J. Chem. Eng. Data **2009,** *54,* 627–635

Isopiestic Determination of the Osmotic Coefficients of an 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[†]

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This paper, written in celebration of Professor Robin H. Stokes' 90th birthday anniversary, describes isopiestic measurements and the development of a thermodynamic model for the highly important $MgCl_2 + CaCl_2 + H_2O$ system at (25 and 50) °C. The isopiestic method has been used to determine the osmotic coefficients of the mixed solutions from low to high concentrations. Sodium chloride and sulfuric acid solutions have been used as isopiestic reference standards. The isopiestic results obtained have been combined with all other experimental thermodynamic quantities available in the literature (osmotic coefficients, water activities, calcium and magnesium chloride mineral's solubilties) to construct a chemical model that calculates solute and solvent activities and solid−liquid equilibria in the $MgCl_2 + H_2O$ and $MgCl_2 + CaCl_2 + H_2O$ systems. The mixed solution model created here used $CaCl_2 + H_2O$ system parametrization established in our previous study (Christov and Moller, *GCA* **2004b**, *68*, 3717). The model incorporates the concentration-dependent specific interaction equations of Pitzer for aqueous solutions (*J. Phys. Chem.* **1973**, *77*, 268). The model for the binary $MgCl_2 + H_2O$ system is validated by comparing activity coefficient predictions with those given in the literature and not used in the parametrization process. The model predictions on the effect of mixing on the deliquescence relative humidity in $MgCl_2 + CaCl_2 + H_2O$ solutions saturated with highly soluble $MgCl_2\cdot 6H_2O$(cr), $CaCl_2\cdot 6H_2O$(cr), and $2MgCl_2\cdot CaCl_2\cdot 2H_2O$ (cr) sea-salt minerals are also given.

Introduction

Computer models that predict solution behavior and solid−liquid−gas equilibria close to experimental accuracy have wide applicability. They can simulate the complex changes that occur in nature and can replicate conditions that are difficult or expensive to duplicate in the laboratory. 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 this approach could be expanded to accurately calculate solubilities in complex brines and to predict the behavior of natural fluids.

The main objective of this study is the development of a thermodynamic model for solution behavior and solid−liquid equilibria in the $MgCl_2 + CaCl_2 + H_2O$ system at (25 and 50) °C. This system is a subsystem of a complex brine system, and magnesium and calcium chloride minerals are the higher solubility minerals of the complex sea-salts. Sea-salts are the largest in terms of amount cycled annually through the atmosphere. Sea-salt aerosols are highly hygroscopic and exhibit physical changes as a function of relative humidity. Solid sea-salt particles take up water in the atmosphere and form aqueous droplets. 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. This process is of special interest in the chemistry of formation of aqueous sea-salt aerosols in the marine boundary layer. 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. Within the salt-solution model, relative humidity is related to water activity, a_w[9,10]

$$a_w = P_w / P\circ_w = RH/100 \tag{1}$$

where P_w and P°_w are the vapor pressure of the saturation solution and pure water, respectively, at given temperature. As a result, both DRH and MDRH of aqueous salt solutions depend on temperature, the salt stoichiometry, and the solution composition.

Because of very high complicity of experiments, the relative humidity data, particularly for the mixed systems, are sparse.[11] Nevertheless, different sophisticated thermodynamic equilibrium models, such as SCAPE and SCAPE2,[12,13] AIM and AIM2,[14] UNAERO,[15] and ISOPROPIA[16] have been proposed and developed to describe the deliquescence behavior of gas −solid−liquid inorganic aerosol equilibrium. All these thermodynamic models are focused on estimation of DRH and/or MDRH of the tropospheric aqueous aerosol system and therefore all include ammonium and nitrate species in combination with some seawater major ions and some sea-salt minerals. These models do not include all possible stable and metastable brine

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[†] Part of the special issue "Robin H. Stokes Festschrift".

10.1021/je8005634 CCC: $40.75

minerals (simple, double, and triple salts), and only certain equilibria are assumed to determine the deliquescence of complex sea-salts. None of the models presented in the literature include into consideration the mixing solution parameters and mineral formation in the $MgCl_2 + CaCl_2 + H_2O$ system.

At moderate-to-low RH, the highly concentrated sea-salt solutions are chemically highly nonideal, and therefore the prediction of relative humidity changes in binary and mixed solutions in equilibrium with high-soluble solids is very important. The accurate description of the deliquescence behavior of single sea-salts or their mixtures as a function of solution composition, the equilibrium minerals stoichiometry, and temperature is critical to understand and describe thermodynamics and chemistry of aqueous sea-salt equilibrium. The preliminary calculations of the author of this study show that accepting sea-salt as a simple halite (NaCl(cr)) salt, which is the main sea-salt component, is a wrong approximation in the construction of the standard temperature model for formation of aqueous sea-salt aerosols. This preliminary thermodynamic equilibria model, which used parametrization established in our previous studies,[7,17,18] predicted a DRH value of ≈ 34 % for saturated with bishofite $MgCl_2 + H_2O$ binary solution, which is much lower than for halite (DRH ≈ 75 %) and lower compared to all other binary systems within the quinary $Na + K + Mg + Cl + SO_4 + H_2O$ sea-type system. This calculation suggested that $MgCl_2 \cdot 6H_2O(cr)$ saturated solutions are the first ones, which are formed on the surface of quinary solid-sea aerosols at wetting conditions, to form reactive aqueous sea aerosols. The recent chemical kinetic studies of Molina and coworkers[19] also show that the wetting behavior of complex sea-salt toward its OH uptake follows that of $MgCl_2 \cdot 6H_2O(cr)$, its lower deliquescence component, rather that of halite, its major component. However, to extend the understanding of the deliquescence behavior of complex solid sea-salt under high relative humidity conditions, it is necessary to develop an accurate thermodynamic model, which also includes the equilibrium of high-soluble calcium chloride minerals, such as antarcticite ($CaCl_2 \cdot 6H_2O(cr)$), $CaCl_2 \cdot 2H_2O(cr)$), and tachyhydrite ($2MgCl_2 \cdot CaCl_2 \cdot 6H_2O(cr)$). In addition to bishofite, the chemical equilibrium of these minerals also can play a key role in the formation of aqueous sea-salt aerosols by decreasing the DRH value of solid sea-salt. Development of the thermodynamic temperature-variable equilibrium model for the $MgCl_2 + CaCl_2 + H_2O$ system can be a powerful predictive tool to solve the above important for atmospheric chemistry problems. Other important applications include design and assessment of nuclear and acid mine waste disposal strategies as well as production of evaporate minerals and utilization of waste solutions during treatment of natural deposits.

