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Chemical Equilibrium Model of Solution Behavior and Bishofite ($MgCl_2 \cdot 6H_2O(cr)$) and Hydrogen−Carnallite ($HCl \cdot MgCl_2 \cdot 7H_2O(cr)$) Solubility in the $MgCl_2 + H_2O$ and $HCl-MgCl_2 + H_2O$ Systems to High Acid Concentration at (0 to 100) °C[†]

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This paper describes the development of a thermodynamic model for the highly important $MgCl_2 + H_2O$ and $HCl + MgCl_2 + H_2O$ systems at (0 to 100) °C. The model incorporates the concentration-dependent specific interaction equations of Pitzer for aqueous solutions (*J. Phys. Chem.* **1973**, *77*, 268). All experimental thermodynamic quantities available in the literature (osmotic coefficients, water activities, magnesium chloride mineral's solubilties) are used to construct a chemical model that calculates solute and solvent activities and solid−liquid equilibria in the $MgCl_2 + H_2O$ and $HCl + MgCl_2 + H_2O$ systems. The (0 to 100) °C model for the binary $MgCl_2 + H_2O$ system gives excellent agreement with activity and solubility data used in parametrization and/or validation processes. To create a temperature-variable mixed solution model for the $HCl + MgCl_2 + H_2O$ system, a $HCl + H_2O$ model parametrization established in our previous study (Christov and Moller, *GCA* **2004a**, *68*, 1309) has been used. To develop an equilibrium solubility model of hydrogen−carnallite ($HCl \cdot MgCl_2 \cdot 7H_2O(cr)$), crystallizing within the $HCl + MgCl_2 + H_2O$ system at very high acid concentration, we extend the application range of H−Cl pure electrolyte parametrization up to very high molality ($\approx 23\ mol \cdot kg^{-1}$ at (0 and 25) °C and $\approx 15\ mol \cdot kg^{-1}$ at higher temperature). The evaluated T-variable single electrolyte and mixing ion interaction parameters and thermodynamic solubility products of minerals give an excellent agreement with $MgCl_2 \cdot 6H_2O(cr)$ and $HCl \cdot MgCl_2 \cdot 7H_2O(cr)$ equilibrium solubility data in mixed solutions at (0 to 100) °C. The model predictions on the effect of temperature and mixing on the deliquescence relative humidity (DRH/MDRH) in $MgCl_2 + H_2O$ and $HCl + MgCl_2 + H_2O$ solutions saturated with highly soluble bishofite and hydrogen−carnallite minerals are also given.

Introduction

Computer models that predict solution behavior and solid−liquid−gas equilibria close to experimental accuracy have wide applicability. Such models can be powerful predictive and interpretive tools to study the geochemistry of natural waters and mineral deposits, solve environmental problems, and optimize industrial processes. The specific interaction approach for describing electrolyte solutions to high concentration introduced by Pitzer[1,2] represents a significant advance in physical chemistry that has facilitated the construction of accurate thermodynamic models. It was showed[3−8] that the Pitzer approach could be expanded to accurately calculate solubilities in complex brines and to predict the behavior of natural fluids.

This paper continues our series concerning parametrization of comprehensive XPT-variable thermodynamic models concerned with complex aqueous equilibrium solutions of highly soluble inorganic salts, which can assist in the development of a complex atmospheric chemistry model that can accurately predict the composition and state of sea-type aerosols over the wide ranges of temperature and relative humidity.[8,9] The main objective of this study is the development of a high accuracy thermodynamic model for solution behavior and highly soluble bishofite and hydrogen−carnallite minerals solubility in $MgCl_2 + H_2O$ and $HCl + MgCl_2 + H_2O$ systems at (0 to 100) °C.

The physical state and size of inorganic atmospheric particles are a function of relative humidity (RH). Deliquescence is a process in which a soluble solid substance sorbs water vapor from the air to form a saturated aqueous solution. Deliquescence of a single inorganic salt or their mixture is a process of spontaneous solid−liquid phase change. The deliquescence occurs when relative humidity (RH) in the gas-phase environment is at or above deliquescence relative humidity (DRH) of the salt or mutual deliquescence relative humidity (MDRH) of a salt mixture. Because of very high complicity of experiments, the relative humidity data, particularly for the mixed systems, are sparse.[10] Nevertheless, different sophisticated thermodynamic equilibrium models, such as SCAPE and SCAPE2,[11,12] AIM and AIM2,[13] UNAERO,[14] and ISOPROPIA[15] have been proposed and developed to describe the deliquescence behavior of gas−solid−liquid inorganic aerosol equilibrium. However, none of the models presented in the literature include a consideration of the mixing solution parameters and minerals formation as a function of temperature and acid concentration in the $HCl + MgCl_2 + H_2O$ system.

In the previous paper of the author, presented in the same journal,[8] new osmotic coefficient data, obtained using isopiestic measurements, are presented for mixed $MgCl_2 + CaCl_2 + H_2O$ solutions. These data were combined with all other thermody-

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namic quantities available in the literature to construct a high accuracy model for $MgCl_2 + H_2O$ and $CaCl_2 + H_2O$ binary and $MgCl_2 + CaCl_2 + H_2O$ ternary systems at (25 and 50) °C. The model was used to calculate DRH/MDRH of mixed $MgCl_2 + CaCl_2 + H_2O$ solutions in equilibrium with $MgCl_2 \cdot 6H_2O(cr)$, $CaCl_2 \cdot 6H_2O(cr)$, and $2MgCl_2 \cdot CaCl_2 \cdot 12H_2O(cr)$ minerals against the composition of saturated solutions. According to the calculated deliquescence diagram, the addition of highly soluble calcium chloride decreased the DRH of bishofite (DRH ($MgCl_2 \cdot 6H_2O(cr)$; 25 °C) $\approx$ 34.4 %) in the mixed system. It was concluded that mixed $MgCl_2 + CaCl_2 + H_2O$ solutions saturated with bishofite and with a molal ratio of magnesium and calcium chloride corresponding to the composition of solid sea-salt aerosols (Lin et al.:[16] $m(MgCl_2)/m(CaCl_2) = 7/2$) will be the first equilibrium solutions which are formed during the formation of liquid sea-salt aerosols at standard temperature. The solid−liquid equilibrium model for the mixed system predicts a MDRH value of $\approx$ 32 % for this bishofite equilibrium solution, respectively, for the lowest deliquescence of complex solid sea-salt. Our recent chemical kinetic experiments[9] on OH uptake of solid $MgCl_2 + CaCl_2$ mixtures completely validate these model predictions. It was established that the effect of relative humidity (RH) on OH uptake by the solid magnesium chloride + solid calcium chloride mixture reproduces quantitatively that of solid sea-salt.

However, to extend the understanding of the deliquescence behavior of complex solid sea-salt in an acidic atmospheric environment and under high relative humidity conditions, it is necessary to develop an accurate thermodynamic model which also considers the acid interaction solution parameters and highly soluble acidic minerals, such as hydrogen−carnallite ($HCl \cdot MgCl_2 \cdot 7H_2O(cr)$). In addition to bishofite, the chemical equilibrium of this double salt also can play a key role on formation of aqueous sea-salt aerosols by decreasing the DRH value of solid sea-salt. Development of the temperature-variable, pH-dependent thermodynamic model for $MgCl_2 \cdot 6H_2O(cr)$ and $HCl \cdot MgCl_2 \cdot 7H_2O(cr)$ equilibrium in $MgCl_2 + H_2O$ and $HCl + MgCl_2 + H_2O$ systems can be a powerful predictive tool to solve, important for atmospheric chemistry problems. Other important applications include design and assessment of nuclear and acid mine waste disposal strategies,[10] development of high concentration chloride leaching processes,[17] as well as production of evaporate minerals (such as carnallite, magnesium-, and potassium chlorides), and utilization of waste solutions during treatment of natural deposits.[18−20] The model presented here also provides many parameter evaluations which form a good base to develop a highly important T-variable model of geochemical behavior of aluminum in acidic magnesium-rich natural waters.[7]

Methodology

Modeling Approach. In constructing the model for $MgCl_2 + H_2O$ and $HCl + MgCl_2 + H_2O$ systems at (0 to 100) °C, the solubility approach described in previous studies of the author is used.[5−8,20] The model incorporates the concentration-dependent specific interaction equations of Pitzer[1,2] for aqueous solutions. Since Pitzer's representation of the aqueous phase is based on the excess free energy, all the activity expressions are consistent, allowing different kinds of data {e.g., activity (water activity (a_w), osmotic (φ), and activity ($\gamma_\pm$) coefficients), voltage, and solubility measurements} to be used in the parameter evaluations and other thermodynamic functions to be calculated. Model validation involves comparison of model predictions with data not used in the parameter evaluation process.

