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Thermodynamic Model of Natural Brines Accounting for the Presence of Trace Components:
II. System Na^+, K^+, Mg^{2+} || Cl^-, Br^-–H_2O

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Abstract—This paper reports the calculations of parameters for the Pitzer equation and thermodynamic potentials of solid phases crystallizing in water–salt systems modeling chloride brines taking into account the presence of bromide ions in them. Solubility diagrams were calculated for corresponding ternary and quaternary systems containing chlorides and bromides of sodium, potassium, and magnesium at 25°C. The results of calculations are in adequate agreement with the available published experimental data on solubility and can be used to model salt crystallization during the concentration of seawater and brines.

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INTRODUCTION

Bromine (bromide ion) is one of the best studied trace components of natural brines. It does not form its own minerals but substitutes for chloride ion in halite, sylvite, carnallite, and bischofite. The proportion of the contents of chloride and bromide ions in liquid and solid phases (bromine–chlorine index, $Br \cdot 10^3/Cl$) is one of the most widely used geochemical indicators of salt accumulation conditions [1]. The goal of this study is to calculate the thermodynamic parameters of a model of natural brines accounting for the presence of bromide ions in brines and salts crystallizing from them. Modeling was performed in the reciprocal five-component system Na^+, K^+, Mg^{2+} || Cl^-, Br^-–H_2O at 25°C. The equilibrium compositions of the liquid and solid phases can be calculated for this system during all stages of chloride precipitation, starting from halite and completing in the eutonic point.

In this paper, we continue the analysis of phase equilibria in model salt–water systems accounting for the presence of trace components in natural brines, which was commenced in an accompanying paper [2]. The algorithm of thermodynamic modeling used in this study was described in detail elsewhere [3, 4]. The dependence of excess thermodynamic functions (activity coefficients of electrolytes and osmotic coefficient of water) on solution composition was approximated by the Pitzer equations [5], which were also given in [3, 4]. The description of a binary system by the Pitzer method requires no more than four parameters: $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^{φ}, which are independent of ionic strength and characterize binary ($\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$) and ternary (C^{φ}) short-range interactions between the ions of electrolyte only. They are determined on the basis of experimental data on water activity or activity coefficients of electrolytes in binary systems. The parameters θ and ψ describe binary and ternary short-range interactions between ions of different electrolytes and are calculated from experimental data for ternary systems. A transition to systems containing more than three components does not require the introduction of new parameters, and in most cases, all calculations are performed on the basis of data on binary and ternary subsystems. An exception is the case when solid phases crystallizing in a multicomponent system are missing in all its ternary subsystems. This circumstance is one of the advantages of the Pitzer method over other methods for the calculation of activity coefficients in electrolyte solutions.

Thus, the database for the construction of a thermodynamic model of a multicomponent salt–water system on the basis of the Pitzer equations includes an array of parameters for the binary and ternary subsystems of the system and the thermodynamic potentials of solid phases crystallizing in the system ($\ln K_{sp}$, where K_{sp} is the solubility product calculated accounting for the activity coefficients of all components). These parameters are given in Tables 1–3.

The Pitzer parameters of binary and some ternary systems were taken from the literature or previously calculated by us. Missing parameters were constrained in the present study using experimental data on solubility in the three-component salt–water systems $NaBr$–KBr–H_2O, $NaBr$–$MgBr_2$–H_2O, and KBr–$MgBr_2$–H_2O at 25°C. The solubility diagrams of ternary bromide systems calculated using these parameters are shown in Fig. 1. It can be seen that the results of calculations are generally consistent with the experimental data, and most of the three-component systems are adequately described by the Pitzer equations with zero values for θ and ψ.

Table 1. Parameters of Pitzer equations for binary systems at 25°C

System	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{φ}	α_1	α_2	Reference*
$NaCl–H_2O$	0.0765	0.2664	0	0.00124	2	–	[6]
$KCl–H_2O$	0.0484	0.2122	0	–0.00084	2	–	[6]
$MgCl_2–H_2O$	0.3509	1.6508	0	0.00610	2	–	[6]
$NaBr–H_2O$	0.1060	0.2701	–0.0145	–0.00071	2	1	[7]
$KBr–H_2O$	0.0554	0.2307	0	–0.00156	2	–	[8]
$MgBr_2–H_2O$	0.3668	1.8945	–0.1114	0.00324	2	1	[9]

* Here after, the references in which the values of parameters were calculated are given.

Table 2. Parameters of Pitzer equations for three-component systems at 25°C

Ion pair	θ	Referenc	Ion triplet	ψ	Reference
Na^+, K^+	–0.017	[10]	K^+, Mg^{2+}, Cl^-	–0.0140	[12]
Na^+, Mg^{2+}	0	[11]	Na^+, K^+, Br^-	0	Our data
K^+, Mg^{2+}	–0.083	[12]	Na^+, Mg^{2+}, Br^-	0	Our data
Cl^-, Br^-	0	[7]	K^+, Mg^{2+}, Br^-	0	Our data
Ion triplet	ψ	Reference	Na^+, Cl^-, Br^-	0	[7]
Na^+, K^+, Cl^-	–0.0007	[10]	K^+, Cl^-, Br^-	0	[7]
Na^+, Mg^{2+}, Cl^-	0	[11]	Mg^{2+}, Cl^-, Br^-	0	[9]

The five-component reciprocal system Na^+, K^+, Mg^{2+} ‖ Cl^-, $Br^-–H_2O$ includes five four-component subsystems: three reciprocal systems (Na^+, K^+ ‖ Cl^-, $Br^-–H_2O$; K^+, Mg^{2+} ‖ Cl^-, $Br^-–H_2O$) and two system with a common anion (Na^+, K^+, Mg^{2+} ‖ $Cl^-–H_2O$ and Na^+, K^+, Mg^{2+} ‖ $Br^-–H_2O$). Similar to our previous studies (e.g., [3, 4]), four-component systems were chosen for the graphical presentation of the results of calculations and evaluation of their agreement with experimental data. Systems with a higher number of components are difficult to visualize, because their phase diagrams are three- or higher-dimensional. In addition they are studied much less comprehensively. On the other hand, three-component solutions are oversimplified to be regarded as models for natural systems. In our opinion, the calculation of solubility diagrams is a necessary step in the creation of a thermodynamic model for salt deposition, because it provides a means for a graphic comparison of calculated results with experimental data and, thus, the objective assessment of model agreement with real physicochemical processes.

