PITZER MODEL BASED STUDY OF $CsX–NiX_2–H_2O$ (X = Cl, Br) SYSTEMS AT 298.15 K

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The Pitzer ion-interaction model was used for simulating the $CsX–NiX_2–H_2O$ (X = Cl, Br) systems at 298.15 K. The necessary thermodynamic functions (binary and ternary parameters, thermodynamic solubility products) were calculated and the theoretical solubility diagrams plotted. A very good agreement was found between the calculated and observed data.
Key words: Solubility diagram; Double salts; Pitzer model; Thermodynamic functions.

Solutions of the type $(b_1\,MX + b_2\,MeX_2)(aq)$ where M denotes Li, Na, NH_4, K, Rb, or Cs; Me denotes Mg, Mn, Co, Ni, or Cu; X denotes Cl or Br; and b_i are molalities of the respective compounds have been subject to many investigations over a wide temperature range. Fields of equilibrium crystallization of one or more double salts with different stoichiometric compositions (2-1-2, 1-1-2, 4-3-2, 3-1-0, 2-1-0, 1-1-0) have been established in most cases[1]. The only exceptions are solutions with the participation of NaX, which are of a simple eutonic type[2,3]. From solutions containing MgX_2, only carnallite type double salts $MX\,.\,MgX_2\,.\,6\,H_2O$ (1-1-6) crystallize[4–9]. The double salt $CsCl\,.\,NiCl_2\,.\,2\,H_2O$ has been found[10] to crystallize from $(b_1\,CsCl + b_2\,NiCl_2)(aq)$ saturated ternary solutions. Investigating the $(b_1\,CsBr + b_2\,NiBr_2)(aq)$ system, Balarew and coworkers[11,12] established a field of equilibrium crystallization of the anhydrous salt $CsBr\,.\,NiBr_2$. The authors[12] interpreted the crystallization of an anhydrous double salt in the bromide system in terms of Pearson's concept[13] involving "hard" and "soft" Lewis acids (Cs^+ and Ni^{2+} ions) and bases (X^- ions and H_2O molecules).

The basic Pitzer model[14,15] has been applied with success to solve many theoretical and practical problems. Evidence has been obtained that the model can be used for a sufficiently precise description of the properties of saturated and unsaturated binary[14,16], ternary[1,15,17–20] and multicomponent[9] electrolyte solutions from which both phases with a constant stoichiometric composition (simple and double salts)[1,17–20] and solid solutions[9,21,22] crystallize. In our previous studies we simulated and plotted the theoretical solubility isotherms of solutions of the type $(b_1\,MX + b_2\,MeX_2)(aq)$ (refs[1,18–20]) on the basis of the Pitzer model. Thermodynamic investigation of the solutions

{b_1 RbCl + b_2 ($MnCl_2$, $CoCl_2$, $NiCl_2$ or $CuCl_2$)}(aq) (ref.[1]) explained why a second double salt RbCl . $CoCl_2$. 2 H_2O crystallizes at T = 298.15 K and p^0 = 1.01325 . 10^5 Pa in addition to the double salt with the stoichiometric composition 2-1-2 in the solutions (b_1 RbCl + b_2 $CoCl_2$)(aq) only. Simulation of carnallite type ternary solutions (b_1 MX + b_2 MgX_2)(aq) (refs[18–20]) indicated that some of the experimental data presented in the literature were incorrect. It was explained from a thermodynamic viewpoint why at T = 298.15 K a carnallite type double salt does not crystallize from (b_1 LiBr + b_2 $MgBr_2$)(aq) solutions only.

The purpose of the present investigation was thermodynamic simulation of the solutions (b_1 CsX + b_2 NiX_2)(aq) at T = 298.15 K on the basis of the Pitzer model and plotting the theoretical solubility isotherms.

SOLUBILITY CALCULATION

The (b_1 CsX + b_2 NiX_2)(aq) solutions were simulated thermodynamically at T = 298.15 K based on the Pitzer model as follows: (i) determination of the Pitzer binary parameters $\beta^{(0)}$, $\beta^{(1)}$, and C^{φ} which make allowance for the interionic interactions of two ions and three ions in the binary solution, (ii) determination of the Pitzer ternary parameters θ_{MN} and ψ_{MNX} characterizing the interaction between two different ions of the same sign and the interaction between three ions, respectively, in the ternary solution, and (iii) calculation of the solubility isotherms of the three-component solutions.

