THERMOCHEMICAL INVESTIGATIONS OF THE SYSTEMS
KCl–KBr–H2O, K2SO4–(NH4)2SO4–H2O and KNO3–NH4NO3–H2O at 298.15 K

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Abstract

For the equilibrium solid phases occurring in the systems: KCl–KBr–H2O, K2SO4–(NH4)2SO4–H2O and KNO3–NH4NO3–H2O, the concentration dependencies of differential solution enthalpies, $\Delta_{sol}H_2$, for several crystallization paths, were measured. The limiting differential solution enthalpies, $\Delta_{sol}H_2^0$, were determined by extrapolation of the above dependencies to the ionic strength, I_m^0, corresponding to the appropriate binary solutions. For KCl–KBr–H2O system only, the clear dependence between $\Delta_{sol}H_2^0$ and I_m^0 values was found and discussed.

Keywords: differential enthalpy of solution, ternary systems

Introduction

The equilibrium properties of ternary systems: KCl–KBr–H2O (I), K2SO4–(NH4)2SO4–H2O (II) and KNO3–NH4NO3–H2O (III) were earlier examined in our laboratories [1 –3]. It was found that mentioned systems differ significantly from each other. The mixed crystals of the K(Cl, Br) type only are present in the system (I) (Fig. 1). The system (II) exhibits the presence of the mixed crystals of (K, NH4)2SO4 type and a discontinuity region (section AB in the Fig. 2) while in the system (III) (Fig. 3), beside the (K, NH4)NO3 mixed crystals also the double salt KNO3·2NH4NO3 (pt B in Fig. 3) and the wide discontinuity region exist (section C-B in Fig. 3) [3–5].

The crystallization enthalpies of the equilibrium solid phases occurring in these systems were also investigated [6–8]. They were determined from the concentrational dependencies of differential solution enthalpies, $\Delta_{sol}H_2$, measured along the crystallization paths (marked in the Figs 1–3 with the Roman numerals) from the binary, the appropriate salt-water systems to the solubility isotherm. The extrapolation of these functions to the saturated solution gave the
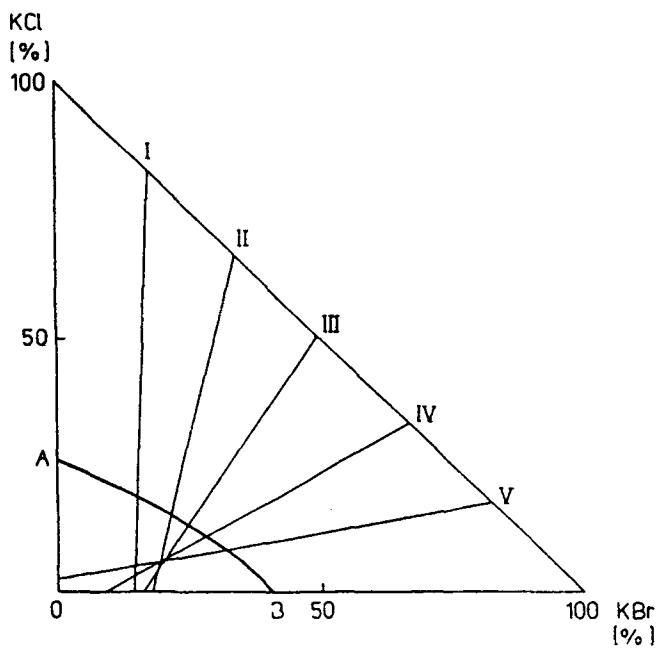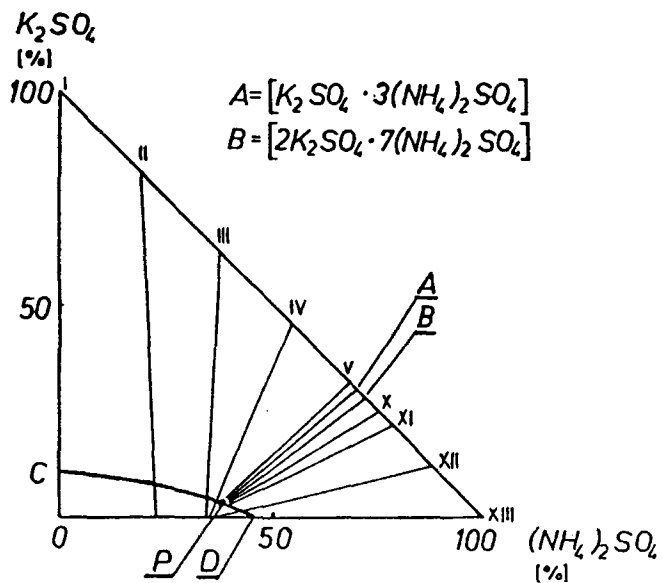
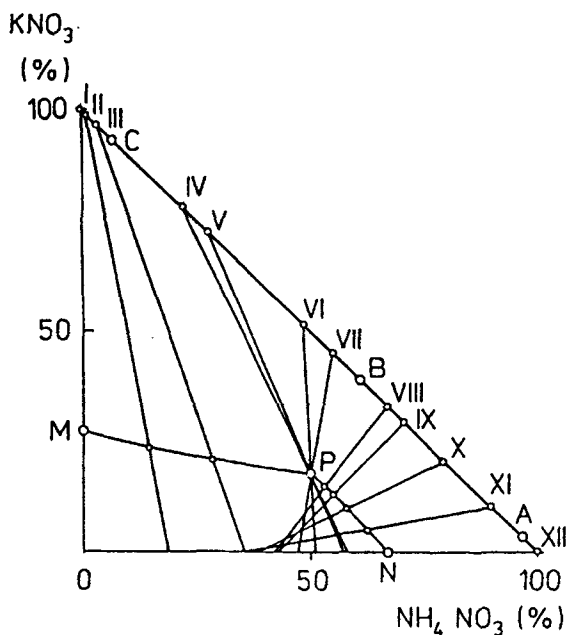Fig. 1 The system KCl–KBr–H$_2$O at 298.15 K