Table 3. Thermodynamic solubility products of solid phases at 25°C

Solid phase	$\ln K_{sp}$	Reference
NaCl (halite)	3.65	[4]
in NaBr-based solid solutions	3.50*	Our data
$NaCl \cdot 2H_2O$ (hydrohalite)	3.61**	[4]
KCl (sylvite)	2.09	[4]
$MgCl_2 \cdot 6H_2O$ (bischofite)	10.52	[4]
$KCl \cdot MgCl_2 \cdot 6H_2O$ (carnallite)	9.90	[4]
in solid solutions based on $KBr \cdot MgBr_2 \cdot 6H_2O$	10.30*	Our data
NaBr	6.50**	Our data
in NaCl-based solid solutions	6.78*	[9]
$NaBr \cdot 2H_2O$	4.76	[9]
KBr	2.60	[8]
$MgBr_2 \cdot 6H_2O$	9.98	[9]
$KBr \cdot MgBr_2 \cdot 6H_2O$	10.90	Our data
in solid solutions based on $KCl \cdot MgCl_2 \cdot 6H_2O$	9.00*	Our data

Notes: * Hypothetical $\ln K_{sp}$ values for the components of solid solutions.

** $\ln K_{sp}$ for modifications, metastable in binary solutions at 25°C.

A specific feature of the system is the crystallization of a number of solid solutions in it. Let us consider an algorithm for the calculation of phase equilibria in a salt–water system with crystallization of solid solutions by the example of a four-component reciprocal water–salt system, M, N ‖ X,Y–H_2O, where M and N are cations and X and Y are anions (as was noted above, such diagrams are used to estimate the consistency of calculated and experimental data). We first briefly address the case when solid phases in equilibrium with a solution have fixed compositions, 1 $l_1^i MX \cdot l_2^i NX \cdot l_3^i MY \cdot l_4^i NY \cdot l_5^i H_2O$, where l_j^i is the stoichiometric coefficient of the *j*th component, salt or water, in the *i*th solid

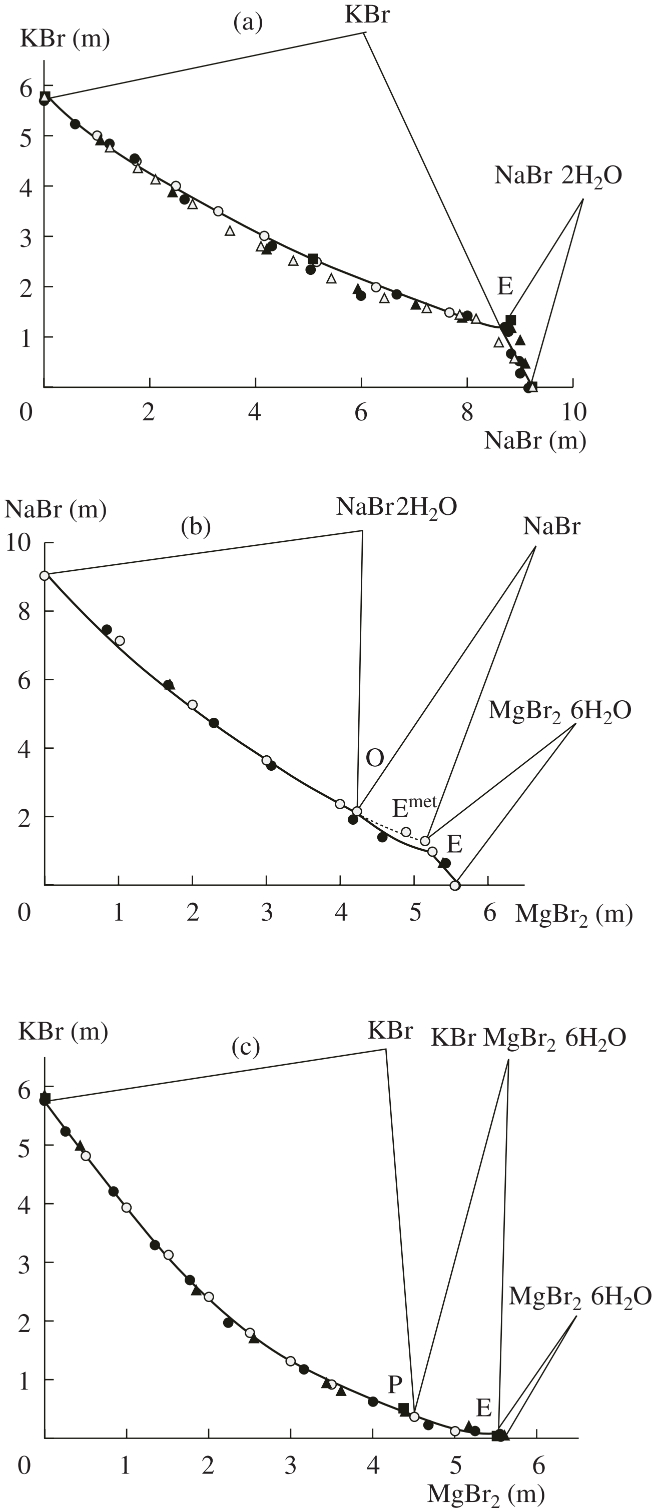

Fig. 1. Solubility diagrams for the three-component systems (a) NaBr–KBr–H_2O, (b) NaBr–$MgBr_2$–H_2O, and (c) KBr–$MgBr_2$–H_2O at 25°C. Here and in other diagrams, unfilled circles and lines correspond to calculated values, and other symbols show the experimental data of various authors [14]. Invariant points: E, eutonic; P, peritonic; and O, tributary point.

