A THERMODYNAMIC MODEL OF AQUEOUS ELECTROLYTE SOLUTION BEHAVIOR AND SOLID-LIQUID EQUILIBRIUM IN THE Li-H-Na-K-Cl-OH-H$_2$O SYSTEM TO VERY HIGH CONCENTRATIONS (40 MOLAL) AND FROM 0 TO 250 °C

ARNAULT LASSIN[*,†], CHRISTOMIR CHRISTOV[**,***], LAURENT ANDRÉ[*], and MOHAMED AZAROUAL[*]

ABSTRACT. This paper describes a chemical model that calculates solute and solvent activities and solid-liquid equilibria in the Li-H-Na-K-Cl-OH-H$_2$O system from dilute to high solution concentration within the 0 to 250 °C temperature range. The model coherently extends to Li the temperature-variable H-Na-K-OH-Cl-H$_2$O model of Christov and Møller (2004b, p. 1309). The solubility modeling approach based on Pitzer's (1973, p. 268) specific interaction equations is used. All binary (LiCl-H$_2$O and LiOH-H$_2$O) and ternary (LiCl-HCl-H$_2$O, LiCl-NaCl-H$_2$O, LiCl-KCl-H$_2$O, LiOH-NaOH-H$_2$O, LiOH-KOH-H$_2$O, and LiOH-LiCl-H$_2$O) lithium subsystems are included in the model parameterization. The model for the LiCl-H$_2$O system is parameterized using two different approaches: (1) with 4 ion interaction binary parameters ($\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^{φ}), and (2) with 3 ion interaction binary parameters ($\beta^{(0)}$, $\beta^{(1)}$, and C^{φ}) and including neutral aqueous LiCl^0(aq) species. Approach (2) provides a better fit of activity data in unsaturated binary solutions and accurately predicts solid solubilities up to 40 mol.kg^{-1} and up to 250 °C. Therefore, this approach was used to parameterize lithium chloride mixed systems. Temperature functions for the thermodynamic solubility product (as log K$^{\circ}_{sp}$) of 5 simple lithium salts (LiCl.2H$_2$O(cr), LiCl.H$_2$O(cr), LiCl(cr), LiOH.H$_2$O(cr), and LiOH(cr)) are determined. The log K$^{\circ}_{sp}$ values of 3 double lithium basic salts precipitating in the LiOH-LiCl-H$_2$O system at 50 °C (3LiOH.LiCl(cr), LiOH.LiCl(cr), and LiOH.3LiCl(cr)) are also estimated using solubility data.

Keywords: Lithium, hypersaline aqueous solutions, Pitzer model, thermodynamic excess properties, solubility, mixed systems

INTRODUCTION

The interest in lithium is increasing because of the difficulties involved in finding oil substitutes for the world's energy supply, taking into account environmental constraints. It is used, in particular, in batteries (including vehicle batteries and energy storage devices) and the demand for lithium is expected to increase greatly in the coming years (Ebensperger and others, 2005; Grosjean and others, 2012; Kushnir and Sandén, 2012). Large amounts of lithium are found in the salt flats (*salars*) of the Altiplanos in South America, mostly in Chile, Argentina and Bolivia (Garrett, 2004; Risacher and Fritz, 2009), in saline lakes in China (Song and Yao, 2001) and the United States, and in the Dead Sea (Warren, 2010). There may be other sources of lithium in other countries and hydrosystems, such as in some geothermal waters (Pauwels and others, 1993, 1995) and oil brines (Gruber and others, 2011). Regardless of the source and geochemical cycle of lithium, an understanding of its chemical behavior is a prerequisite for its exploration, extraction and exploitation, in particular because of the very high concentrations it can reach in aqueous solutions due to the very high solubility of the lithium salts.

* BRGM—3 avenue C. Guillemin, Orléans, France (a.lassin@brgm.fr, l.andre@brgm.fr, m.azaroual@brgm.fr)
** GeoEco Consulting 2010, 13735 Paseo Cevera, San Diego, California 92129, USA (hristovi@sbcglobal.net)
*** Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria (christov@svr.igic.bas.bg)
† Corresponding author: E-mail: a.lassin@brgm.fr

Part of this understanding relies on the development of comprehensive thermodynamic models that accurately predict lithium aqueous chemistry and lithium mineral solubilities as a function of the composition of precipitates and solution concentration at high temperature. For example, the study of lithium salt solubility diagrams is of practical importance with a view to explaining the distribution of lithium ions in natural evaporate deposits during crystallization of salts as a result of sea water evaporation and during treatment of natural deposits (Song and Yao, 2001, 2003).

Several authors (Pitzer and Mayorga, 1973; Kim and Frederick, 1988a; Christov and others, 1994; Ojkova and others, 1998; Song and Yao, 2001; El Guendouzi and others, 2003, 2004; Nasirzadeh and others, 2005) have developed 298.15 K Pitzer equation-based models for Li interactions in binary and mixed sea-type systems. The standard temperature Pitzer models of Christov and others (1994, 2000) for the Li-Mg-Ca-Cl-Br-H_2O system, of Song and Yao (2001) for Li chloride ternary sub-systems within the Li-K-Mg-Cl-SO_4-H_2O system, of Song and Yao (2003) for the Li-Na-K-Mg-Cl-SO_4-H_2O system, and of Christov (1995) for Li-Mg-Br-H_2O at 343.15 K consider precipitation of lithium minerals. On the basis of their own high temperature osmotic coefficient data and reference activity data at lower temperature, Holmes and Mesmer (HM) developed temperature variable models for binary systems LiCl-H_2O (Holmes and Mesmer, 1981, 1983) and LiOH-H_2O (Holmes and Mesmer, 1998a). The models of HM are valid only up to low molality (m_{max} = 6 mol.kg^{-1} for chloride and hydroxide systems) and therefore cannot be used for solid-liquid equilibrium calculations. With only one exception (Li$_2$SeO$_4$-H_2O model), all of the Pitzer models described in the literature for Li binary systems (LiCl-H_2O, LiBr-H_2O, LiI-H_2O, LiOH-H_2O, LiClO$_4$-H_2O, LiNO$_3$-H_2O, Li$_2$SO$_4$-H_2O) have used a standard molality-based Pitzer approach for 1-1 and 1-2 types of electrolytes with three ion interaction pure electrolyte parameters ($\beta^{(0)}$, $\beta^{(1)}$, and C^{φ}). Ojkova and others (1998) include in their model for the Li$_2$SeO$_4$-H_2O system a fourth interaction parameter ($\beta^{(2)}$) from basic Pitzer equations. Only two temperature variable solid-liquid equilibrium models are available in the literature for lithium chloride systems: the one from Monnin and others (2002) for the LiCl-H_2O system, which is based on the Pitzer equations for subzero temperatures (up to about 200 K) and on the mean spherical approximation (MSA) model for temperatures up to 433 K, and the one from Zeng and others (2007) for the H-Li-Mg-Cl-H_2O system who used the BET model over the temperature range from 273 to 473 K. There is no model available in the framework of the Pitzer formulation for temperatures comprised between 273.15 and 523.15 K.

The construction of a comprehensive Pitzer model has, however, been initiated through a series of experimental measurements and parameterization of XTP- and pH-variable thermodynamic solid-liquid equilibrium models of highly soluble chloride, hydroxide, and bromide minerals precipitating within the H-Li-Na-K-Mg-Ca-Al-Fe(II)-Fe(III)-OH-Cl-Br-HSO$_4$-SO$_4$-H_2O system (Christov and others, 2000; Christov, 2004, 2012; Christov and Møller, 2004a, 2004b; Christov and others, 2007). The resulting consistent and extensible geochemical databases are able to describe complex systems that can be applied to natural and industrial contexts.

The objective of the present work is to continue the development of such a database, providing the Pitzer parameters that enable the accurate description of the Li-H-Na-K-Cl-OH-H_2O system from diluted aqueous solutions up to saturation with respect to minerals, and from low (273.15 K) to high temperatures (up to 523.15 K).

<div align="center">METHODOLOGY</div>

The specific interaction approach for describing electrolyte solutions to high concentration introduced by Pitzer (1973, 1991) represents a significant advance in physical chemistry that has facilitated the construction of accurate thermodynamic

models (Gueddari and others, 1983; Harvie and others, 1984). It has been shown that the Pitzer approach could be expanded to accurately calculate ion activity products, and thus solubilities, in complex brines and to predict the behavior of natural fluids from subzero temperatures (Marion and others, 2003) to a very high temperature up to 573.15 K (Pabalan and Pitzer, 1987; Møller, 1988; Christov and Møller, 2004a, 2004b; Møller and others, 2005, 2006, 2007; Christov and others, 2007; Christov, 2009, 2012).

The Pitzer Approach

The Pitzer specific interaction approach (Pitzer, 1973) and model equations for osmotic and activity coefficients have been discussed in detail in many publications (see references below). Depending on the chemical system or the range of salinity studied, the basic Pitzer approach has been used, modified and extended in various ways. We review here these practices in order to explain our modeling technology, which has been used to create a model for extremely high concentrated lithium chloride solutions, with a very strong association at high molality.

Pitzer equations.—We give here only the equation for calculating the logarithm of the activity coefficient, γ_M, of a cation M of charge z_M. Equation (1) refers to the basic Pitzer theory (Pitzer, 1973; Pitzer and Mayorga, 1973) and it is expressed here according to Harvie and Weare (1980). The additional terms given here with equation (1A) have been introduced later in order to take into account the contribution of neutral species (Pitzer and Silvester, 1976; Harvie and others, 1984; Felmy and Weare, 1986).

$$ln\ \gamma_M = z_M^2 F + \sum_a m_a(2B_{Ma} + ZC_{Ma}) + \sum_c m_c\left(2\Phi_{Mc} + \sum_a m_a\psi_{Mca}\right)$$
$$+ \sum_{a\ <\ a'}\sum m_a m_{a'}\psi_{Maa'} + |z_M|\sum_c\sum_a m_c m_a C_{ca} \quad (1)$$

$$+ \sum_n m_n(2\lambda_{Mn}) + \sum_n\sum_a m_n m_a\zeta_{Mna} \quad (1A)$$

Subscripts c, a and n refer to cations, anions, and neutral species, and the summations are over the total number of cations, anions, or neutral species. The double summation index, $a < a'$, denotes the sum over all distinguishable pairs of dissimilar anions. In equation (1), B and Φ are measurable combinations of the second virial coefficients. C and ψ are measurable combinations of the third virial coefficients. B and C are parameterized from single electrolyte data, and Φ and ψ are parameterized from mixed system data. m_i is the molality of species i ($i = M$, a, c, n).

The function F is the sum of the Debye-Hückel term,

$$F = -A^\varphi\left[\frac{\sqrt{I}}{(1 + b\sqrt{I})} + \frac{2}{b}(1 + b\sqrt{I})\right] \quad (2)$$

and terms with the derivatives of the second virial coefficients with respect to ionic strength (see Harvie and others, 1984). In equation (2), b is a universal empirical constant assigned to be equal to 1.2. A^φ, the Debye-Hückel limiting law slope for osmotic coefficients, is a function of temperature, density and the dielectric constant of water (see, Møller, 1988).

For the interaction of any cation M and any anion a, Pitzer assumes that in equation (1), B has the ionic strength dependent form:

$$B_{Ma} = \beta^{(0)}_{Ma} + \beta^{(1)}_{Ma}g(\alpha_1\sqrt{I}) \tag{3}$$

$$+ \ \beta^{(2)}_{Ma}g(\alpha_2\sqrt{I}) \tag{3A}$$

where $g(x) = 2[1 - (1 + x)e^{-x}]$, with $x = \alpha_1\sqrt{I}$ and $\alpha_1 = 2.0$

Equation (3) refers to the basic Pitzer theory, while the additional term corresponding to equation (3A) was introduced afterwards to deal with 2-2 electrolytes (Pitzer and Mayorga, 1974). Its use has been extended to other types of electrolytes as detailed below.

The C_{Ma} third virial coefficients (see eq 1) are assumed to be ionic strength independent. However, some terms containing C_{Ma} parameters have a concentration dependence given by Z, as:

$$z = \sum_i m_i |z_i| \tag{4}$$

In equation 1, the Φ terms account for interactions between two ions i and j of like charges. In the equation for Φ,

$$\Phi_{ij} = \theta_{ij} + {}^E\theta_{ij}(I) \tag{5}$$

θ_{ij} is the only adjustable parameter. The ${}^E\theta_{ij}(I)$ term accounts for electrostatic unsymmetric mixing effects that depend only on the charges of ions i and j and the total ionic strength.

The ψ_{ijk} parameters are used for each triple ion interaction where the ions i, j, k do not all have the same sign. Their inclusion is generally important for describing solubilities in concentrated multicomponent systems.

According to the basic Pitzer equations, therefore, at constant temperature and pressure, the solution model parameters to be estimated are: 1) $\beta^{(0)}$, $\beta^{(1)}$, and C^φ for each cation-anion pair in the pure electrolytes; 2) θ for each unlike cation-cation or anion-anion pair in electrolyte mixtures; 3) ψ for each triple ion interaction where the ions do not all have the same sign in electrolyte mixtures.