The Pitzer equations are described in many publications.[3−8,20,21] Equations 1 to 3 give the expression for the activity coefficient, γ, for the interaction of a cation, M, with the other solutes (m is molality; c is cation; a is anion; n is neutral species; I is ionic strength; A^φ is the Debye−Huckel constant). This expression is symmetric for anions. The adjustable parameters describing binary solution interactions are the ionic strength dependent $B(I)$ coefficients and C, which is independent of ionic strength. The adjustable Θ_{ij} coefficients for mixing between two ions of like charges are ionic strength dependent. The adjustable Ψ terms, which account for mixing between two ions of like charges and an ion of opposite charge, are independent of ionic strength.

$$\ln \gamma_M = z_M^2 F + \sum_a m_a(2B_{Ma}(I) + ZC_{Ma}) + \sum_c m_c(2\Phi_{Mc} + \sum_a m_a \psi_{Mca}) + \sum_a \sum_{a<a'} m_a m_{a'} \psi_{Maa'} + |z_M| \sum_c \sum_a m_c m_a C_{ca} + \sum_n m_n(2\lambda_{nM}) + \sum_n \sum_a m_n m_a \varsigma_{naM} \tag{1}$$

$$F = -A^\varphi\{I^{.5}/(1 + 1.2I^{.5}) + (2/1.2)\ln(1 + 1.2I^{.5})\} + \sum_c \sum_a m_c m_a B'_{ca} + \sum_c \sum_{c'<c} m_c m_{c'} \Phi'_{cc'} + \sum_a \sum_{a'<a} m_a m_{a'} \Phi'_{a,a'} \tag{2}$$

$$B_{ma} = \beta^0_{Ma} + \beta^1_{Ma} g(\alpha, I^{.5}) + \beta^2_{Ma} g(12I^{.5}), g(x) = 2(1 - (1 + x)e^{-x})/x^2, \Phi_{ij} = \Theta_{ij} + {}^E\Theta_{ij}(I), Z = \sum_i |z_i| m_i \tag{3}$$

To extend the application of the model for predictions of solution properties at very high concentrations, Pitzer and Simonson[22] introduced in their approach mole fraction concentrations. Their approach has been used successfully for modeling of aerosol mixtures.[23] In the parametrization proposed here, we use a standard molality based on the ion interaction model. To fit the binary solution properties with a lower sigma value and to high concentration, some authors used in their single electrolyte parametrization an extended version of the Pitzer model, introducing two C^φ parameter values.[24,25] In our single electrolyte parametrization, we use the standard Pitzer approach with one C^φ parameter. In our previous studies,[6,20,21] we show that the above standard Pitzer approach gives excellent model reliability to very high concentration and temperature (for example, to 64 $mol \cdot kg^{-1}$ in the $NaOH + H_2O$ system[6] and up to 300 °C and 18 $mol \cdot kg^{-1}$ in the $NaBr + H_2O$ and $KBr + H_2O$ systems[26]). Note that in the model presented here we do not include the neutral species (such as $MgCl_2^o(aq)$); i.e., neutral species−ion interaction parameters (λ and ξ in eq 1)[3,6,21] will be not considered in this model. Therefore, at constant temperature and pressure, the solution model parameters to be evaluated are ($\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^φ) pure electrolyte and (θ and Ψ) mixing parameters.

Because of the theoretical and practical importance of the binary and mixed systems studied in this work, there is a considerable volume of experimental data and theoretical analysis reported in the literature. Our comprehensive acid−base (0 to 250) °C models[6,7,21] the for H−Na−K−Ca−OH−Cl−HSO_4−SO_4−H_2O system do not include magnesium interactions and minerals. However, in our sodium−potassium−acid model[6] we present a new well validated $HCl + H_2O$ model, which is valid for temperatures from (0 to 250) °C and relatively low acid molality for the $HCl + H_2O$ solution behavior and chloride minerals solubilities in mixed systems. The model is in excellent agreement with all recent activity data and with solubility data

Table 1. Values of the $MgCl_2 + H_2O$ and $HCl + H_2O$ Pure Electrolyte and $MgCl_2 + HCl + H_2O$ Mixing Parameters, Determined and/or Validated in This Study at (0, 25, 50, 75, and 100) °C, Where A^{φ} Is the Debye−Huckel Constant[a]

parameters	0 °C	25 °C	50 °C	75 °C	100 °C
$A^{\phi b}$	0.376704	0.391475	0.410330	0.433275	0.460525
$\beta^{(0)}(H,Cl)^b$	0.190681	0.176092	0.165712	0.154655	0.142776
$\beta^{(1)}(H,Cl)^b$	0.275353	0.298974	0.311600	0.331738	0.358190
$C^{\varphi}(H,Cl)^b$	0.0	0.0	0.0	0.0	0.0
$\beta^{(0)}(Mg,Cl)$	0.383722	0.36193^c	0.34448^c	0.330448	0.319140
$\beta^{(1)}(Mg,Cl)$	1.392948	1.58114^c	1.77455^c	1.972060	2.172843
$C^{\varphi}(Mg,Cl)$	0.002684	0.002380^c	0.001695^c	0.000716	−0.000501
	$(0.00930)^d$	$(0.0065)^e$	$(0.00403)^d$	$(0.0018)^d$	$(-0.00008)^d$
$\theta(Mg,H)$	0.0965	0.100	0.115	0.132	0.160
$\Psi(Mg,H,Cl)$	−0.01	−0.011	−0.012	−0.013	−0.014

[a] Values of $C^{\varphi}(Mg,Cl)$ solution parameters presented in the literature are given in branches. [b] Parameters calculated from temperature dependence equations [covering the (0 to 250) °C range] presented in Christov and Moller[6] and used in this study. [c] From Christov.[8] [d] Parameters calculated from temperature dependence equations given by Pabalan and Pitzer.[4] [e] From Balarew et al.[18]

in binary and multicomponent systems.[6,7,21] The $HCl + H_2O$ model described in our previous studies was developed to describe the acid interactions in subsurface natural fluids and therefore cover a relatively low acid concentration range (up to 10 $mol \cdot kg^{-1}$ HCl). Here we develop a equilibrium model for application in modeling of atmospheric chemistry processes. Because of relatively low water content in the atmosphere, the acid concentration in the acidic atmosphere environment becomes very high (as a molal ratio of moles of acid to the moles of water). To account for this, in this study we extend the concentration range of application of our recent $HCl + H_2O$ parametrization by using, in our equilibrium mixed $HCl + MgCl_2 + H_2O$ model parametrization, the hydrogen−carnallite ($HCl \cdot MgCl_2 \cdot 7H_2O(cr)$) solubility data at very high acid concentration (≈ 23 $mol \cdot kg^{-1}$ at (0 and 25) °C and ≈ 15 $mol \cdot kg^{-1}$ at higher temperature).

The comprehensive T-variable model of Pabalan and Pitzer[4] for the $Na-K-Mg-Cl-SO_4-H_2O$ system does not include acid interactions and solids. The authors used in their magnesium chloride model $\beta^{(0)}(Mg,Cl)$, $\beta^{(1)}(Mg,Cl)$ binaries from De Lima and Pitzer.[27] To fit the binary solution solubility data, the authors modified the values of $C^{\varphi}(Mg,Cl)$. To determine the chemical potential of magnesium chloride solids, Pabalan and Pitzer[4] used the heat capacity values determined by calorimetric measurements. Following our well-defined solubility approach,[6,20,21,26] in this study the chemical potential of minerals is directly determined from equilibrium solubility data. The ORNL group (Holmes and Mesmer[28]) has derived a (0 to 250) °C Pitzer model for magnesium chloride solutions. The $MgCl_2 + H_2O$ model is based on their own high temperature (>110 °C) isopiestic data and calorimetric and isopiestic data at lower temperature. The widely used model of Holmes and Mesmer is valid only for low concentrated solutions ($m(MgCl_2) < 4$ $mol \cdot kg^{-1}$) and therefore does not consider solid phase formation. In this study, the model for the $MgCl_2 + H_2O$ system was reparametrized at (0 to 100) °C. To better reflect the high concentration behavior of the $MgCl_2 + H_2O$ system, we included all available low concentration activity data as well as bishofite solubility measurements to evaluate pure electrolyte parameters of Mg−Cl interactions and the chemical potential of $MgCl_2 \cdot 6H_2O$.

Several authors (Harvie et al.,[3] Koenigsberger et al.,[17] Khoo et al.,[29] Roy et al.,[30] and Yahong et al.,[31−33]) have constructed models for the mixed $HCl + MgCl_2 + H_2O$ system. The models of Khoo et al.[29] (25 °C; $I^{max} = 3$ $mol \cdot kg^{-1}$) and of Roy et al.[30] ((5 to 45) °C; $I^{max} = 5$ $mol \cdot kg^{-1}$) have been developed to describe only their own HCl activity coefficient data for mixed solutions with low ionic strength (I) values, obtained on the basis of electromotive force (EMF) measurements. Therefore, Yahong et al.[31−33] show that the mixing parameters ($\theta(Mg,H)$ and $\Psi(Mg,H,Cl)$), derived by Roy and extrapolated to (0 and 50) °C, give unreliable solubility predictions in the ternary system. The standard temperature model of Harvie et al.[3] and the model of Koenigsberger et al.[17] at (25 to 125) °C do not consider precipitation of hydrogen−carnallite. The computer code of Koenigsberger et al. has been developed to predict mostly the component activity coefficients and water activity in unsaturated solutions. Therefore, in their calculations, the authors used low molality Mg−Cl pure electrolyte parametrization of Holmes and Mesmer.[28] The authors did not give the values of mixing parameters and the solubility product of solids, which they used in their activity and solubility calculations. In their series of three publications, Yahong et al.[31−33] present their bishofite and hydrogen−carnallite solubility models for the $HCl + MgCl_2 + H_2O$ system at (0, 20, 40, and 50) °C. Although the authors show that the model predictions are in good agreement with experimental equilibrium data, their models are not well-defined and, respectively, not reliable because: (1) the thermodynamic solubility product of hydrogen−carnallite at (0 and 20) °C is not determined, (2) the authors evaluate extremely high values of the binary mixing $\theta(Mg,H)$ parameter even at low temperatures of (40 and 50) °C, and (3) the values of mixing parameters ($\theta(Mg,H)$ and $\Psi(Mg,H,Cl)$) at each temperature are not consistent with their values at other temperatures, even in a narrow temperature range from (0 to 50) °C (see discussion in next paragraph). Therefore, reparametrization of the mixed $MgCl_2 + CaCl_2 + H_2O$ system at (0 to 100) °C is necessary.