phase (see [4] for more detail). Then, the sum $l_1^i \ln a_{MX} + l_2^i \ln a_{NX} + l_3^i \ln a_{MY} + l_4^i \ln a_{NY} + l_5^i \ln a_{H_2O}$ must be constant and equal the logarithm of the solubility product of the respective compound:

$$\ln K_{sp}(i) = [\mu_i^{0(s)} - \mu_i^{0(1)}]/RT,$$

where $\mu_i^{0(s)}$ and $\mu_i^{0(1)}$ are the standard chemical potentials of the ith compound in the solid and liquid phases, respectively; R is the universal gas constant; T is the temperature; and a_j are the activities of solution species, which are calculated by the expressions

$$\ln a_{MX} = \nu_M \ln m_M + \nu_X \ln m_X + \nu \ln \gamma_{MX}$$

and

$$\ln a_{H_2O} = -(\sum m_i)\varphi/55.51.$$

In these equations, ν_M and ν_X are the numbers of M and X ions in the electrolyte formula MX; $\nu = \nu_M + \nu_X$. The values of γ_{MX} (average ion activity coefficient of salt) and φ (osmotic coefficient of water) are determined on the basis of an accepted calculation method, the Pitzer method in our case.

Using the molalities of ions, m_M, m_N, m_X, and m_Y, as independent compositional variables, the composition of solution in an invariant point is obtained by solving a system of four equations, three of which describe the conditions of phase and chemical equilibria, and the fourth is the electroneutrality equation.

$$\begin{cases} \sum_{j=1}^{5} l_j^1 \ln a_j(m_M, m_N, m_X, m_Y) = \ln K_{sp1} \\ \sum_{j=1}^{5} l_j^2 \ln a_j(m_M, m_N, m_X, m_Y) = \ln K_{sp2} \\ \sum_{j=1}^{5} l_j^3 \ln a_j(m_M, m_N, m_X, m_Y) = \ln K_{sp3} \\ m_M z_M + m_N z_N = m_X|z_X| + m_Y|z_Y|. \end{cases} \qquad (1)$$

Lines corresponding to the simultaneous crystallization of two salts are calculated from equation system (1) under the condition that one compositional variable remains constant, for instance m_N = const. The crystallization fields of particular solid phases can be constructed in a similar way.

Consider now the case when solid solutions are crystallized in the M, N || X, Y system. Let a liquid phase be in equilibrium with a solid solution based on two anhydrous electrolytes, MX and MY, and having the composition $MX_{x_1}Y_{1-x_1}$; in the case considered, it can be exemplified by the solid solution $NaCl_{x_1}Br_{1-x_1}$ or $KCl_{x_2}Br_{1-x_2}$. The thermodynamic description of the solid phase is based on the model of regular solid solu-

Table 4. Regular parameters describing the nonideality of binary solid solutions at 25°C

System	Solid solution	Basis of solid solution	$\tilde{\alpha}$, relative unit	Reference
NaCl–NaBr–H_2O	$NaCl_xBr_{1-x}$	NaCl	1.01	[7]
NaCl–NaBr–H_2O	$NaCl_xBr_{1-x} \cdot 2H_2O$	$NaBr \cdot 2H_2O$	1.01	[7]
$Na^+, Mg^{2+} \| Cl^-, Br^-$–$H_2O$	$NaCl_xBr_{1-x}$	NaBr	1.01	Our data
KCl–KBr–H_2O	KCl_xBr_{1-x}	Continuous series	1.21	[8]
$MgCl_2$–$MgBr_2$–H_2O	$MgCl_{2x}Br_{2(1-x)} \cdot 6H_2O$	Continuous series	1.01	[9]
$K^+, Mg^{2+} \| Cl^-, Br^-$–$H_2O$	$KMgCl_{3x}Br_{3(1-x)} \cdot 6H_2O$	$KCl \cdot MgCl_2 \cdot 6H_2O$	0.00	Our data
$K^+, Mg^{2+} \| Cl^-, Br^-$–$H_2O$	$KMgCl_{3x}Br_{3(1-x)} \cdot 6H_2O$	$KBr \cdot MgBr_2 \cdot 6H_2O$	0.00	Our data

tions, according to which the activity coefficients of salt components (for the symmetrical normalization of activities, i.e., $\ln\gamma_i^s = 0$ for the pure ith salt) can be calculated by the equations

$$RT\ln\gamma_{MX}^{s} = \alpha(1-x_1)^2,$$

$$RT\ln\gamma_{MX}^{s} = \alpha x_1^2,$$

where α is the parameter of nonideality for the regular solid solutions under question. Then, in accordance with the conditions of phase and chemical equilibria, the following equation is satisfied for the activity of the salt component MX in the liquid phase (a_{MX}):

$$\ln a_{MX} = \frac{\mu^{(0)s} - \mu^{(0)1}}{RT} + \ln x_1 + \frac{\alpha}{RT}(1-x_1)^2.$$

Thus, the equilibrium of a liquid solution saturated with respect to the solid solution $MX_{x_1}Y_{1-x_1}$ is described by the system of equations

$$\begin{cases} \ln a_{MX} = \ln K_{sp}(MX) + \ln x_1 + \tilde{\alpha}(1-x_1)^2 \\ \ln a_{MY} = \ln K_{sp}(MY) + \ln(1-x_1) + \tilde{\alpha}x_1^2. \end{cases} \quad (2)$$

Hereafter, $\tilde{\alpha} = \frac{\alpha}{RT}$. The values of $\ln K_{sp}$ for anhydrous salts, as well as their crystal hydrates, are determined from solubility measurements in binary systems. Note that if the crystallizing solid solutions are irregular, the problem does not change fundamentally and only the form of the function $\ln\gamma^s = f(x)$ will be modified.

Similarly, for the equilibrium of a liquid phase with solid solutions based on crystal hydrates, $MX_{x_2}Y_{1-x_2} \cdot nH_2O$ (for instance, $NaCl_{x_2}Br_{1-x_2} \cdot 2H_2O$ in the system considered below), the following system is derived:

$$\begin{cases} \ln a_{MX} + n\ln a_{H_2O} = \ln K_{sp}(MX \cdot nH_2O) \\ \qquad + \ln x_2 + \tilde{\alpha}(1-x_2)^2 \\ \ln a_{MY} + n\ln a_{H_2O} = \ln K_{sp}(MY \cdot nH_2O) \\ \qquad + \ln(1-x_2) + \tilde{\alpha}x_2^2. \end{cases} \quad (3)$$

In this case, it is assumed that the crystal hydrates have identical numbers of water molecules, because such solid solutions are formed in the systems considered below. The algorithm of computations for salt components with different numbers of crystallization water molecules was described by Rumyantsev et al. [8].