During the 1970's, Pitzer and co-authors determined the ion interaction parameters for a large number of binary and ternary unsaturated solutions of electrolytes. Using the standard Pitzer approach with three ($\beta^{(0)}$, $\beta^{(1)}$, and C^φ) ion-interaction binary parameters, Pitzer and Mayorga (1973) developed models for 227 pure aqueous electrolyte systems of the 1-1, 2-1, 1-2, 3-1 and 4-1 types, and Kim and Frederick (1988a) developed models for 294 binary systems of the same types plus four 1-3 electrolyte systems. These binary systems models were developed using only activity data (osmotic coefficients) in unsaturated solutions. That is the precipitation of solid phases was not considered. Furthermore, the parameterization of Pitzer and Mayorga (1973) (summarized also in Pitzer, 1991) focused on a good representation of activity properties (osmotic coefficients) of low to moderate molality unsaturated binary solutions alone, with a maximum molality of 6 m for each model. The parameterization of Kim and Frederick (1988a) extends the concentration range of application of pure electrolyte ion-interaction parameters, focusing on the fit of data at high molality. However, for many binary systems of the type 1-1, 2-1, and 3-1 the concentration extension of Kim and Frederick parameterization leads to a disagreement with the low molality osmotic coefficients data, and to much higher standard deviation values, compared to Pitzer and Mayorga (1973) parameterizations (see Christov 1994, 2004, 2005). More recent studies have also shown that, for a binary electrolytic solution containing a univalent species, either cationic or anionic, the standard Pitzer approach gives excellent model reliability from 273.15 K to very high temperatures (up to 573 K), and from extremely

low ($[Al_{total}] \approx 10^{-7}$ mol.kg^{-1} in the aluminum hydroxide speciation model (Møller and others, 2006, 2007) to very high concentrations [for example, up to 523.15 K and 64 mol.kg^{-1} in the NaOH-H$_2$O system (Christov and Møller, 2004b); up to 383.15 K and ≈ 14.5 mol.kg^{-1} in the CaCl$_2$-H$_2$O system (Christov and Møller, 2004a); up to 373.15 K and 7.64 mol.kg^{-1} in the MgCl$_2$-H$_2$O system (Christov, 2009); up to 573.15 K and 18 mol.kg^{-1} in the NaBr-H$_2$O, and KBr-H$_2$O systems; and up to 523 K and 16.5 mol.kg^{-1}in the CaBr$_2$-H$_2$O system (Christov, 2012)].

Using the binary system parameterization of Pitzer and Mayorga (1973), Pitzer and Kim (1974) developed models for 52 ternary mixtures of 1-1+1-1 (for example HCl-LiCl-H$_2$O), 1-1+2-1 (for example NaCl-MgCl$_2$-H$_2$O), 1-1+1-2, 2-1+2-1, and 2-1+2-1 brine-type electrolytes. Once again, mixed system models of Pitzer and Kim (1974) were developed using only activity data (osmotic coefficients) in unsaturated solutions, and the precipitation of solid phases was not considered. Pitzer and Kim (1974) concluded that the mixed models enabled the calculation of the activity coefficients in the ternary systems under consideration with an accuracy of 2 to 6 percent. Kim and Frederick (1988b) performed the same work, including in their parameterization some transition metal chloride systems, for which data were available.

The $\beta^{(2)}$ parameter.—Pitzer and Mayorga (1973) did not study 2-2 (for example MgSO$_4$-H$_2$O) or higher (for example Al$_2$(SO$_4$)$_3$-H$_2$O) electrolytes. Indeed, they found that the three-parameter approach ($\beta^{(0)}$, $\beta^{(1)}$, and C^φ, see eq 1) could not accurately fit the activity data for these types of solutions. For these electrolytes, the mean activity coefficient, $\gamma_\pm$, and the osmotic coefficient, φ, drop very sharply in dilute solutions, while showing a very gradual increase, with a very broad minimum at intermediate concentrations. Pitzer and Mayorga (1974) concluded that this behavior was due to ion association reactions and that the standard approach with three estimated solution parameters cannot reproduce it. This led to a further modification of the original equations for the description of binary solutions by introducing an additional parameter, $\beta^{(2)}_{Ma}$, and its associated $\alpha_2\sqrt{I}$ term in the B_{Ma} equation (see eq 3A). Pitzer and Mayorga (1974) presented these parameterizations assuming that the form of the excess functions (that is 3 or 4β and C^φ values, as well as the values of the α terms) vary with the type of electrolyte. For binary electrolyte solutions in which either the cationic or anionic species are univalent (for example NaCl, Na$_2$SO$_4$, or MgCl$_2$), the standard Pitzer approach uses 3 parameters (that is omits the $\beta^{(2)}$ term) and α_1 equals 2.0. For the 2-2 type of electrolytes, the model includes the $\beta^{(2)}$ parameter, α_1 equals 1.4, and α_2 equals 12. This approach provides accurate models for many 2-2 electrolytes, and gives an excellent representation of activity data covering the entire concentration range from low molality up to saturation and beyond.

On the other hand, some authors found that some restrictions limit the potential of the standard Pitzer model to correctly describe activity and solubility properties in some binary electrolyte systems containing a univalent species at very high molality. One major factor determined these restrictions: type of φ vs. m, or $\gamma_\pm$ vs. m dependences at high concentration. For all of these systems, φ vs. m, or $\gamma_\pm$ vs. m curves have a broad maximum at molality approaching the molality of saturation ("CaCl$_2$ type)". This "broad maximum" type of φ vs. m, or $\gamma_\pm$ vs. m dependence for highly concentrated solutions has been modeled using various extended versions of the Pitzer model, such as mole fraction models (Petrenko and Pitzer, 1997), multi-parameters models (Gruszkiewicz and Simonson, 2005), two C^φ extension models (Palmer and others, 2002), by inclusion of complex aqueous species [such as CaCl$^+$(aq), Sterner and others, 1998], or by accounting for temperature variations in α_1 and α_2 terms (Holmes and Mesmer, 1998b). In the case of the 3-2 electrolyte, Al$_2$(SO$_4$)$_3$, Reardon (1988) used the 4-parameter Pitzer approach (that is including $\beta^{(2)}$) and values of 2 and 50 for α_1 and α_2, respectively. To describe the high concentration solution behavior of systems

showing a "smooth" maximum on $\gamma_{\pm}$ vs. m dependence, and to take strong association reactions at high molality into account, a very simple modeling technique was proposed: using the 4-parameter Pitzer approach and varying the values of α_1 and α_2 terms. This approach was used for various types of binary electrolyte systems at 298.15 K: 1-1 (for example, HNO_3-H_2O in Christov, 2005), 2-1 (for example, $CuCl_2$-H_2O in Christov, 1994), 1-2 (for example, $Na_2Cr_2O_7$-H_2O in Christov and others, 1999), 3-1 (for example, $FeCl_3$-H_2O in Christov, 2004), and 3-2 types (for example, $Al_2(SO_4)_3$(aq)-H_2O in Christov, 2001a). The resulting models reduce the standard deviation (σ) values of experimental activity data fitting and extend the application range of the binary system models to the highest molality, close or equal to the molality of saturation, m(sat). It was found that by varying the values of α_1 and α_2 terms, it was possible to vary the concentration range of binary solutions at which association reactions became more important, and this should be taken into account when introducing the $\beta^{(2)}$ parameter. According to Christov (2005), a model that uses $\alpha_1 = 1.4$ and $\alpha_2 = 12$ takes association reactions into account only for low molality solutions, while combinations of $\alpha_1 = 2$ and $\alpha_2 = (1$ or $-1)$ can be used if ion association occurs at higher molality. All these approaches for binary systems were successfully used to develop models of multicomponent systems such as Na-K-Cl-SO$_4$-Cr$_2$O$_7$-H$_2$O (Christov, 1998, 2001b), or K-Mg-Al-Cl-SO$_4$-H$_2$O (Christov, 2001a). On the other hand, to correctly describe the very low solubility of portlandite ($Ca(OH)_2$(cr)) in pure water, a case of 2-1 electrolyte: $Ca(OH)_2$-H_2O, Christov and Møller (2004a) also used the $\beta^{(2)}$ 4-parameter approach (with $\alpha_1 = 1.4$ and $\alpha_2 = 12$) in their $273.15 - 573.15$ K model instead of introducing the well-defined $Ca(OH)^+$(aq) species.

For many of the binary solutions considered above, there is, however, experimental evidence of the formation of aqueous complexes [for example $CuCl^+$(aq), $AlSO_4^+$(aq), or $FeCl^{2+}$(aq)] that are taken into account in other approaches of aqueous solution chemistry. Although the solution model developed with the 4-parameter Pitzer approach with no aqueous complexes differs from others that take into account aqueous complexes for the same solutions, it is simple and provides an accurate description of the thermodynamic properties, including solubilities.

Ion association.—In some instances, there are much stronger bonds formed between some ionic species than can be modeled with Pitzer type equations, and it is necessary to consider the formation of particular aqueous species (Harvie and others, 1984; Felmy and Weare, 1986; Møller, 1988; Greenberg and Møller, 1989; Rard and Clegg, 1997; Sterner and others, 1998; Pitzer and others, 1999; Christov and Møller, 2004b; Møller and others, 2005, 2006, 2007). Harvie and others (1984) discussed the correlation between the ion pairing and the $\beta^{(2)}$ parameter for rather low molality. They provided a key for selecting one option instead of another: for strong ion associations, $\beta^{(2)}$ takes strong negative values indicating that using an ion association approach, with an association constant, is more efficient and should be preferred. The adding of a charged contact ion pair to the solution model requires the determination of not only a stability constant to describe the ion pair, but also ion interaction parameters between the ion pair and each of the other species in the solution. For example the 273.15 K–523.15 K model of Christov and Møller (2004b) for the binary system H_2SO_4-H_2O was developed by including the contact ion pair HSO_4^-(aq) and therefore the system is considered to be a mixed system H-HSO_4-SO_4-H_2O. As a result, the model development required the determination of the chemical potential of the bisulfate ion ($\mu^0(HSO_4^-$(aq))) and the consideration of many potential interactions: H-HSO_4, H-SO_4, SO_4-HSO_4, H-SO_4-HSO_4. The complications associated with adding the HSO_4^-(aq) ion pair increase in the case of mixed sulfuric acid systems. For example, in order to develop an accurate model for H_2SO_4-K_2SO_4-H_2O, it was necessary to estimate, in addition to all of the sulfate parameters, T-variation bisulfate

parameters of K-HSO$_4$, K-H-HSO$_4$, and K-SO$_4$-HSO$_4$ interactions, and to determine the chemical potential of bisulfate solids, using only the available solubility data. However, in most cases, the very limited experimental database that does exist does not make it possible to determine the pure electrolyte parameters for these ion pairs (for example parameters for FeCl^{2+}-Cl$^-$ interactions). The inclusion of an ion association reaction in a Pitzer-based model without appropriate ion interaction binary and mixing parameters determined from an extensive and parameters-sensitive experimental database can lead to inappropriate and even completely wrong activity and solubility model predictions.

In spite of spectroscopic or other experimental indications that a particular complex exists in a solution, it might be possible to develop a sufficiently accurate solution model to describe the excess properties without including explicitly these complexes. Indeed, in light of the above considerations, simple evidence of ion-association in concentrated solutions is not a sufficient reason for incorporating ion pairs in a Pitzer-based activity model. Reasons for introducing a contact ion pair in the Pitzer based activity model would include 1) a failure to accurately predict observed thermodynamic properties such as osmotic/activity coefficients and solubilities in binary and complex systems, 2) a pH-dependent behavior of binary systems, and 3) experimental evidence of the abundance of the contact ion pair compared to the dissociated aqueous species, which evidences the strength of the ion association.

Binary and Mixed Systems Including Neutral Species [see eq (1A)]

Fluids commonly encountered in natural systems include dissolved neutral species such as carbon dioxide ($CO_{2(aq)}$) and silica ($SiO_{2(aq)}$). Further development of Harvie and Weare's (1980) model to include carbon dioxide and its hydrolysis products (Harvie and others, 1984) required an additional modification of fundamental Pitzer equations. This modification included terms, λ_{nc} or λ_{na}, to account for interactions between neutral solutes, n, and dissolved cations, c, and anions, a. The behavior of $CO_{2(aq)}$ in NaCl-H$_2$O solutions could then be described by the following neutral species-ion interaction parameters: $\lambda_{CO2,Na}$, $\lambda_{CO2,Cl}$. Analyses of interactions in more complex natural waters demonstrated the need to add an additional interaction parameter, ζ_{nca}, to account for ternary interactions between an anion, a cation and a neutral solute (such as $\zeta_{SiO2,Na,Cl}$: Felmy and Weare, 1986). Using spectroscopic measurements, Felmy and others (2001) further developed their model by introducing polymerized silica species in order to describe the behavior of silica at high pH. To describe the extremely low solubility of calcium sulfate solids in pure water and in the mixed Na-K-Ca-Cl-SO$_4$-H$_2$O system, Møller (1988) and Greenberg and Møller (1989) also included the neutral $CaSO_4^0$(aq) species without evaluating $CaSO_4^0$(aq)-ion interaction parameters. The neutral $Al(OH)_3^0$(aq) species is also included in the aluminum hydroxide speciation 273.15-563.15 K model described in (Møller and others, 2006, 2007). The inclusion of this aqueous complex together with estimated $Al(OH)_3^0$(aq)-ion interaction parameters into a model gives an excellent fit of experimental gibbsite $Al(OH)_3$(cr) and boehmite AlOOH(cr) solubility data in the intermediate pH range.