Model Parametrization and Results

In constructing the model of the $HCl + MgCl_2 + H_2O$ system at (0 to 100) °C, the Debye−Huckel constants, A^{φ} (see Table 1), at (0, 25, 50, 75, and 100) °C are calculated from temperature function given in Moller.[34] See also the discussion in our previous study[6] for A^{φ} parametrization and validation. Pure electrolyte parameters of H−Cl interactions (Table 1) at (0 to 100) °C are calculated from our temperature function given in our acid−base models.[6,7,21] In this study, we extend the concentration range of application of our $HCl + H_2O$ parametrization up to very high acid concentration (see the text below). Evaluations of the remaining model parameters are discussed in the sections below. They are the binary solution model parameters, $\beta^{(0)}$, $\beta^{(1)}$, and C^{φ}, for the Mg−Cl ion interactions (Table 1); the mixed solution model parameters $\theta(Mg,H)$ and $\Psi(Mg,H,Cl)$ for ion interactions in $HCl + MgCl_2 + H_2O$ ternary solutions (see Table 1); and the standard chemical potentials of the bishofite $MgCl_2 \cdot 6H_2O(cr)$ and hydrogen−carnallite $HCl \cdot MgCl_2 \cdot 7H_2O(cr)$ solid phases (see Table 3) contained within the $MgCl_2 + H_2O$ binary and $HCl + MgCl_2 + H_2O$ ternary

Table 2. Predicted Mean Activity Coefficient ($\gamma_\pm$) of $MgCl_2$ in Binary $MgCl_2 + H_2O$ Solutions as a Function of Molality *m* (in $mol \cdot kg^{-1}$) Up to 6*m* at (0 and 100) °C

calcd values of:	$m(MgCl_2)$ ($mol \cdot kg^{-1}$)	activity coefficient $\gamma_\pm$ ($MgCl_2$) 0.1	0.25	0.5	1.0	2.0	4.0	6.0
	t/(°C)							
this study[a]	0	0.52346	0.488	0.4978	0.618	1.2342	7.1214	50.955
calcd[b]		0.5438		0.5046	0.618	1.21	7.29	
this study[a]	100	0.4709		0.385	0.4114	0.6212	2.0858	
calcd[b]		0.45326	0.409	0.3662	0.394	0.60	2.003	8.377

[a] Predictions of the model presented here (Table 1). [b] Predictions of the model of Holmes and Mesmer.[28]

Table 3. Calculated Values of the Logarithm of the Thermodynamic Solubility Product (ln K^o_{sp}) of $MgCl_2 \cdot 6H_2O(cr)$ and $HCl \cdot MgCl_2 \cdot 7H_2O(cr)$ at (0, 25, 50, 75, and 100) °C, Where *m*(sat) Is the Molality of the Saturated Binary $MgCl_2 + H_2O$ Solutions[a]

salt composition	m(sat)/($mol \cdot kg^{-1}$) calcd	exptl[b]	ln K^o_{sp} calcd	ref data
		0 °C		
$MgCl_2 \cdot 6H_2O(cr)$	5.63	5.55	10.818 (± 0.08)	
$HCl \cdot MgCl_2 \cdot 7H_2O(cr)$			22.7 (± 0.20)	
		25 °C		
$MgCl_2 \cdot 6H_2O(cr)$	5.79	5.80	10.114 (± 0.06)	10.26[c] 10.39 to 10.6[d]
$HCl \cdot MgCl_2 \cdot 7H_2O(cr)$			21.7 (± 0.10)	
		50 °C		
$MgCl_2 \cdot 6H_2O(cr)$	6.26	6.27	9.714 (± 0.08)	9.86[e]
$HCl \cdot MgCl_2 \cdot 7H_2O(cr)$			20.82 (± 0.10)	50 °C: 19.31[f] 40 °C: 20.03[g]
		75 °C		
$MgCl_2 \cdot 6H_2O(cr)$	6.715	6.58 to 6.8	9.266 (± 0.09)	9.22[e]
$HCl \cdot MgCl_2 \cdot 7H_2O(cr)$			20.05	
		100 °C		
$MgCl_2 \cdot 6H_2O(cr)$	7.64	7.66	8.685 (± 0.10)	
$HCl \cdot MgCl_2 \cdot 7H_2O(cr)$			19.0	

[a] Numbers in parentheses are the deviations of the ln K^o_{sp} constants in experimental equilibrium ternary solutions (refs 45 to 52). [b] From Linke[43] and Zdanovskii and Cheremnyh.[42] [c] Harvie et al.[3] [d] Christov et al.[19] and Christov.[20] [e] Balarew et al.[44] [f] Yahong et al.[33] [g] Yahong et al.[32]

systems at temperatures ranging from (0 to 100) °C. Reference osmotic coefficient data for the $MgCl_2 + H_2O$ binary are used to evaluate solution parameters for low and moderate chloride concentration. Solubility data in binary and mixed systems are also used to broaden the concentration range of parametrization. Following the approach in our previous studies,[5,20] to avoid the overlapping effect of pure electrolytes and mixing solution parameters, the model for the binary $MgCl_2 + H_2O$ system was developed using only the data for this binary system, and the mixed solutions model was parametrized on the basis of the data only for the $HCl + MgCl_2 + H_2O$ system. Note that in our $MgCl_2 + H_2O$ binary and $HCl + MgCl_2 + H_2O$ mixed model parametrization we used only raw experimental thermodynamic quantities (osmotic coefficients, water activity, and minerals solubility), which are directly derived from experimental measurements (isopiestic studies, voltage (EMF), and solubility experiments). The mean activity coefficient recommendations available in the literature are model dependent and therefore are not used in the parametrization process. However, some of these data are used here to validate the $MgCl_2 + H_2O$ solution model (see Table 2).

Evaluation of Parameters in the $MgCl_2 + H_2O$ System from (0 to 100) °C. In this study, the (0 to 100) °C model for the $MgCl_2 + H_2O$ system is constructed retaining the same parametrization at (25 and 50) °C established previously[8] (see Table 1 for Mg−Cl solution parameters and Table 3 for thermodynamic solubility product of $MgCl_2 \cdot 6H_2O(cr)$). Here, the (25 and 50) °C $MgCl_2 + H_2O$ model is extended to low (0 °C) and to high temperature (100 °C). The $MgCl_2 + H_2O$ binary solution interaction parameters are evaluated from activity data (osmotic coefficients and water activity) for unsaturated solutions. To better reflect the high concentration behavior of the system, we include in parametrization solubility measurements of bishofite in the binary system. Osmotic coefficient (φ) and water activity (a_w) data for binary solutions are used to help define the concentration variation of $\beta^{(0)}$(Mg,Cl), $\beta^{(1)}$(Mg,Cl), and C^{φ}(Mg,Cl). The osmotic coefficient data sets which are included in parametrization are (*n* is the number of experimental data points): (1) data of Snipes et al.[35] at (40, 50, 60, 70, and 80) °C and up to $m = 2.0$ $mol \cdot kg^{-1}$ ($n = 75$); (2) data of Patll et al.[36] up to $m = 4.8$ $mol \cdot kg^{-1}$ ($n = 40$), and at (30, 40, 50, 60, and 70) °C; (3) the 25 °C data of Stokes[37] up to saturation ($m(\text{sat}) = 5.84$ $mol \cdot kg^{-1}$, $n = 19$); (4) the recommendations of Robinson and Stokes[38] up to $m = 5$ $mol \cdot kg^{-1}$ ($n = 21$) and at 25 °C; (5) the standard temperature data of Rard and Miller[39] up to $m = 5.81$ $mol \cdot kg^{-1}$ (saturated solution; $n = 37$). For a broad concentration and temperature ranges of pure electrolyte parametrization, the high molality smoothed water activity (a_w) values, given in refs 40 and 41 are also included. The a_w sets, included in Mg−Cl parametrization, are from: Suhotin[40] (set 6), $m(\text{max}) = 6.30$ $mol \cdot kg^{-1}$, at (0, 25, 50, 75, and 100) °C ($n = 60$), and from Zaizev et al.[41] (set 7), temperature ranging from (0 to 100) °C and $m(\text{max}) = 7.00$ $mol \cdot kg^{-1}$ ($n = 200$). There is a very good agreement between all sets of osmotic coefficient and water activity data at (0 to 100) °C. Note that in our parametrization the osmotic data in the supersaturated solutions are not considered (i.e., 25 °C data of Stokes[37] and of Rard and Miller[39] at (5.92 $mol \cdot kg^{-1}$ < $m(MgCl_2)$ < 6.0 $mol \cdot kg^{-1}$).

