Thermodynamic Simulation of Four-Component Carnallite Type Systems

C. Christov[1,*], S. Petrenko[2], C. Balarew[1], and V. Valyashko[2]

[1] Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
[2] Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 117907 Moscow, Russia

Summary. The standard method of *Pitzer* for predicting the solubility isotherms of systems in which solid phases with a constant composition crystallize is applied to cases when mixed crystals are formed. The four-component carnallite type systems $RbCl-CsCl-MgCl_2-H_2O$, $RbCl-KCl-MgCl_2-H_2O$, and $RbCl-RbBr-MgCl_2-MgBr_2-H_2O$ and the corresponding subsystems are thermodynamically simulated at 25 °C. It is established that the solubility diagrams consist of crystallization regions of the simple salts MX, $M'X'$, $MgX_2 \cdot 6H_2O$, and $MgX'_2 \cdot 6H_2O$ and of the corresponding carnallite type double salts with the composition $1:1:6$. A method of calculation of the integral *Gibbs* energy of mixing $G^{mix}(s)$ of crystals formed in water-salt systems has been proposed. The results on the systems $RbCl-KCl-H_2O$, $RbCl-RbBr-H_2O$, and $MgCl_2-MgBr_2-H_2O$ are compared with experimental data from the literature and with values calculated using various models.

Keywords. Phase diagrams; Solubility; Double salts; Carnallite; Bromocarnallite; *Pitzer* model; *Gibbs* energy of mixing.

Thermodynamische Simulation von Vierkomponentensystemen des Carnallit-Types

Zusammenfassung. Die *Pitzer*-Methode zur Voraussage der Löslichkeitsisothermen in Mehrstoffsystemen, in welchen feste Phasen mit konstanter Zusammensetzung auskristallisieren, wurde auch für Fälle angewendet, bei denen sich Mischkristalle bilden. Die Vierstoffsysteme $RbCl-CsCl-MgCl_2-H_2O$, $RbCl-KCl-MgCl_2-H_2O$ und $RbCl-RbBr-MgCl_2-MgBr_2-H_2O$, aus welchen Carnallit-Typ-Mischkristalle auskristallisieren, und die dazugehörigen Dreistoff-Randsysteme wurden bei 25 °C simuliert. Man stellt fest, daß die Löslichkeitsdiagramme sowohl Kristallisationsbereiche der einfachen Salze MX, $M'X$, $MgX_2 \cdot 6H_2O$ und $MgX'_2 \cdot 6H_2O$ als auch der entsprechenden carnallitartigen Doppelsalze mit der Zusammensetzung $1:1:6$ umfassen. Eine Methode zur Berechnung der *Gibbs*-Energie $G^{mix}(s)$ für die in Wasser-Salz-Systemen gebildeten Mischkristalle wird vorgeschlagen. Die für die Systeme $RbCl-KCl-H_2O$, $RbCl-RbBr-H_2O$ und $MgCl_2-MgBr_2-H_2O$ erhaltenen Ergebnisse werden mit experimentellen Literaturdaten und Resultaten von Berechnungen aufgrund verschiedener Modelle verglichen.

Introduction

In the literature there is a relatively small number of data on four-component systems of the type M^+, M'^+, $Mg^{2+/}$ $Cl^{-//}$ H_2O and M^+, $Mg^{2+/}$ Cl^-, $Br^{-//}$ H_2O,

where M^+, $M'^+ = K^+$, NH_4^+, Rb^+, and Cs^+. The $KCl-NH_4Cl-MgCl_2-H_2O$ system has been investigated at 25 °C [1]. It has been established that a discontinuous series of mixed crystals based on ammonium and potassium carnallities is formed. *D'Ans* and *Bush* [2] have established the formation of limited solid solutions between potassium and rubidium carnallites in the four-component system $KCl-RbCl-MgCl_2-H_2O$ at 25 °C. These results are confirmed by the experimental data of *Makarov et al.* [3] obtained by investigation of the same system at 100 °C. *Balarew et al.* [4, 5] have studied the cocrystallization of isostructural carnallite type double salts and found that in systems where continuous series of mixed crystals are formed, the distribution coefficients D correspond to the theoretical values calculated according to the equation of isomorphic cocrystallization [6], where $M_{1,0}$ and $M_{2,0}$ are the molalities of the salts in their binary saturated solutions.

$$D_{2/1} = \left(\frac{M_{1,0}}{M_{2,0}}\right)^2 \qquad\qquad 1$$

The experimental investigation of the systems carnallite type double salt I–carnallite type double salt II–water is difficult because most carnallite type double salts are incongruently soluble in water at temperatures up to 75 °C.