Finally, the crystallization of solid solutions based on $MNX_{x_3}Y_{1-x_3} \cdot nH_2O$ (e.g., mixed chloride–bromide carnallite in our systems) is described by the similar system of equations:

$$\begin{cases} \ln a_{MX} + \ln a_{NX} + n\ln a_{H_2O} \\ = \ln K_{sp}(MX \cdot NX \cdot nH_2O) + \ln x_3 + \tilde{\alpha}(1-x_3)^2 \\ \ln a_{MY} + \ln a_{NY} + n\ln a_{H_2O} \\ = \ln K_{sp}(MY \cdot NY \cdot nH_2O) + \ln(1-x_3) + \tilde{\alpha}x_3^2. \end{cases} \quad (4)$$

In such a case, the values of $\ln K_{sp}$ are determined from solubility data in ternary systems.

If experimental data on the compositions of coexisting liquid and solid phases are available in the literature, the regular nonideality parameter of the solid phase, α, can be determined by minimizing the difference between the left-hand and right-hand sides of Eqs. (2)–(4). These parameters were previously determined for the chloride–bromide solid solutions of sodium, potassium, and magnesium [7–9] and are given in Table 4. Preliminary calculations of phase equilibria for the system $Na^+, Mg^{2+} \| Cl^-, Br^-$–$H_2O$, in which chloride–bromide carnallite solid solutions ($KMgCl_{3x}Br_{3(1-x)} \cdot 6H_2O$) are crystallized, showed that they are well described by the model of ideal solid solutions, i.e., with $\alpha = 0$.

After the general description of the algorithm, consider particular four-component reciprocal systems. We

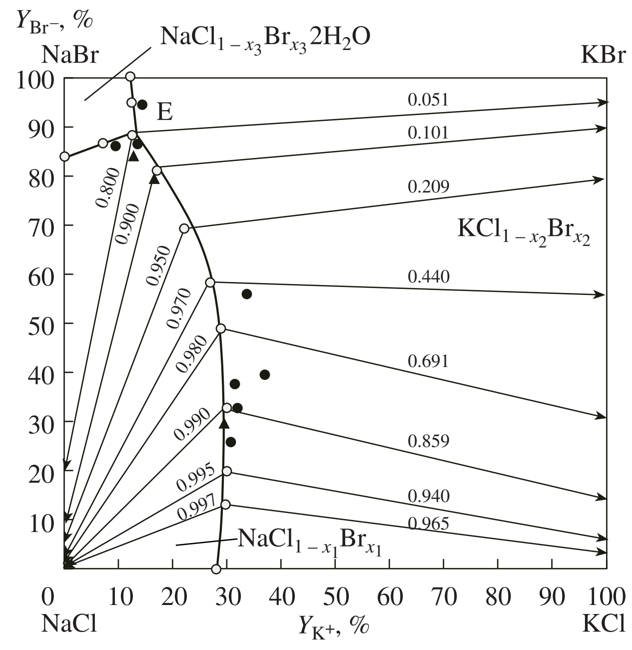

Fig. 2. Solubility diagram for the system Na^+, K^+ || Cl^-, $Br–H_2O$ at 25°C. See text for further explanation.

begin with the system Na^+, K^+ || Cl^-, $Br^-–H_2O$ at 25°C (Fig. 2). Three solid phases of variable composition crystallize in this system: $NaCl_{x_1}Br_{1-x_1}$, $KCl_{x_2}Br_{1-x_2}$, and $NaCl_{x_3}Br_{1-x_3} \cdot 3H_2O$. Correspondingly, the solubility diagram includes three crystallization fields, three limbs of univariant equilibria between a liquid solution and two solid phases, and one invariant point of the eutonic type corresponding to the simultaneous saturation of the liquid phase with respect to three solid solutions. As an example, consider the calculation of the limb of $NaCl_{x_1}Br_{1-x_1}$ and $NaCl_{x_3}Br_{1-x_3} \cdot 2H_2O$ cocrystallization. The following conditions of phase and chemical equilibrium must be satisfied for any compositions of equilibrium liquid and solid phases:

$$\begin{aligned} \ln a_{NaCl} &= \ln K_{sp}(NaCl) + \ln x_1 + \tilde{\alpha}_1(1-x_1)^2, \\ \ln a_{NaBr} &= \ln K_{sp}(NaBr) + \ln(1-x_1) + \tilde{\alpha}_1 x_1^2, \\ \ln a_{NaCl} + 2\ln a_{H_2O} &= \ln K_{sp}(NaCl \cdot 2H_2O) \\ &\quad + \ln x_3 + \tilde{\alpha}_3(1-x_3)^2, \\ \ln a_{NaBr} + 2\ln a_{H_2O} &= \ln K_{sp}(NaBr \cdot 2H_2O) \\ &\quad + \ln(1-x_3) + \tilde{\alpha}_3 x_3^2. \end{aligned} \tag{5}$$

This equation system includes five independent variables. Three variables characterize the composition of the liquid solution; in the case considered, these are the molalities of three ions, for instance, m_{Na}, m_K, and m_{Cl}, because the molality of the fourth ion, m_{Br}, is not independent and can be found from the electroneutrality constraint. Two variables, x_1 and x_3, describe the compositions of two solid solutions. Thus, the system defines a univariant line of the compositions of liquid phase (liquidus) and the corresponding compositions of solid phases (solidi).