Since the simulation is primarily aimed at obtaining the compositions of the saturated ternary solutions, applicability of the binary parameters to high concentrations of the binary solutions up to saturation at the lowest value of the standard deviation (σ) is a very important criterion for the choice of the binary parameters. The values of the Pitzer parameters for all the four binary solutions were taken from the literature (Table I). The parameters for CsCl(aq), CsBr(aq), and $NiCl_2$(aq) are applicable up to saturation of the binary solutions. The applicability of parameters for CsX(aq) has been proved by

TABLE I

Pitzer binary parameters for CsX(aq) and NiX_2(aq) (X = Cl, Br) at T = 298.15 K where σ is the standard deviation of the osmotic coefficients

Solution	$\beta^{(0)}$	$\beta^{(1)}$	C^{φ}	b_{max} / mol kg^{-1}	σ
CsCl(aq)[a]	0.03900	–0.03740	–0.00120	11.30	0.0030
CsBr(aq)[a]	0.03010	0.00290	–0.00050	5.67	0.0010
$NiCl_2$(aq)[b]	0.39304	0.99773	–0.01658	5.50	0.0139
$NiBr_2$(aq)[b]	0.44305	1.48323	–0.00590	4.50	0.0087

[a] Refs[9,18,21]; [b] ref.[16].

simulation of (b_1 CsX + MgX_2)(aq) (ref.[18]) and four-component carnallite type systems[9], and calculation of the Gibbs free energy of mixing ΔG^{mix}(s) of crystals in alkali-halide solutions with the participation of CsX (ref.[21]). Experimental isopiestic data exist concerning the dependence of the activity of water (or the osmotic coefficients) for $NiBr_2$(aq) (electrolyte of type 2-1) up to 4.693 mol kg^{-1} (ref.[23]). On the basis of these initial data, Kim and Frederick[16] determined $\beta^{(0)}$, $\beta^{(1)}$, and C^{φ} (three parameters) which hold up to 4.500 mol kg^{-1}. In order to extend the concentration range to 4.693 mol kg^{-1}, we calculated the parameters using (i) the approach of Filippov[24] (who proposes calculation of a fourth parameter $\beta^{(2)}$ with indices $\alpha_1 = 2$ and $\alpha_2 = 1$ for 2-1 electrolytes) and (ii) the approach given in ref.[1] (with $\beta^{(2)}$ and indices $\alpha_1 = 2$ and $\alpha_2 = -1$). In both cases, however, the widening of the molality range was associated with an increase in σ. For that reason we used the parameters by Kim and Frederick[16].

By using the data for $\beta^{(0)}$, $\beta^{(1)}$, and C^{φ} and the molality b^s of the saturated binary solutions, we calculated the logarithms of the thermodynamic solubility product ln K^0_{sp} for CsX and NiX_2 . 6 H_2O (Table II). The small differences between the ln K^0_{sp} values obtained in this paper and those presented in refs[1,9,18,21,24,25] are mainly due to the different b^s values used in calculations.

The ternary parameters of the systems investigated were calculated from the experimental solubility data reported by Lileev et al.[10] for (b_1 CsCl + b_2 $NiCl_2$)(aq) and by Balarew et al.[12] for (b_1 CsBr + b_2 $NiBr_2$)(aq). The choice of the parameters was based on the minimum deviation of the logarithm of the solubility product ln K^0_{sp} for the whole crystallization curve of the component from its value for the binary system. In addition, the ln K^0_{sp} value for the double salts CsCl . $NiCl_2$. 2 H_2O and CsBr . $NiBr_2$ crystallizing in the systems was to be constant along the whole crystallization branch of the double salt. In our calculations of θ_{MN} and ψ_{MNX} we included the unsymmetrical

TABLE II
Calculated values of the logarithm of the thermodynamic solubility products K^0_{sp} and molalities of the saturated binary solutions b^s

Salt composition	ln K^0_{sp}	b^s mol kg^{-1}
CsCl	3.45	11.25
CsBr	1.94	5.80
$NiCl_2$. 6 H_2O	6.90	4.95
$NiBr_2$. 6 H_2O	12.20	6.73
CsCl . $NiCl_2$. 2 H_2O	8.25 ± 0.30	–
CsBr . $NiBr_2$	17.05 ± 0.45	–

mixing terms ${}^{E}\theta$ and ${}^{E}\theta'$, following ref.[15]. Since parameter $\theta_{Cs,Ni}$ makes allowance for Cs-Ni interionic interactions in the ternary solutions only, its value had to be constant for the chloride and bromide systems. For that reason both systems were processed simultaneously, i.e. we varied the values of $\psi_{Cs,Ni,Cl}$ and $\psi_{Cs,Ni,Br}$ with a preset $\theta_{Cs,Ni}$ value. The values found for $\ln K^0_{sp}$ of the double salts are given in Table II, while the ternary parameters are presented in Table III. The absolute value of the sum of ternary parameters for the bromide system exceeds the sum of parameter values for the chloride system. The same has been observed with the corresponding carnallite type ternary chloride and bromide systems[18]. Since θ_{MN} is constant for systems with common cations M and N, it can be concluded that in the ternary solutions (b_1 MX + b_2 NX_2)(aq) the ternary interionic interactions of the type M–N–X are stronger with a larger halide ion X^-.