K. Pitzer has suggested a method [7, 8] allowing the calculation of the activity coefficients in saturated and unsaturated solutions of electrolytes with an accuracy of 2–6% [9]. *Harvie* and *Weare* [10] and *Filippov, Dmitriev,* and *Yakovleva* [11] were the first to apply the *Pitzer* model under the conditions of chemical and phase equilibrium in order to predict the phase diagrams of multi-component water–salt systems in which phases with constant compositions crystallize. The authors have used data on the properties of the corresponding subsystems with a smaller number of components.

The purpose of the present work is the thermodynamical simulation of four- component carnillite type systems in which mixed crystals are formed by means of the *Pitzer* model. This would allow drawing conclusions on the applicability of the standard method to the simulation of water–salt systems in cases when solid phases with varying compositions crystallize in them. The systems $RbCl-CsCl-MgCl_2-H_2O$, $RbCl-KCl-MgCl_2-H_2O$, and $RbCl-RbBr-MgCl_2-MgBr_2-H_2O$ are investigated at 25 °C.

Harvie, Møller, and *Weare* [12] and *Filippov* and *Rumjanzev* [13] have used the *Pitzer* model for systems where mixed crystals are formed. The authors have calculated the *Gibbs* energy of mixing $G^{mix}(s)$ by the following equation:

$$G^{mix}(s)/RT = x_1\ln a_1(s) + x_2\ln a_2(s) = x_1[\ln a_1(l) - \ln a_1(l_0)] + x_2[\ln a_2(l) - \ln a_2(l_0)],$$

$$2$$

where the indices s, l and l_0 concern mixed crystals and saturated ternary and binary solutions, respectively [13]. In a detailed study we have proved the applicability of these equations to the determination of $G^{mix}(s)$ for a series of systems in which mixed crystals of both anhydrous salts and crystalline hydrates are formed [14].

Königsberger has determined the excess *Gibbs* energy of the solid phase according to equation 3 deduced from the subregular mixing model

$$G^E(s) = x(1-x)\left[G^E(s) + G^E(s)(1-2x)\right], \qquad\qquad 3$$

where $G_1^E(s)$ and $G_2^E(s)$ are the thermodynamic excess parameters [15]. They are obtained from fits to *Lippmann* diagrams [16], in which the total solubility constant ΣK is plotted *vs.* the mole fractions x of the solid phase and activity fractions x_{act} of the aqueous phase at thermodynamic equilibrium. In Ref. [17], the authors have determined the thermodynamic properties from the thermodynamic equilibrium conditions for a system with a variable composition of the solid phase (equality of the chemical potential in the solid and liquid phases) and the condition concerning stoichiometric saturation, $dx = 0$. *Königsberger* has proposed the method of recursive *Bayesian* estimation which allows the improvement of the thermodynamic excess parameters [18].

In Refs. [19, 20], the $G^{mix}(s)$ values for mixed crystals of the type (K, Rb)Cl and Rb(Cl, Br) are obtained from data on the solubilities of single salts and mixed crystals in aqueous solutions and from measurement of the activity coefficients in saturated ternary solutions by the isopiestic method. The authors have calculated the Gibbs energy of mixing by the following equation:

$$G^{mix}(s) = RT(x_1 \ln x_1 + x_2 \ln x_2 + x_1 \ln f_1 + x_2 \ln f_2), \qquad 4$$

where f_1 is the rational activity coefficient in the solid phase. In a detailed study, *Sangster* and *Pelton* [21] have summarized the data published before 1985 on 70 binary alkali halide systems. The authors have proposed simplified expressions for the dependence of the excess parameters H^E, S^E, and G^E on the solid solution compositions given in molar fractions x_1. in cases of insufficient data they have assumed that the excess entropy S^E is equal to zero and G^E is independent of temperature.

In the present investigation, we propose a new method of determination of the thermodynamic excess parameters of mixed crystals. The results obtained on ternary subsystems with isomorphic cocrystallization (RbCl–KCl–H$_2$O, RbCl–RbBr–H$_2$O, and MgCl$_2$–MgBr$_2$–H$_2$O) are compared with the experimental data reported in the literature and with values calculated on the basis of different mathematical models.

Results and Discussion

Calculation of Solubilities

The four-component carnallite type systems were simulated on the basis of the *Pitzer* model using the following approach:

1. Determination of the binary *Pitzer* parameters $\beta^{(0)}$, $\beta^{(1)}$ and C^φ, taking into account the interionic interactions between two ions of the same sign, two ions of different signs and three ions, respectively
2. Determination of the ternary *Pitzer* parameters θ_{MN} and ψ_{MNX} characterizing interactions between two different ions of the same sign and interactions between three ions
3. Calculation of the solubility isotherms of the three-component systems
4. Calculation of the solubility isotherms of the four-component systems.