Methodology

Modeling Approach. In constructing the model for the $MgCl_2 + CaCl_2 + H_2O$ system at (25 and 50) °C, the solubility approach described in previous studies of the author is used. The model incorporates the concentration-dependent specific interaction equations of Pitzer[1,2] for aqueous solutions. Since the Pitzer 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 parameter evaluation.

Pitzer's equations are described and widely discussed in the literature.[4,7,8,20] Here, we give only the expression for the activity coefficient of the interaction of cation (M) with other solutes, $\gamma_{(M^+)}$

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

Equation 2 is symmetric for anions. The subscripts c and a in eq 2 refer to cations and anions; m is their molality; B and Φ represent measurable combinations of the second virial coefficients; and C and Ψ represent measurable combinations of third virial coefficients. B and C are parametrized from single electrolyte data, and Φ and Ψ are parametrized from mixed solution data.

To extend the application of the model for predictions of solution properties at very high concentrations, Pitzer and Simonson[21] introduced in their approach mole fraction concentrations. Their approach has been used successfully for modeling $CaCl_2(aq)$[22] and aerosol mixtures.[23] In the parametrization presented here, we used a standard molality-based ion interaction model. To fit the binary solution properties with 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 used the standard Pitzer approach with one C^φ parameter. In our previous studies[7,18,20] we show that the above standard Pitzer approach gives excellent model reliability to very high concentration (for example, to 64 $mol \cdot kg^{-1}$ in the $NaOH + H_2O$ system[7]). Note that in the model presented we accepted that the electrolytes are completely dissociated and there are only independent ions in the solution; i.e., the equilibrium constant of complexes (such as $MgCl_2°(aq)$) are not included in the model. Therefore, at constant temperature and pressure, the solution model parameters to be evaluated are $\beta^{(0)}$, $\beta^{(1)}$, and C^φ for each cation−anion pair; θ for each unlike cation−cation or anion−anion pair; Ψ for each triple-ion interaction where the ions are not all of the same sign.

The brine system models of Harvie et al.[3,4] are the only models which include interaction parameters and solid−liquid equilibria in the mixed $MgCl_2 + CaCl_2 + H_2O$ system at 25 °C. However, this system model is not well defined. In construction of their mixing model, the authors used pure electrolyte parameters for $MgCl_2 + H_2O$ and $CaCl_2 + H_2O$ from Pitzer and Mayorga,[26] which are valid up to much lower molalities than the molality of saturated solutions (see Table 2). Moreover, in constructing the 25 °C model for the corresponding sulfate system with the same cations ($MgSO_4 + CaSO_4 + H_2O$), the authors used different values of the ternary mixing Ψ (Mg, Ca, SO_4) parameter: $\Psi(Mg, Ca, SO_4) = 0.05$ in the earlier study[3] and $\Psi(Mg, Ca, SO_4) = 0.024$ in the next one.[4] Therefore, reparameterization of the mixed $MgCl_2 + CaCl_2 + H_2O$ system at 25 °C is necessary. The temperature-variable models for this ternary system are not available in the literature. The model of Pabalan and Pitzer[5] does not include calcium 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^φ(Mg,Cl). To determine the chemical potential of magnesium chloride solids, Pabalan and Pitzer[5] used the heat capacity values determined

Table 1. Isopiestic Molalities *m* of Aqueous $CaCl_2$ and $MgCl_2$, Activity of Water a_w, and Osmotic Coefficients φ(exp) in Mixed $MgCl_2 + CaCl_2 + H_2O$ Solutions and the Difference between Experimental and Model Calculated Osmotic Coefficients [$\Delta = \varphi(\text{exp}) - \varphi(\text{cal})$] at 25 °C and 50 °C[a]