Fig. 2 The system K$_2$SO$_4$–(NH$_4$)$_2$SO$_4$–H$_2$O at 298.15 K

Fig. 3 The system KNO_3–NH_4NO_3–H_2O at 298.15 K

last differential enthalpies of solution, $\Delta_{sol}H_2^{sat}$, which are numerically equal to the crystallization enthalpies, $\Delta_{cryst}H_m$. These investigations were obviously focused on the highly concentrated and almost saturated solutions. It seemed interesting to analyze the thermochemical properties of the same systems, but now in the area of low concentration of the salt. To this aim it was necessary to perform some additional measurements of the salt dissolution enthalpy in dilute solutions region.

Experimental

The salts KCl, KBr, KNO_3, NH_4NO_3, K_2SO_4 and $(NH_4)_2SO_4$, all analytical grade (POCh, Gliwice), were dried to a constant weight prior the use. All solutions were prepared by weight using double distilled and deionized water.

In order to obtain appropriate solid phases, the equilibrium data, examined in our laboratories [1–3], were used. Those 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 for every system and amounted to $4.625 \cdot 10^{-3}$ of mole for system (I), $2.462 \cdot 10^{-3}$ of mole for system (II) and $1.877 \cdot 10^{-3}$ of mole

for system (III). The crystallization paths were the same as described previously [6–8].

The experiments were carried out using a solution calorimeter of 'isoperibol' type, made in Technical University of Gdańsk [9, 10]. The experimental data are available on request.

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

Results and discussion

The differential solution enthalpies, $\Delta_{sol}H_2$, of the equilibrium solid phases within the range of low concentration of the solution were fitted to the equation:

$$\Delta_{sol}H_2 (I_m) = \sum_{i=0}^{2} a_i I_m^i \qquad (1)$$

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

The coefficients in Eq. (1), for every investigated system, are given in Tables 1–3, together with the number of experimental points used in each fit and maximal ionic strength reaching in given series of measurements.

The limiting differential solution enthalpies, $\Delta_{sol}H_2^0$, were determined by extrapolation of the above dependencies to the ionic strength corresponding to appropriate binary solutions. In the case of the system (I) the binary solutions were: KBr–H$_2$O (for paths I–IV) and KCl–H$_2$O (for path V); in the system (II) – (NH$_4$)$_2$SO$_4$–H$_2$O (paths II–XII); and in the system (III) – NH$_4$NO$_3$–H$_2$O (paths II–XI). These mixtures were treated as binary solvents in infinitely diluted solutions.

The determined as above the values of $\Delta_{sol}H_2^0$ and the concentrations of the proper binary solutions, I_m^0, are presented in Tables 4–6.

The Fig. 4 presents the limiting differential solution enthalpies in the KBr–H$_2$O (points I–IV) and KCl–H$_2$O (point V) binary solvents as a function of their ionic strength. The points marked KCl and KBr denote the standard solution enthalpies of these salts in pure water, taken from Parker's data [11]. As it is seen from the Figure, two straight lines were obtained; the one corresponding to the mixed crystals based on KCl (points: KCl, I, III and II) and the other corresponding to the mixed crystals based on KBr (points: KBr, V and IV).