This scheme was used for simulating the systems of the type MX–MgX$_2$–H$_2$O, where $M = $ Li, K, NH$_4$, Rb and Cs, and $X = $ Cl and Br [22, 23]. The very good

agreement between the calculated solubility isotherms and the experimental data permitted an application of the results obtained to the simulation of the four-component systems whose subsystems were MX-MgX_2-H_2O. Since the interaction between more than three ions is not taken into consideration in the *Pitzer* model, the simulation was performed on the basis of data on binary and ternary subsystems alone.

All binary parameters such as $\beta^{(0)}$, $\beta^{(1)}$, and C^φ needed for the simulation were taken from the literature (Table 1). We calculated phase diagrams with parameters which were valid up to saturated solutions.

The ternary parameters θ_{MN} and ψ_{MNX} for the subsystems MX-MgX_2-H_2O in which phases with constant compositions (simple salts and carnallite type double salts) crystallize are also given in the literature. They are calculated from the experimental data on the solubility in the ternary systems. The minimum deviation of the logarithm of the solubility product $\ln K^0_{sp}$ for each of the crystallization fields from its value in the corresponding binary system was the criterion used for the choice of parameters. The $\ln K^0_{sp}$ values of the binary systems were calculated on the basis of the binary parameters (Table 1) and of the saturated solutions' composition. The values used by us are presented in Table 2. The differences between the calculated values of the logarithm of the solubility product in this paper and those presented in Refs. [22] and [23] are due to differences in the data on the solubilities used.

Table 1. *Pitzer* binary parameters for the MX-H_2O and MgX_2-H_2O (M = K, Rb, Cs; X = Cl, Br) systems at 25 °C

System	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^φ	max m	Ref.
KCl-H_2O	0.0483	0.2122	0.0000	−0.0008	4.88	[12]
$RbCl$-H_2O	0.0409	0.1919	0.0000	−0.0007	7.51	[22]
$RbBr$-H_2O	0.0370	0.1520	0.0000	−0.0007	6.40	[22]
$CsCl$-H_2O	0.0390	−0.0374	0.0000	−0.0012	11.30	[22]
$MgCl_2$-H_2O	0.3511	1.6512	0.0000	0.0065	5.76	[22, 23]
$MgBr_2$-H_2O	0.4328	1.7457	0.0000	0.0029	5.37	[22, 23]

Table 2. *Pitzer* ternary parameters for MX-MgX_2-H_2O, MX-$M'X'$-H_2O, and $MgCl_2 \cdot 6H_2O$-$MgBr_2 \cdot 6H_2O$-H_2O systems at 25 °C

System	θ_{MN}	ψ_{MNX}	Ref.
KCl-$MgCl_2$-H_2O	0.00000	−0.02200	[12]
$RbCl$-$MgCl_2$-H_2O	−0.10400	0.00000	[22]
$RbBr$-$MgBr_2$-H_2O	−0.10400	−0.01900	[22]
$CsCl$-$MgCl_2$-H_2O	−0.12600	0.00000	[22]
$RbCl$-KCl-H_2O	−0.00007	−0.00001	[33]
$RbCl$-$CsCl$-H_2O	+0.00025	−0.00060	[33]
$RbCl$-$RbBr$-H_2O	−0.00001	−0.00001	[33]
$MgCl_2 \cdot 6H_2O$-$MgBr_2 \cdot 6H_2O$-H_2O	+0.00110	+0.00020	[33]

The experimental results on the systems $RbCl-CsCl-H_2O$ [24], $RbCl-KCl-H_2O$ [24, 25], $RbCl-RbBr-H_2O$ [20], and $MgCl_2-MgBr_2-H_2O$ [26, 27] at 25 °C indicate the formation of mixed crystals. As in known, many of the water–salt systems in which solid solutions are formed, obey the rule of *Zdanovskii* [28], *i.e.* isoactivities of water fall on straight lines over the whole concentration region of the solutions. Assuming the applicability of the rule of *Zdanovskii* to the four systems under investigation, we have calculated the ternary parameters on the basis of data for the binary subsystems only [13, 29]. We have found no data on θ_{MN} and ψ_{MNX} for the considered systems with varying solid phase compositions crystallizing in them in the literature. The values found for θ_{MN} and ψ_{MNX} (Table 3) are very low, and in our calculations we have assumed $\theta_{MN} = \psi_{MNX} = 0$. This approach has been proposed by *Pitzer* and *Kim* [9] for a series of systems and is also used by *Königsberger* [15]. The solubility isotherms of the ternary carnallite type systems are given in Ref. [22].