$m(MgCl_2)$ ($mol \cdot kg^{-1}$)	$m(CaCl_2)$ ($mol \cdot kg^{-1}$)	φ(exp)	$\Delta = \varphi(\text{exp}) - \varphi(\text{cal})$
	25 °C		
	$a_w = 0.9275$ (NaCl reference standard)		
1.1772	0.0	1.183	0.0019
1.08	0.1189	1.1614	−0.0164
0.9804	0.2403	1.1406	−0.0351
0.89	0.3486	1.1241	−0.0492
0.762	0.5089	1.0956	−0.0777
	$a_w = 0.917$ (NaCl reference standard)		
0.6463	0.6499	1.2364	0.0638
0.530	0.8404	1.1694	−0.0186
0.4892	0.8596	1.1061	−0.0723
0.2739	1.0133	1.1553	0.0099
0.1399	1.1741	1.1334	−0.0131
0.0	1.3535	1.1025	−0.0498
	$a_w = 0.885$ (NaCl reference standard)		
1.6373	0.0	1.4704	0.0914
1.4104	0.1638	1.436	0.1003
1.2905	0.3414	1.385	0.0519
1.1586	0.5023	1.361	0.0302
1.0291	0.6665	1.3332	0.0016
0.8721	0.8904	1.2826	−0.0594
	$a_w = 0.871$ (NaCl reference standard)		
0.5425	1.4235	1.2998	−0.0917
0.5569	1.3071	1.371	0.0148
0.3805	1.5492	1.3243	−0.0455
0.3044	1.7814	1.2865	−0.0952
0.0	2.0376	1.2537	−0.0992
	$a_w = 0.7945$ (NaCl reference standard)		
2.4224	0.0	1.7572	0.0370
2.2113	0.2447	1.733	0.0265
1.9956	0.5013	1.7047	0.0078
1.783	0.7592	1.6744	−0.0171
1.556	1.0362	1.6421	−0.0467
1.3181	1.3267	1.6094	−0.0795
	$a_w = 0.7633$ (H_2SO_4 reference standard)		
1.073	1.6398	1.8421	0.1050
0.8145	1.9557	1.8033	0.0994
0.5684	2.2632	1.7648	0.0487
0.2812	2.4999	1.7345	0.0482
0.0	2.8538	1.6917	−0.0169
	$a_w = 0.6645$ (H_2SO_4 reference standard)		
3.3225	0.0	2.2762	0.0969
3.0588	0.3357	2.2279	0.0900
2.7864	0.6843	2.179	0.0484
2.4828	1.0842	2.1202	−0.0111
2.1714	1.447	2.0914	−0.0276
1.860	1.8517	2.0375	−0.0915
	$a_w = 0.6035$ (H_2SO_4 reference standard)		
0.4008	3.7015	2.2776	0.0529
0.0	4.2393	2.204	−0.0800
	$a_w = 0.5028$ (H_2SO_4 reference standard)		
4.5271	0.0	2.8102	0.0598
4.0869	0.5666	2.734	0.0110
3.7365	1.0045	2.6834	−0.0207
3.3767	1.4557	2.6327	−0.0594
2.9655	1.9773	2.5739	−0.1152
2.5136	2.3332	2.5208	−0.0921
	$a_w = 0.4075$ (H_2SO_4 reference standard)		
0.5595	4.9945	2.9906	0.1087
0.0	5.667	2.9307	0.0213
	50 °C		
	$a_w = 0.925$ (NaCl reference standard)		
1.2396	0.0	1.1637	0.0050
1.1199	0.1227	1.1609	0.0110
1.0096	0.2453	1.1495	0.0044
0.8238	0.4729	1.1125	−0.0317
0.7754	0.5109	1.1215	−0.0167
0.6513	0.6546	1.1046	−0.0319
0.5327	0.8297	1.0588	−0.0879
	$a_w = 0.918$ (NaCl reference standard)		
0.4165	0.9827	1.131	−0.0212
0.2732	1.0763	1.1725	0.0413
0.1313	1.2507	1.145	0.0091
0.0	1.4296	1.1070	−0.0397
	$a_w = 0.8940$ (NaCl reference standard)		
1.608	0.0	1.289	−0.0091
1.4378	0.209	1.2589	−0.0353
1.3313	0.3468	1.2355	−0.0592
1.1806	0.5076	1.2281	−0.0578
1.0257	0.6843	1.2124	−0.0692
0.8713	0.8803	1.1836	−0.0912
0.7103	1.0741	1.1619	−0.1042
	$a_w = 0.878$ (NaCl reference standard)		
0.5517	1.2749	1.3181	0.0260
0.3725	1.4869	1.2947	−0.0009
0.1914	1.7251	1.2562	−0.0527
0.0	1.955	1.2314	−0.0864

[a] The reported molalities are the average of duplicate determinations.

by calorimetric measurements. In this study, the model for the $MgCl_2 + H_2O$ binary system was reparameterized at (25 and 50) °C. The pure electrolyte parameters of Mg−Cl interactions are evaluated using binary solution osmotic coefficient data up to saturation of solutions. The chemical potential of bishofite is determined directly from solubility data in the $MgCl_2 + H_2O$ binary system. Our comprehensive acid−base (0 to 250) °C models[7,20] do not include magnesium interactions and minerals.

Table 2. Values of the $MgCl_2 + H_2O$ and $CaCl_2 + H_2O$ Pure Electrolyte and $MgCl_2 + CaCl_2 + H_2O$ Mixing Parameters Determined in This Study and Those Presented in the Literature at (25 and 50) °C, Where m^{max} Is the Maximum Molality (in $mol \cdot kg^{-1}$) of the Experimental Data Used in Magnesium and Calcium Chloride Model Parameterization and/or Validation and A^{φ} is the Debye−Huckel Constant

	25 °C				50 °C	
parameters	this study ($m^{max} = m(sat)$)	Pitzer and Mayorga;[26] Harvie et al.[4]	Kim and Frederick[40]	Balarew et al.;[17] Christov[18]	this study ($m^{max} = m(sat)$)	Pabalan and Pitzer[5]
$A^{\varphi a}$	0.391475				0.41033	
$\beta^{(0)}(Ca,Cl)^a$	0.30532	$0.3159(m^{max} = 2.5)$	$0.32579(m^{max} = 6)$		0.30698	
$\beta^{(1)}(Ca,Cl)^a$	1.70813	$1.614(m^{max} = 2.5)$	$1.38412(m^{max} = 6)$		1.81650	
$C^{\varphi}(Ca,Cl)^a$	0.00234	$-0.00034(m^{max} = 2.5)$	$-0.00174(m^{max} = 6)$		−0.001518	
$\beta^{(0)}(Mg,Cl)$	0.36193	$0.35235(m^{max} = 4.5)$	$0.35573(m^{max} = 5.75)$	$0.3511(m^{max} = 5.76)$	0.34448	0.33703^b
$\beta^{(1)}(Mg,Cl)$	1.58114	$1.6815(m^{max} = 4.5)$	$1.61738(m^{max} = 5.75)$	$1.6512(m^{max} = 5.76)$	1.77455	1.79758^b
$C^{\varphi}(Mg,Cl)$	0.00238	$0.00519(m^{max} = 4.5)$	$0.00474(m^{max} = 5.75)$	$0.0065(m^{max} = 5.76)$	0.001695	0.00403^b
θ (Mg,Ca)	0.007				0.007	
Ψ(Mg,CaCl)	−0.0166	-0.012^c			−0.01906	

[a] Parameters calculated from temperature dependence equations (covering the (0 to 250) °C range) presented in Christov and Moller[20] and used in this study. [b] Parameters calculated from temperature dependence equations given by Pabalan and Pitzer.[5] [c] Harvie et al.[4]

However, in our calcium acid−base model, we present a new model valid for temperatures from (0 to 250) °C for the $CaCl_2 + H_2O$ solution behavior and calcium chloride solid ($CaCl_2 \cdot nH_2O$ (n = 2, 4, 6)) solubilities. The model is in excellent agreement with all recent activity data and with solubility data in binary and multicomponent systems. In the development of the mixed solution model, in this study, a $CaCl_2 + H_2O$ system parametrization model[20] was used, adapted to (25 and 50) °C.