The cross point of these lines corresponding to the KBr content equal to about 12% in binary KBr–H$_2$O solution. From the equilibrium data [1], it is known, that KBr content in mixed crystal K(Cl,Br) corresponding to this solu-

Table 1 Coefficients of Eq. (1) for the system KCl–KBr–H_2O; N–number of experimental points used in each fit, R–correlation coefficient, I_m^{max}–maximal ionic strength

Crystallization path	N	$a_0/$ J·mol^{-1}	$a_1/$ J·kg·mol^{-2}	$a_2/$ J·kg^2·mol^{-3}	R	$I_m^{max}/$ mol·kg^{-1}
I	18	1.92085 E4	–3.70623E3	6.80936E2	0.9866	2.7033
II	18	1.68421 E4	–1.25100E3	6.46774E1	0.9960	2.9836
III	20	1.58976 E4	–2.92502E2	–1.35708E2	0.9816	2.9565
IV	19	1.79260 E4	–1.27615E3	1.46735E1	0.9940	2.7869
V	19	1.89115 E4	–8.44760E2	–3.85717E2	0.9967	2.8070

Table 2 Coefficients of Eq. (1) for the system $K_2SO_4-(NH_4)_2SO_4-H_2O$; N-number of experimental points used in each fit, R-correlation coefficient, I_m^{max}-maximal ionic strength

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	I_m^{max} $mol \cdot kg^{-1}$
II	19	3.30891E4	-3.40094E3	1.51839E2	0.9987	7.8789
III	19	3.44633E4	-2.99106E3	9.35842E1	0.9809	12.5595
IV	18	2.63043E4	-1.95992E3	5.43906E1	0.9855	13.6533
V	20	2.51533E4	-1.85877E3	5.09749E1	0.9969	13.8264
VI	21	8.44094E3	4.94960E2	-3.56693E1	0.9781	13.8744
VII	21	2.91657E3	1.05812E3	-5.07564E1	0.9863	13.8159
VIII	20	-1.54766E4	3.56566E3	-1.35442E2	0.9015	13.8000
IX	22	-1.18090E4	2.92831E3	-1.09407E2	0.9103	13.7178
X	22	-1.14897E3	1.18189E3	-4.00385E1	0.9901	13.8108
XI	23	-1.43000E2	9.61967E2	-3.21077E1	0.9891	13.9623
XII	27	-1.26251E3	1.01609E3	-3.10984E1	0.9913	13.9029

Table 3 Coefficients of Eq. (1) for the system KNO_3–NH_4NO_3–H_2O; N-number of experimental points used in each fit, R-correlation coefficient, I_m^{max}-maximal ionic strength

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	I_m^{max} / $mol \cdot kg^{-1}$
II	19	4.94769E4	-1.32319E4	1.59731E3	0.9881	3.9770
III	21	1.79126E4	1.10701E3	-1.40823E2	0.9803	8.8440
IV	21	2.38329E5	-2.45390E4	6.61283E2	0.9927	19.1522
V	20	-5.56081E5	6.42747E4	-1.81808E3	0.9834	18.5234
VI	23	-2.21302E5	3.29554E4	-1.15641E3	0.9767	15.5147
VII	20	2.22547E4	-1.10935E3	2.85598E1	0.9897	15.9296
VIII	20	2.59657E4	-1.99881E3	7.53196E1	0.9701	12.2734
IX	21	9.43668E3	1.16162E3	-7.36634E1	0.9738	12.2418
X	20	1.81903E4	-6.73036E2	1.64435E1	0.9833	15.7203
XI	21	1.86429E4	-7.22164E2	1.65119E1	0.9954	17.9604

Table 4 The system KC l–KBr–H$_2$O at 298.15 K; the values of limiting differential enthalpies of solution, $\Delta_{sol}H_2^0$, for binary solutions of KBr–H$_2$O (paths I–IV) and KCL–H$_2$O (path V), I_m^0