Figure 1 shows the calculated and experimentally obtained solubility isotherms of the ternary subsystems in which mixed crystals appear. The solubilities are calculated on the basis of the binary and ternary parameters obtained, assuming that only simple salt components of the system crystallize in them. This approximation is used by *Fanghänel* and *Emons* [30] for predicting the solubility isotherm of $KCl-MgCl_2-H_2O$ system at 200 °C. In the system $RbCl-KCl-H_2O$, $RbCl-RbBr-H_2O$, and $MgCl_2-MgBr_2-H_2O$, where a continuous series of mixed crystals appear, the experimental solubility isotherms are below the calculated. The difference between experimentally found and calculated solubilities is obviously associated with the Gibbs energy of mixing $G^{mix}(s)$ of crystals. This problem will be discussed in the next section. For the system $RbCl-CsCl-H_2O$, in which a discontinuous series of mixed crystals is formed, the experimental data are in very good agreement with the calculated ones. In the literature there are no data on the solid phase compositions [24]. The results obtained from the thermodynamic simulation of the system show that the composition of the mixed crystals is very close to that of the pure salts RbCl and CsCl, only small amounts of admixture being present.

Table 3. Calculated logarithm of the solubility product ($\ln K_{sp}^0$) values

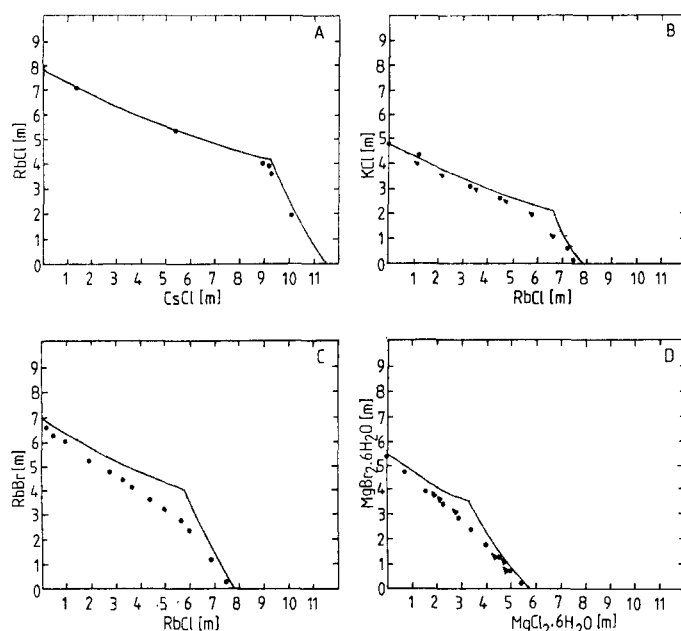| salt composition	$\ln K_{sp}^0$
$MgCl_2 \cdot 6H_2O$	10.397
KCl	2.090
$KCl \cdot MgCl_2 \cdot 6H_2O$	10.109
RbCl	3.050
$RbCl \cdot MgCl_2 \cdot 6H_2O$	7.100
CsCl	3.485
$CsCl \cdot MgCl_2 \cdot 6H_2O$	10.400
$MgBr_2 \cdot 6H_2O$	12.120
RbBr	2.526
$RbBr \cdot MgBr_2 \cdot 6H_2O$	10.620

Fig 1. Solubility isotherms of MX–$M'X'$–H_2O and $MgCl_2 \cdot 6H_2O$–$MgBr_2 \cdot 6H_2O$–H_2O type systems at 25 °C (—); calculated values: A: ● ([24]); B: ●, ▲ ([24] and [25], respectively); C: ● ([20]); D: ●, ▲ ([26] and [27], respectively)

The solubility isotherms of the carnallite type four-component systems RbCl–CsCl–MgCl$_2$–H$_2$O, RbCl–KCl–MgCl$_2$–H$_2$O, and RbCl–RbBr–MgCl$_2$–MgBr$_2$–H$_2$O at 25 °C are plotted assuming that no new solid phases crystallizes in them. The results obtained are given in Figs. 2 to 4 as horizontal nonaqueous projections of the corresponding solubility diagrams, presented as triangular or quadrangular prisms. The salt composition of the systems is given in ion-equivalent percentage.
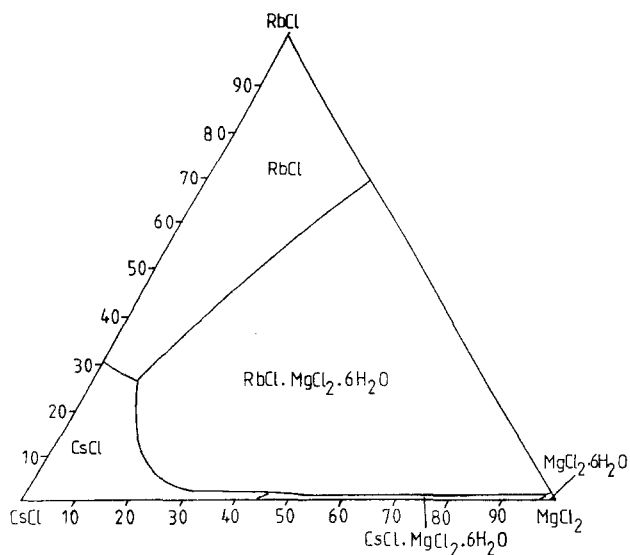