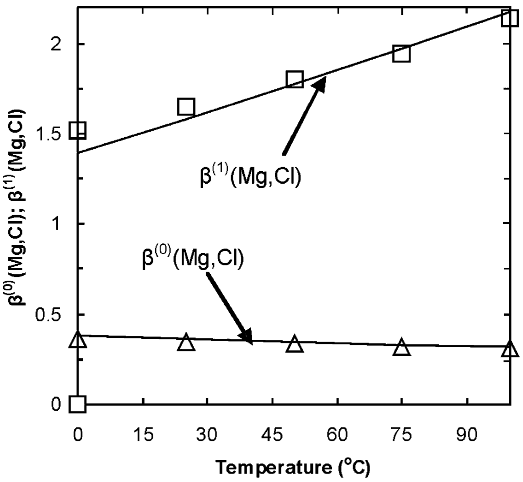

Figure 1. Comparison of $\beta^{(0)}$(Mg,Cl) and $\beta^{(1)}$(Mg,Cl) pure electrolyte parameters evaluated in this study [solid lines: (0 to 100) °C)] with the recommended values (symbols) of Christov[20] (at 25 °C) and Pabalan and Pitzer[4] at (0, 50, 75, and 100) °C.

The bishofite solubility data in the $MgCl_2 + H_2O$ system at (0 to 100) °C are used to evaluate the chemical potential of solid mineral. The agreement between the bishofite equilibrium solubility data presented in the literature is very good. The smoothed solubility data of Zdanovskii and Cheremnyh[42] and those summarized by Linke[43] are used in parametrization. According to the data, $MgCl_2 \cdot 6H_2O$(cr) is the only stable phase in this binary system from (0 to 100) °C.

The resulting $\beta^{(0)}$(Mg,Cl), $\beta^{(1)}$(Mg,Cl), and C^{φ}(Mg,Cl) parametrization for the binary $MgCl_2 + H_2O$ system is presented in Table 1. It gives excellent agreement with the data for unsaturated binary solutions. The model fits the T-variable osmotic data of Snipes et al.[35] (set 1) and of Patll et al.[36] (set 2) with sigma values (σ) of 0.044 and 0.065, respectively. For definition of sigma, see Christov and Moller.[21] The summary sigma value (σ) for the fit of the osmotic data at standard temperature (sets 3 to 5) is 0.038. The summary sigma value for water activity data (sets 6 and 7) is 0.094. Figure 1 compares the $\beta^{(0)}$(Mg,Cl) and $\beta^{(1)}$(Mg,Cl) parametrization vs temperature, established in this study with the most widely used recommendations of Balarew et al.,[18] and Christov[20] at 25 °C, and by Pabalan and Pitzer[4] at (0, 50, 75, and 100) °C. The parameters of Pabalan and Pitzer at each temperature are calculated from their temperature dependence equations. As is shown, the T- variable $\beta^{(0)}$(Mg,Cl) and $\beta^{(1)}$(Mg,Cl) binary parameter values obtained in this study are very close to those given in the literature[4,18,20] at (0 to 100) °C (see Figure 1). Similarly to the recommendations of Pabalan and Pitzer we determined $\beta^{(0)}$(Mg,Cl) parameters which very smoothly decrease with temperature, while $\beta^{(1)}$(Mg,Cl) increases with temperature more sharply. The C^{φ}(Mg,Cl) parametrization established here follows the same trend with temperature from (0 to 100) °C as those established by Christov[18,20] and Pabalan and Pitzer:[4] C^{φ}(Mg,Cl) decreases with temperature and has a negative value at 100 °C only (see Table 1). In this study, we evaluate lower C^{φ} values than those given in the literature. The relatively high difference of C^{φ}(Mg,Cl) values is not surprising since the Mg−Cl parametrization uses a different concentration range of experimental data. Following our solubility approach, the pure electrolyte Mg−Cl parameters are evaluated here using binary system activity data for unsaturated solutions and bishofite solubility data. Therefore, Mg−Cl pure electrolyte parametrization established here is valid up to saturated binary solutions and from (0 to 100) °C.

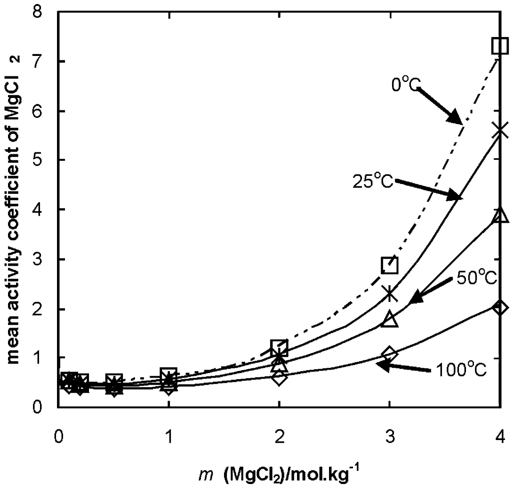

Figure 2. Comparison of mean $MgCl_2$ activity coefficients in $MgCl_2 + H_2O$ solutions calculated by the model (solid lines: (25, 50, 75, and 100) °C; dashed-dotted line: 0 °C) with the recommended values of Holmes and Mesmer[28] (symbols) from (0 to 100) °C (symbols: open squares, 0 °C; crosses, 25 °C; open triangles, 50 °C; open diamonds, 100 °C).

The magnesium chloride mean activity coefficient values, available in the literature, are used here to validate the solution model predictions. The solution model predicts mean activity coefficients ($\gamma_{\pm}$) of $MgCl_2$ which are in very good agreement with recommended values of Stokes,[37] Robinson and Stokes,[38] and Rard and Miller[39] at 25 °C (up to saturation) and of Holmes and Mesmer[28] at 50 °C (to 6 $mol \cdot kg^{-1}$ $MgCl_2$). The (25 and 50) °C comparison is given in the previous study of the author (see Table 3 in Christov[8]). Here, in Table 2 we compare our $\gamma_{\pm}$ ($MgCl_2$) calculations with recommendations of Holmes and Mesmer[28] at (0 and 100) °C and up to 4 $mol \cdot kg^{-1}$ $MgCl_2$. Figure 2 shows the comparison of the model presented here (Table 1) and the calculations of Holmes and Mesmer (see their Table 6 at saturation pressure) vs concentration and temperature [from (0 to 100) °C]. The low molality ($\leq$ 4 $mol \cdot kg^{-1}$ $MgCl_2$) predictions of both models are in excellent agreement. According to both models, the magnesium chloride mean activity coefficient sharply decreases with temperature ranging from (0 to 100) °C and at high molality (> 2 $mol \cdot kg^{-1}$). Note that the T-variable ORNL researchers model is valid only for low molality $MgCl_2 + H_2O$ binary solutions, up to 4 $mol \cdot kg^{-1}$ $MgCl_2$. The $MgCl_2 + H_2O$ model presented here describes precisely not only low molality solution behavior (see Table 2 and Figure 2) but also bishofite equilibrium at much higher solution concentration (up to 7.64 $mol \cdot kg^{-1}$ $MgCl_2$ at 100 °C; see Figure 4 and text below). This finding permits a conclusion that the concentration extension of the Mg−Cl parametrization up to saturation do not decrease the accuracy of the model for describing the solution behavior at low molality.

The temperature-variable thermodynamic solubility product (as ln K^{o}_{sp}) at (0 to 100) °C of bishofite is evaluated from solubility data in the $MgCl_2 + H_2O$ binary system using the evaluation of the Mg−Cl binary interaction parameters. The calculated ln K^{o}_{sp} values are given in Table 3 and Figure 3 (as a solid line). The model predicts solubility product values, which are in very good agreement with recommendations given in other publications (Christov[20] at 25 °C and Balarew et al.[44] at (50 and 75) °C; see triangles on Figure 3). The main reason for the small ln K^{o}_{sp} differences is the differences in m(sat) values used in calculations. The established thermodynamic solubility product of $MgCl_2 \cdot 6H_2O$(cr) gives a very good agreement with bishofite pure water (0 to 100) °C solubility data of Zdanovskii

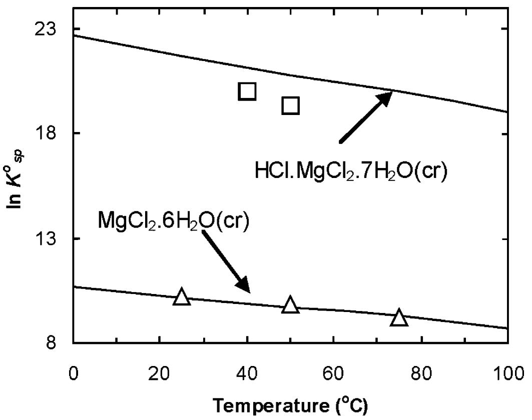

Figure 3. Comparison of thermodynamic solubility product (ln K°_{sp}) of $MgCl_2 \cdot 6H_2O(cr)$ and $HCl \cdot MgCl_2 \cdot 7H_2O(cr)$ determined in this study [solid lines: (0 to 100) °C] with the recommended values (symbols). Symbols: open triangles, recommendations of Christov et al.[19] (25 °C) and Balarew et al.[44] at (50 and 75) °C; open squares, recommendations of Yahong et al. at (40 and 50) °C.