Experimental Approach and Results. New isopiestic measurements have been carried out in the $MgCl_2 + CaCl_2 + H_2O$ ternary system at (25 and 50) °C. The osmotic coefficients in this ternary sytem, obtained here, are critical for developing a comprehensive ion-interaction model which accurately describes mixing ion interactions in magnesium−calcium solutions. Low and high molality osmotic/activity coefficient data, determined on the basis of isopiestic measurements, are the most reliable thermodynamic data, which can be used in parametrization of equilibrium models which can accurately predict not only solution behaviors but also solid−liquid equilibria in binary and complex systems.[28]

The osmotic coefficients of the $MgCl_2 + CaCl_2 + H_2O$ solutions were determined by the isopiestic method described in our previous studies.[28−31] Sodium chloride and sulfuric acid solutions were used as isopiestic reference standards. Stock aqueous solutions were prepared from solid samples and deionized water. Merck (A.R.) solid sodium chloride and sulfuric acid were used. The solid magnesium and calcium chloride samples were from Aldrich (99.99 %). The solids were used without further purification. To remove the residual moisture in the solids, the salts were dried slowly (for several hours) in air at the 160 °C temperature. The solutions were prepared by the mass method. The salts were weighed with an accuracy of $\pm 1 \cdot 10^{-5}$ g giving, after the addition of 3 mL of water, a solution of the desired concentration. The samples were placed in a copper low-pressure desiccator which, after evacuation, was placed in a thermostat whose temperature was maintained at (25 ± 0.01) °C and (50 ± 0.01) °C. After attaining equilibrium, the samples were weighed again, and the concentrations of the isopiestic solutions obtained were calculated.

Table 1 shows the isopiestic equilibrium molalities of $MgCl_2(aq)$ and $CaCl_2(aq)$, with NaCl(aq) and $H_2SO_4(aq)$ reference solutions. Reported molalities are the average of duplicate determinations. We found that an equilibrium period of 45 days at 25 °C and 20 days at 50 °C yielded results with a good agreement of molalities for duplicate samples of the same electrolyte. This relatively long time needed to obtain equilibrium can be attributed to the fact that we have not shaken the desiccator with solutions investigated. We weighed the clean and dry copper cups before and after experiments. The initial and final weights of the cups were not changed. This fact brings us to a conclusion that corrosion was not a problem in our isopiestic experiments. The molalities in Table 1 are accurate to within 0.2 % or better. The osmotic coefficients φ of mixed $MgCl_2 + CaCl_2 + H_2O$ solutions were calculated from the equation

$$\varphi = -55.51 \ln a_w / \{y(MgCl_2) \cdot m(MgCl_2) + y(CaCl_2) \cdot m(CaCl_2)\} \quad (3)$$

where a_w is the activity of water; m is the molality of magnesium and calcium chloride in isopiestic equilibrium with reference solution; and y is the stoichiometric ionization number of $MgCl_2$ and $CaCl_2$ (y = 3 for both). Activities of water a_w for isopiestic standards NaCl(aq) and $H_2SO_4(aq)$ were calculated from our temperature-variable acid−base model[7,20] adapted to (25 and 50) °C. Table 1 contains the derived values of a_w and ϕ for mixed $MgCl_2 + CaCl_2 + H_2O$ solutions.

Model Parametrization and Results

In constructing the model of the $MgCl_2 + CaCl_2 + H_2O$ system at (25 and 50) °C, the Debye−Huckel constants, A^{φ} (see Table 2), at (25 and 50) °C are calculated from the temperature function given in Moller.[32] See also the discussion in our previous study[7] for A^{φ} parametrization and validation. Pure electrolyte parameters of Ca−Cl interactions (Table 2) and chemical potentials of $CaCl_2 \cdot nH_2O$ (n = 2, 6) (Table 4) at (25 and 50) °C are calculated from our temperature functions given in our calcium acid−base model.[20] Evaluations of temperature functions for 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 2); the mixed solution model parameters θ(Mg,Ca) and Ψ(Mg,Ca,Cl) for ion interactions in $MgCl_2 + CaCl_2 + H_2O$ ternary solutions (see Table 2); and the standard chemical potentials of the bishofite $MgCl_2 \cdot 6H_2O(cr)$ and tachyhydrite $2MgCl_2 \cdot CaCl_2 \cdot 12H_2O(cr)$ solid phases (see Table 4) contained within the $MgCl_2 + H_2O$ binary and $MgCl_2 + CaCl_2 + H_2O$ ternary systems at (25 and 50) °C. Reference osmotic coefficient data for $MgCl_2 + H_2O$ binary and those obtained here for mixing solutions are used to evaluate solution parameters for low and moderate chloride concentration. Solubility data in binary and mixing solutions are also used to broaden the concentration range of parametrization. Note that following the

Table 3. 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 Saturation *m*(sat) at (25 and 50) °C

		activity coefficient $\gamma_\pm$ ($MgCl_2$)						
calculated values of:	$m(MgCl_2)/(mol \cdot kg^{-1})$	0.1	0.25	0.5	1.0	2.0	4.0	sat'd at 25 °C; 6.0 at 50 °C
	t/(°C)							
this study[a]	25	0.5242	0.474	0.474	0.5668	1.157	5.2524	32.603
calcd[b]		0.528 to 0.532		0.48 to 0.484	0.569 to 0.574	1.051 to 1.059	5.53 to 5.66	32.2
calcd[c]		0.5241		0.4741	0.5646	1.046	5.648	32.68
this study[a]	50	0.51306	0.456	0.4475	0.5153	0.8898	3.8838	20.825
calcd[d]		0.5052		0.4423	0.5110	0.8875	3.9200	

[a] Predictions of the model presented here (Table 2). [b] Predictions of the models of Stokes[33] and Robinson and Stokes.[34] [c] Predictions of the model of Rard and Miller.[35] [d] Predictions of the model of Holmes and Mesmer.[42]