Parameterization

We therefore propose the following parameterization procedure for models based on Pitzer formalism for binary electrolyte systems with at least one univalent ion, or of 3-2 type:

(i) Parameterize a standard Pitzer equation model using three single electrolyte interaction parameters ($\beta^{(0)}$, $\beta^{(1)}$, and C$^\varphi$).

(ii) If model predictions are not in agreement with raw experimental activity and solubility data, develop a new model using four interaction parameters from basic Pitzer equations ($\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C$^\varphi$). Vary the values of α_1 and α_2

terms to achieve the best fit of data for the entire concentration and temperature range.

(iii) If neither (i) nor (ii) provides an acceptable fit, include in the model one or more ion pairs with their stability constant and binary and mixing ion interaction or neutral species-ion interaction parameters for all aqueous species. To avoid the redundancy of having both the $\beta^{(2)}$ parameter and the contact ion pair to account for the ionic association in solutions it is preferable to develop a three parameter model ($\beta^{(0)}$, $\beta^{(1)}$, and C^{φ}) adapted to complex-free solutions.

(iv) Confirm the suitability of the accepted models for binary systems by developing accurate models for higher-order mixed systems, where aqueous solutions can be more concentrated than in the binary systems.

According to Pitzer's theory, the $\beta^{(2)}$ parameter fully accounts for association reactions at low molality for 2-2 electrolyte systems. Therefore, including a contact ion pair in a model for this type of system is inappropriate and can lead to erroneous model calculations of the solubility product of precipitating solids (Christov, 2012).

The temperature-variation model for lithium binary and mixed system solubility is developed using the following classical approach. Activity data for unsaturated solutions are used to estimate interaction parameters for low and moderate electrolyte concentrations. Solubility data in binary and mixed solutions are also used to broaden the temperature and concentration ranges of parameterization. Using the same approach as in previous studies, in order to avoid the overlapping of pure electrolyte and mixed solution parameters, we developed the models for Li binary systems using only the data for these binary systems, and mixed solution models were parameterized using only data for a mixed system. In our binary and mixed model parameterization we used only raw experimental thermodynamic values (osmotic coefficients, water activity, and minerals solubility) derived directly from experimental measurements (isopiestic and vapor pressure studies, and solubility experiments). Results of the parameterization are expressed in terms of standard deviation (σ), as defined in Christov and Møller (2004a). Note that the mean activity coefficients recommended in the literature are model-dependent and are therefore not used in the parameterization process. However, some of these data are compared to our results to evaluate the solution models for Li binary systems.

The new Li models are parameterized using PEST (Doherty, 2004), a software for model-independent parameter estimation and uncertainty analysis, in combination with PhreeqC v2.15 (Parkhurst and Appelo, 1999), used for the calculation of the excess properties of aqueous solutions. PhreeqC includes the Phrqpitz modules (Plummer and others, 1988), which are based on the Pitzer formalism. We modified the PhreeqC code in order to be consistent with the temperature function used by Christov and Møller (2004b) for the solution parameters. The Debye-Hückel parameter A^{φ} is adapted in PhreeqC using the equations of Bradley and Pitzer (1979) and of Pitzer and others (1984). Møller (1988) used the same A^{φ} data (from Pitzer and others, 1984) to develop her T-function. Therefore, both temperature functions give almost the same A^{φ} values (with less than 0.066% difference) at every temperature between 273.15 and 523.15 K.

We used two different equations to describe the temperature dependence of model parameters. Temperature dependence for the thermodynamic solubility product (as Log K$^{o}_{sp}$) and the equilibrium dissociation constants of ion pairs (as Log K) is built into the model by adjusting selected constants in the following equation:

$$\text{Log K} = A_1 + A_2 T + A_3/T + A_4 \text{Log(T)} + A_5/T^2 \tag{6}$$

For Pitzer ion-ion and neutral species-ion binary and ternary interaction parameters (P), the temperature function is the same as in (Christov and Møller, 2004a, 2004b):

$$P(T) = a_1 + a_2T + a_3 T^2 + a_4T^3 + a_5/T + a_6 \ln(T) + a_7/(T\text{-}263) + a_8/(680\text{-}T)$$

$$(7)$$

In equations (6) and (7), temperature is in Kelvin, and A_i ($i = 1$ to 5) and a_j ($j = 1$ to 8) are the parameters to be adjusted. In some cases, parameters A_i can be directly derived from sets of standard thermodynamic properties including Gibbs free energy, enthalpy, entropy and heat capacity (see for instance Blanc and others, 2012). We determined Log K_{sp}^o values for Li minerals using the estimated model solution parameters and experimental equilibrium solubility data in binary and mixed Li systems.

<div align="center">MODEL PARAMETERIZATION AND RESULTS</div>

Christov and Møller (2004b) described the temperature dependent (from 273.15 K to 523.15 K) high quality models of solution behavior and (solid-liquid) equilibrium for all binary and mixed sub-systems in the quinary H-Na-K-Cl-OH-H$_2$O system. These models are in excellent agreement with data for low molality activity, E.M.F, and K_w/Q_w for unsaturated solutions, and with data for high-concentration acid-base mineral solubility data. We have developed a model for lithium mixed systems (Li-H-Na-K-Cl-OH-H$_2$O) using the parameterization from Christov and Møller (2004b) without any additional adjustments of the values for the binary and mixed ion-interaction parameters and the chemical potential of sodium and potassium chloride and hydroxide minerals. The remaining models to be considered to complete the Li brine system series are those for binary (LiCl-H$_2$O and LiOH-H$_2$O) and ternary (LiCl-HCl-H$_2$O, LiCl-NaCl-H$_2$O, LiCl-KCl-H$_2$O, LiOH-NaOH-H$_2$O, LiOH-KOH-H$_2$O, and LiOH-LiCl-H$_2$O) systems. All of these lithium subsystems are included in the model parameterization presented here.

For parameterizing equilibrium models that can predict aqueous solution behavior and solid-liquid equilibria in binary and complex systems, the most reliable and complementary experimental data are low- and high-molality osmotic coefficient and/or water activity data and solid solubility data (Christov, 2005, 2012). This type of data is therefore used throughout our study.

<div align="center">*Binary LiCl-H$_2$O System*</div>

Selection of experimental data.—Numerous experimental data, both for solution properties and solid solubility, are available for the simple binary LiCl-H$_2$O system at various temperatures and molality (table 1). Aqueous solution properties are mostly restricted to moderate salinities and seldom reach or approach the solubility of solid phases for the LiCl-H$_2$O system (fig. 1). Osmotic data are available for LiCl molalities ranging from 0.001 to 20.95 mol/kg at 298.15 K (Robinson and Stokes, 1949; Hamer and Wu, 1972), from 0.1 to 18.6 mol/kg between 273.15 and 373.15 K (Gibbard and Scatchard, 1973; Patil and others, 1990), from 7.42 to 20.95 at 428.15 K (Brendler and Voigt, 1994), from 0.68 to 6.30 between 498.15 and 523.15 K (Holmes and Mesmer, 1983). Additional osmotic data are provided at 318.15 and 353.15 K, but only for LiCl molalities up to 4.8 mol/kg (Hellams and others, 1965; Moore and others, 1972) and between 383.15 and 473.15 K for molalities up to 6 mol/kg (Holmes and Mesmer, 1981). Vapor pressure measurements above LiCl aqueous solutions have been done by Kangro and Groeneveld (1962) up to 20 mol/kg, at 293.15 and 298.15 K. These data are not used in the parameterization. However, we used these high molality data to validate the model with an independent check, after conversion of vapor pressure into osmotic coefficient.

TABLE 1

Standard deviation (σ) values of activity (osmotic coefficients (φ)) and solubility data in the Li-Na-K-Cl-H$_2$O (model 2) and Li-Na-K-OH-H$_2$O systems. n is the number of experimental data points and m(sat) is the molality of solutions saturated with the corresponding solid phase

SYSTEM	Method [a]	Type of data	t°C-tot°C	Molality Range	Reference	σ	n [b]
ACTIVITY DATA							
LiCl-H$_2$O	vap	φ	20, 25	1-18	*Kangro and Groeneveld (1962)*	*0.0666 [c]* / *0.0244*	*36*
	iso	φ	25	m(LiCl): 0.1-20.0	Robinson and Stokes (1949)	0.0672 [c] / 0.0263 [d]	37
	comp	φ	25	m(LiCl): 0.001-19.219	Hamer and Wu (1972)	0.0568 [c] / 0.0299 [d]	43
	iso	φ	45	m(LiCl): 0.6-2.2	Hellams and others (1965)	0.0275 [c] / 0.0104 [d]	11
	iso	φ	80	m(LiCl): 1.3-4.8	Moore and others (1972)	0.0418 [c] / 0.0133 [d]	14
	iso	φ	0-100	m(LiCl): 0.1-18.6	Gibbard and Scatchard (1973), Patil and others (1990)	0.0744 [c] / 0.0241 [d]	130
	iso	φ	110-200	m(LiCl): 0.5-6.0	Holmes and Mesmer (1981)	0.0347 [c] / 0.0121 [d]	28
	iso	φ	155	m(LiCl): 7.42-20.95	*Brendler and Voigt (1994)*	*0.0714 [c]* / *0.0432 [d]*	*16*
	iso	φ	225-250	m(LiCl): 0.68-6.30	Holmes and Mesmer (1983)	0.0187 [c] / 0.0061 [d]	34
LiOH-H$_2$O	vap	φ	25-90	m(LiOH): 0.07-4.77	Nasirzadeh and others (2005)	0.0114	308
		φ	25	m(LiOH): 0.1-5.0	Mikulin (1968)	0.0333	21
	iso	φ	110-170	m(LiOH): 0.62-7.22	Holmes and Mesmer (1998)	0.0102	54
LiCl-KCl-H$_2$O	hyg	φ	25	m(LiCl+KCl): 0.0-6.0	El Guendouzi and others (2003)	0.0218	45
LiCl-NaCl-H$_2$O	hyg	φ	25	m(LiCl+NaCl): 0.0-6.0	El Guendouzi and others (2004)	0.0362	45

TABLE 1
(*continued*)

SOLUBILITY DATA

SYSTEM	Type of salt	Method [a]	t°C-t°C	Molality Range	Reference	σ [e]	n
LiCl-H$_2$O	LiCl.2H$_2$O(cr) m(sat)	sol	0-20	m(LiCl): 16.06-19.52	Linke (1965)	0.3081 [c] / 0.1556 [d]	5
	LiCl.H$_2$O(cr) m(sat)	sol	19.4-99	m(LiCl): 19.46-30.27	Linke (1965), Farelo and others (2005)	0.3359 [c] / 0.1578 [d]	28
	LiCl(cr) m(sat)	sol	96-160	m(LiCl): 29.83-34.23	Linke (1965)	0.0193 [c] / 0.0089 [d]	8
	LiCl(cr) m(sat)	sol	200-250	m(LiCl): 36.46-40.74	Monnin and others (2002)	0.1301 [c] / 0.0026 [d]	2
LiOH-H$_2$O	LiOH.H$_2$O(cr)m(sat)	sol	0-108.9	m(LiOH): 4.97-7.98	Linke (1965), Kirgintsev and others (1972)	0.2202	16
	LiOH(cr)m(sat)	sol	108.9-200	m(LiOH): 7.06-7.85	Itkina and others (1967), Kirgintsev and others (1972)	0.0001	3
LiCl-KCl-H$_2$O	LiCl.2H$_2$O(cr), LiCl.H$_2$O(cr), LiCl(cr), KCl(cr) Sylvite m(sat)	sol	0-100	m(LiCl): 0-31.50 / m(KCl): 0.0-7.46	Plyushchev and others (1959), Akopov (1962), Campbell and Kartzmark (1956), Zatloukal and others (1959), Yanko and Goldanel (1964)	0.0686	181
LiCl-NaCl-H$_2$O	LiCl.2H$_2$O(cr), LiCl.H$_2$O(cr), LiCl(cr), NaCl(cr) Halite m(sat)	sol	0-100	m(LiCl): 0-30.40 / m(NaCl): 0.0-6.70	Akopov (1963), Khy (1960)	0.0730	56
LiOH-KOH-H$_2$O	LiOH.H$_2$O(cr),LiOH (cr), KOH.H$_2$O(cr) m(sat)	sol	0-150	m(LiOH): 0-7.85 / m(KOH): 0.0-30.0	Itkina and others (1967, 1968)	0.0964	18
LiOH-NaOH-H$_2$O	LiOH.H$_2$O(cr),LiOH (cr), NaOH.H$_2$O(cr) NaOH.4H$_2$O(cr) m(sat)	sol	0-150	m(LiOH): 0-7.85 / m(NaOH): 0.0-20.0	Evteeva (1965), Itkina and others (1968)	0.1081	22

