THERMODYNAMIC STUDY OF THE $CuCl_2$–MCl_2–H_2O SYSTEMS (M = Mg, Co) AT 298.15 K

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The Pitzer ion-interaction model was used for a simulation of the $CuCl_2$–MCl_2–H_2O (M = Mg, Co) systems at 298.15 K. The necessary thermodynamic functions (binary and ternary ion-interaction parameters and thermodynamic solubility products) were calculated and the theoretical solubility diagrams plotted. A very good agreement was obtained between the calculated and observed data.

Key words: Pitzer equations; Three-component systems; Phase diagrams.

Experimental solubility data of ternary water–salt systems of the MCl_2–$M'Cl_2$–H_2O type (M, M′ = Mg, Mn, Fe, Co, Ni, Cu, Cd) indicate a great variety of solid phases involved. Crystallization of a continuous or discontinuous series of mixed crystals[1] is possible, as well as of double salts with various stoichiometric compositions[2]. Only the systems derived from $CuCl_2$ and the $CaCl_2$–$CoCl_2$–H_2O (ref.[3]) and $MgCl_2$–$NiCl_2$–H_2O systems (ref.[4]) are of a simple eutonic type. Pitzer[5] simulated the $MgCl_2$–$NiCl_2$–H_2O system and obtained a very close similarity between the observed and calculated solubility isotherms. A strong distortion of the coordination octahedra around the Cu^{2+} ions in $CuCl_2 . 2\,H_2O$ due to the Jahn–Teller effect is responsible for the fact that no substitution of Cu^{2+}–ions occurs, i.e. no mixed crystals are formed[6]. Studying the $MgCl_2$–$CuCl_2$–H_2O system, Balarew and Spassov[6] established separate crystallization of $MgCl_2 . 6\,H_2O$ and $CuCl_2 . 2\,H_2O$. Bassett et al.[7] investigated the $CoCl_2$–$CuCl_2$–H_2O system and found fields of equilibrium crystallization of the corresponding crystalline hydrates ($CoCl_2 . 6\,H_2O$ and $CuCl_2 . 2\,H_2O$) only.

The present study is concerned with a thermodynamic simulation of the $MgCl_2$–$CuCl_2$–H_2O and $CoCl_2$–$CuCl_2$–H_2O systems at T = 298.15 K using the Pitzer model. The necessary thermodynamic functions (binary and ternary parameters of interionic interaction and thermodynamic solubility products of the corresponding crystalline hydrates) were calculated and the theoretical solubility isotherms plotted.

CALCULATION OF THE SOLUBILITY ISOTHERMS

With the aim as formulated above, we used the Pitzer ion-interaction model[8,9], allowing the activity coefficients in saturated and unsaturated solutions of electrolytes to be determined with an accuracy of 2 to 6 per cent[10]. The Pitzer model has found application to the determination of the thermodynamic characteristics and plotting the different types of theoretical solubility isotherms of three- and multi-component systems[5,11–17].

The systems were investigated using the approach which had already been applied to the systems of the $MeX–MX_2–H_2O$ type (Me = Li, NH_4, K, Rb, Cs; M = Mg, Mn, Co, Ni, Cu; X = Cl, Br) (refs[13–17]). This approach consists in: (i) determination of the Pitzer binary parameters ($\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, C^{φ}) which allow for interionic interactions of two ions and three ions; (ii) determination of the Pitzer ternary parameters (θ_{MN} and ψ_{MNX}) characterizing interaction between two different ions of the same sign and interaction between three ions, respectively; (iii) calculation of the solubility isotherms of the three-component systems.

The values of the Pitzer binary parameters ($\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^{φ}) for the $MCl_2–H_2O$ systems (M = Mg, Co, Cu) were taken from the literature (Table I). The parameters are applicable up to saturation or nearly saturation of the binary solutions. Their applicability has been proved in refs[14–18]. Based on the data for $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^{φ} and molality (m^s) of the saturated binary solutions, we calculated the logarithms of the thermodynamic solubility product $\ln K^0_{sp}$ for the hydrates (Table II). The small differences between the $\ln K^0_{sp}$ values obtained in this paper and those presented in refs[14-18] are mainly due to the different m^s values used in the calculation.

The ternary parameters of the systems investigated were calculated from the experimental solubility data by Balarew and Spassov[6] for the $CuCl_2–MgCl_2–H_2O$ system and by Bassett et al.[7] for the $CuCl_2–CoCl_2–H_2O$ system. 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 saturated binary solution. In our calculations of Θ_{MN} and Ψ_{MNX} we included the unsymmetrical

TABLE I
Pitzer binary parameters for the $MCl_2–H_2O$ (M = Mg, Co, Cu) systems at T = 298.15 K where σ is the standard deviation of the osmotic coefficients

System	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{φ}	max m	σ
$MgCl_2–H_2O^a$	0.35110	1.65120	0.00000	0.00650	5.76	–
$CoCl_2–H_2O^b$	0.34723	1.66470	–0.00350	0.00559	4.26	0.00079
$CuCl_2–H_2O^b$	0.17661	0.57402	0.63405	–0.01089	5.73	0.00213

[a] Refs[14,16,17]; [b] refs[15,18].

mixing terms $^{E}\theta$ and $^{E}\theta'$, following ref.[9]. The values found for θ_{MN} and ψ_{MNX} are given in Table III.

