	0.9943	12563 ±168

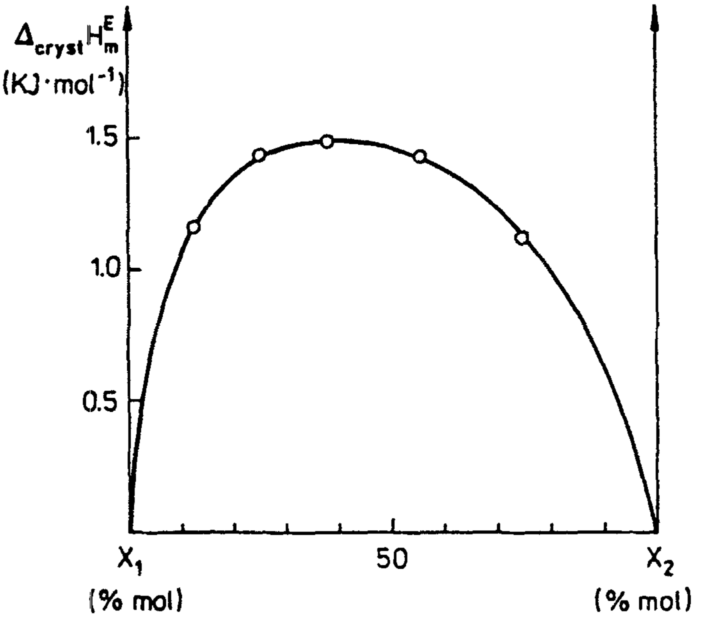

Fig. 2 The excess molar enthalpies of crystallization of mixed crystals K(Cl, Br), $\Delta_{cryst}H_m^E$, as a function of their contents; x_1 and x_2 are the molar fractions of KCl and KBr, respectively

The calculations yielded $\Delta_{cryst}H_{m(1)} = -13779\pm143$ J·mol^{-1} [12] and $\Delta_{cryst}H_{m(2)} = -13673\pm84$ J·mol^{-1} [13] (calculated from integral enthalpies of solution).

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

As it can be seen from the graph, the values $\Delta_{cryst}H_m^E$ lie on a parabola. It confirms the existence of mixed crystals in equilibrium solid phases and maximum interactions occur at 40 mol % of KCl content.

References

1 A. Chmarzynski, J. Thermal Anal., 38 (1992) 2027.
2 A. G. Bergmann and N. P. Vlasov, DAN S.S.S.R., 36 (1942) 64.
3 E. Cornec and P. Klug, Bull. Soc. Chim., 41 (1927) 1016.
4 G. Flatt and G. Burgkhardt, Helv. Chim. Acta, 27 (1944) 1605.
5 V. I. Nikolayev, Izv. IFKhA A.N. S.S.S.R., 7 (1935) 146.
6 N. A. Schlesinger, F. P. Zorkin and L. V. Novozhenova, Zhurn. Neorg. Khim., 11 (1938) 1259.
7 A. K. Zhdanov, Uzb. Khim. Zhurn., 5 (1959) 39.
8 V. Ja. Anosov, M. I. Ozerova and Ju. Je. Fialkov, Osnovy Fizikhokhimicheskovo Analiza, Moscow 1976.

9 M. Męcik, Proc. IV. International Conference on Calorimetry and Thermal Analysis, Zakopane 1988.
10 M. Męcik, Proc. XII. International Conference on Calorimetry, Salt Lake City, U.S.A. 1993.
11 B. Dejewska and A. Sędzimir, Cryst. Res. Technol., 24 (1989) 1003.
12 A. Chmarzyński and H. Piekarski, J. Thermal Anal., 38 (1992) 2019.
13 V. B. Parker, Thermal Properties of Aqueous Uni-univalent Electrolytes Natl. Bur. Stand. (U.S.), Washington D.C. 1965.

Zusammenfassung — Für das System $KCl-KBr-H_2O$ wurden in Abhängigkeit von der Konzentration und des Kristallisationsweges die differentiellen Lösungsenthalpien $\Delta_{sol}H_2$, gemessen. Ausgehend von diesen Messungen wurden die Kristallisationsenthalpien $\Delta_{cryst}H_m$ von Mischkristallen berechnet, die als stabile feste Phase in diesem System vorkommen.