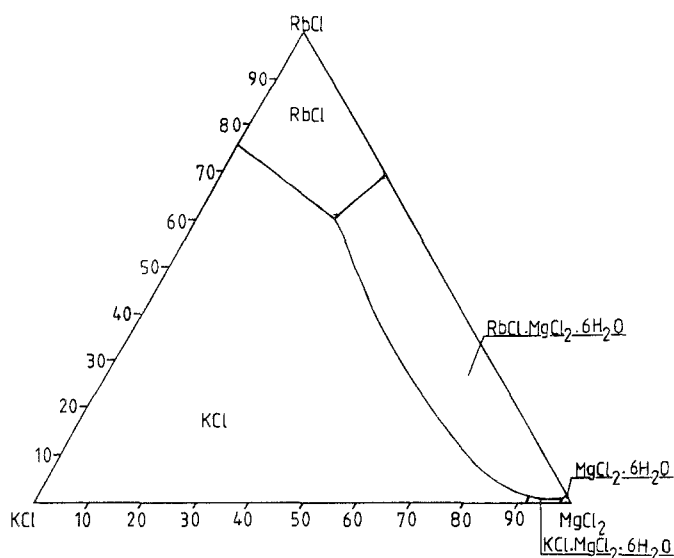**Fig. 2.** Calculated solubility isotherms of the RbCl–CsCl–MgCl$_2$–H$_2$O system at 25 °C (in ion-equivalent %)

Fig. 3. Calculated solubility iso-
therms of the RbCl–KCl–
MgCl$_2$–H$_2$O system at 25 °C (in
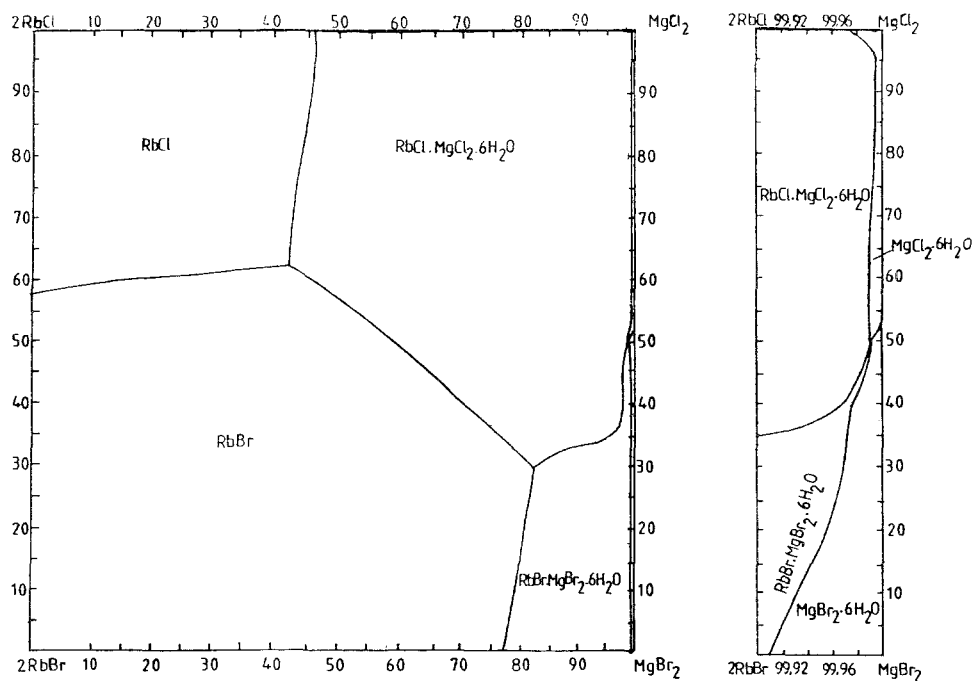ion-equivalent %)

Fig. 4. Calculated solubility isotherms of the RbCl–RbBr–MgCl$_2$–MgBr$_2$–H$_2$O system at 25 °C (in
ion-equivalent %)

The simulation is realized on the basis of data concerning the binary and ternary
subsystems, the chemical potential for each crystallization region being the same
over the whole surface of the solubility isotherm.