[a] Experimental method: iso = isopiestic; comp = compilation; v.p. = vapor pressure; hyg = hygroscopic; sol = salt solubility.
[b] Some of the experimental data are not used in the parameterization as explained in the text.
[c] Standard deviation calculated for model 1 (without LiCl^0(aq) species).
[d] Standard deviation calculated for model 2 (with LiCl^0(aq) species).
[e] Average saturation index = $[\Sigma(SI)^2/n]^{0.5}$, where $SI = \log(IAP/K^\circ_{sp})$ is the saturation index of a mineral. Information in italics: data excluded from parameterization (see text).
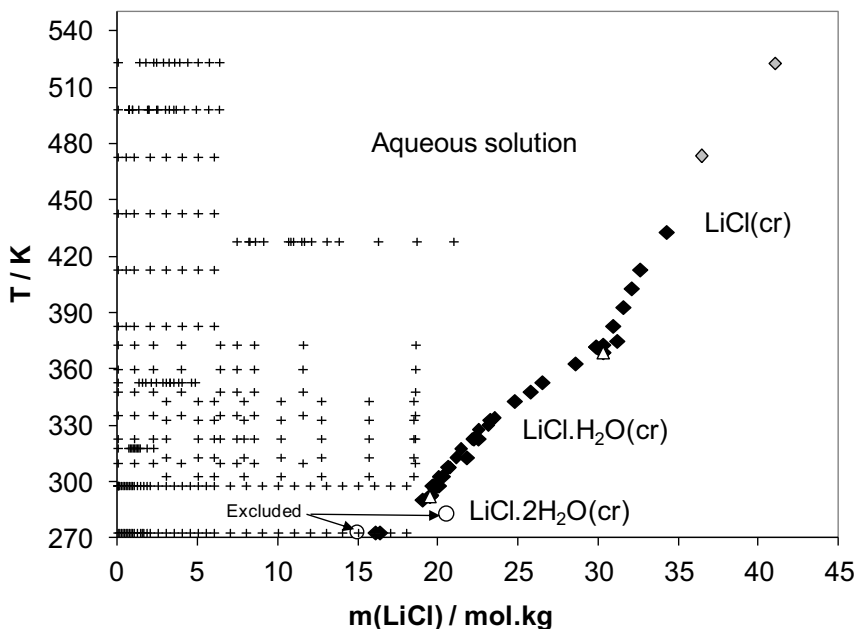
Fig. 1. Experimental aqueous (osmotic coefficient, φ) and solubility data used for the LiCl-H$_2$O binary system, as a function of temperature. Crosses represent aqueous data: from Gibbard and Scatchard (1973) for 273.15 to 373.15 K; from Robinson and Stokes (1949) and from Mikulin (1968) at 298.15 K; from Hellams and others (1965) at 318.15 K; from Moore and others (1972) at 353.15 K; from Holmes and Mesmer (1981) for 383.15 to 473.15 K; from Brendler and Voigt (1994) at 428.15 K (not included in parameterization); from Holmes and Mesmer (1983) for 498.15 to 523.15 K. Black diamonds represent solubility data for LiCl.nH$_2$O(cr) solids (n = 0, 1 or 2) from compilations of Linke (1965), Zdanovskii and others (1973), and Garrett (2004), and from Farelo and others (2005). Triangles represent phase transition (292.55 K: LiCl.2H$_2$O(cr) to LiCl.H$_2$O(cr) and 369.15 K: LiCl.H$_2$O(cr) to LiCl(cr)) points of Kirgintsev and others (1972). Gray diamonds represent high temperature (473.15 K and 523.15 K) LiCl(cr) solubility calculated using solubility-temperature relationship given by Monnin and others (2002) (their table 1) and based on the compilation of Cohen-Adad (1991). Circles represent LiCl.H$_2$O(cr) solubility at 273.15 K (Garrett, 2004) and 283.15 K (Zdanovskii and others, 1973) (not included in parameterization).

Data from Brendler and Voigt (1994) at 428.15 K have been excluded from parameterization. The main reason for exclusion of these data is their inconsistency with data from others at other temperatures, and with predictions of our final LiCl model. According to our test, this inconsistency is mainly due to an inappropriate solution model for the reference solutions used in Brendler and Voigt (1994) experiments. They used MgCl$_2$ as the reference electrolyte. According to the authors, the reported osmotic coefficient data for MgCl$_2$ do not permit development of accurate model for aqueous MgCl$_2$-H$_2$O solutions. Therefore, in their calculations of the osmotic coefficient of LiCl, Brendler and Voigt (1994) used the data for reference standard from Valyashko and others (1987), and not a prediction of the MgCl$_2$-H$_2$O model of Pabalan and Pitzer (1987). This may in turn lead to questionable calculated values of the osmotic coefficient of LiCl aqueous solutions. The model for MgCl$_2$ implemented in our database is from Christov (2009), which gives osmotic coefficients predictions much closer to the Pabalan and Pitzer (1987) model, than to the data from Valyashko and others (1987), at least up to 100 °C. Using Christov (2009) model for interpreting isopiestic measurements of Brendler and Voigt (1994) leads to values of osmotic coefficients for LiCl aqueous solutions lower than recommended by these authors. All osmotic coefficients data available in literature for LiCl-H$_2$O systems are shown on figure 1.

According to the experimental solubility data there are three solid phases, which precipitated from saturated binary LiCl-H$_2$O solutions from 273.15 K to 523.15 K: LiCl.2H$_2$O(cr) (from 273.15 K to ≈293.15 K), LiCl.H$_2$O(cr) (from ≈293.15 K to ≈367.15 K), and LiCl(cr) (from ≈367.15 K to ≈523.15 K). According to Kirgintsev and others (1972), LiCl.2H$_2$O(cr) to LiCl.H$_2$O(cr) and LiCl.H$_2$O(cr) to LiCl(cr) phase transitions in contact with the aqueous solution occur at 292.55 and 19.45 mol/kg, and 369.15 K and 30.27 mol/kg, respectively. According to solubility data, as well as to the solubility-temperature relationship given by Monnin and others (2002) (see their table 1), which is based on the compilation of Cohen-Adad (1991), the solubility of lithium chloride solids sharply increases with temperature: from ≈20 mol/kg at a temperature of 293.15 to 41 mol/kg at 523.15 K. The LiCl.2H$_2$O(cr), LiCl.H$_2$O(cr), and LiCl(cr) solubility data used in parameterization for temperatures between 273.15 and 433.15 K are from Farelo and others (2005) and from compilations of Linke (1965), Zdanovskii and others (1973) and Garrett (2004). At higher temperature (473.15 and 523.15 K) the smoothed data of Monnin and others (2002) are used. With only two exception sets [LiCl.2H$_2$O(cr) solubility at 273.15 K (Garrett, 2004) and at 283.15 K (Zdanovskii and others, 1973)] the data are in a very good agreement. Therefore, only these two inconsistent data points were excluded from parameterization. All available solubility data are also given in figure 1. As can be seen, there is a lack of activity data for high concentrated unsaturated LiCl-H$_2$O solutions at high temperatures above 373.15 K. Therefore, it was a big challenge to evaluate pure electrolyte parameters describing accurately the solution behavior for the whole molality range up to saturation, especially at high temperature.

Model parameterization.—The parameterization procedure involves two different steps for each system under consideration: first binaries, then ternary sub-systems. For a monovalent electrolyte like LiCl, a simple fully dissociated representation of the system should allow the description of its behavior as a function of salinity and temperature, the associated Li$^+$-Cl$^-$ temperature-dependent specific interaction parameters being $\beta^{(0)}$, $\beta^{(1)}$, and C^φ. However, as pointed out by Monnin and others (2002) and discussed below, due to the very high solubility of lithium chloride, this simple chemical representation does not describe the experimental data accurately enough. For systems that can be very highly concentrated or show a strong curvature of the osmotic coefficient at high salinities, some authors add the $\beta^{(2)}$ interaction parameter in their fitting procedure (Zhou and others, 2003; Christov, 2005), with a value of ±1 for the related α_2 parameter. In some cases, α_2 is also adjusted (Rumyantsev and others, 2004; Zhang and others, 2005). The $\beta^{(2)}$ parameter was originally introduced by Pitzer (see *The $\beta^{(2)}$ parameter* section above) to deal with symmetrical 2:2 electrolytes. We tested this option and call it "model 1" below.

This work aimed to produce interaction parameters that are compatible with an extensive existing database. Instead of the $\beta^{(2)}$ interaction parameter, we included the LiCl^0(aq) neutral aqueous species in the chemical description of the system, in addition to the Li$^+$ and Cl$^-$ ions, in order to improve model performance. As a consequence, the specific interaction parameters, $\lambda_{\text{Li-LiCl}}$, $\lambda_{\text{Cl-LiCl}}$, and $\zeta_{\text{Li-Cl-LiCl}}$, and the equilibrium constant for the Li$^+$ + Cl$^-$ = LiCl^0(aq) reaction had to be included in what we call "model 2" below. However, in order to reduce the number of parameters to be fitted, we set these neutral species-ions interaction parameters to 0 in a first approximation. This enabled us to describe with a high level of confidence the whole set of experimental data for both osmotic coefficient and minerals solubility (see below).

There are few available data on aqueous properties up to saturation with respect to mineral phases at high temperatures (>373.15 K). Depending on the model (1 or

2), we were able to fill this gap using aqueous and solubility data simultaneously in the fitting procedure.

For both models, parameters were fitted with the numerous experimental data that cover a wide range of temperatures (from 273.15–523.15 K) and salinities (from 0 to 20 mol/kg for osmotic coefficients (fig. 2) and up to 41 mol/kg for mineral solubility data (fig. 3). On the whole, model 2 describes experimental data better than model 1. The standard deviation, σ, for the entire set of osmotic coefficient data (349 points) is 0.0534 for model 1 and 0.0221 for model 2. The 16 experimental osmotic coefficients from Brendler and Voigt (1994) and the 36 data points (calculated from vapor pressure measurements) from Kangro and Groeneveld (1962) were included in the calculation of the deviation. They are only used here to check the quality of parameterization and point out discrepancies. The standard deviation, σ, for the whole set of solubility data (43 points), is 0.2922 for model 1 and 0.1380 for model 2. Model 2 reproduces experimental solubility data up to 523.15 K and 41 M of LiCl, whereas model 1 fails at temperatures above 490 K and molalities above 37 M.

More detailed information on standard deviations for the two experimental datasets (osmotic coefficient and mineral solubility) is given in table 1.

Specific interaction parameters were plotted as a function of temperature (fig. 4). For model 2, all parameters vary smoothly with temperature, and $\beta^{(0)}$ and $\beta^{(1)}$ even have an almost linear temperature dependence. These are good model stability criteria. The parameters of the temperature functions consistent with equation (2) are given in table 2.

The adjustment procedure also provides temperature functions for equilibrium constants for the dissolution reaction of LiCl.nH₂O(cr) salts ($n = 0, 1$ or 2): LiCl.nH₂O(cr) = Li⁺ + Cl⁻ + n H₂O, and for the formation of the contact ion pair LiCl⁰aq in model 2. The relevant parameters are given in table 3 and equilibrium constants have been plotted, alongside literature values for comparison, as a function of temperature (fig. 5). Equilibrium constants for LiCl.H₂O(cr) and LiCl.2H₂O(cr) come from Monnin and others (2002). The value at 298.15 K for LiCl.H₂O(cr) is from Christov (2005). The functions determined by us are in rather good agreement with these data. Values for LiCl(cr) come either from Monnin and others (2002) or were calculated using the standard thermodynamic properties of LiCl(cr) formation (ΔH_f°, S° and C_p) determined by Chase (1998) from calorimetric measurements, and of Li⁺ and Cl⁻ ions determined by Shock and Helgeson (1988) using the CODATA (1978) recommended values for the elements and aqueous species. Our results are much more consistent with the calorimetric data of Chase (1998) than with those of Monnin and others (2002). We also checked our models by comparing the invariant points in the LiCl-H₂O system calculated using models 1 and 2 to experimental data (table 4). The match is satisfactory—the slight discrepancy being due to the smoothing of the temperature function of the salt crystal solubility products.