Table 4. Calculated Values of the Logarithm of the Thermodynamic Solubility Product (ln K^o_{sp}) and the Standard Molar Gibbs Free Energy ($\Delta_f G^o_m$) of Formation of $CaCl_2 \cdot 6H_2O$(cr), $CaCl_2 \cdot 2H_2O$(cr), $MgCl_2 \cdot 6H_2O$(cr), and $2MgCl_2 \cdot CaCl_2 \cdot 12H_2O$(cr), at 25 °C and 50 °C, Where *m*(sat) Is the Molality of the Saturated Binary Solutions

	25 °C						50 °C			
	$m(sat)/(mol \cdot kg^{-1})$		ln $K°_{sp}$		$\Delta_f G°_m/(kJ \cdot mol^{-1})$		$m(sat)/(mol \cdot kg^{-1})$		ln $K°_{sp}$	
salt composition	cal	exp	cal	ref data	cal	ref data	cal	exp	cal	ref data
$CaCl_2 \cdot 6H_2O$(cr)	7.436	7.38[a]	9.751[b]	9.544[c]	−2214.64[b]	−2215.19[c]				
$CaCl_2 \cdot 2H_2O$(cr)			22.883[b]		−1233.57[b]		11.90[b]	11.92[a]	20.752[b]	
$MgCl_2 \cdot 6H_2O$(cr)	5.79	5.80[a]	10.114	10.26[c] 10.39 to 10.60[d]	−2114.96[e]	−2114.68[c] −2113.75[d]	6.26	6.27[a]	9.714	9.86[f]
$2MgCl_2 \cdot CaCl_2 \cdot 12H_2O$(cr)			39.25	40.02[c]	−4998.80[e]	−4997.05[c]			35.332	

[a] From Linke[39] and Zdanovskii et al.[51] [b] Parameters calculated from temperature dependence equations (covering the (0 to 250) °C range) presented in Christov and Moller[20] and used in this study. [c] Harvie et al.[4] [d] From Christov.[18] [e] Calculated using standard chemical potentials for ions in solutions from Wagman et al.[53] [f] Balarew et al.[41]

approach in previous studies of the author,[6,18] to avoid an 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 $MgCl_2 + CaCl_2 + H_2O$ system. Activity coefficient values, presented in the literature and not used in the parametrization process, are used here to validate the solution model (see Table 3).

Evaluation of Parameters in the $MgCl_2 + H_2O$ System. The $MgCl_2 + H_2O$ binary solution interaction parameters are evaluated from osmotic coefficient data in this sytem. To better reflect the high concentration behavior of the system, we include, in parametrization solubility, measurements of bishofite in the binary system. Osmotic coefficient 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) at 25 °C and at 50 °C. The 25 °C osmotic coefficient data sets which are included in parametrization are (*n* is the number of experimental data points): (1) Stokes data[33] up to saturation ($m(sat) = 5.84\ mol \cdot kg^{-1}$; $n = 19$); (2) the recommendations of Robinson and Stokes[34] up to $m = 5\ mol \cdot kg^{-1}$ ($n = 21$); the data of Rard and Miler[35] up to $m = 5.81\ mol \cdot kg^{-1}$ (saturated solution; $n = 37$). At 50 °C, the included osmotic $MgCl_2 + H_2O$ binary data are from: (1) Patll et al.[36] up to $m = 4.80\ mol \cdot kg^{-1}$ ($n = 8$), and (2) Snipes et al.[37] up to $m = 2.0\ mol \cdot kg^{-1}$ ($n = 15$). For a broad concentration range of pure electrolyte parametrization, the high molality smoothed water activity values, given in ref 38, are also included (set (3): $m(max) = 5.857\ mol \cdot kg^{-1}$; $n = 12$). There is a very good agreement between all sets of osmotic coefficient data at (25 and 50) °C. Note that in our final parametrization the osmotic 25 °C data of Stokes[33] and of Rard and Miler[35] in the supersaturated solution ($5.92\ mol \cdot kg^{-1} < m(MgCl_2) < 6.0\ mol \cdot kg^{-1}$) are not considered.

The bishofite solubility data in the $MgCl_2 + H_2O$ system at (25 and 50) °C are used to evaluate the chemical potential of solid mineral. Solubility data, which are in very good agreement, are taken from Linke.[39] According to the data, $MgCl_2 \cdot 6H_2O$(cr) is the only stable phase in this binary at (25 and 50) °C. The model's $\beta^{(0)}$(Mg,Cl), $\beta^{(1)}$(Mg,Cl), and C^{φ}(Mg,Cl) parametrization for the binary $MgCl_2 + H_2O$ system (Table 2) gives excellent agreement with the data for unsaturated binary solutions. The summary sigma values (σ) for the fit of the osmotic data (sets 1 to 3) are 0.043 and 0.032 at 25 °C and 50 °C, respectively. For definition of sigma, see Christov and Moller.[20] The $\beta^{(0)}$(Mg,Cl) and $\beta^{(1)}$(Mg,Cl) binary [(25 and 50) °C] parameter values obtained in this study are very close to those given in the literature at both temperatures[4,5,17,18,40] (see Table 2). The relatively high difference of C^{φ}(Mg,Cl) values can be explained by a different concentration range of experimental data used in parametrization. The pure electrolyte Mg−Cl parameters evaluated here are valid up to saturated binary solutions. The constructed solid−liquid bishofite equilibrium model gives the (25 and 50) °C thermodynamic solubility product (as ln $K°_{sp}$) and 25 °C standard Gibbs energy of formation ($\Delta_f G°_m$) values, which are also in good agreement with the Pitzer calculations of other authors[4,18,41] (Table 4). The main reason for the small ln $K°_{sp}$ differences is the differences in *m*(sat) values used in calculations.

The solution model predicts mean activity coefficients ($\gamma_\pm$) of $MgCl_2$ which are in very good agreement with recommended values of Stokes,[33] Robinson and Stokes,[34] and Rard and Miller[35] at 25 °C (up to saturation), and of Holmes and Mesmer[42] at 50 °C (to $6\ mol \cdot kg^{-1}$ $MgCl_2$). The comparison is given in Table 3. According to all models, the magnesium chloride mean activity coefficient sharply decreases in temperature ranging from (25 to 50) °C and at high molality ($> 2\ mol \cdot kg^{-1}$). Note that recommended magnesium chloride mean activity coefficients values, available in the literature, are not used in the parametrization of $MgCl_2 + H_2O$ model. Therefore, these data are used here to validate the solution model predictions.