The calculated solubility isotherms give information on the thermodynamically
most favourable position of the surface separating the crystallization regions of the
simple and double salts. Since it is assumed that the ternary subsystems RbCl–KCl–

H_2O, $RbCl-RbBr-H_2O$, and $MgCl_2-MgBr_2-H_2O$ are of a simple eutonic type, the surfaces separating the crystallization regions of the simple salts are absent in the real solubility diagrams of the systems $RbCl-KCl-MgCl_2-H_2O$ and $RbCl-RbBr-MgCl_2-MgBr_2-H_2O$. In Ref. [31], the results from the experimental study of the systems with the participation of two carnallite type double salts are summarized. It is established that a continuous series of mixed crystals appear when not only the carnallite type double salts are isostructural, but also the parameters of their unit cells are close. A quantitative criterion in this respect is the value of the parameter $\Delta\delta$ which takes into account the difference between the volumes V_1 and V_2 of the unit cells of pure salts participating in the formation of mixed crystals according to the formula

$$\Delta\delta = \frac{(V_2 - V_1)^2}{V_1 \cdot V_2} \qquad 5$$

In agreement with the generalization made in Ref. [31], a continuous series of mixed crystals should be formed between the isostructural rubidium and cesium chlor-carnallites ($\Delta\delta = 1.2 \times 10^{-3}$), whereas isostructural rubidium chlorocarnallite and rubidium bromocarnallite should form a discontinuous series of mixed crystals ($\Delta\delta = 8.2 \times 10^{-3}$). A discontinuous series of mixed crystals should also be formed by isodimorphic potassium and rubidium chlorocarnallites.

Calculation of Gibbs Energies of Mixed Crystals

The good agreement between our results [14] on $G^{mix}(s)$ and $G^E(s)$ and those available in the literature for all the systems investigated has proved the applicability of the method chosen which is based on $Pitzer$'s equations. This has permitted the application of equation 2 to the determination of the thermodynamic characteristics of $Mg(Cl, Br)_2 \cdot 6H_2O$ mixed crystals formed in the system $MgCl_2-MgBr_2-H_2O$ at 25 °C for which we have found no data in the literature. We have used data on the solubility given by different authors [26, 27]. The results obtained for $G^{mix}(s)$ vs. x_1 are presented in Fig. 5. The dependence presented has a symmetrical shape and a minimum point at $x_1 \approx 0.5$. This allows using the regular mixing model and generalizing the results by a simplified correlation equation:

$$G^E(s) = (-4.28 \pm 0.16)x_1 x_2 \, \text{kJ mol}^{-1} \qquad 6$$

The mixed crystals show considerable negative deviations from ideal mixed crystals. This may be associated with the same type of crystal lattice, the closeness of chemical bonds, and the small difference in size of the exchanging ions. On the basis of the calculated activities of the components in the solid phase ($a_1(s)$) and the experimental data on the composition of the mixed crystals (x_1), and after asumming the presence of a stoichiometric saturation [17] ($x_{aq} = x_{act} = x$), we have determined the rational activity coefficients f_1. In accordance with dependence 4, the activity coefficients of the solid solution components are smaller than unity (if $G^E(s) < 0$) and, in contrast to the alkali halide systems [14], decrease with the molar fraction of the components x_1.

The theoretical solubility isotherms for the ternary subsystems (Fig. 1) have been plotted assuming that only simple salt components of the systems crystallize
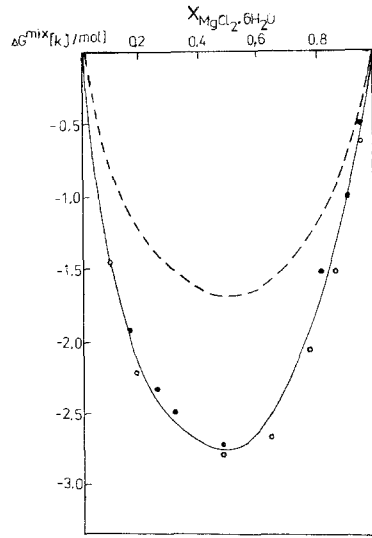
Fig. 5. Plot of the *Gibbs* energy of mixing $G^{mix}(s)$ [kJ·mol^{-1}] *vs.* the mole fraction of $MgCl_2·6H_2O$ in $Mg(Cl,Br)_2·6H_2O$ mixed crystals at 25 °C; $\circ$, $\bullet$: calculated values according to eqn. 2 from experimental data of *Boeke* [26] and *Nikolaev et al.* [27], respectively; ———: G_{id}^{mix} $(f_1 = f_2 = 1)$