The above-mentioned solid solutions are joined in the invariant point by a third solid solution, $KCl_{x_2}Br_{1-x_2}$. Correspondingly, the following two equations are added to equation system (5) describing phase and chemical equilibrium:

$$\begin{aligned} \ln a_{KCl} &= \ln K_{sp}(KCl) + \ln x_2 + \tilde{\alpha}_2(1-x_2)^2, \\ \text{and } \ln a_{KBr} &= \ln K_{sp}(KBr) + \ln(1-x_2) + \tilde{\alpha}_2 x_2^2. \end{aligned} \tag{6}$$

This results in a system of six equations with six variables: three variables for the composition of liquid phase (m_{Na}, m_K, and m_{Cl}) and three variables characterizing the compositions of three solid solutions: x_1, x_2, and x_3. The solution to this system yields the invariant compositions of liquid and solid solutions corresponding to the eutonic point in the solubility diagram. There is a complication in that the activity of water in the invariant eutonic solution must be known for calculations. Even if there is an adequate thermodynamic model for the solution (for instance, the Pitzer model), such a calculation is a priori impossible, because the composition of solution (m_{Na}, m_K, and m_{Cl}) cannot be determined, if the values of x_1, x_2, and x_3 in the eutonic point are not known. Thus, the systems of Eqs. (5) and (6) can be used only in combination with direct experimental data for a_{H_2O}, which can be obtained, for instance, by the isopiestic method. To our knowledge, there are no such data in the literature. Therefore, the values of a_{H_2O} must be preliminarily calculated from the data on the composition of liquid eutonic solution (using an appropriate thermodynamic model).

It was found that the procedure of thermodynamic calculations can be significantly facilitated, if, instead of simultaneous solution for the variables describing the compositions of liquid and solid phases, the equilibrium compositions of solid solutions are first determined. The equilibrium composition of the liquid phase can be obtained then from the values of x_i in the coexisting solid solutions, because the solid solutions are in equilibrium with each other independent of the state of liquid solution. Let us illustrate this approach by the example of equation system (5). Sum the right-hand and left-hand sides of the first and fourth equations and subtract the sums of the right-hand and left-hand sides of the second and third equations. This yields the following expression:

$$\begin{aligned} &\ln K_{sp}(NaCl) + \ln K_{sp}(NaBr \cdot 2H_2O) \\ &- \ln K_{sp}(NaBr) - \ln K_{sp}(NaCl \cdot 2H_2O) \\ &+ \ln\frac{x_1(1-x_3)}{(1-x_1)x_3} + \alpha_1(1-2x_1) + \alpha_3(2x_3-1) = 0. \end{aligned}$$

Any linear combination of $\ln K_{sp}$ is constant under given temperature and pressure; consequently, the equilibrium value of x_3 can be determined for any given x_1 value.

Using the described algorithm, two remaining lines of univariant equilibrium were constructed: liquid solution $NaCl_{x_1}Br_{1-x_1}$–$KCl_{x_2}Br_{1-x_2}$ and liquid solution $KCl_{x_2}Br_{1-x_2}$–$NaCl_{x_3}Br_{1-x_3} \cdot 2H_2O$.

The parameters of liquid and solid phases necessary for thermodynamic description are given in Tables 1–4. Consider in more detail the characteristics of components of solid solutions and methods of their calculation (Table 3). As was noted above, the values of $\ln K_{sp}$ for anhydrous salts or crystal hydrates can be readily calculated (using for instance, the Pitzer equation) from the data on solubility in binary systems for those temperatures at which the salts are stable phases. At 25°C, such solid phases in the systems considered are halite, sylvite, bischofite, carnallite, $NaBr \cdot 2H_2O$, KBr, and $MgBr_2 \cdot 6H_2O$. In a similar way, using solubility data for ternary systems, $\ln K_{sp}$ values are determined for ternary compounds, carnallite and its bromide analog, $KBr \cdot MgBr_2 \cdot 6H_2O$, in our case. The situation is more complicated for the solid phases that are metastable under the given temperatures; their characteristics at 25°C can be derived by the extrapolation of $\ln K_{sp}(T)$, if there are sufficiently reliable measurements of the temperature effect on solubility. In particular, this procedure was performed for hydrohalite, which crystallizes in the NaCl–H_2O binary system at negative temperatures, but the knowledge of its potential at 25°C is necessary for the calculation of equilibria involving the $NaCl_xBr_{1-x} \cdot 2H_2O$ solid solutions. Furthermore, the calculation of equilibria with the $NaCl_xBr_{1-x}$ solid solutions requires the knowledge of $\ln K_{sp}$ for anhydrous sodium bromide at 25°C. However, at temperatures of lower than 50.2°C, $NaBr \cdot 2H_2O$ is a stable solid phase in the NaBr–H_2O binary [13].

Another problem emerges during the calculation of different modifications of solid solutions of the same qualitative compositions. In the systems considered, there are two types of $NaCl_xBr_{1-x}$ solutions, those based on NaCl and NaBr (a small crystallization field of the latter variety of these solid solutions is present in the solubility diagram of the system $Na^+, Mg^{2+} \parallel Cl^-, Br^-$–$H_2O$ at high $MgBr_2$ contents). Thus, $\ln K_{sp}(NaCl)$ values for solid solutions based on NaBr are needed for calculations. A similar problem is related to the existence of three types of solid solutions of chloride–bromide carnallite join, $KMgCl_{3x}Br_{3(1-x)} \cdot 6H_2O$. In such cases, the values of $\ln K_{sp}$ can be calculated on the basis of experimental data in respective four-component systems.