Activity Coefficients, Activity of Water and Relative Humidity

As a result of the fitting procedure, individual activity coefficients for Li⁺ and Cl⁻ can be calculated as a function of total molality of dissolved LiCl at various temperatures. As indicated by Plummer and others (1988), individual-ion activities and activity coefficients (eq 1) cannot be measured independently: only the mean activity coefficient of a neutral combination of two ions of interest can be measured. If the dissolved electrolyte is fully dissociated, the mean activity coefficient ($\gamma_\pm$) is calculated from the individual activity coefficients according to: $\gamma_\pm = (\gamma_{Li+} \, \gamma_{Cl-})^{1/2}$. If dissociation is not complete, the degree of dissociation (δ) must be taken into account (Zhang and others, 2011). The mean activity coefficient is then rewritten as: $\gamma_\pm = \delta \times (\gamma_{Li+} \, \gamma_{Cl-})^{1/2}$, where $\delta = m(Li^+)/[m(Li^+) + m(LiCl^0)]$.
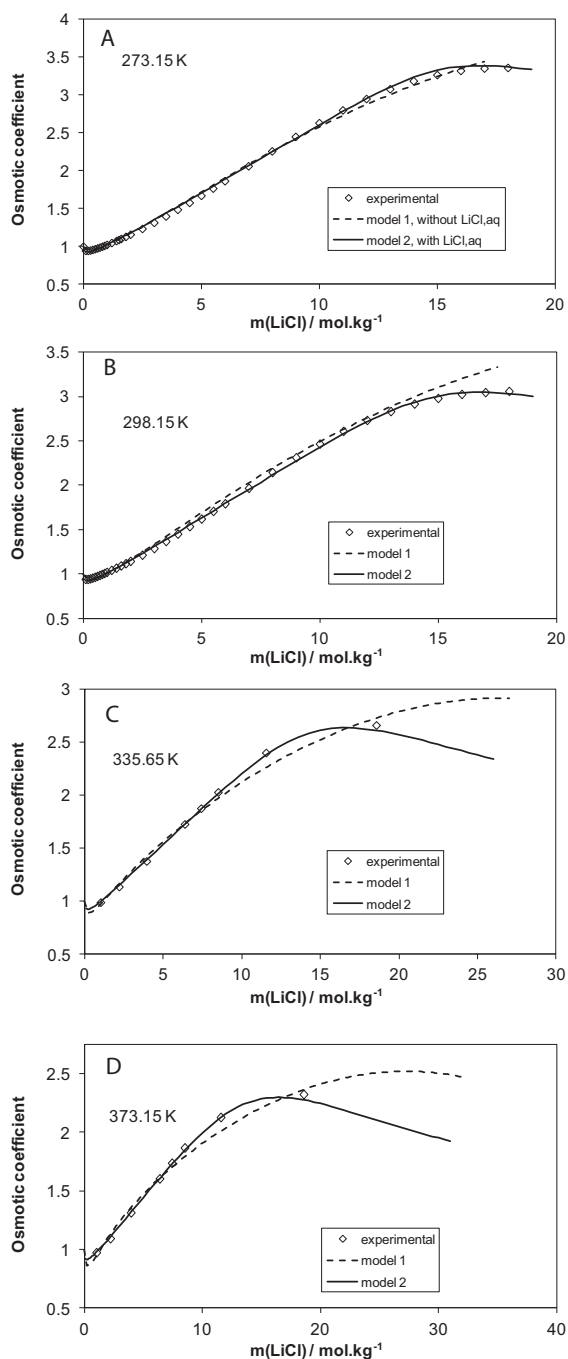
Fig. 2. Calculated (lines) and experimental (diamonds) osmotic coefficients, φ, for the LiCl-H$_2$O binary system as a function of total molality of LiCl: (A) at 273.15 K, (B) at 298.15 K, (C) at 335.65 K, (D) at 373.15 K, (E) at 443.15 K, (F) at 523.15 K, and (G) at 428.15 K (not used in parameterization). Experimental data—see figure 1 caption. Dashed lines are values calculated with model 1 (without the LiCl^0(aq) neutral species, but with α_2 and $\beta^{(2)}$ parameters) and solid lines are values calculated with model 2.
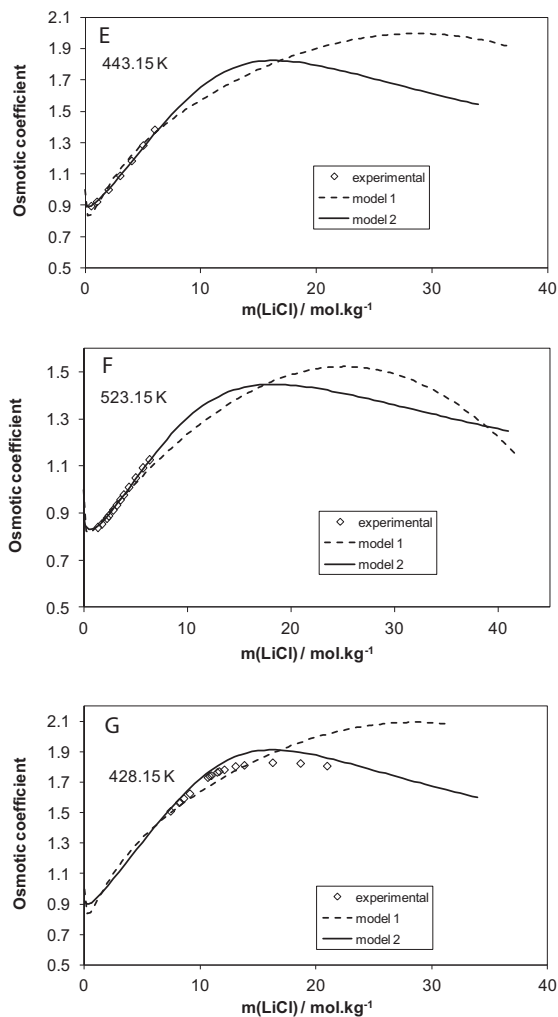
Fig. 2 (continued)

Mean activity coefficients calculated in this manner were plotted (fig. 6) and given in table 5 for comparison with recommended values from the literature. LiCl mean activity coefficients are extremely variable (between <1 at low salinities and/or at high temperatures and >60 close to mineral saturation at low temperatures). Mean activity coefficients calculated with model 2 are generally closer to the values recommended in the literature than results of model 1 (table 5). None of the models available in the literature provide mean activity coefficients over the entire range of temperatures and concentrations covered in table 5. This illustrates the complexity of the system and the good performance of the models described here.

As an ultimate test of our models, calculated values for deliquescence relative humidity (DRH), the osmotic coefficient and the mean activity coefficient of LiCl at saturated lithium binary solution at 298.15 K are compared to recommended experimental values and the results of reference models (table 6). A good agreement is obtained with recommended experimental data, in particular for model 2 that provides better results than the reference models listed in the table.
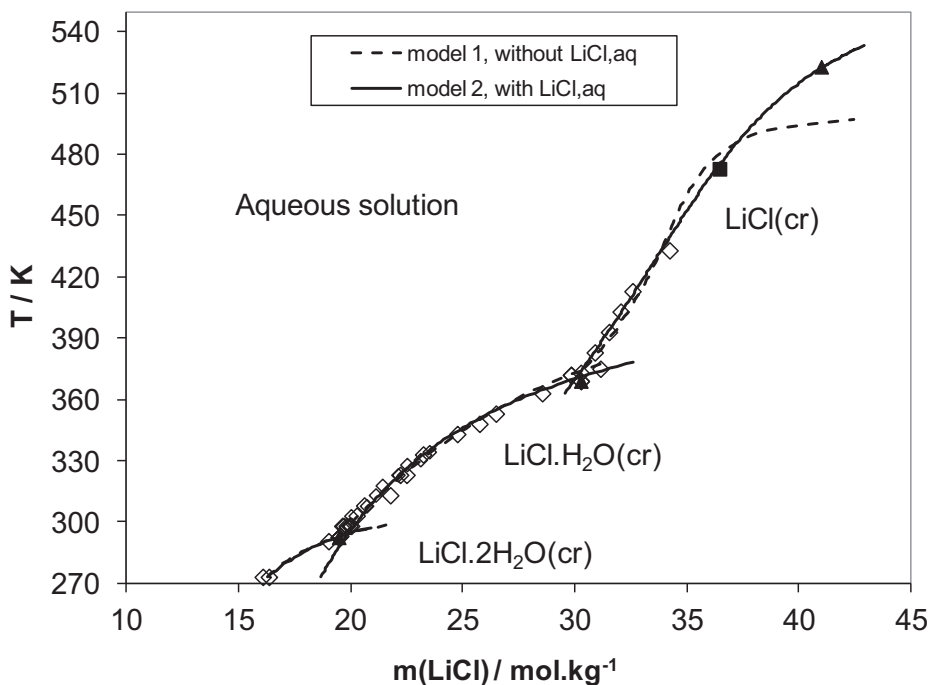
Fig. 3. Experimental (symbols) and calculated (lines) solubility of LiCl.nH$_2$O(cr) (n = 0, 1 or 2) solids as a function of temperature in the LiCl-H$_2$O binary system. Experimental data—see figure 1 caption. Dashed lines are values calculated with model 1 (without the LiCl^0(aq) neutral species, but with α_2 and $\beta^{(2)}$ parameters) and solid lines are values calculated with model 2.

All performed tests and calculations show that predictions of model 2, which uses the neutral ion pair LiCl^0(aq), are more consistent with experimental data than the predictions of more widely used model 1. It is possible that total dissociation of dissolved species in extremely high salinity LiCl-H$_2$O solutions is not complete, and to account for the strong association at high molality it is necessary to introduce the ion pair LiCl^0(aq) into the model.

Aqueous Speciation

Since dissolved LiCl is not fully dissociated, Li and Cl speciation in the aqueous solution was calculated. The LiCl^0(aq) mol percent, equal to 100 m(LiCl^0(aq))/ [m(Li$^+$) + m(LiCl^0(aq))], is plotted in figure 7 as a function of total LiCl molality at various temperatures. At low temperatures, from low concentrations up to about a molality of 10 mol/kg, the dissolved LiCl is almost fully dissociated. This is consistent with the classic use of the Pitzer approach. At higher molalities, the neutral LiCl^0(aq) contact ion pair is increasingly abundant, which is in agreement with the experimental observation of a contact ion pair made by Rudolph and others (1995), using Raman spectroscopy, in LiCl aqueous solutions at 295 K. These authors observed this neutral species for salt/water molar ratios of less than 1:4, which corresponds to a molality of about 14 M and is consistent with the results of model 2. Moreover, as the temperature increases, the fractions of the LiCl^0(aq) species increase, indicating a stabilization of this species with temperature. This is in agreement with the evolution of the dissociation constant with temperature (above 673.15 K) as reported by Sverjensky and others (1997). As an illustration of this, we have plotted LiCl speciation along the solution-
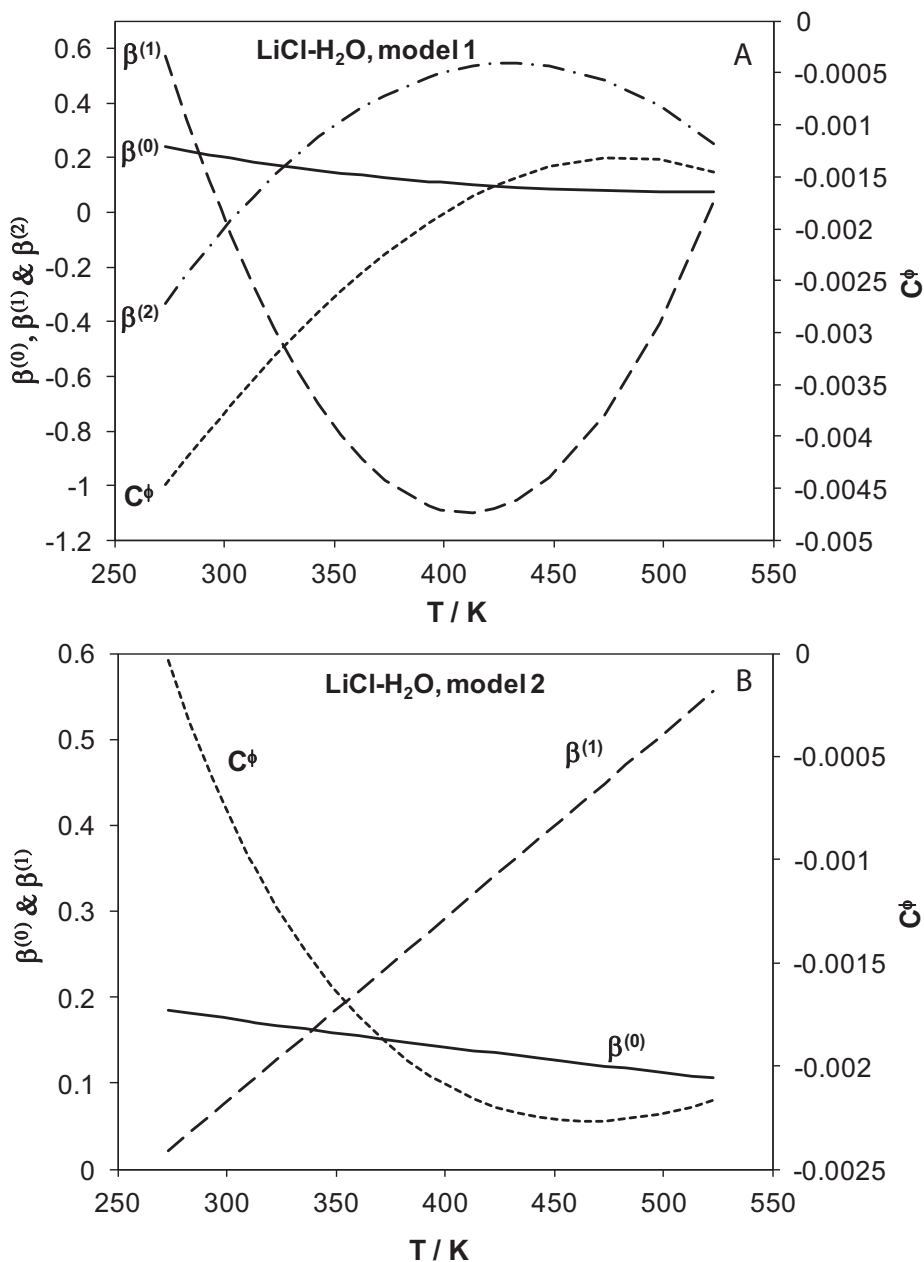
Fig. 4. Estimated pure electrolyte parameters for the LiCl-H$_2$O binary system from 273.15 to 523.15 K: (A) model 1 (no LiCl^0(aq)): $\beta^{(0)}$(Li$^+$,Cl$^-$) (solid line), $\beta^{(1)}$(Li$^+$,Cl$^-$) (long-dashed line), $\beta^{(2)}$(Li$^+$,Cl$^-$) (dot-dashed line), and C$^\phi$ (Li$^+$,Cl$^-$) (short-dashed line), (B) model 2: $\beta^{(0)}$(Li$^+$,Cl$^-$) (solid line), $\beta^{(1)}$(Li$^+$,Cl$^-$) (long-dashed line), and C$^\phi$ (Li$^+$,Cl$^-$) (short-dashed line)

mineral equilibrium line (fig. 8). Up to 523.15 K, the total number of aqueous ions (m$_{Li+}$ + m$_{Cl-}$) never exceeds the number of water molecules (55.508 mol/kg). This is qualitatively consistent with studies that report that at high concentrations—up to at