Evaluation of Parameters in the $MgCl_2 + CaCl_2 + H_2O$ System. The osmotic coefficient data, obtained in this study and given in Table 1, and the solubility data in this ternary system are used to evaluate θ(Mg,Ca) and Ψ(Mg,Ca,Cl) mixing parameters and the standard chemical potential of the $2MgCl_2 \cdot CaCl_2 \cdot 12H_2O$(cr) double salt, which precipitates from saturated ternary solutions. With only one exception (25 °C data of Shevchuk and Vaisfeld[47]), the solubility data in the $MgCl_2 + CaCl_2 + H_2O$ system at (25 and 50) °C, available in the literature, are in excellent agreement. Reported phase diagrams at 25 °C of Van't Hoff,[43] Lee and Egerton,[44] Bury and Davies,[45] and Kurnakov and Nikolaev[46] consist of fields of equilibrium crystallization of $MgCl_2 \cdot 6H_2O$(cr), $CaCl_2 \cdot 6H_2O$(cr), and $2MgCl_2 \cdot CaCl_2 \cdot 12H_2O$(cr). In addition to these solids, Shevchuk and Vaisfeld[47] reported also precipitation of $CaCl_2 \cdot 4H_2O$(cr) from saturated solutions at the same temperature. According to all solubility data found in the literature (Smith and Prutton,[48] Assarsson,[49] and Majima et al.[50]), the type of phase diagrams of the $MgCl_2 + CaCl_2 + H_2O$ system at 50 °C is very similar to those at 25 °C: at 50 °C, $CaCl_2 \cdot 2H_2O$(cr) is a stable phase, instead of $CaCl_2 \cdot 6H_2O$(cr). All these solubility data are summarized in Zdanovskii et al.[51]

In the activity and solubility data correlations, the evaluations of the binary parameters for aqueous $MgCl_2$ and of the $MgCl_2 \cdot 6H_2O$(s) standard chemical potential established above are used. In this parametrization, the Ca−Cl pure electrolyte parameters and standard chemical potentials of $CaCl_2 \cdot 6H_2O$(s) and $CaCl_2 \cdot 2H_2O$(s) are taken from our previous study (Tables 2 and 4). The resulting θ(Mg,Ca) and Ψ(Mg,Ca,Cl) and ln $K^{\circ}_{sp}(2MgCl_2 \cdot CaCl_2 \cdot 12H_2O(cr))$ model is presented in Tables 2 and 4. It was found that variation with temperature of the θ(Mg,Ca) parameter does not improve the data fit (Table 2). Therefore, a constant value of 0.007 is accepted in the model. The same value is also accepted in the 25 °C model of Harvie et al.[4] However, the present 25 °C mixing model uses a lower Ψ(Mg,Ca,Cl) value (−0.0166) than the model presented in ref 4 (−0.012; Table 2). Note that the present 25 °C mixing model was parametrized using activity and solubility data in mixed solutions and uses different Mg−Cl binary parameters, which are determined from the osmotic data at much higher concentration (up to saturation). The mixing $MgCl_2 + CaCl_2 + H_2O$ model of Harvie et al.[4] has been parametrized using only solubility data and uses Mg−Cl pure electrolyte parameters, which are valid up to 4.5 $mol \cdot kg^{-1}$. However, at 25 °C, both models calculate very consistent values for the thermodynamic solubility product of the $2MgCl_2 \cdot CaCl_2 \cdot 12H_2O$(cr) double salt. The model presented here gives very good agreement with the osmotic coefficient data obtained in this study. The sigma values of the fit of the data at (25 and 50) °C are 0.069 and 0.053, respectively. The last column in Table 1 gives the difference between experimental and model calculated osmotic coefficients [$\Delta = \varphi(\text{exp}) - \varphi(\text{cal})$]. In Figure 1, we compare the calculated (25 °C, solid line; 50 °C, dashed-dotted line) and experimental (from Table 1; symbols: open squares, 25 °C; stars, 50 °C) osmotic coefficients (φ) in mixed $MgCl_2 + CaCl_2 + H_2O$ solutions with equal magnesium and calcium chloride molality $\{m(MgCl_2)/mol \cdot kg^{-1} = m(CaCl_2)/mol \cdot kg^{-1}\}$ against total molality (m^{total}) and up to 8 $mol \cdot kg^{-1}$. According to the data and the model predictions, the mixed solution osmotic coefficients very smoothly decrease with temperature. The mixed solution model is also in excellent agreement with magnesium and calcium chloride solid solubility data at (25 and 50) °C in the ternary $MgCl_2 + CaCl_2 + H_2O$ system. Figures 2a,b compare the model predictions and the experimental solubility isotherms. According to the model, at 25 °C the solubility isotherm consists of three branches corresponding to the crystallization of $MgCl_2 \cdot 6H_2O$(cr), $CaCl_2 \cdot 6H_2O$(cr), and $2MgCl_2 \cdot CaCl_2 \cdot 12H_2O$(cr). Therefore, the data points of Shevchuk and Vaisfeld[47] on $CaCl_2 \cdot 4H_2O$(cr) precipitation (crosses on Figure 2a) are estimated as not correct and excluded in parametrization. The good agreement between the mixing model predictions and experimental osmotic data obtained in this study and solubility data given in the literature shows the consistency of both types of data.