The solubility isotherms of the ternary solutions at T = 298.15 K were calculated by using the thermodynamic functions obtained. At the phase and chemical equilibria of a given salt with its saturated solution, the equation

TABLE II
Calculated logarithms of the thermodynamic solubility products ($\ln K_{sp}^0$)

Salt composition	$\ln K_{sp}^0$
$MgCl_2 \cdot 6\,H_2O$	10.47
$CoCl_2 \cdot 6\,H_2O$	5.81
$CuCl_2 \cdot 2\,H_2O$	4.51

TABLE III
Pitzer ternary parameters for the $CuCl_2$–MCl_2–H_2O (M = Mg, Co) systems at T = 298.15 K

System	θ_{MN}	ψ_{MNX}
$CuCl_2$–$MgCl_2$–H_2O	–0.0600	–0.0450
$CuCl_2$–$CoCl_2$–H_2O	0.0015	0.0040

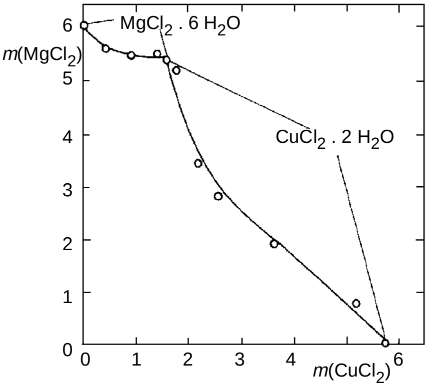

FIG. 1
Solubility isotherm of the $CuCl_2$–$MgCl_2$–H_2O system at 298.15 K: ❍ experimental data from ref.[6]; ——— calculated values (in molality)

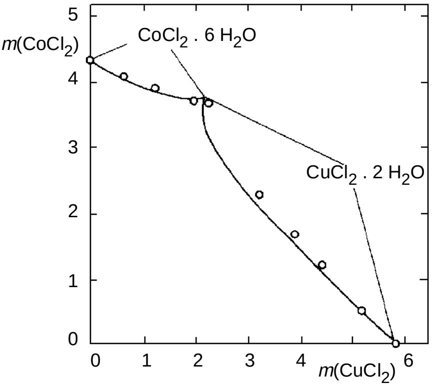

FIG. 2
Solubility isotherm of the $CuCl_2$–$CoCl_2$–H_2O system at 298.15 K: ❍ experimental data from ref.[7]; ——— calculated values (in molality)

$$\ln \{K^0_{sp}(1,0,2)\} = \ln a(CuCl_2) + 2 \ln a_w = 4.51 \qquad (1)$$

is applied to the isotherm branches that correspond to the crystallization of $CuCl_2 . 2 H_2O$, while

$$\ln \{K^0_{sp}(0,1,6)\} = \ln a(MgCl_2) + 6 \ln a_w = 10.47, \text{ and} \qquad (2)$$

$$\ln \{K^0_{sp}(0,1,6)\} = \ln a(CoCl_2) + 6 \ln a_w = 5.81 \qquad (3)$$

are used for the $MgCl_2 . 6 H_2O$ and for the $CoCl_2 . 6 H_2O$ branches. The quantities $a(CuCl_2)$, $a(MgCl_2)$, $a(CoCl_2)$, and a_w are the activities of $CuCl_2$, $MgCl_2$, $CoCl_2$, and H_2O in the saturated solution, respectively. Then the solubility isotherms can be calculated as the geometric site of points meeting conditions (*1*) and (*2*) for the $MgCl_2$–$CuCl_2$–H_2O system and conditions (*1*) and (*3*) for the $CoCl_2$–$CuCl_2$–H_2O system.

The calculated solubility isotherms are shown in Figs 1 and 2. The $\ln K^0_{sp}$ values on the isotherm branches for the $MgCl_2$–$CuCl_2$–H_2O system vary within the following limits: $\ln \{K^0_{sp}(1,0,2)\} = 4.33$–$4.69$ and $\ln \{K^0_{sp}(0,1,6)\} = 10.32$–$10.62$. For the $CoCl_2$–$CuCl_2$–H_2O system: $\ln \{K^0_{sp}(1,0,2)\} = 4.49$–$4.53$ and $\ln \{K^0_{sp}(0,1,6)\} = 5.80$–$5.82$. The calculated values agree very well with the observed data.

The thermodynamic functions of the binary and ternary electrolyte systems can be used for simulation of other multicomponent systems with respect to which the systems under study are subsystems.

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