Table 2

Fitting constant values (eq 7) for the binary solution interaction parameters[a]

Binary system	Parameters	T range (°C)	Constants (T in degrees Kelvin)				
			$a_1(-)$	$a_2(T)$	$a_3(T^2)$	$a_5(1/T)$	$a_6(ln(T))$
LiCl-H$_2$O Model 1[b]	$\beta^{(0)}(Li^+-Cl^-)$	0-220	0.5015472	-2.206d-03	2.349d-06	45.28407	0
	$\beta^{(1)}(Li^+-Cl^-)$	0-220	13.21831	-0.071394	8.772d-05	85.25804	0
	$\beta^{(2)}(Li^+-Cl^-)$	0-220	-6.01484	0.030441	-3.530d-05	0	0
	$C^\varphi(Li^+-Cl^-)$	0-220	-0.02991	9.91d-05	-9.60d-08	1.51258	0
LiCl-H$_2$O Model 2[c]	$\beta^{(0)}(Li^+-Cl^-)$	0-250	0.2185836	-2.51d-04	0	9.696362	0
	$\beta^{(1)}(Li^+-Cl^-)$	0-250	-0.583294	2.165d-03	0	3.722014	0
	$C^\varphi(Li^+-Cl^-)$	0-250	-0.01755	1.64d-05	0	3.56052	0
LiOH-H$_2$O	$\beta^{(0)}(Li^+-OH^-)$	0-200	0.121114	-3.45d-04	0	3.917769	0
	$\beta^{(1)}(Li^+-OH^-)$	0-200	1.235033	-3.984d-03	0	101.9411	0
	$C^\varphi(Li^+-OH^-)$	0-200	1.00d-10	2.51d-06	0	-0.51131	0

[a] The constants a_4, a_7 and a_8 in equation (7) are zero for all of the above interaction parameters. The temperature range for each parameter is the temperature range of experimental data used in model parameterization and/or validation.
[b] Model 1 includes only Li^+ and Cl^- aqueous species, with $\alpha_1 = 2$ and $\alpha_2 = 1$.
[c] Model 2 includes the three aqueous species Li^+, Cl^- and neutral $LiCl^0(aq)$.

least 18.5 m—a hydration shell is preserved around Li^+ ions (Tanaka and others, 1987; Egorov and others, 2003; Petit and others, 2008), even if the water content of this hydration shell can drop to two water molecules (Harsányi and others, 2011). However, for such high salinities, the system can hardly be considered to be an aqueous solution. This means that, using the specific interaction parameters, the Pitzer formalism can describe, in the same way, different chemical processes.

Conversely, with a fully dissociated description of the dissolved LiCl, the relative quantities of water molecules and ionic species would be conducive to the formation of a majority of contact ion pairs, but without any possibility of creating covalent bonds. The creation of covalent bonds would lead to the formation of neutral complexes, which is impossible due to the initial hypothesis of fully dissociated LiCl. These contradictory arguments support the second model proposed here, which is used hereafter for dealing with ternary systems.

Binary LiOH-H$_2$O System

The recent parameters provided by Monnin and Dubois (2005) allow describing the osmotic coefficients of LiOH aqueous solutions as a function of temperature up to the solubility of LiOH solid salts. However, new experimental measurements of osmotic coefficient were published at the same time by Nasirzadeh and others (2005), which could not be used by Monnin and Dubois (2005). Furthermore, the behavior of osmotic coefficients calculated with Monnin and Dubois' parameters beyond the solubility limit of LiOH salts become instable, and the possibility to extend the use of this set of parameters to ternary systems involving highly soluble salts, like LiCl, NaOH or KOH, is questionable. For these reasons, a new set of temperature-dependent interaction parameters for the LiOH-H$_2$O binary system is determined hereafter.

Selection of experimental data.—Solution property data cover the aqueous solution domain in terms of molalities and temperatures better in the LiOH-H$_2$O binary system than in the LiCl-H$_2$O system (fig. 9). However, aqueous data is still lacking for the region near the solid-aqueous solution equilibrium at temperatures above 298.15 K. They range from 0.1 to 5.0 mol/kg for temperatures comprised between 298.15 and 363.15 K (Mikulin, 1968; Nasirzadeh and others, 2005). At 383.15 K [close to the

TABLE 3

Values of fitting constants (eq 6) for log K of formation of aqueous complex and dissolution of solid phases

	Compound	T range (°C) [a]	Constants (T in degrees Kelvin)				
			$A_1(-)$	$A_2(T)$	$A_3(1/T)$	$A_4(\log T)$	$A_5(1/T^2)$
Model 1	LiCl.2H₂O(cr)	0-20	160.892123	0.11350914	1.1932293	-76.955468	0
	LiCl.H₂O(cr)	0-110	19.720829	-0.0036038	1.1316800	-5.410474	0
	LiCl(cr)	90-160	14.6380406	-0.0140304	1.2298564	-1.458678	0
Model 2	LiCl⁰(aq)	0-250	-3.5869	0.007566	-1254.4	0	0
	LiCl.2H₂O(cr)	0-20	6.1532	-0.0064179	0	0	0
	LiCl.H₂O(cr)	0-110	36.2702	0.005655998	2.696341	-13.2627354	0
	LiCl(cr)	90-250	29.9783	-0.004068	1.15421	-9.05005	0
	3LiOH.LiCl(cr)	50	9.269	0	0	0	0
	LiOH.LiCl(cr)	50	6.593	0	0	0	0
	LiOH.3LiCl(cr)	50	17.95	0	0	0	0
	LiOH.H₂O(cr)	0-110	-3.8702256	-0.00914328	0.4129607	3.0072101	0
	LiOH(cr)	50-200	-256.08895	-0.06047962	9290.232715	98.8913449	142.35284
	Sylvite [b]	0-250	6.496259873	-0.012323368	-1537.997915	1.507740146	-42632.32102
	Halite [c]	0-250	-752.24954	-0.11904958	41385.703	274.17933	-2480.9109d+03
	KOH.H₂O(cr) [d]	0-70	-444.0232678	-0.285906703	-18.23476494	216.5607191	0.831249816

[a] The temperature range of the solubility data used in parameter estimation and verification.
[b] Fitted using data of Greenberg and Møller (1989) for the sake of consistency with equation (6).
[c] Taken from the Thermoddem database (Blanc and others, 2012).
[d] Adapted to equation (6) using data of Christov and Møller (2004).

temperature of LiOH.H₂O(cr) to LiOH(cr) phase transition, see below], experimental data draw near to the solubility limit with osmotic coefficient values measured at molalities up to 7.2 mol/kg (Holmes and Mesmer, 1998a). These authors also provided aqueous properties at 413.12 and 443.09 K for molalities up to 5.6 and 5.1 mol/kg, respectively. No aqueous data are available at temperatures below 298.15 K.

Solubility data from the compilations of Linke (1965) and Zdanovskii and others (1973) range from 273.15 K to 373.15 K and concern the equilibrium between the aqueous solution and the LiOH.H₂O(cr) solid phase. At higher temperatures, solubility data for the LiOH(cr) solid phase are given by Itkina and others (1967). The phase transition point (382.05 K) between these two solid phases at equilibrium with the aqueous solution is given by Kirgintsev and others (1972). One inconsistent solubility point for LiOH.H₂O(cr) at 273.15 K (Zdanovskii and others, 1973), is excluded from parameterization.

Model parameterization.—Because Li hydroxides are moderately soluble (much less so than Li chlorides) and experimental aqueous properties show simple shapes in the 298.15 to 443.15 K temperature range, the binary LiOH-H₂O system can be described
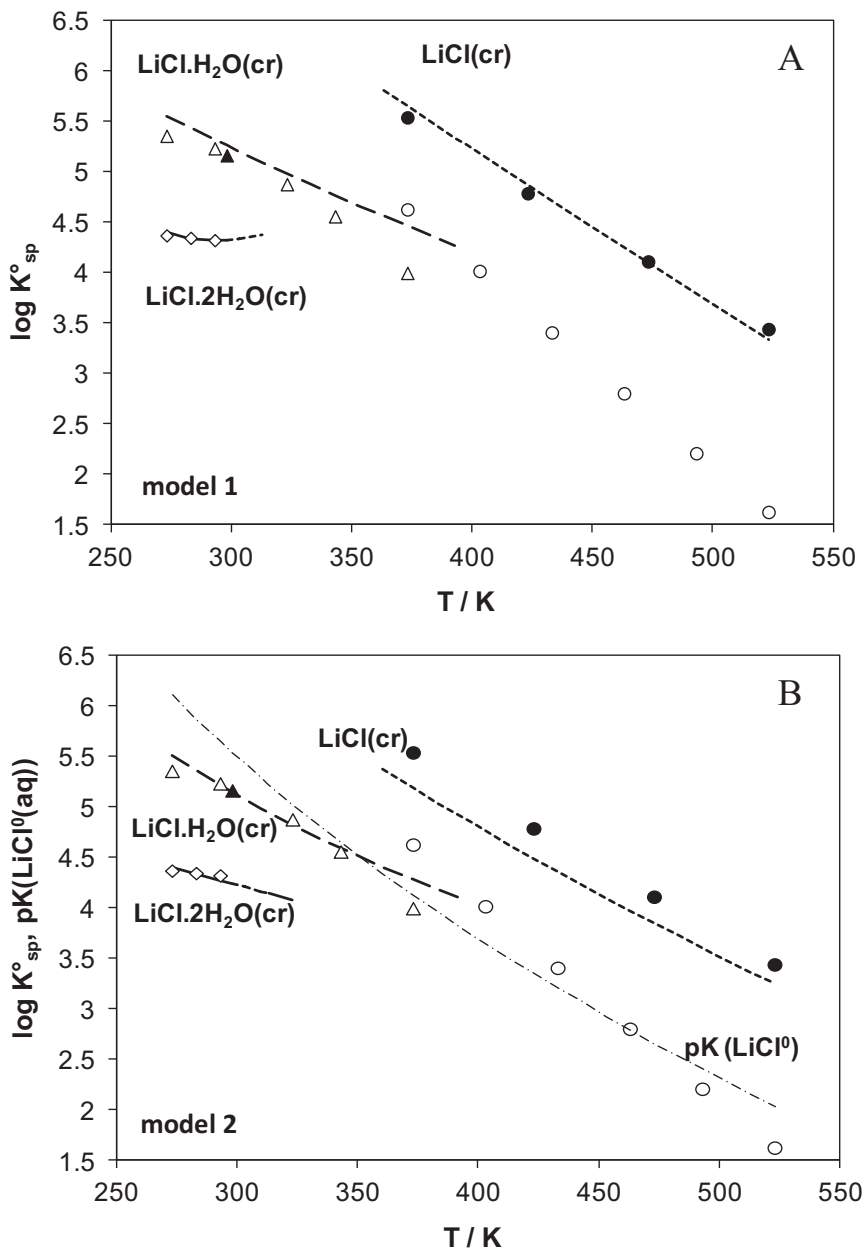
Fig. 5. Comparison of the thermodynamic solubility product (as log K°_{sp}) of lithium chloride solids determined in this study (lines) with the recommended values (symbols) from 0 to 250 °C: (A) model 1 (without the $LiCl^0$(aq) neutral species, but with α_2 and $\beta^{(2)}$ parameters), (B) model 2. Dot-dashed line: $LiCl.2H_2O$(cr); long-dashed line: $LiCl.H_2O$(cr); short-dashed line: $LiCl$(cr); solid line: $LiCl^0$(aq). White diamonds, triangles and circles: log K°_{sp} recommended by Monnin and others (2002) for $LiCl.2H_2O$(cr), $LiCl.H_2O$(cr) and $LiCl$(cr), respectively. Black triangle: log K°_{sp} ($LiCl.H_2O$(cr)) from Christov (2005). Black circles: log K°_{sp} of $LiCl$(cr) calculated using the $LiCl$(cr) calorimetric data (ΔH°_f, S° and C_p) from Chase (1998) and the standard thermodynamic properties (ΔG°_f, S°, HKF parameters) of Li^+ and Cl^- aqueous species from Shock and Helgeson (1988). For model 2, the equilibrium dissociation constant pK($LiCl^0$(aq)) of the neutral aqueous specie $LiCl^0$(aq), determined in this study, is also plotted (dot-dashed line).