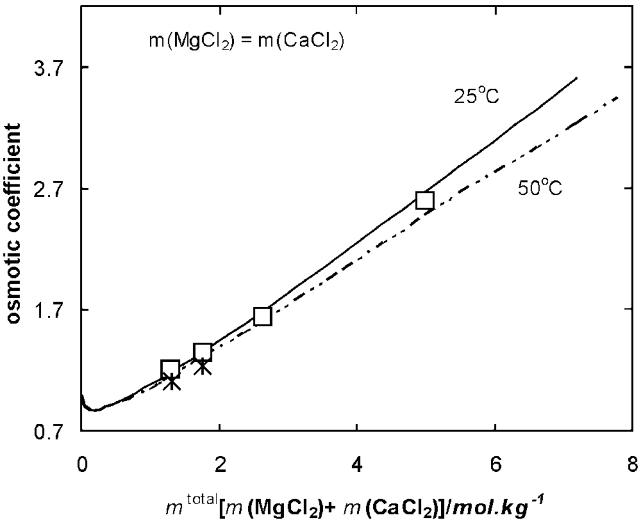

Figure 1. Calculated (25 °C, solid line; 50 °C, dashed-dotted line) and experimental (symbols: open squares, 25 °C; stars, 50 °C) osmotic coefficients (φ) in mixed $MgCl_2 + CaCl_2 + H_2O$ solutions with equal components molality [$m(MgCl_2) = m(CaCl_2)$] against total molality ($m^{\text{total}}/mol \cdot kg^{-1}$). Experimental data are from this study (Table 1).

Applications and Conclusions

The equilibrium model presented here has also been used to calculate deliquescence relative humidity (DRH) of pure minerals in their saturated binary solutions, as well as mutual deliquescence relative humidity (MDRH) of mixed $MgCl_2 + CaCl_2 + H_2O$ solutions in equilibrium with simple salt minerals and their mixtures. The results are summarized in Table 5. According to the equilibrium model, MRDH of mixed $MgCl_2 + CaCl_2 + H_2O$ solutions in equilibrium with antarcticite decreases with increasing the concentration of the $MgCl_2$ (DRH = 22.4 % in binary $CaCl_2-H_2O$ solutions; MRDH = 16.5 % in ($CaCl_2 \cdot 6H_2O$(cr) + $2MgCl_2 \cdot CaCl_2 \cdot 12H_2O$(cr)) invariant point at $m(MgCl_2) = 1.95\ mol \cdot kg^{-1}$. The effect of mixing on the DRH/MDRH values of $MgCl_2 + CaCl_2 + H_2O$ solutions, saturated with bischofite, is stronger. Relative humidity decreases from 34.4 % in binary $MgCl_2 + H_2O$ to MRDH = 19.1 % in ($MgCl_2 \cdot 6H_2O$(cr) + $2MgCl_2 \cdot CaCl_2 \cdot 12H_2O$(cr)) invariant point at $m(CaCl_2) = 4.6\ mol \cdot kg^{-1}$ (see Table 5). According to the model, the saturated $2MgCl_2 \cdot CaCl_2 \cdot 12H_2O$(cr) solutions are formed at RH values from 16.4 % to 19.1 %. On Figure 3, we present the model predictions on the effect of mixing on the deliquescence relative humidity of bishofite, tachyhydrate, and antarcticite against mole fraction (x) of calcium chloride over the full composition range ($0 < x(CaCl_2) < 1$).

According to Lin et al.,[52] the sea-salt aerosols are comprised of its five major components, that is, NaCl (68 %), $MgCl_2$ (14 %), Na_2SO_4 (11 %), $CaCl_2$ (4 %), and KCl (2 %). The percentages represent the mass fraction of each component in a sea-salt aerosol. Preliminary calculations,

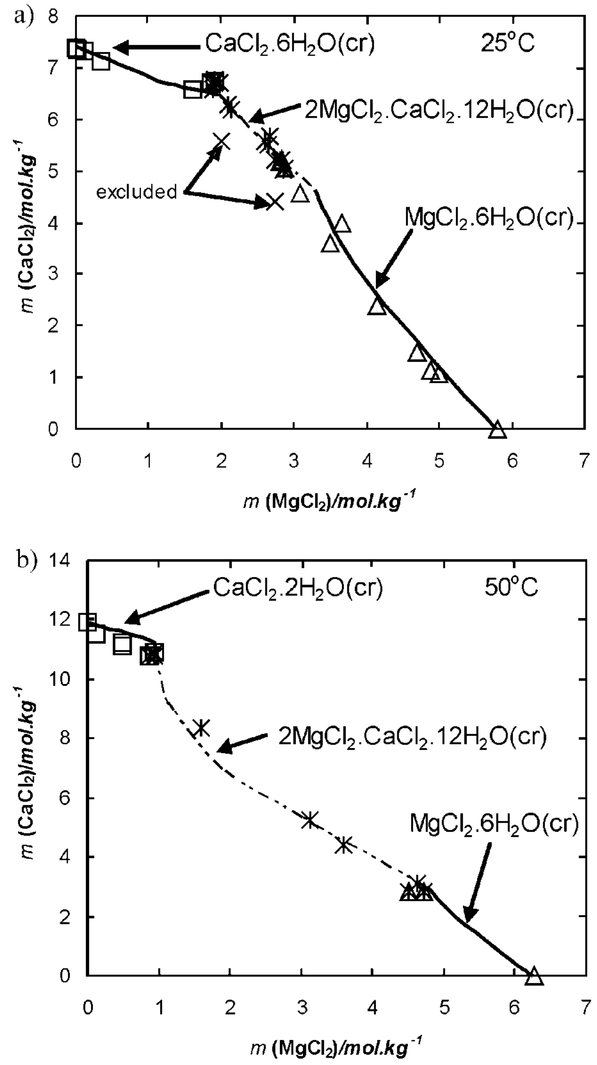

Figure 2. Calculated (solid and dashed-dotted lines) and experimental solubility of $CaCl_2\cdot 6H_2O(cr)$ (open squares at 25 °C), $CaCl_2\cdot 2H_2O(cr)$ (open squares at 50 °C), $MgCl_2\cdot 6H_2O(cr)$ (open triangles at (25 and 50) °C), and $2MgCl_2\cdot CaCl_2\cdot 12H_2O(cr)$ (stars at (25 and 50) °C) solid phases in the $MgCl_2 + CaCl_2 + H_2O$ system. (a) 25 °C; (b) 50 °C. The ternary system experimental solubility data are from at 25 °C: Van't Hoff,[43] Lee and Egerton,[44] Bury and Davies,[45] Kurnakov and Nikolaev,[46] and Shevchuk and Vaisfeld.[47] At 50 °C: Smith and Prutton,[48] Assarsson,[49] and Majima et al.[50] The cross symbols on Figure 2a (from Shevchuk and Vaisfeld[47]) corresponding to the crystallization of $CaCl_2\cdot 4H_2O(cr)$ at 25 °C are excluded in model parametrization.