The results obtained were used for calculation of the solubility isotherms of the ternary solutions at T = 298.15 K. At phase and chemical equilibria of a given salt (ν_1A_1 . ν_2A_2 . ν_3A_3) with its saturated solution, the following equation is applied[1,9,17–19]:

$$\ln K^0_{sp}(\nu_1,\nu_2,\nu_3) = \nu_1 \ln a_1 + \nu_2 \ln a_2 + \nu_3 \ln a_3 = \text{constant} \ , \qquad (1)$$

where a_1, a_2 and a_3 are activities of the components A_1, A_2 and H_2O in the saturated solution, and ν_1, ν_2 and ν_3 denote the stoichiometric coefficients in the salt. Then the solubility isotherm can be calculated as a geometric site of points meeting condition (*1*). The eutonic of the ternary system is a point that satisfies two equations which describe the solubility isotherms of two solid phases, respectively. This eutonic represents the solution of the system:

$$\ln K^0_{sp}(\nu_1,\nu_2,\nu_3,b_1,b_2) = \text{constant}' \ ,$$
$$\ln K^0_{sp}(\nu'_1,\nu'_2,\nu'_3,b_1,b_2) = \text{constant}'' \ . \qquad (2)$$

TABLE III
Pitzer ternary parameters for the (b_1 CsX + b_2 NiX_2)(aq) systems at T = 298.15 K

Solution	θ_{MN}	ψ_{MNX}
(b_1 CsCl + b_2 $NiCl_2$)(aq)	–0.2300	0.0000
(b_1 CsBr + b_2 $NiBr_2$)(aq)	–0.2300	–0.0199

The calculated solubility isotherms are in a good agreement with the experimental data (Figs 1 and 2). The thermodynamic functions of the binary and ternary electrolyte systems can be used for simulating other multicomponent systems with respect to which the systems under consideration are subsystems.

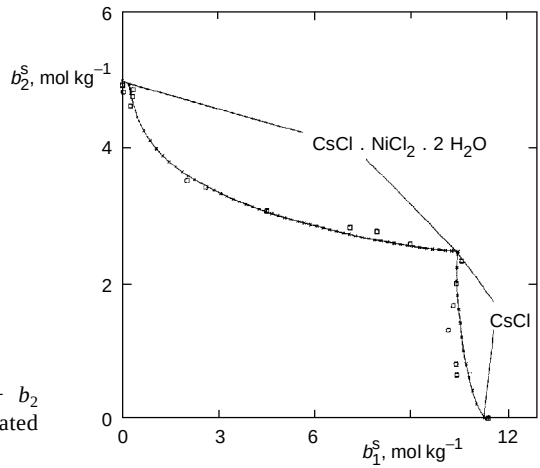

FIG. 1
Molality b^s solubilities in (b_1 CsCl + b_2 $NiCl_2$)(aq) at T = 298.15 K: × calculated values; ❒ ref.[10]

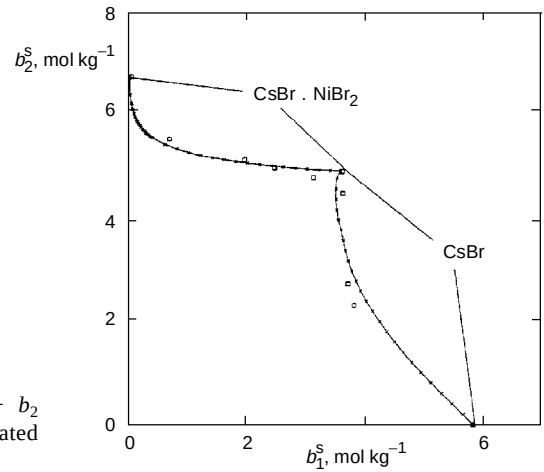

FIG. 2
Molality b^s solubilities in (b_1 CsBr + b_2 $NiBr_2$)(aq) at T = 348.15 K: × calculated values; ❒ ref.[12]

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