TABLE 4

Molality and temperature of the invariant points in the LiCl-H₂O (Models 1 & 2) and LiOH-H₂O binary systems

Co-crystallization solids	$m^s/(mol.kg^{-1})$		T / °C	
	Calculated	Reference data	Calculated	Reference data
$LiCl.2H_2O(cr) + LiCl.H_2O(cr)$	Model 1: 19.34	19.57[a]	Model 1: 19.02	20.79[a]
	Model 2: 19.875	19.46[b]	Model 2: 20.94	19.4 [b]
		19.46[c]		20.0[c]
$LiCl.H_2O(cr) + LiCl(cr)$	Model 1: 30.28	30.26[a]	Model 1: 101.56	96.59[a]
	Model 2: 30.03	30.27[d]	Model 2: 96.97	96.0 [d]
		29.88[c]		93.5±0.5[e]
				93.51±0.03[e]
				94.0[f]
$LiOH.H_2O(cr) + LiOH(cr)$	7.67	7.78[g]	105.63	108.9[g]

[a] Calculated using the MSA model of Monnin and others (2002).
[b] Experimental values of Kessis (1961), included in the compilation of Kirgintsev and others (1972).
[c] Experimental values of Benrath (1934).
[d] Experimental values of Akopov (1962), included in the compilations of Kirgintsev and others (1972).
[e] Phase Transition Temperature (PTT) given by Applebey and Cook (1938).
[f] Phase Transition Temperature (PTT) given in the compilation of Garrett (2004).
[g] Experimental values of Rollet and Cohen-Adad (1964), included in the compilations of Kirgintsev and others (1972).

satisfactorily with the simple Li^+-OH^--H_2O chemical representation and the $\beta^{(0)}$, $\beta^{(1)}$, and C^φ specific interaction parameters (table 2). The standard deviation σ is 0.013 for the entire set of osmotic data (383 points) (fig. 10). The standard deviation σ is 0.202 for the entire set of solubility data that are available from 273.15 up to 473.15 K (19 points) (fig. 11). Detailed σ for the various data sets are given in table 1. The monotonous behavior of the specific interaction parameters $\beta^{(0)}$, $\beta^{(1)}$, and C^φ when plotted against temperature (fig. 12) is an indication of mathematical stability, and extrapolation to temperatures higher than 473.15 K could be done with relatively good confidence. Temperature functions for the LiOH(cr) and $LiOH.H_2O(cr)$ solubility products were determined during the fitting procedure (table 3) for the following chemical reactions where $n = 0$ or 1: $LiOH.nH_2O(cr) = Li^+ + OH^- + nH_2O$. For comparison, our equilibrium constants are plotted against temperature alongside those estimated by Monnin and Dubois (2005) (fig. 13). The two sets of values are in good agreement. However, a comparison of the calculated invariant points in the $LiOH-H_2O$ system with experimental data (table 4) reveals a slight discrepancy. The calculated temperature transition between $LiOH.H_2O(cr)$ and LiOH(cr) is 382.05 K, whereas the experimental value reported by Kirgintsev and others (1972) in their compilation is 378.78 K. This is due to the smoothing of the temperature function of the salt crystal solubility products.

The fitting procedure also provides an intrinsically consistent extrapolation of the osmotic coefficient for LiOH aqueous solutions down to 273.15 K and up to 473.15 K for which solubility data are available (fig. 10). Li^+ and OH^- activity coefficients can, therefore, also be calculated with a good confidence at these temperatures. The mean activity coefficients of LiOH are compared to recommended values over the whole range of temperatures and molalities covered in the literature: from 273.15 to 523.15 K
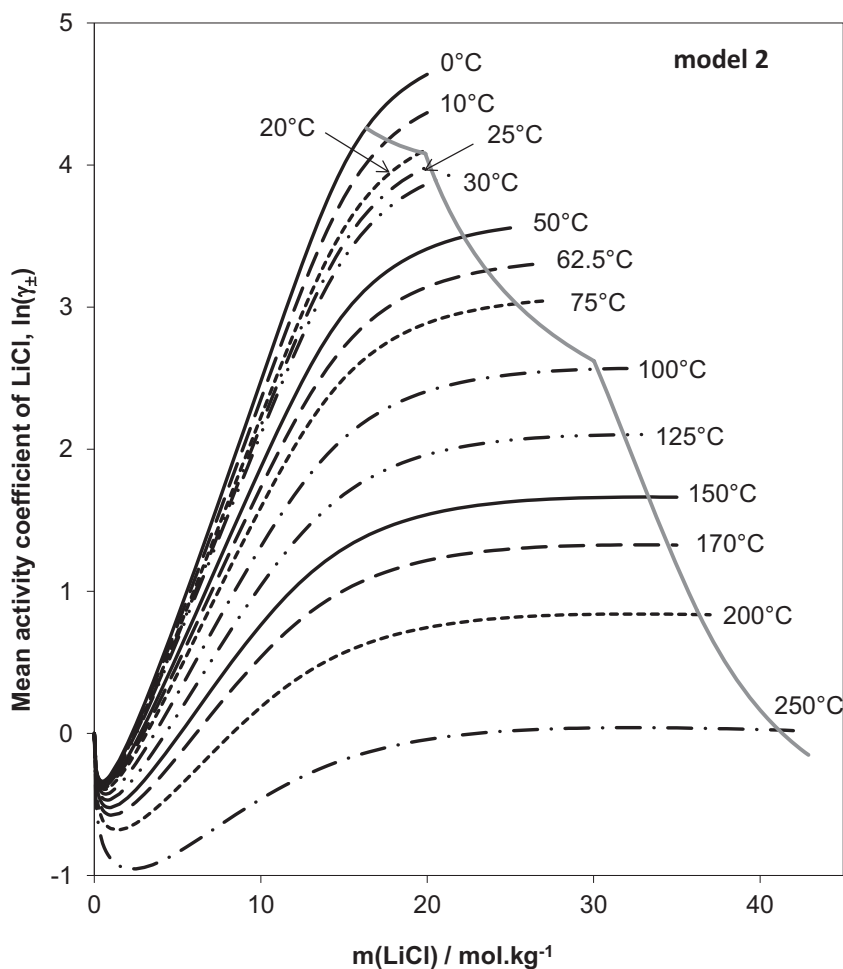
Fig. 6. Calculated mean LiCl activity coefficients in LiCl-H$_2$O solutions vs. molality, from 273.15 to 523.15 K according to model 2. The gray solid line represents the calculated solubility of LiCl.nH$_2$O(cr) (n = 0, 1 or 2) solids (see also fig. 3).

and from 0.1 to 5 *m* (table 7). Our calculated values fall between those recommended by Holmes and Mesmer (1998a) and by Nasirzadeh and others (2005) at 298.15 and 323.15 K, for LiOH molalities ranging from 0.1 to 3 *m*. At higher temperatures, our calculated values are in very good agreement with those of Holmes and Mesmer (1998a). Significant discrepancies appear at 273.15 K throughout the entire molality range because Holmes and Mesmer (1998a) were interested in the behavior of alkali aqueous solutions at high temperatures. On the other hand, our calculations are in good agreement with the recommended experimental deliquescence relative humidity and osmotic coefficient in the saturated LiOH binary system at 298.15 K (table 6). Our model provides even better results than the reference model of Pitzer and Mayorga (1973), the results of which are also shown in the table.

In mixed systems, parameterization of LiOH may be applied under conditions where the ionic strength of the aqueous mixtures is far greater than the values found along the solubility limit of Li hydroxides in the binary Li-OH-H$_2$O system. For

Predicted mean activity coefficient ($\gamma_\pm$) of LiCl in binary solutions as a function of molality ($mol.kg^{-1}$) and temperature

Recommended values of:	T °C	$\gamma_\pm$ (LiCl)							
		0.1 $mol.kg^{-1}$	0.5 $mol.kg^{-1}$	1.0 $mol.kg^{-1}$	4.0 $mol.kg^{-1}$	6.0 $mol.kg^{-1}$	10.0 $mol.kg^{-1}$	14.0 $mol.kg^{-1}$	18.0 $mol.kg^{-1}$
Model 1 [1]	0	0.800	0.747	0.784	1.731	3.329	12.188	39.205	105.510
Model 2 [1]		0.780	0.714	0.751	1.657	3.128	11.925	42.656	88.062
Calc. [2]		0.800	0.758	0.792	1.636	3.117	12.51	41.4	87.94
Model 1 [1]	25	0.764	0.680	0.703	1.477	2.635	8.031	21.518	49.254
Model 2 [1]		0.774	0.704	0.734	1.495	2.653	8.709	25.614	46.805
Calc. [2]		0.794	0.741	0.782	1.501	2.697	9.333	25.94	49.14
Calc. [3]		0.790	0.739	0.774	1.510	2.72	9.40	26.2	
Calc. [4]		0.789	0.739	0.775	1.499	2.73	9.60	25.5	50.3
Calc. [5]		0.790	0.739	0.774	1.51	2.72	9.40	26.2	49.9
Calc. [6]			0.739	0.770	1.495	2.717			
Model 1 [1]	50	0.734	0.626	0.640	1.279	2.137	5.570	12.82	25.733
Model 2 [1]		0.767	0.692	0.714	1.349	2.263	6.506	16.195	26.736
Calc. [2]		0.783	0.722	0.746	1.357	2.308	6.973	16.68	28.81
Model 1 [1]	100	0.685	0.548	0.547	0.976	1.454	2.945	5.357	8.832
Model 2 [1]		0.745	0.657	0.661	1.078	1.632	3.726	7.128	10.116
Calc. [2]		0.756	0.676	0.681	1.088	1.665	3.889	7.155	10.52
Model 1 [1]	140	0.656	0.506	0.494	0.788	1.083	1.872	2.967	4.372
Model 2 [1]		0.721	0.618	0.608	0.879	1.235	2.399	3.924	5.115
Calc. [7]			0.626	0.616	0.889	1.273			
Model 1 [1]	170	0.638	0.483	0.463	0.667	0.864	1.353	1.977	2.727
Model 2 [1]		0.698	0.584	0.562	0.740	0.983	1.711	2.552	3.173
Calc. [7]			0.587	0.566	0.753	1.028			
Model 1 [1]	200	0.622	0.464	0.436	0.557	0.681	0.978	1.337	1.747
Model 2 [1]		0.671	0.544	0.511	0.609	0.765	1.204	1.667	1.998
Calc. [7]			0.544	0.511	0.619	0.802			

[1] Predictions of models No. 1 and No. 2 presented here (see table 2).
[2] Predictions of the model of Gibbard and Scatchard (1973).
[3] Recommended values of Robinson and Stokes (1949).
[4] Recommended values of Hamer and Wu (1972).
[5] Recommended values of Mikulin (1968).
[6] Predictions of the model of El Guendouzi and others (2001).
[7] Predictions of the model of Holmes and Mesmer (1981).

instance, this may occur in the ternary Li-Cl-OH-H₂O system, because of the high solubility of Li chlorides. The extended use of this parameterization is thought to be feasible only if it is stable, that is only if its behavior is relatively smooth and monotonous with respect to salinity. We therefore verified this for various temperatures ranging from 273.15 to 473.15 K (fig. 14).

Ternary LiCl-LiOH-H₂O and LiCl-HCl-H₂O Systems

Selection of experimental data.—Solution property data are rare for ternary systems. Only two sets are available at 273.15 and 323.15 K (Chernyh and others, 1987) for the LiCl-LiOH-H₂O ternary system (fig. 15A). At 323.15 K, experimental data show a very complex lithium solubility behavior at very high concentrations. These authors suggest that the existence of double salts, such as LiCl.3LiOH(cr) and LiCl.LiOH(cr), might control this solubility.

TABLE 6

Comparison of model calculations and experimental or recommended values for the activity properties in saturated (s) Lithium binary solutions at T = 298.15 K: Deliquescence Relative Humidity DRH (DRH = $a_w^s \times 100$); a_w^s, φ^s and γ^s, activity of water, osmotic and activity coefficients at saturation, respectively

Binary System	DRH, % (a_w^s x 100)			φ^s			γ^s		
	Exp. data	Calculated		Exp. data	Calculated		Recom's	Calculated	
		Reference models	This study[g]		Reference models	This study[g]		Reference models	This study[g]
LiCl-H₂O	11.05[a] 11.3[b] 11.30[c]	10.16[d] 10.12[e]	Model 1: 9.576 Model 2: 11.682	3.07[a]	3.184[d] 3.19[e]	Model 1: 3.265 Model 2: 2.956	≈ 62[a]	70.3[e] >> 100[f]	Model 1: 69.311 Model 2: 54.41
LiOH-H₂O	83.4[a]	84.8[f]	83.823	0.934[a]	0.848[f]	0.920	0.461[a]	0.42[f]	0.544

[a] Experimental data and recommendations of Mikulin (1968).
[b] DRH data at 294.75 K of Hedlin and Trofimenkoff (1965).
[c] Smoothed DRH data of Greenspan (1977).
[d] Data calculated using parameterization of Kim and Frederick (1988a).
[e] Data calculated using parameterization of Song and Yao (2001).
[f] Data calculated using parameterization of Pitzer and Mayorga (1973).
[g] Data calculated using chemical equilibrium models developed during this study using two different model parameterization approaches (see table 2).

Three sets of solubility data are also available for the LiCl-HCl-H₂O ternary system, at 273.15 (Engel, 1888; Chu and Zai, 1965), 293.15 (Li and others, 2000) and 298.15 K (Herz, 1912) and for relatively limited ranges of salinities (fig. 16). Data at 273.15 and 298.15 K come from the compilation of Zdanovskii and others (1973). Chu and Zai (1965) give the composition of the aqueous solution at the eutonic point at 273.15 K, where LiCl.H₂O(cr) and LiCl.2H₂O(cr) coexist: 8.253 *m* LiCl + 11.736 *m* HCl.

Despite the scarcity of experimental data, these two ternary systems must be considered so that the pH can be taken into account when dealing with natural or industrial Li-containing brines.