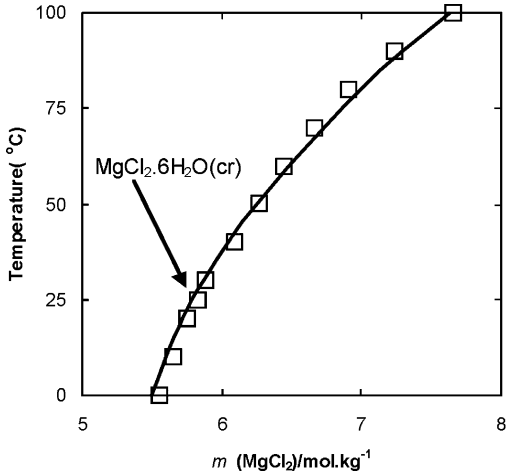

Figure 4. Calculated (solid line) and experimental (open squares: Linke,[43] Zdanovskii and Cheremnyh[42]) solubility of $MgCl_2 \cdot 6H_2O(cr)$ in the $MgCl_2 + H_2O$ system as a function of temperature at (0 to 100) °C.

and Cheremnyh[42] and Linke[43] ($\sigma = 0.050$). Figure 4 compares calculated (solid line) and experimental (open squares) $MgCl_2 \cdot 6H_2O(cr)$ solubility in the $MgCl_2 + H_2O$ system as a function of temperature from (0 to 100) °C.

Evaluation of Parameters in the $HCl + MgCl_2 + H_2O$ System. The (0 to 100) °C solubility data in this ternary system are used to evaluate T-variable θ(Mg,H) and Ψ(Mg,H,Cl) mixing parameters and the standard chemical potential (as ln K°_{sp}) of hydrogen carnallite ($HCl \cdot MgCl_2 \cdot 7H_2O(cr)$) double salt, which precipitate from saturated ternary solutions. There is some inconsistency in the data given in the literature on the composition of solids, which are in equilibrium with saturated solutions. Some authors did not identify crystallization of $HCl \cdot MgCl_2 \cdot 7H_2O(cr)$ at high acid concentration and reported a solubility diagram which consists of the crystallization field of $MgCl_2 \cdot 6H_2O(cr)$ only. Other authors reported diagrams which consist of fields of equilibrium crystallization of two solids: bishofite and hydrogen carnallite. However, the composition of equilibrium solutions in all data sets and from (0 to 100) °C are in good agreement. The following $MgCl_2 \cdot 6H_2O(cr)$ equilibrium data in the ternary $HCl + MgCl_2 + H_2O$ system are used in mixed model parametrization: data of Engel[45] (0 °C), of Obuhov and Lavrov[46] [(0, 25, 50, 82, and 100) °C], of Obuhov and Mihailov[47] [(60, 70, and 90) °C], of Grushvizkii and Shmidt[48] [(0 and 25) °C], of Ke Juan and Wen-Tschi[49] (0 °C), of Voelz-Fladrich[50] [(0, 25, 35, and 45) °C], and of Dahne[51] [(0, 50, 60, 70, and 80) °C]. In addition to these data we also included in evaluations all high acid concentration data available in the literature on $HCl \cdot MgCl_2 \cdot 7H_2O(cr)$ equilibrium. These data are given by Ke Juan and Wen-Tschi (at 0 °C and up to $m(HCl) = 19.7\ mol \cdot kg^{-1}$), by Voelz-Fladrich (at 0 °C up to $m(HCl) = 18.83\ mol \cdot kg^{-1}$; at 25 °C up to $m(HCl) = 18.0\ mol \cdot kg^{-1}$; at 35 °C up to $m(HCl) = 14.84\ mol \cdot kg^{-1}$, and at 45 °C up to $m(HCl) = 10.23\ mol \cdot kg^{-1}$), and by Dahne (0 °C up to $m(HCl) = 22.7\ mol \cdot kg^{-1}$, at 50 °C up to $m(HCl) = 14.04\ mol \cdot kg^{-1}$, and at 60 °C up to $m(HCl) = 8.69\ mol \cdot kg^{-1}$). Note that hydrogen−carnallite equilibrium solubility data cover a temperature range from (0 to 60) °C. All these ternary system solubility data are summarized in Zdanovskii et al.[52]

In the solubility data correlations, the evaluations of the binary parameters for aqueous $MgCl_2$ and of $MgCl_2 \cdot 6H_2O(s)$ standard chemical potential established above are used (Tables 1 and 3). In this parametrization, the H−Cl pure electrolyte parameters at (0 to 100) °C are calculated from temperature dependence equations (covering the (0 to 250) °C range) presented in our previous study (Christov and Moller[6]) (Table 1). The parametrization of a mixed system model began at standard temperature, for which the experimental data are more complete. As a first step in θ(Mg,H) and Ψ(Mg,H,Cl) parametrization, we introduced in our model the same mixing parameter values as in the brine system model of Harvie et al.[3] Nevertheless, using different Mg−Cl and H−Cl pure electrolyte parameters, which are used in both models, and different molality ranges of mixed system solubility data used in parametrization (Harvie et al.[3] model is valid only up to $m(HCl) = 7.0\ mol \cdot kg^{-1}$ and do not consider $HCl \cdot MgCl_2 \cdot 7H_2O(cr)$ precipitation), it was found that Harvie et al. mixing parametrization fit very well the experimental solubility data in this mixed system up to $m(HCl) = 18\ mol \cdot kg^{-1}$. To extend the parametrization to low (0 °C) and high (100 °C) temperature, it was necessary to vary both θ(Mg,H) and Ψ(Mg,H,Cl) parameters with temperature. To extend our $HCl \cdot MgCl_2 \cdot 7H_2O(cr)$ equilibrium precipitation model to high temperature (100 °C), outside the temperature range of experimental data [(0 to 60) °C], an approach described in a previous study[7] of the author is used. We plot the polythermal diagram predicted by the model for the composition of $HCl + MgCl_2 + H_2O$ solutions saturated with two solid phases ($MgCl_2 \cdot 6H_2O(s) + HCl \cdot MgCl_2 \cdot 7H_2O(cr)$). At $60\ °C < T < 100\ °C$ we vary θ(Mg,H) and Ψ(Mg,Ha,Cl) mixing parameters, as well as the standard chemical potential of hydrogen−carnallite, trying to keep a smooth parametrization with temperature [ranging (from 0 to 100) °C] and smooth magnesium chloride and HCl concentrations for invariant ($MgCl_2 \cdot 6H_2O(s) + HCl \cdot MgCl_2 \cdot 7H_2O(cr)$) points. The resulting θ(Mg,H) and Ψ(Mg,H,Cl) and ln $K^\circ_{sp}(HCl \cdot MgCl_2 \cdot 7H_2O(cr))$ model is presented in Tables 1 and 3. According to the model calculations, the thermodynamic solubility product of hydrogen−carnallite smoothly decreases with temperature from 22.7 at 0 °C to 19.0 at 100 °C (see also the upper solid line on Figure 3). The model predicts slightly higher ln $K^\circ_{sp}(HCl \cdot MgCl_2 \cdot 7H_2O(cr)$ values at (40 and 50) °C than the model of Yahong et al.[32,33] (open squares on Figure 3; max difference of 0.65 log units). Figure 5 compares θ(Mg,H) and Ψ(Mg,H,Cl) mixing parameters evaluated here (solid lines), with those determined by other authors (symbols) and from (0 to 100) °C. Our θ(Mg,H) evaluations give a smooth increase with temperature and an approximately linear decrease of Ψ(Mg,H,Cl) with increasing temperature from (0 to 100) °C. As shown in Figure 5, the (0 to 50) °C mixing parameters of

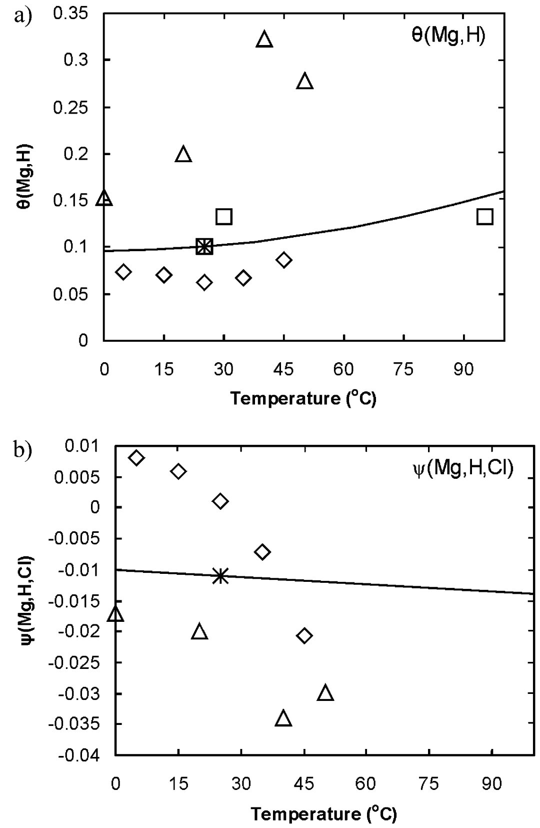

Figure 5. Comparison of θ(Mg,H) and Ψ(Mg,H,Cl) mixing ion interaction parameters evaluated in this study [solid lines: (0 to 100) °C)] with the reference values (symbols). (a) θ(Mg,H); (b) Ψ(Mg,H,Cl). On both figures, stars, open triangles, and open diamonds represent the parameters determined by Harvie et al.[3] (25 °C), Yahong et al.[31−33] at (0 to 50) °C, and Roy et al.[30] at (5 to 45) °C. The open squares in Figure 5a show the θ(Mg,H) values of Koenigsberger et al.[17]