in them. According to the conditions of chemical and phase equilibrium in solutions saturated towards a given salt with the composition $\alpha_1A_1·\alpha_2A_2·\alpha_3A_3$, the value of the logarithm of activity of this salt will be a constant equal to the logarithm of activity in the saturated binary solution $\ln a(l_0)$, $(\ln a(l_0) = \ln K_{sp}^0)$

$$\ln a(\alpha_1, \alpha_2, \alpha_3) = \alpha_1 \ln a_1 + \alpha_2 \ln a_2 + \alpha_3 \ln a_3 = \ln K_{sp}^0(\alpha_1, \alpha_2, \alpha_3) = const, \qquad 7$$

where a_1, a_2, and a_3 are the activities of the components A_1, A_2, and H_2O in the saturated solution, and α_1, α_2, and α_3 denote the stoichiometric coefficients in the salt. The solubility isotherms are calculated as a geometrical site of points satisfying condition 7. The eutectic in the ternary systems is a point simultaneously satisfying two equations (which describe the solubility isotherms of two solid phases) and represent the solution of the system

$$\ln a(\alpha_1, \alpha_2, \alpha_3; m_1, m_2) = \ln K_{sp}^0(\alpha_1, \alpha_2, \alpha_3) = const$$
$$\ln a(\alpha_1, \alpha_2, \alpha_3; m_1, m_2) = \ln K_{sp}^0(\alpha_1, \alpha_2, \alpha_3) = const' \qquad 8$$

i.e. in the eutectic point the activities of the components in the ternary solution (a_1^{eut}, a_2^{eut}) are equal to the activities of the components in the corresponding binary solutions:

$$a_1^{eut} = a_1(l_0); \quad a_2^{eut} = a_2(l_0) \qquad 9$$

Proceeding from these conditions and using the binary and ternary parameters of interionic interaction obtained as well as the values for $\ln K_{sp}^0$, we have plotted the theoretical solubility isotherms and determined the molalities of the solution components (m_1^{eut} and m_2^{eut}) at the eutectic point.

According to the method proposed by *McCoy* and *Wallace* [32] and used by *Filippov* and *Rumjanzev* [12], the *Gibbs* energy of mixing, $G^{mix}(s)$, is determined by the ratio between the component activities in the saturated ternary and binary solutions. In agreement with condition 9, the maximum absolute value of $G^{mix}(s)$ will depend on the activities at the eutectic point and the activities ($a_1(l)$, $a_2(l)$) at the solubility isotherm point (m_1, m_2) corresponding to the eutectic (the "transition"

eutectic solution – a saturated ternary solution corresponds to the transition saturated binary solutions – saturated ternary solution). The use of *Pitzer*'s equations permits calculating $a_1(l)$ and $a_2(l)$. The task consists in determining the composition of the corresponding saturated ternary solution.

As was already pointed out, a large part of the water-salt systems in which solid solutions are formed obey the rule of *Zdanovskii*, and the numerical values for a series of properties of the mixed ternary solutions of electrolytes are additive with respect to the properties of the binary solutions being mixed. When this rule is valid, the integral of the *Mckay-Perring* equation becomes equal to zero and the equations for the activity coefficients γ_1 and γ_2 of the components in the ternary solution can be written as [13]

$$\gamma_1 = \frac{a_1(l_0)}{m_1 + m_2} \quad \text{and} \quad \gamma_2 = \frac{a_2(l_0)}{m_1 + m_2}. \qquad 10$$

The index l_0 concerns the binary solution which is isopiestic to the ternary solution (m_1, m_2).

After simple transformations, equations 10 can be written as

$$\frac{a_1(l)}{a_1(l_0)} = \frac{m_1}{m_1 + m_2} \quad \text{and} \quad \frac{a_2(l)}{a_2(l_0)} = \frac{m_2}{m_1 + m_2}. \qquad 11$$

From the latter equation it is evident that when the systems follow the rule of *Zdanovskii*, the activity ratio is constant with a constant molar fraction in the liquid phase. Then, in the corresponding saturated ternary solution the molar fraction x_{aq} of each component should be the same as in an eutectic solution (x_{aq}):

$$\frac{m_1}{m_1 + m_2} = \frac{m_1^{eut}}{m_1^{eut} + m_2^{eut}} \quad \text{and} \quad \frac{m_2}{m_1 + m_2} = \frac{m_2^{eut}}{m_1^{eut} + m_2^{eut}}. \qquad 12$$