SYSTEM $Na^+, K^+ \parallel Cl^-, Br^-$–$H_2O$

The calculated phase diagram for the system $Na^+, K^+ \parallel Cl^-, Br^-$—$H_2O$ at 25°C is shown in Fig. 2. Similar to the solubility diagrams of other reciprocal four-component systems, Fig. 2 was constructed in the Jänecke indexes of ions, Y_i: $Y_{K^+} = \frac{m_{K^+}}{m_{Na^+} + m_{K^+}} \cdot 100$ and $Y_{Br^-} = \frac{m_{Br^-}}{m_{Cl^-} + m_{Br^-}} \cdot 100$. As was noted above, the solubility diagram includes three crystallization fields of solid solutions, $NaCl_{x_1}Br_{1-x_1}$, $KCl_{x_2}Br_{1-x_2}$, and $NaCl_{x_3}Br_{1-x_3} \cdot 2H_2O$; three univariant limbs of liquid solution in equilibrium with two solid solutions; and one invariant point. Let us consider three-component subsystems, which correspond to the sides of the Le Chatelier–Jänecke square in Fig. 2. The solubility isotherms in two of them (NaCl–KCl–H_2O and NaBr–KBr–H_2O) are simple eutonic ones. Only solid phases of fixed composition crystallize in them at 25°C: NaCl, KCl, $NaBr \cdot 2H_2O$, and KBr. A continuous solid solution series is formed in the KCl–KBr–H_2O system. The NaCl–NaBr–H_2O system is the most interesting. Its 25°C solubility isotherm includes two limbs of crystallization of solid solutions: $NaCl_{x_1}Br_{1-x_1}$ on the basis of NaCl having a face-centered cubic lattice and $NaCl_{x_3}Br_{1-x_3} \cdot 2H_2O$ based on monoclinic $NaBr \cdot 2H_2O$ and one invariant point of the eutonic type corresponding to the coexistence of liquid and two solid solutions. It is interesting that the type of the solubility diagram of the system considered changes in response to temperature variations. At –10°C, the diagram contains a single limb of crystallization of the continuous solid solution $NaCl_{x_3}Br_{1-x_3} \cdot 2H_2O$; and at 108.7–120.1°C, there is also only one limb of crystallization, but the composition of crystallizing solid solution is different, $NaCl_{x_1}Br_{1-x_1}$ [14]. A diagram containing solid solutions with a miscibility gap can be observed within the temperature range limited by the temperatures of the following transitions: $NaCl \cdot 2H_2O \rightleftharpoons NaCl + 2H_2O$ (0.15°C) and $NaBr \cdot 2H_2O \rightleftharpoons NaBr + 2H_2O$ (50.2°C) [13]. The temperature interval must extend beyond the temperatures of phase transitions, because the loss of crystallization water in a ternary system must be lower than in its binary subsystem.

The results of calculations of the composition of liquid solution in the system $Na^+, K^+ \parallel Cl^-, Br^-$–$H_2O$ at 25°C corresponding to univariant equilibria with two solid solutions, are shown in Fig. 2 by bold lines. For comparison, also shown are experimental data on the compositions of liquid phase reported by various authors (compositions of coexisting solid phases are unfortunately unknown) [14]. As can be seen from Fig. 2, the experimental data are in good agreement with the results of calculations. The direction of tie lines is shown schematically by thin lines labeled with the val-

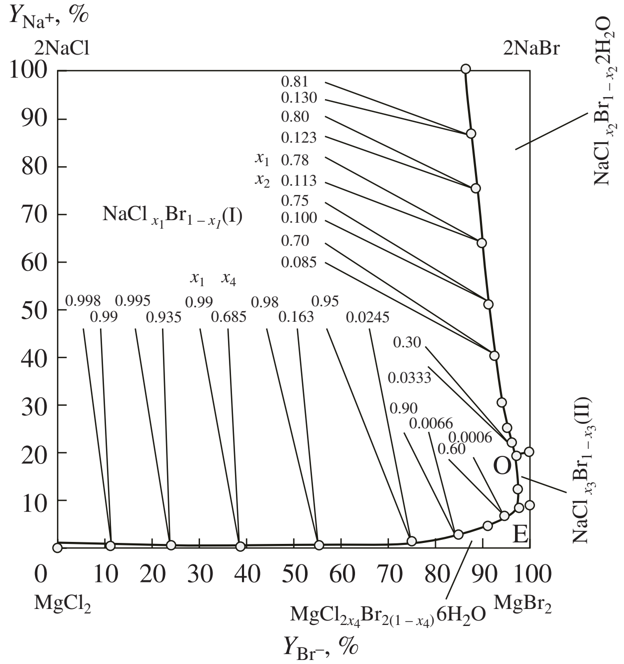

Fig. 3. Solubility diagram for the system Na^+, Mg^{2+} || Cl^-, Br^-–H_2O at 25°C.

ues of the mole fraction of chloride ion in the respective solid solution (x_1, x_2, and x_3).

The notation of invariant points used in this and other diagrams corresponds to the terminology accepted in our publications [2, 3]. The invariant point is designated by E, because it is a eutonic. Indeed, it can be seen that the point of the liquid solution lies within the triangle formed by the points of coexisting solid solutions; this implies their simultaneous crystallization during water evaporation. By the way, other relations are impossible in this system, because its diagram includes only one invariant point.

SYSTEM Na^+, MG^{2+} || Cl^-, Br^-–H_2O

In contrast to the previous system, no experimental data were found in the literature, and the diagram presented in Fig. 2 for this system was obtained theoretically on the basis of the 25°C solubility isotherms of three-component subsystems and general thermodynamic relations governing the topology of phase diagrams.

Similar to the previous system, only solid phases of fixed composition crystallize in two ternary subsystems. The diagram of one of them, $NaCl$–$MgCl_2$–H_2O, is of the simple eutonic type with the limbs of halite and bischofite crystallization; it is one of the best known halurgic systems. The handbook of [14] provides experimental data of two authors for the $NaBr$–$MgBr_2$–H_2O system. One of these studies contains two points only, one of which is a eutonic point corresponding to the equilibrium of solution with $NaBr \cdot 2H_2O$ and $MgBr_2 \cdot 6H_2O$. According to more recent and comprehensive data, the solubility isotherm includes three crystallization limbs and two invariant points (Fig. 1). One of these points is a eutonic and the other is a tributary point (O) corresponding to the transition $NaBr \cdot 2H_2O \rightleftarrows NaBr + 2H_2O$. As was noted above, this transition occurs in the $NaBr$–H_2O binary at 50.2°C, but the addition of magnesium bromide to the solution strongly depresses water activity, and this reaction may occur already at 25°C. We calculated two variants of the solubility diagram: stable, consisting of three limbs ($NaBr \cdot 2H_2O$, $NaBr$, and $MgBr_2 \cdot 6H_2O$), and metastable, consisting of two limbs ($NaBr \cdot 2H_2O$ and $MgBr_2 \cdot 6H_2O$). As can be seen from Fig. 1, the results of calculations accounting for $NaBr \cdot 2H_2O$ dehydration is distinctly more consistent with the experimental results of both authors, and this variant was therefore accepted for further calculations.