Yahong et al.[31−33] (see open triangles), which are determined using $MgCl_2 \cdot 6H_2O$(cr) and $HCl \cdot MgCl_2 \cdot 7H_2O$(cr) solubility data in the mixed system, are very scattered and different from those evaluated here, especially at (40 and 50) °C. The main reason for this difference can be the application range of HCl(aq) pure electrolyte parameters, which Yahong et al. used in their mixed model. The θ(Mg,H) model presented here is in relatively good agreement with the models of Roy et al.[30] (open diamonds in Figure 5a) and Koenigsberger et al.[17] (open squares). The differences in Ψ(Mg,H,Cl) mixing parameters evaluated here (solid line on Figure 5b) and in the model of Roy et al.[30] (open diamonds) can be explained with a very big difference in HCl m(max) values of experimental data used in model development. The model predicts high consistency with temperature composition of ($MgCl_2 \cdot 6H_2O$(cr) + $HCl \cdot MgCl_2 \cdot 7H_2O$(cr)) coexistence point (see Figure 6). According to the model predictions, in the invariant point the molality of $MgCl_2$ increases, and the molality of HCl decreases with temperature from (0 to 100) °C. The model predictions (crosses-solid line) are in excellent agreement with available experimental data, from (0 to 50) °C (see open symbols in Figure 6).

As a final test of the solid−liquid equilibria model developed in this study, in Figure 7 we compare the model predictions and the experimental solubility isotherms. The T-variable (0 to 100) °C mixed system model is in excellent agreement with all bishofite [from (0 to 100) °C] and hydrogen−carnallite [from (0 to 60) °C] solubility data available in the literature. In all five figures, the solid symbols represent bishofite equilibrium data, and the open symbols correspond to the hydrogen−carnallite saturation data. According to the model, at (0 to 100) °C the solubility isotherm consists of two branches corresponding to the crystallization of $MgCl_2 \cdot 6H_2O$(cr) and $HCl \cdot MgCl_2 \cdot 7H_2O$(cr). Therefore, the high acid molality data points of Obuhov and Lavrov[46] at (0 and 25) °C on $MgCl_2 \cdot 6H_2O$(cr) precipitation (see solid circles at high HCl concentration in Figure 7a and 7b) are estimated as not correct and excluded in parametrization. The summary standard deviation values of bishofite and hydrogen−carnallite solubility data in the mixed HCl + $MgCl_2$ + H_2O system are 0.076 and 0.065, respectively. The deviations of the thermodynamic solubility constants of $MgCl_2 \cdot 6H_2O$(cr) and $HCl \cdot MgCl_2 \cdot 7H_2O$(cr) in their saturated ternary solutions, which are experimentally determined, are given in branches in Table 3.

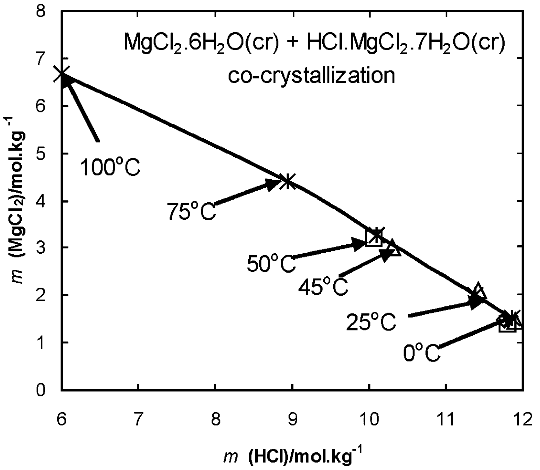

Figure 6. Comparison between calculated (stars-solid line) and experimental (open symbols) composition of ($MgCl_2 \cdot 6H_2O$ (cr) + $HCl \cdot MgCl_2 \cdot 7H_2O$ (cr)) invariant point in the HCl + $MgCl_2$ + H_2O system from (0 to 100) °C. Symbols: open diamond, Ke Juan and Wen-Tschi;[49] open triangles, Voelz-Fladrich;[50] open squares, Dahne.[51]

Note that the low molality binary system HCl + H_2O model, which has been established in our previous study using experimental activity and solubility data up to m(HCl) = 8 $mol \cdot kg^{-1}$, was used here in construction of the present mixed model without any changes. The accurate prediction of $HCl \cdot MgCl_2 \cdot 7H_2O$(cr) solubility up to 25 $mol \cdot kg^{-1}$ HCl also proves the accuracy of the concentration extension of our HCl + H_2O parametrization. The good agreement between the mixing model predictions and solubility data given in the literature also shows the consistency of (1) binary systems HCl + H_2O and $MgCl_2$ + H_2O models and (2) the ternary system HCl + $MgCl_2$ + H_2O model, established here and presented in Tables 1 and 3.

Applications

The equilibrium (0 to 100) °C models for $MgCl_2$ + H_2O binary and HCl + $MgCl_2$ + H_2O ternary systems have also been used to calculate deliquescence relative humidity (DRH) of bishofite in its saturated binary solutions, as well as deliquescence relative humidity (DRH/MDRH) of mixed HCl + $MgCl_2$ + H_2O solutions in equilibrium with $MgCl_2 \cdot 6H_2O$(cr) and $HCl \cdot MgCl_2 \cdot 7H_2O$(cr). Within the salt-solution model, relative humidity is related to water activity, a_w, according to the equation[53,54]

$$a_{\mathrm{w}} = P_{\mathrm{w}}/P_{\mathrm{w}}^{\mathrm{o}} = \mathrm{RH}/100 \tag{4}$$

where P_w and P_w^o are the vapor pressure of the saturation solution and pure water, respectively, at given temperature.