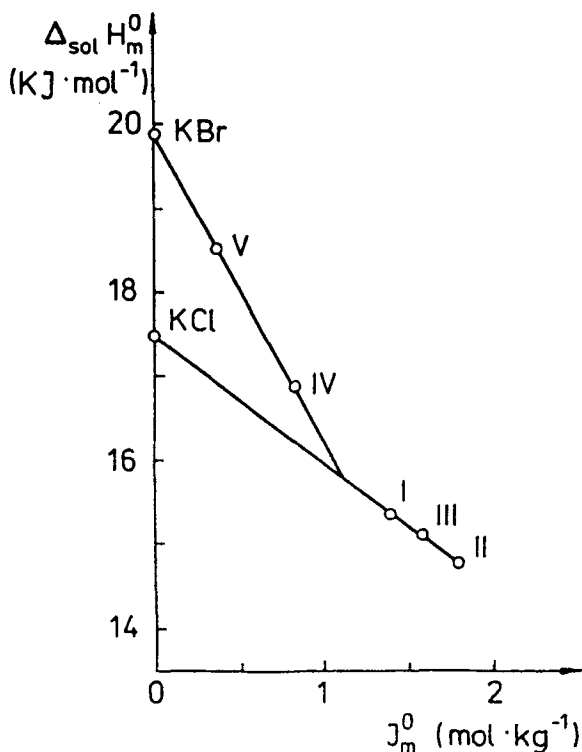| Path	I_m^0 /mol·kg^{-1}	$\Delta_{sol}H_2^0$ /J·mol^{-1}
I	1.3920	15369±67
II	1.8077	14792±33
III	1.5935	15087±84
IV	0.8362	16869±74
V	0.3627	18554±68

Fig. 4 The limiting differential enthalpies of solution, $\Delta_{sol}H_2^0$, in the binary solutions KBr–H$_2$O (I–IV) and KCl–H$_2$O (V) as a function of their ionic strength, I_m^0

tion amounts to about 40 mole%. Additionally, in the work described the crystallization enthalpies investigations [7], the supposition was put forward, that in this region the transition of mixed crystals based on KCl to mixed crystals based on KBr, occurs. It seems that results given in presented work confirm this supposition.

Table 5 The system K_2SO_4–$(NH_4)_2SO_4$–H_2O at 298.15 K; the values of limiting differential enthalpies of solution, $\Delta_{sol}H_2^0$, for binary solutions of $(NH_4)_2SO_4$–H_2O, I_m^0

Path	I_m^0 /mol·kg^{-1}	$\Delta_{sol}H_2^0$ /J·mol^{-1}
II	6.6937	17127±36
III	11.4729	12465±77
IV	12.1177	10541±70
V	11.8579	10280±54
VI	11.9900	9248±83
VII	11.8842	8323±56
VIII	11.8579	7760±103
IX	11.7060	7478±103
X	11.5503	7160±43
XI	11.4267	6657±50
XII	10.9112	6122±48

Table 6 The system KNO_3–NH_4NO_3–H_2O at 298.15 K; the values of limiting differential enthalpies of solution, $\Delta_{sol}H_2^0$, for binary solutions of NH_4NO_3–H_2O, I_m^0

Path	I_m^0 /mol·kg^{-1}	$\Delta_{sol}H_2^0$ /J·mol^{-1}
II	2.9056	24516±69
III	6.9311	18820±117
IV	17.7084	11148±42
V	16.9988	11160±110
VI	13.2402	12311±122
VII	11.2281	13399±104
VIII	9.3853	13840±156
IX	9.0546	13915±147
X	7.5184	14060±98
XI	6.7786	14506±38

Unfortunately, such simple and clear picture was obtained only for the system (I). The results obtained in the case of other investigated systems are more complicated and they did not give any explicit relations. It is probably connected with the fact that solutions representing binary solvents in those systems contain a great number of diluted salts and their ionic strength ranges between 2.9056–17.7084 of mol·kg^{-1}. Additionally, the equilibrium solid phases occurring there are more complicated than in the case of the system (I).

However, this is the first work relating to the problems discussed above and needs, of course, further investigations.

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Zusammenfassung — Für die festen Gleichgewichtsphasen in den Systemen KCl–KBr–H_2O, K_2SO_4–$(NH_4)_2SO_4$–H_2O und KNO_3–NH_4NO_3–H_2O, wurde die Konzentrationsabhängigkeit der differentiellen Lösungsenthalpien $\Delta_{sol}H_2$ für verschiedene Kristallisationswege gemessen. Die Werte $\Delta_{sol}H_2^0$ wurden mittels Extrapolation obiger Abhängigkeiten zur Ionenstärke I_m^0 der entsprechenden binären Lösungen bestimmt. Lediglich für das System KCl–KBr–H_2O wurde ein eindeutiger Zusammenhang zwischen $\Delta_{sol}H_2^0$ und I_m^0 gefunden und diskutiert.