Using the solubility data from [14] for the limb of anhydrous NaBr crystallization in the $NaBr$–$MgBr_2$–H_2O system at 25°C, we calculated also for the first time the thermodynamic potential $\ln K_{sp}(NaBr)$ in the crystal lattice of anhydrous NaBr. Similarly, the thermodynamic potential $\ln K_{sp}(NaCl)$ in the solid solutions on the basis of anhydrous NaBr was calculated in the four-component system Na^+, Mg^{2+} || Cl^-, Br^-—H_2O.

Solid solutions are formed in two other ternary subsystems, $NaCl$–$NaBr$–H_2O and $MgCl_2$–$MgBr_2$–H_2O. The former system was discussed above, and the latter system crystallizes as a continuous series from $MgCl_2 \cdot 6H_2O$ to $MgBr_2 \cdot 6H_2O$; its diagram was calculated in [9].

The results of calculations for the solubility diagram of the four-component system Na^+, Mg^{2+} || Cl^-, Br^-–H_2O at 25°C are shown in Fig. 3. It can be seen that it includes four crystallization fields of various solid solutions: $NaCl_{x_1}Br_{1-x_1}$ (I), $NaCl_{x_2}Br_{1-x_2} \cdot 2H_2O$, $NaCl_{x_3}Br_{1-x_3}$ (II), and $MgCl_{2x_4}Br_{2(1-x_4)} \cdot 6H_2O$. The two types of solid solutions on the basis of sodium chloride and bromide were discussed above: one of them, $NaCl_{x_1}Br_{1-x_1}$ (I), is based on halite and crystallizes within a wide compositional range; its field occupies the major portion of the diagram in Fig. 2. The second type solid solution, $NaCl_{x_3}Br_{1-x_3}$ (II), is formed by the dehydration of $NaCl_{x_2}Br_{1-x_2} \cdot 2H_2O$ solid solutions on the basis of $NaBr \cdot 2H_2O$ at a significant decrease in water activity in the liquid phase (at high concentrations of $MgBr_2$). Its crystal structure corresponds to that of NaBr.

The solubility diagram of the system Na^+, Mg^{2+} || Cl^-, Br^-–H_2O at 25°C contains five lines of univariant equilibria and two invariant points, one tributary point (O) and one eutonic point (E). Unfortunately, the directions of tie lines cannot be shown in the diagram because of the large number of various solid solutions. Therefore, the compositions of solid phases were characterized in the following way: two arrows emanate from the calculated points of liquid phase composition, near which the values of x_1, x_2, x_3, and x_4 are indicated. For each crystallization limb, the sequence of description of the composition of two solid solutions is indicated for one of the points (for instance, x_1, x_2).

SYSTEM K^+, Mg^{2+} ‖ Cl^-, Br^-–H_2O

This system is the most complex and interesting among all of the four-component reciprocal systems considered in this paper. Similar to the previous cases, we begin from the characteristics of its ternary subsystems. Two of them crystallize continuous solid solution series: $KCl_{x_1}Br_{1-x_1}$ in the KCl–KBr–H_2O system and $MgCl_{2x_2}Br_{2(1-x_2)} \cdot 6H_2O$ in the $MgCl_2$–$MgBr_2$–H_2O system. The solubility diagrams of the other two subsystems, KCl–$MgCl_2$–H_2O and KBr–$MgBr_2$–H_2O, have similar structures. Each of them includes three limbs of crystallization of solid phases of fixed composition: the anhydrous potassium salt KCl (KBr), the bischofite-type crystal hydrate $MgCl_2 \cdot 6H_2O$ ($MgBr_2 \cdot 6H_2O$), and the binary salt $KCl \cdot MgCl_2 \cdot 6H_2O$ ($KBr \cdot MgBr_2 \cdot 6H_2O$).

The solubility diagram of the four-component reciprocal system K^+, Mg^{2+} ‖ Cl^-, Br^-—H_2O includes five crystallization fields of solid solutions (Fig. 4). In addition to the aforementioned $KCl_{x_1}Br_{1-x_1}$ and $MgCl_{2x_2}Br_{2(1-x_2)} \cdot 6H_2O$, which are formed in ternary subsystems, carnallite-type solid solutions crystallize in the quaternary system. According to the available experimental data, there are three possible modifications of these compounds: rhombic pseudohexagonal with a low content of bromide-ion (0–12.2 at %), rhombic pseudotetragonal with a high content of bromide-ion (85–100 at %), and an intermediate tetragonal variety [15]. Nikolaev [16] studied in detail the system K^+, Mg^{2+} ‖ Cl^-, Br^-–H_2O at 25°C and referred to these three types of solid solutions as rhombic chlorine-carnallite, rhombic bromine-carnallite, and quadratic carnallite. The stability boundaries of bromine-carnallite coincide with the data of [15], and the boundary between rhombic chlorine-carnallite and quadratic carnallite was constrained by the observation that the intermediate modification appeared at a Br^- content of 15.5 at %, but it was unstable at concentrations from 15.5 to 33.5 at % and transformed with time into rhombic chlorine-carnallite.

The results of calculations are shown in Fig. 4. The solubility diagram is dominated by the crystallization field of potassium chloride–bromide solid solutions; other fields, univariant lines, and invariant points are crowded near the side of the quadrate corresponding to the ternary subsystem $MgCl_2$–$MgBr_2$–H_2O. Because of this, the respective enlarged portion of the solubility diagram is shown in Fig. 4. It includes the crystallization fields of five solid solutions, ten lines of univariant equilibria between a liquid solution and two solid phases, and four invariant points (peritonic points P_1 and P_2 and eutonic points E_1 and E_2).