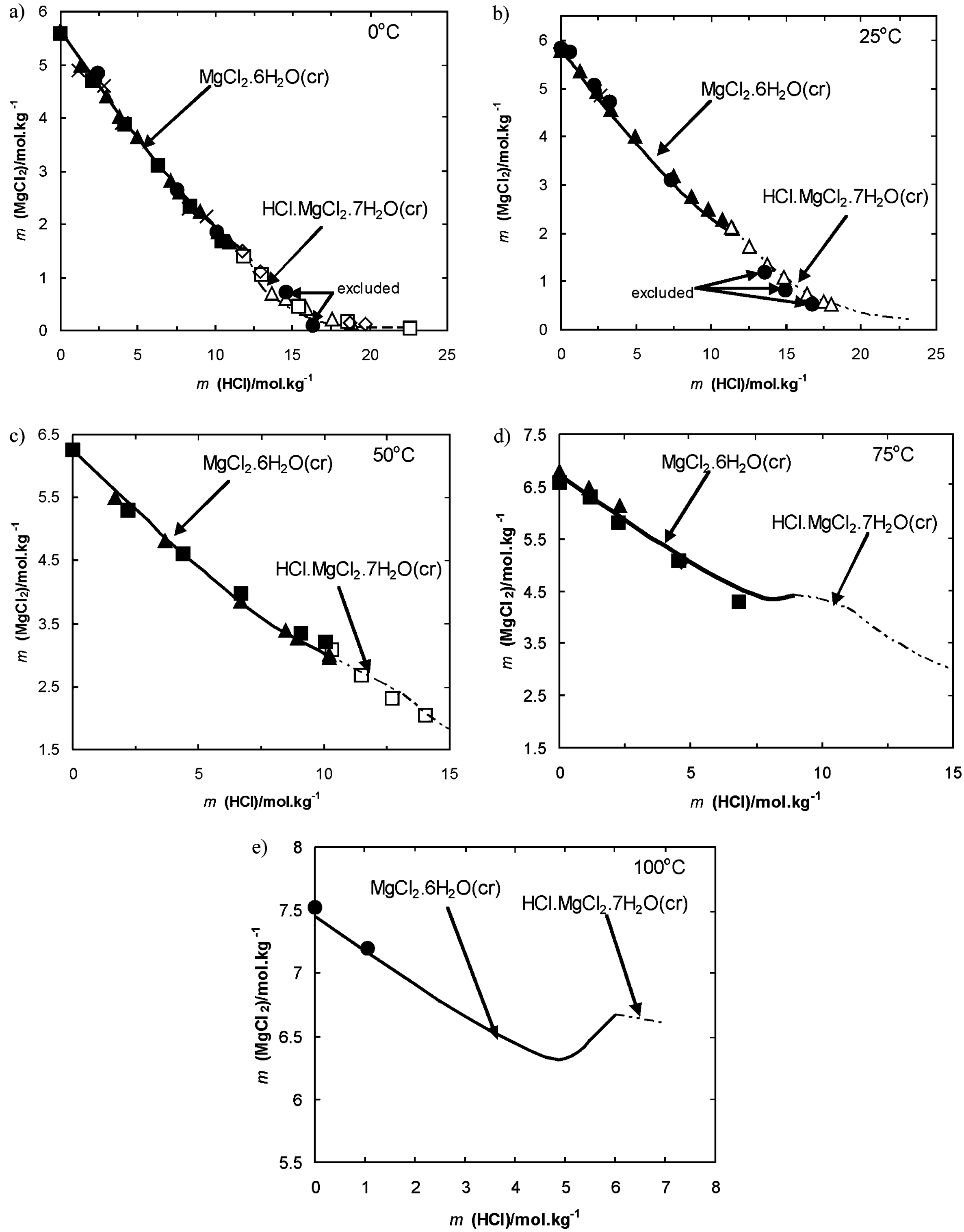

Figure 7. Calculated (solid lines, $MgCl_2 \cdot 6H_2O(cr)$ equilibrium; dashed-dotted lines, $HCl \cdot MgCl_2 \cdot 7H_2O(cr)$ equilibrium) and experimental solubility of $MgCl_2 \cdot 6H_2O(cr)$ (solid symbols) and $HCl \cdot MgCl_2 \cdot 7H_2O(cr)$ (open symbols) solid phases in the $HCl + MgCl_2 + H_2O$ system. (a) 0 °C; (b) 25 °C; (c) 50 °C; (d) 75 °C; (e) 100 °C. The ternary system experimental solubility data are from: (a) Circles, Obuhov and Lavrov;[46] squares, Dahne;[51] triangles, Voelz-Fladrich;[50] open diamonds, Ke Juan and Wen-Tschi;[49] crosses, and Engel.[45] (b) Circles, Obuhov and Lavrov;[46] triangles, Voelz-Fladrich;[50] stars, Grushvizkii and Shmidt.[48] (c) Squares, Dahne;[51] Voelz-Fladrich[50] (data at 45 °C: triangles). (d) Squares, data of Dahne[51] at 70 °C; triangles, data of Dahne[51] at 80 °C; diamonds, data of Obuhov and Mihailov[47] at 70 °C. (e) Circles, Obuhov and Lavrov.[46]

The results of DRH (bishofite) calculations are presented in Table 4. According to the equilibrium model DRH of bishofite in binary system $MgCl_2 + H_2O$ is about constant ($\approx$ 34.4 %) at low temperature. The calculated DRH value at 25 °C is in good agreement with the determinations of Rard and Miller[39] and Stokes.[37] At higher temperature, DRH ($MgCl_2 \cdot 6H_2O(cr)$) sharply decreases and at 100 °C is about 23 %. According to the $HCl + MgCl_2 + H_2O$ equilibrium model, the effect of HCl on the DRH/MDRH values of the bishofite solid phase is very strong (see Table 5). At 25 °C the relative humidity decreases from 34.4 % in saturated binary $MgCl_2 + H_2O$ solutions to MRDH = 16.1 % in the ($MgCl_2 \cdot 6H_2O(cr)$ + $HCl \cdot MgCl_2 \cdot$

Table 4. Deliquescence Relative Humidity (DRH, %) Values of Bishofite ($MgCl_2 \cdot 6H_2O(cr)$) from (0 to 100) °C[a]

T, °C	0	25	50	75	100
DRH	34.3	34.4 (33.0)[b] (32.8)[c]	32.2	28.7	23.0

[a] Values presented in the literature are given in branches. [b] From Stokes.[37] [c] From Rard and Miller.[39]

Table 5. Deliquescence Relative Humidity/Mutual Deliquescence Relative Humidity (DRH/MDRH) Values of Solid Minerals Precipitating in $HCl + MgCl_2 + H_2O$ System at 25 °C

precipitated mineral	mixed solutions molality range ($mol \cdot kg^{-1}$)	DRH−MDRH or MDRH−DRH
$MgCl_2 \cdot 6H_2O(cr)$	$m(HCl) = 0.0$ to 11.4 $m(MgCl_2) = 5.79$ to 2.01	34.4 to 16.1
$HCl \cdot MgCl_2 \cdot 7H_2O(cr)$	$m(HCl) = 11.4$ to 15.0 $m(MgCl_2) = 2.01$ to 0.84	16.1 to 9.15

$7H_2O(cr)$) invariant point. The model predicts a very low relative humidity value for hydrogen−carnallite. With increasing HCl molality from 11.4 $mol \cdot kg^{-1}$ (cocrystallization point) to 15.0 $mol \cdot kg^{-1}$, MDRH/DRH ($HCl \cdot MgCl_2 \cdot 7H_2O(cr)$) decreases from 16.1 % to 9.15 %. New chemical kinetic experiments are needed to validate these model predictions.

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Literature Cited

(1) Pitzer, K. S. Thermodynamics of electrolytes. I. Theoretical basis and general equations. *J. Phys. Chem.* **1973**, *77*, 268–277.

(2) Pitzer, K. S. *Activity Coefficients in Electrolyte Solutions*, 2nd ed.; Pitzer, K., Ed.; CRC Press: Boca Raton, 1991; pp 75−153.

(3) Harvie, C.; Moller, N.; Weare, J. The prediction of mineral solubilities in natural waters: The Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_3-CO2-H_2O system from zero to high concentration at 25°C. *Geochim. Cosmochim. Acta* **1984**, *48*, 723–751.

(4) Pabalan, R.; Pitzer, K. S. Thermodynamics of concentrated electrolyte mixtures and the prediction of mineral solubilities to high temperatures for mixtures in the system Na-K-Mg-Cl-SO_4-OH-H_2O. *Geochim. Cosmochim. Acta* **1987**, *51*, 2429–2443.

(5) Christov, C. Pitzer ion-interaction parameters for Fe(II) and Fe(III) in the quinary {$Na + K + Mg + Cl + SO_4 + H_2O$} system at $T =$ 298.15 K. *J. Chem. Thermodyn.* **2004**, *36*, 223–235.

(6) Christov, C.; Moller, N. Chemical equilibrium model of solution behaviour and solubility in the H-Na-K-OH-Cl-HSO_4-SO_4-H_2O system to high concentration and temperature. *Geochim. Cosmochim. Acta* **2004a**, *68*, 1309–1331.

(7) Christov, C.; Dickson, A.; Moller, N. Thermodynamic modeling of aqueous aluminum chemistry and solid liquid equilibria to high solution concentration and temperature. I. The acidic H-Al-Na-K-Cl-H_2O system from 0° to 100°C. *J. Solution Chem.* **2007**, *36*, 1495–1523.

(8) Christov, C. Isopiestic Determination of the osmotic coefficients of aqueous $MgCl_2 + CaCl_2$ mixed solution at (25 and 50) °C. Chemical equilibrium model of solution behavior and solubility in the $MgCl_2 + H_2O$, and $MgCl_2 + CaCl_2 + H_2O$ systems to high concentration at (25 and 50) °C. *J. Chem. Eng. Data* **2009**, *54*, 627–635.

(9) Park, J.-H.; Christov, C.; Ivanov, A.; Molina, M. On OH uptake by sea salt under humid conditions. *Geophys. Res. Lett.* **2009**, *36*, L02802(DOI: 10.1029/2009GL036160).

(10) Yang, L.; Pabalan, R.; Juckett, M. Deliquescence relative humidity measurements using an electrical conductivity method. *J. Solution Chem.* **2006**, *35*, 583–604.

(11) Kim, Y.; Seinfeld, J.; Saxena, P. Atmospheric gas-aerosol equilibrium I. Thermodynamic model. *Aerosol Sci. Technol.* **1993**, *19*, 157–181.

(12) Kim, Y.; Seinfeld, J. Atmospheric gas-aerosol equilibrium III. Thermodynamic of crustal elements Ca^{2+}, K^+ and Mg^{2+}. *Aerosol Sci. Technol.* **1995**, *22*, 93–110.

(13) Wexler, A.; Clegg, S. Atmospheric aerosol models of the systems including the ions H^+, NH_4^+, Na^+, SO_4^{2-}, NO_3^-, Cl^-, Br^- and H_2O at 298.15 K. *J. Geophys. Res.* **2002**, *107*, 4207.

(14) Amundson, N.; Caboussat, A.; He, J.; Martynenko, A.; Savarin, V.; Seinfeld, J.; Yoo, K. A new inorganic atmospheric aerosol phase equilibrium models (UNAERO). *Atmos. Chem. Phys.* **2006**, *6*, 975–992.

(15) Nenes, A.; Pandis, S.; Pilinis, C. ISOPROPIA: A new thermodynamic equilibrium model for multiphase multicomponent inorganic aerosols. *Aquat. Geochem.* **1998**, *4*, 123–152.

(16) Lin, T.; Gilbert, J.; Naggar, J.; Imblum, T. Seawater conductivity enhancement by acid injection for MHD thrusters. *Proceedings IEEE's OCEANS 91*, Honolulu, HI, 1991; Vol. 3, pp 1629−1635.