Table 5. Deliquescence Relative Humidity/Mutual Deliquescence Relative Humidity (DRH/MDRH) Values of Solid Minerals in $MgCl_2 + CaCl_2 + H_2O$ System at 25 °C

precipitated mineral	mixed solutions molality range (mol·kg^{-1})	DRH−MDRH or MRDH−MRDH %
$CaCl_2\cdot 6H_2O(cr)$	$m(CaCl_2) = 7.436$ to 6.49; $m(MgCl_2) = 0.0$ to 1.95	22.4 to 16.5
$MgCl_2\cdot 6H_2O(cr)$	$m(CaCl_2) = 0.0$ to 4.63; $m(MgCl_2) = 5.79$ to 3.29	34.4 to 19.1
$2MgCl_2\cdot CaCl_2\cdot 12H_2O(cr)$	$m(CaCl_2) = 6.49$ to 4.63; $m(MgCl_2) = 1.95$ to 3.29	19.1 to 16.4

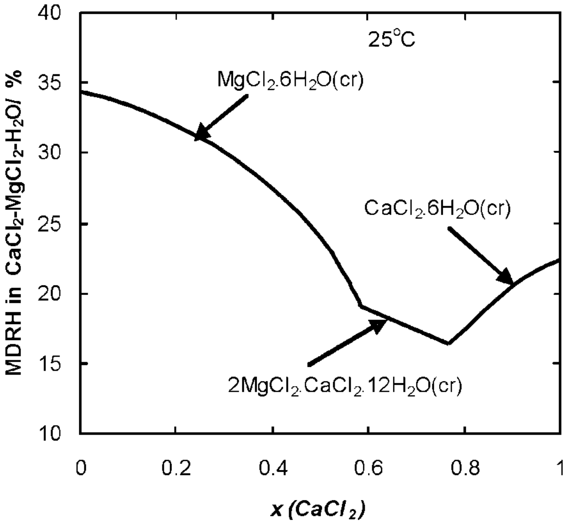

Figure 3. Calculated MDRH of mixed $MgCl_2 + CaCl_2 + H_2O$ solutions in equilibrium with $MgCl_2\cdot 6H_2O(cr)$, $2MgCl_2\cdot CaCl_2\cdot 12H_2O(cr)$, and $CaCl_2\cdot 6H_2O(cr)$ at 25 °C against mole fraction of calcium chloride $\{x(CaCl_2)\}$ in saturated solutions.

based on parametrization established in our previous studies,[7,18,20] give the following DRH values of pure sea-salt minerals in saturated binary solutions at 25 °C: NaCl(cr) = 75.2 %; $Na_2SO_4\cdot 10H_2O(cr) = 93.6$ %; and KCl(cr) = 84.09 %. According to the calculations made in this study (Table 5), the high-soluble magnesium and calcium chloride minerals are the lowest deliquescence sea-salt minerals, and therefore these minerals determined the deliquescence behavior of complex solid sea-salt under humidity conditions. The recent chemical kinetic studies of Park et al.[19] confirm the above conclusion. The experiments of these authors show that solid sea-salt and solid magnesium chloride have a similar deliquescence behavior. However, according to present equilibrium model calculations, the addition of high-soluble calcium chloride decreases the DRH of bishofite, and therefore it should be expected that the magnesium−calcium salt mixture will reproduce even more adequately the deliquescence of solid sea-salt. Taking into account the molal ratio of magnesium and calcium chloride in solid sea-salt aerosols and the calculated phase diagrams of the $MgCl_2 + CaCl_2 + H_2O$ system (Figure 2a), it can be concluded that mixed solutions with composition (≈ 1.25 mol·kg^{-1} $CaCl_2$ + ≈ 4.4 mol·kg^{-1} $MgCl_2$) and saturated with bishofite will be the first saturated solution which is formed during the formation of liquid sea-salt aerosols at standard temperature. The solid−liquid equilibrium model for mixed system predicts a MDRH value of ≈ 32 % for this bishofite equilibrium solution, respectively, for the lowest deliquescence of complex solid sea-salt. However, the equilibrium model for the $MgCl_2 + CaCl_2 + H_2O$ system presented in this study is a small fragment of the complex sea system. Only the development of a comprehensive, temperature-variable model, including all possible pure electrolyte and mixing ion-interaction parameters, and the equilibrium of all stable and metastable sea-type minerals, can accurately describe the deliquescence behavior of sea-salt aerosols and provide important information on the formation of reactive aqueous aerosols in atmosphere. Such a model can be used for accurate calculation of the sequence of formation of saturated solutions on the surface of the solid sea-salt under humidity conditions, and for correct estimation of the thermodynamic stability of supersaturation states, as a function of temperature, solution composition, and solid salt stoichiometry. Conctruction of such a model is one of the main goals in my future studies. The model for highly soluble magnesium and calcium chloride minerals, as well as the experimental activity data, presented in this study represents a good base for development of such a comprehensive model.

Acknowledgment

For more than 20 years, my research was focused on development of standard temperature and XTP-variable thermodynamic models for binary, ternary, and multicomponent industrial and natural systems with a wide range of applications. Almost all standard-temperature binary systems models were parametrized using the comprehensive database of R. A. Robinson and R. H. Stokes. The main criterion in the solution parameter evaluation process was how the resulting model agrees with the accurate activity data presented by Robinson and Stokes. Therefore, without the contribution of Professor Robin H. Stokes to fundamental thermodynamics, more than 50 years ago, development of such accurate models would not be possible. With his contribution to thermodynamics, Professor Stokes made a significant impact in the area of chemical modeling studies and in my career. I wish Professor Stokes the very best in the years to come. I wish to thank S. Velikova and K. Ivanova for help in the isopiestic measurements. I also thank Editor Kenneth N. Marsh and three anonymous reviewers for their constructive suggestions.

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Received for review July 19, 2008. Accepted August 26, 2008. This work has been supported partially by the U.S. National Science Foundation and National Science Fund of the Bulgarian Ministry of Science and Education.

JE8005634