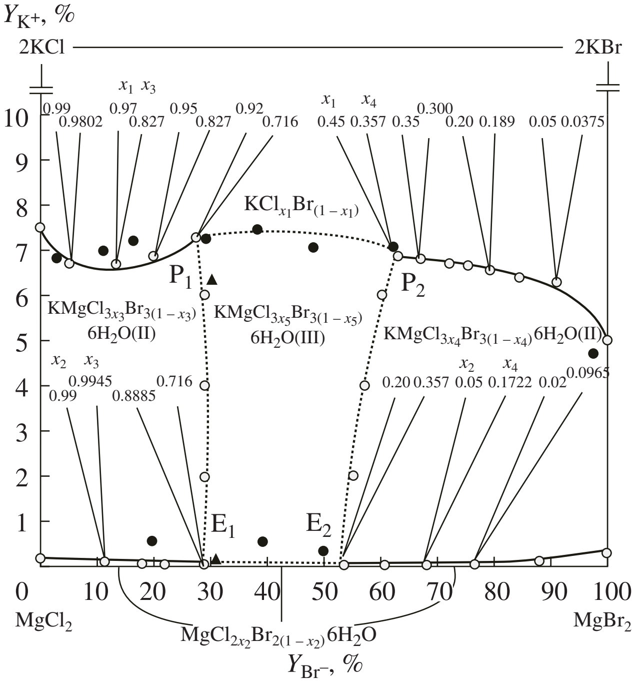

Fig. 4. Fragment of the solubility diagram for the system K^+, Mg^{2+} ‖ Cl^-, Br^-–H_2O at 25°C.

Preliminary calculations showed that the crystallization limbs involving chlorine- and bromine-carnallite in the system K^+, Mg^{2+} ‖ Cl^-, Br^-–H_2O can be adequately reproduced by the model of ideal solid solutions (both $\tilde{\alpha}_i = 0$). Thus, using the data on solubility from [14–16], only two independent parameters were separately varied: the thermodynamic potential of chloride carnallite in the lattice of bromide carnallite and the thermodynamic potential of bromide carnallite in the lattice of chloride carnallite (Table 3).

Thermodynamic analysis on the basis of stability criteria with respect to infinitesimal changes in the state [17] showed that such an unusual phase transition of both carnallites (chloride and bromide) into a transitional modification can occur only in one case, when the thermodynamic potential of both carnallites in the solid solution of the transitional modification is different from the thermodynamic potentials of these phases in their own lattices. The parameter of nonideality in the transitional solid solutions should also be different from the $\tilde{\alpha}$ values of end-member modifications. Otherwise, four variants of stable equilibrium would be observed: (1) the transitional phase does not form at all (its thermodynamic potential in the components of solid solution is higher than that in the components of

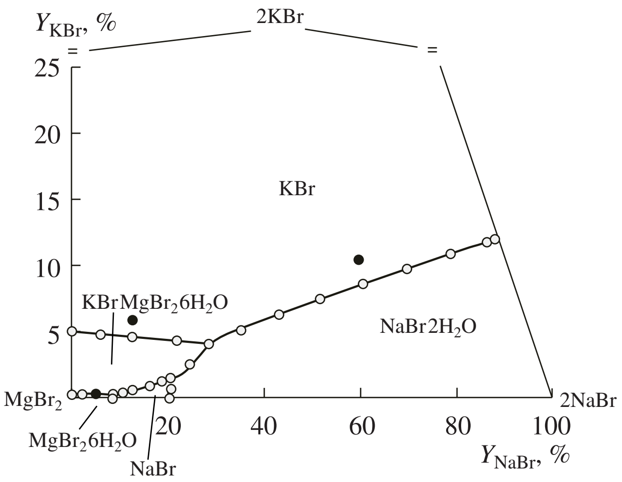

Fig. 5. Fragment of the solubility diagram for the system Na^+, K^+, Mg^{2+} || Br^-–H_2O at 25°C.

adjoining phases); (2) the transitional phase overlaps the crystallization fields of solid solutions on the basis of chloride carnallite; (3) the transitional phase overlaps the crystallization fields of solid solutions on the basis of bromide carnallite; and (4) the transitional phase overlaps both the adjoining fields of crystallization of solid solutions. In such cases, another topology would have been observed in the carnallite part of the phase diagram: the topology of an open book in cases (1)–(3) and band-type topology in case (4).

Thus, in order to calculate the crystallization field of solid solutions on the basis of the transitional carnallite modification, three independent parameters must be simultaneously varied: two thermodynamic potentials, $\ln K_{sp}(KCl \cdot MgCl_2 \cdot 6H_2O)$ and $\ln K_{sp}(KBr \cdot MgBr_2 \cdot 6H_2O)$ in the transitional modification, and the nonideality parameter $\tilde{\alpha}$ for this phase. As can be seen from Fig. 4, the available experimental data are insufficient for such variations: there are five points with relatively high K^+ contents and three points with very low K^+, which are practically not suitable for variation. Therefore, we did not calculate the crystallization field of the transitional carnallite modification, and its boundaries are arbitrarily drawn in the diagram by dotted lines.

SYSTEMS Na^+, K^+, Mg^{2+} || Cl^-–H_2O AND Na^+, K^+, Mg^{2+} || Br^-–H_2O

In addition to the three four-component subsystems considered above, the proposed model five-component reciprocal system Na^+, K^+, Mg^{2+} || Cl^-, Br^-–H_2O includes two four-component systems with a common anion. The solubility diagram of one of them, Na^+, K^+, Mg^{2+} || Cl^-–H_2O, has been repeatedly studied experimentally and calculated using Pitzer equations (e.g., [4, 18, 19]). Halite, sylvite, carnallite, and bischofite crystallize in this system at 25°C. For the bromide system, there is very few experimental data in the literature. They are shown in Fig. 5 together with the results of our calculations (in Jänecke indexes of salt components). The crystallization field of potassium bromide occupies a major portion of the diagram. Other four fields ($NaBr \cdot 2H_2O$, NaBr, $MgBr_2 \cdot 6H_2O$, and $KBr \cdot MgBr_2 \cdot 6H_2O$) occur near the side of the concentration triangle; a fragment of the diagram is therefore presented. It contains several lines of univariant equilibria and three invariant points, peritonic point P, tributary point O, and eutonic point E.

CONCLUSIONS

The results of phase equilibrium calculations on the basis of Pitzer equations are in general in adequate agreement with experimental solubility measurements. Thus, the developed algorithm of calculation of brine–solid solution equilibria, the obtained values of the parameters of Pitzer equations, and the thermodynamic potentials of solid phases crystallizing in the system can be used for the calculation of partition coefficients of Br^- between solid phases and brines, quantitative modeling of the behavior of bromide ion during the processes of evaporite sedimentation under natural condition, and the concentration of brines during the commercial production of bromine.

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