(17) Koenigsberger, E.; May, P.; Harris, B. Properties of electrolyte solutions relevant to high concentration chloride leaching. I. Mixed aqueous solutions of hydrochloric acid and magnesium chloride. *Hydrometallyrgy* **2008**, *90*, 177–191.

(18) Balarew, C.; Christov, C.; Petrenko, S.; Valyashko, V. Thermodynamics of formation of carnallite type double salts. *J. Solution Chem.* **1993**, *22*, 173–181.

(19) Christov, C.; Balarew, C.; Valyashko, V.; Petrenko, S. Investigation of the aqueous lithium and magnesium halide systems. *J. Solution Chem.* **1994**, *23*, 595–604.

(20) Christov, C. Thermodynamics of formation of double salts and solid solutions from aqueous solutions. *J. Chem. Thermodyn.* **2005**, *37*, 1036–1060.

(21) Christov, C.; Moller, N. A Chemical equilibrium model of solution behaviour and solubility in the H-Na-K-Ca-OH-Cl-HSO_4-SO_4-H_2O system to high concentration and temperature. *Geochim. Cosmochim. Acta* **2004b**, *68*, 3717–3739.

(22) Pitzer, K.; Simonson, J. Thermodynamics of multicomponent, miscible, ionic system: Theory and equations. *J. Phys. Chem.* **1986**, *90*, 3005–3009.

(23) Clegg, S.; Brimblecombe, P.; Wexler, A. Thermodynamic model of the system H^+-NH_4^+-Na^+- SO_4^{2-}-NO_3^--Cl^+-H_2O at 298.15 K. *J. Phys. Chem. A* **1998**, *102*, 2155–2171.

(24) Rard, J. A.; Archer, D. Isopiestic investigation of the osmotic and activity coefficients of aqueous NaBr and the solubility of $NaBr \cdot 2H_2O(cr)$ at 298.15K: Thermodynamic properties of the $NaBr + H_2O$ system over wide ranges of temperature and pressure. *J. Chem. Eng. Data* **1995**, *40*, 170–185.

(25) Palmer, D.; Rard, J. A.; Clegg, S. Isopiestic determination of the osmotic and activity coefficients of $Rb_2SO_4(aq)$ and $Cs_2SO_4(aq)$ at $T =$ (298.15 and 323.15) K, and representation with an extended ion-interaction (Pitzer) model. *J. Chem. Thermody.* **2002**, *34*, 63–102.

(26) Christov, C. An isopiestic study of aqueous NaBr and KBr at 50°C. Chemical Equilibrium model of solution behavior and solubility in the NaBr-H_2O, KBr-H_2O and Na-K-Br-H_2O systems to high concentration and temperature. *Geochim. Cosmochim. Acta* **2007**, *71*, 3357–3369.

(27) De Lima, M.; Pitzer, K. S. Thermodynamics of saturated electrolyte mixtures of NaCl with Na_2SO_4 and with $MgCl_2$. *J. Solution Chem.* **1983**, *12*, 187–199.

(28) Holmes, H.; Mesmer, R. Aqueous solutions of the alkaline-earth metal chlorides at elevated temperatures. Isopiestic molalities and thermodynamic properties. *J. Chem. Thermodyn.* **1996**, *28*, 1325–1358.

(29) Khoo, K.; Chan, C.-Y.; Lim, T. Activity coefficients in binary electrolyte mixture $HCl + MgCl_2 + H_2O$ at 298.15 K. *J. Solution Chem.* **1977**, *6*, 855–864.

(30) Roy, R.; Gibbons, J.; Bliss, D.; Casebolt, R.; Baker, R. Activity coefficients for ternary systems: VI. The system $HCl + MgCl_2 + H_2O$ at different temperatures; Application of Pitzer's equations. *J. Solution Chem.* **1980**, *9*, 911–930.

(31) Yahong, L.; Pengshang, S.; Shuping, X.; Shiyang, G. Prediction of the component solubilityin the ternary systems HCl-LiCl-H_2O, HCl-$MgCl_2$-H_2O and LiCl-$MgCl_2$-H_2O at 0° and 20°C using the ion-interaction model. *CALPHAD* **2000**, *24*, 295–308.

(32) Yahong, L.; Pengsheng, S.; Shuping, X.; Wu, L.; Shiyang, G. Solubility prediction of HCl-$MgCl_2$-H_2O system at 50 °C and solubility equilibrium constant for $HCl.MgCl_2 \cdot 7H_2O$ at 40°C. *CALPHAD* **2006a**, *30*, 61–64.

(33) Yahong, L.; Pengsheng, S.; Wu, L.; Shuping, X. Solubility prediction for the HCl-$MgCl_2$-H_2O system at 50 °C using the ion-interaction model. *CALPHAD* **2006b**, *30*, 393–396.

(34) Moller, N. The prediction of mineral solubilities in natural waters: A chemical equilibrium model for the Na-Ca-Cl-SO_4-H_2O system to high temperature and concentration. *Geochim. Cosmochim. Acta* **1988**, *52*, 821–837.

(35) Snipes, H.; Manly, C.; Ensot, D. Heats of dilution of aqueous electrolytes. Temperature dependence. *J. Chem. Eng. Data* **1975**, *20*, 287–291.

(36) Patll, K.; Tripathi, A.; Pathak, G.; Kattl, S. Thermodynamic properties of aqueous electrolyte solutions. 2. Vapour pressure of aqueous solutions of NaBr, NaI, KCl, KBr, KI, RbCl, CsCl, CsBr, CsI, $MgCl_2$,

$CaCl_2$, $CaBr_2$, CaI_2, $SrCl_2$, $SrBr_2$, SrI_2, BaCl2, and $BaBr_2$. *J. Chem. Eng. Data* **1991**, *36*, 225–230.

(37) Stokes, R. H. Thermodynamic Study of bivalent metal halides in aqueous solutions. 14. Concentrated solutions of magnesium chloride. *Trans. Faraday Soc.* **1945**, *41*, 642–645.

(38) Robinson, R. A.; Stokes, R. H. *Electrolyte solutions*, 2nd ed.; Butterworths: London, 1965.

(39) Rard, J. A.; Miller, D. G. Isopiestic investigation of the osmotic and activity coefficients of aqueous $MgCl_2$ solutions at 25°C. *J. Chem. Eng. Data* **1981**, *26*, 38–43.

(40) Suhotin, A. M. *Spravochnik po elektrokhimii*; Khimia: St. Petersburg, 1981.

(41) Zaizev, I.; Zozulia, A.; Aseev G. *Mashinny raschet phisicochimicheskih parametrov neorganicheskih veshetstv*; Khimia: Moscow, 1983.

(42) Zdanovskii, A.; Cheremnyh, L. *Phisicochimicheskie svoistva galurgicheskih rastvorov i solei. Chloridy natriya, kaliya i magniya*; Khimia: St. Petersburg, 1997.

(43) Linke, W. *Solubilities Inorganic and Metal-organic Compounds*, 4th ed.; Amer. Chem. Soc.: WA, 1965; Vols. 1 and 2.

(44) Balarew, C.; Tepavitcharova, S.; Rabadjieva, D.; Voigt, W. Solubility and crystallization in the system $MgCl_2$-$MgSO_4$-H_2O at 50 and 75°C. *J. Solution Chem.* **2001**, *30*, 815–823.

(45) Engel, R. *Ann. Chim. Phys.* **1888**, *13*, 384 (in Zdanovskii et al. 1973, Vol. I-2, p 910).

(46) Obuhov, A.; Lavrov, V. *J. Prikladnoi Khim.* **1931**, *4*, 996–998 (in Zdanovskii et al. 1973, Vol. I-2, p 910).

(47) Obuhov, A.; Mihailov, M. *Kalii* **1932**, *3*, 21 (in Zdanovskii et al. 1973, Vol. I-2, p 911).

(48) Grushvizkii, V.; Shmidt, N. *Bolshaya Elba, USSR* **1937**, *1*, 671–675 (in Zdanovskii et al. 1973, Vol. I-2, p 912).

(49) Ke Juan, C.; Wen-Tschi, Z. *Acta Chim. Sin.* **1965**, *31*, 190 (in Zdanovskii et al. 1973, Vol. I-2, p 914).

(50) Voelz-Fladrich, H. *Freiberger Forsch.* **1962**, *C134*, 79 (in Zdanovskii et al. 1973, Vol. I-2, p 912−913).

(51) Dahne, C. *Z. Anorg. Chem.* **1939**, *371*, 64–66 (in Zdanovskii et al. 1973, Vol. I-2, p 914).

(52) Zdanovskii A.; Soloveva, E.; Liahovskaia, E.; Shestakov, N.; Shleimovich, P.; Abutkova, L. *Experimentalnie dannie po rastvorimosti mnogokomponentnih vodno-solevih system*; Khimiya: St. Petersburg, 1973; Vols. I-1 and I-2.

(53) Seinfeld, J.; Pandis, S. *Atmospheric Chemistry and Physics: From air pollution to climate change*; John Wiley & Sons Inc.: New York, 1998.

(54) Clegg, S.; Brimblecombe, P. A generalised multicomponent thermodynamic model applied to the $(NH_4)_2SO_4$-H_2SO_4-H_2O system to high supersaturation and low relative humidity at 298.15 K. *J. Aerosol Sci.* **1995**, *26*, 19–38.

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