The composition (m_1, m_2) can also be determined graphically. It corresponds to the point of interaction of the solubility isotherm with the beam connecting the hypothetic eutectic and water angle. If the model regular solution describes the system under consideration sufficiently exactly and the condition of stoichiometric saturation is satisfied $(x_{aq} = x_{act} = x)$, then the maximum $G^{mix}(s)$ value can be calculated using the equation

$$G^{mix}(s) = 0.5RT \ln \frac{a_1(l)a_2(l)}{a_1(l_0)a_2(l_0)} \qquad 13$$

where $a_1(l)$ and $a_2(l)$ are the activities of components in the saturated ternary solution in which the molar fraction of each component is equal to the molar fraction in the hypothetic eutectic. The method presented allows calculating the *Gibbs* energy of mixed crystals from the solubility in saturated binary and ternary solutions alone, using the approximation that the corresponding system follows the rule of *Zdanovskii*.

In the present paper we have calculated $G^{mix}(s)$ for the systems $RbCl–KCl–H_2O$, $RbCl–RbBr–H_2O$, and $MgCl_2–MgBr_2–H_2O$. The results obtained (Table 4) are approximated as simplified equations illustrating the $G^E(s)$ vs. x_1 dependence in the

Table 4. Excess parameters at 298.15 K

Mixed crystals	Composition of "hypothetic" eutectic in molalities	$G_1^E(s)/J \cdot mol^{-1}$				
		a	b	c	d	e
(K, Rb)Cl	$m_{KCl} = 2.21$; $m_{RbCl} = 6.44$	3335	4100	3345	1500	3000
Rb(Cl, Br)	$m_{RbCl} = 5.73$; $m_{RbBr} = 3.94$	2690	2800	2915	2000	3100
Mg(Cl, Br)$_2 \cdot 6H_2O$	$m_{MgCl_2} = 3.40$; $m_{MgBr_2} = 3.40$	-4315	-4280	–	–	–

[a] The $G_1^E(s)$ values are calculated on the basis of the proposed method and experimental data of *D'Ans* and *Busch* [25] concerning the KCl–RbCl system, of *Makarov et al.* [20] for the RbCl–RbBr system, and of *Boeke* [26] for the MgCl$_2$–MgBr$_2$ system; [b] $G_1^E(s)$ are calculated according to equation 2 and are presented in Ref. [14] and [33]; [c] $G_1^E(s)$ from fits to *Lippmann* diagrams [15]; [d] generalized parameters of *Sangster* and *Pelton* [21]; [e] experimental results of *Ratner* and *Makarov* [19] for the KCl–RbCl system and of *Makarov et al.* [20] for the RbCl–RbBr system

case of a regular mixing model ($G_2^E(s) = 0$ in equation 3). Our results are compared with the experimental data reported in the literature and with values calculated on the basis of different theoretical models.

Using isopiestic data on the ternary solutions, *Pitzer* and *Kim* [9] have calculated the ternary parameters of interionic interaction for more than 50 systems where mixed crystals are formed. The results presented by these authors show that the θ_{MN} and ψ_{MNX} values are very low and their use (and not the assumption about $\theta_{MN} = \psi_{MNX} = 0$) does not lead to better results in all cases when describing the properties of the ternary solutions ($\ln\gamma$ or φ). In the present study we have calculated θ_{MN} and ψ_{MNX} according to the rule of *Zdanovskii* and have also obtained very low values. This permits the assumption that the systems under consideration follow, to a sufficient extent, the rule of *Zdanovskii*. In addition, the very low values of θ_{MN} and ψ_{MNX} also determine the very weak ionic interactions of the type $M-N$ and $M-N-X$ in ternary solutions of the type $MX-NX-H_2O$. On this basis it can be assumed that for the above systems the active fraction x_{act} is equal to the molar fraction x_{aq} in the liquid phase and equations 2 and 13 can be used for determining $G^{mix}(s)$. This is confirmed by the very good agreement between the results obtained by us ($G_1^E(s)/J \cdot mol^{-1} = 3335$) and those presented in Ref. [15] ($G_1^E(s)/J \cdot mol^{-1} = 3345$) on the RbCl–KCl system, which are derived from the experimental solubility data obtained by *D'Ans* and *Busch* [25]. Similarly to *Königsberger* [15], in our calculations we have neglected the ternary parameters; the binary parameter values are very close. That is why the differences in data obtained for the RbCl–RbBr system are, according to our opinion, due mainly to the different experimental data used. This is also the reason for the different values obtained for excess parameters after applying equations 2 and 13.

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