Model parameterization.—In order to be able to add Li to the existing Christov and Møller (2004a, 2004b) model, the ternary-specific interaction parameter θ for the (OH⁻,Cl⁻) couple must be the same as the one proposed by these authors. The description of the Li-OH-Cl-H₂O system therefore only requires fitting of the binary $\lambda_{OH\text{-}LiCl}$ and of the ternary $\psi_{Li\text{-}OH\text{-}Cl}$, and $\zeta_{Li\text{-}OH\text{-}LiCl}$ interaction parameters. The best results that could be obtained with the constraint on $\theta_{OH\text{-}Cl}$ were plotted (fig. 15A) and are, as expected, more satisfying at 273.15 K than at 323.15 K, with σ values of 0.101 and 0.122, respectively. At 323.15 K, the model was not able to reproduce the data points corresponding to the assumed LiCl.LiOH(cr)—solution equilibrium and are not included in the calculated standard deviation. On the other hand, the best results for salt-solution equilibrium in this composition domain were obtained with a hypothetical 3LiCl.LiOH(cr) double salt rather than with the LiCl.LiOH(cr) double salt as suggested by Chernyh and others (1987). At this stage, there is not enough information to settle the issue. The calculated solubility product of the double salt 3LiCl.LiOH(cr) is log K_{sp} = 17.95 at 323.15 K, for the dissolution reaction: 3LiCl.LiOH(cr) = 4 Li⁺(aq) + 3 Cl⁻(aq) + OH⁻(aq).

Specific interaction parameters were extrapolated up to 523.15 K so that solubility calculations could be done at least between 273.15 and 323.15 K. In particular, we can plot the behavior of the system at 298.15 K as suggested in figure 15B, where the composition of the solution is controlled mainly by LiOH.H₂O(cr) and LiCl.H₂O(cr) salts. Only a small domain could be controlled by LiOH(cr). The specific interaction
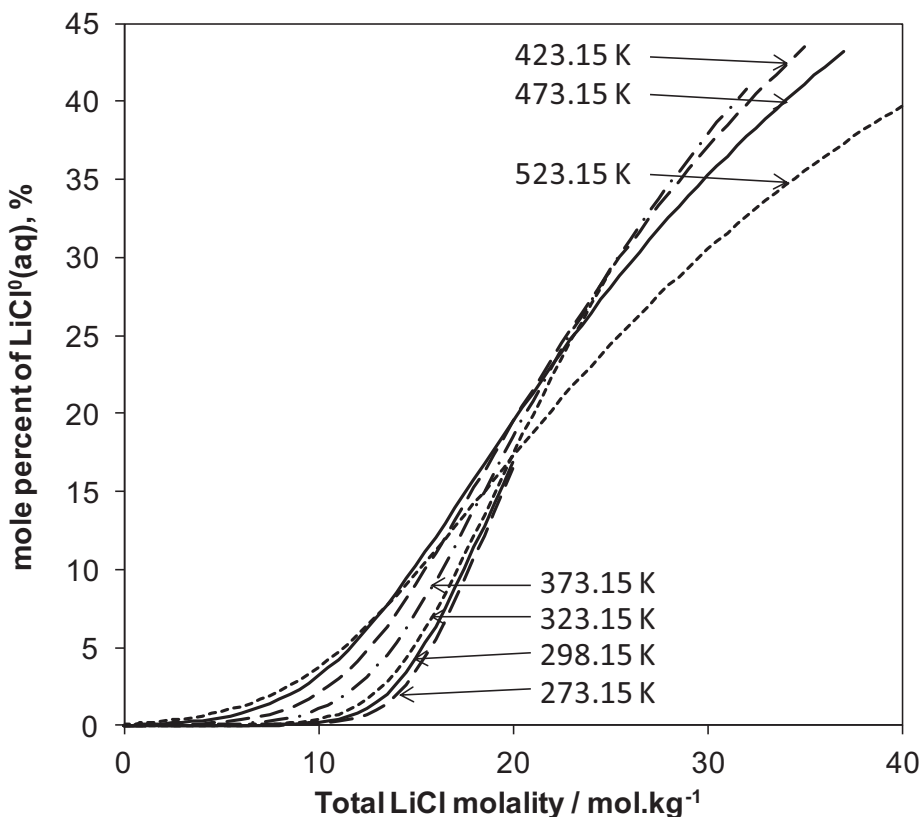
Fig. 7. Model 2 predictions for the distribution of ionic (Li^+, Cl^-) and neutral ($LiCl^0(aq)$) aqueous species in $LiCl$-H_2O solutions vs. total molality of solutions at different temperatures. Results are given as mole percent of $LiCl^0(aq)$, calculated as $100 \times m(LiCl^0(aq))/[m(LiCl(aq)) + m(LiCl^0(aq))]$, where $m(LiCl(aq)) = m(Li^+(aq)) = m(Cl^-(aq))$.

parameters (table 8) were plotted against temperature (fig. 17). $\psi_{Li\text{-}OH\text{-}Cl}$ is almost constant with temperature and has been extrapolated linearly to 523.15 K. On the other hand, $\lambda_{OH\text{-}LiCl}$ and $\zeta_{Li\text{-}OH\text{-}LiCl}$ are much more temperature-sensitive. They have been extrapolated here to 523.15 K assuming they are nil at this temperature.

Description of the Li-H-Cl-H₂O system requires fitting of the $\theta_{Li\text{-}H}$, $\psi_{Li\text{-}H\text{-}Cl}$, and $\zeta_{H\text{-}Cl\text{-}LiCl}$ ternary interaction parameters. The $\zeta_{H\text{-}Cl\text{-}LiCl}$ parameter did not seem to be needed and was set at 0. The fitting of $\theta_{Li\text{-}H}$ and $\psi_{Li\text{-}H\text{-}Cl}$ leads to a good simulation of experimental data (fig. 16), with σ values of 0.039 at 273.15 K, 0.022 at 293.15 K, and 0.101 at 298.15 K. The high σ value at 298.15 K is due to the relative dispersion of the experimental data points. $\theta_{Li\text{-}H}$ and $\psi_{Li\text{-}H\text{-}Cl}$ vary only slightly with temperature and were extrapolated linearly up to about 400 K (fig. 18 and table 8), suggesting the plotted behavior of the LiCl(cr)-HCl solution equilibrium at 373.15 K (fig. 16).

Ternary LiCl-KCl-H₂O System

Selection of experimental data.—Few solution property data exist for the ternary LiCl-KCl-H₂O system. El Guendouzi and others (2003) provide osmotic coefficients, measured at 298.15 K with the hygroscopic method, for aqueous solutions with total Cl molalities ranging from 0.3 to 6 mol/kg and Li/K ratios of 1/2, 1/1, and 2/1 (fig. 19).
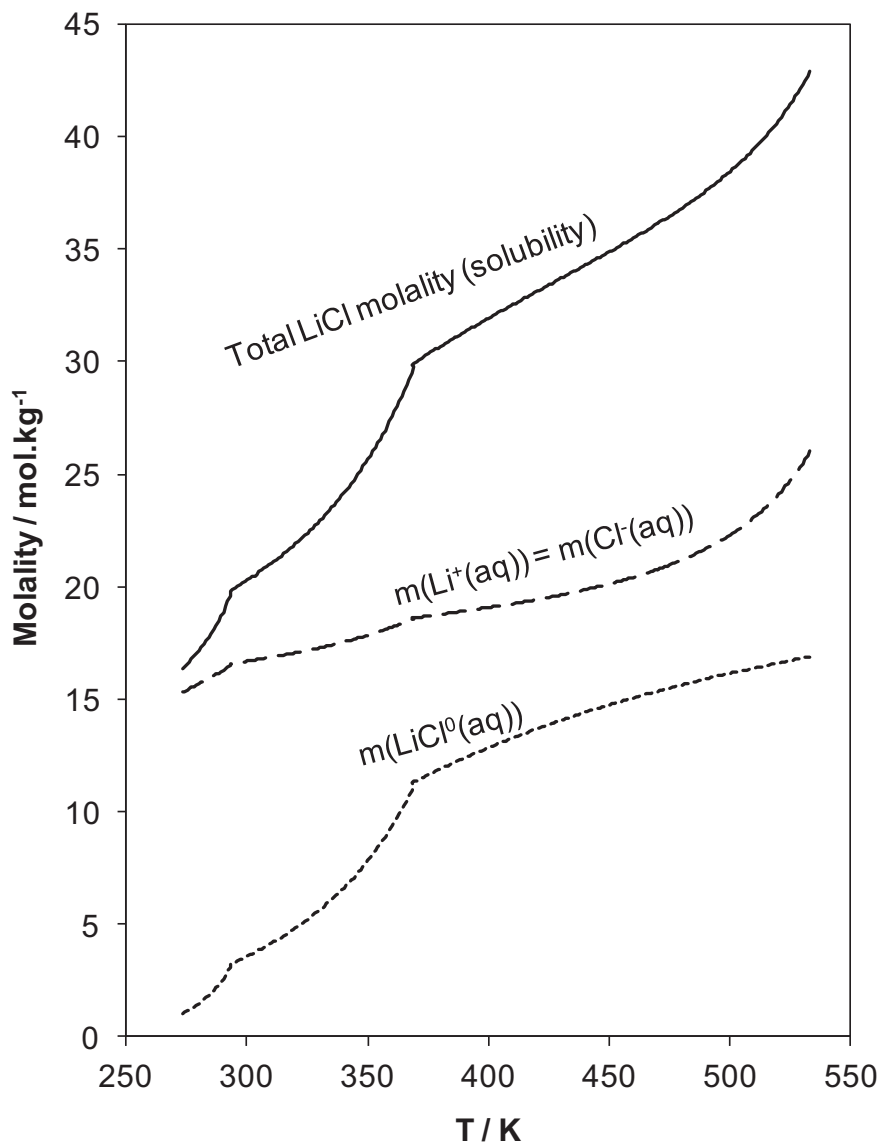
Fig. 8. Model 2 predictions for the contribution of ionic (Li$^+$ and Cl$^-$, with m(Li$^+$(aq)) = m(Cl$^-$(aq)): long-dashed line) and neutral (LiCl^0(aq): short-dashed line) aqueous species on the total molality (solid line) of saturated LiCl-H$_2$O solutions (273.15 to 523.15 K).

More abundant information exists concerning solubility measurements between 273.15 and 373.15 K (Campbell and Kartzmark, 1956; Plyushchev and others, 1959; Akopov, 1962; Yanko and Goldanel, 1964, in Zdanovskii and others, 1973). These solubility data were plotted to show the phase diagram at low temperatures (at 273.15 and 283.15 K), involving the LiCl.2H$_2$O(cr) and KCl(cr) (sylvite) mineral phases (fig. 20A), the phase diagram involving the LiCl.H$_2$O(cr) and KCl(cr) mineral phases for temperatures ranging from 298.15 to 348.15 K (fig. 20B), and the phase diagram at 373.15 K involving the LiCl(cr) and KCl(cr) mineral phases (fig. 20C). These data show that
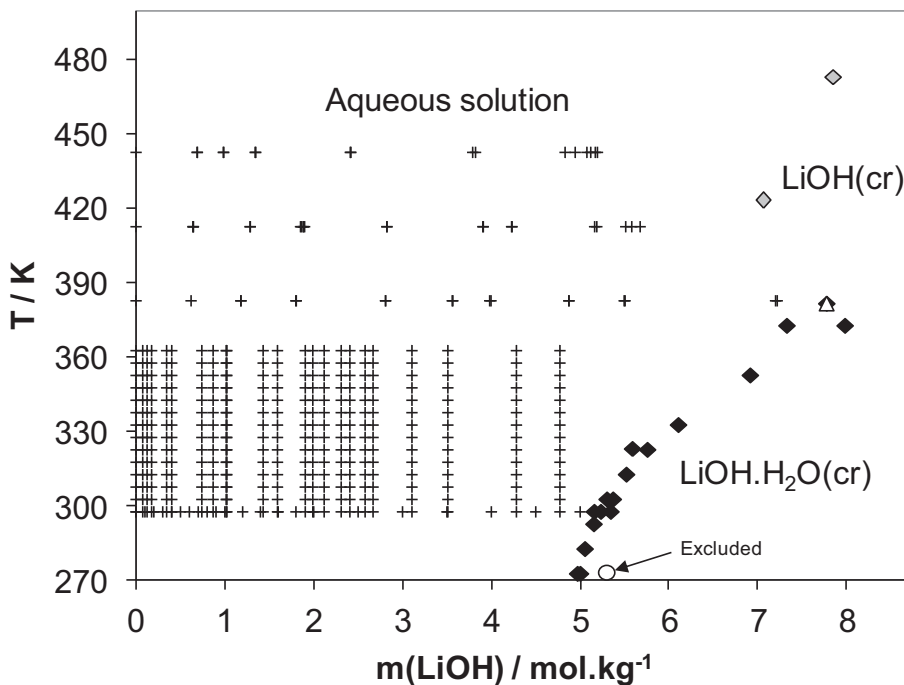
Fig. 9. Experimental aqueous (osmotic coefficient, φ) and solubility data used for the LiOH-H₂O binary system, as a function of temperature. Crosses represent aqueous data: from Nasirzadeh and others (2005) for 298.15 to 365.15 K; from Mikulin (1968) at 298.15 K; from Holmes and Mesmer (1998a) for 383.25 to 443.09 K. Black diamonds represent solubility data of LiOH(cr) and LiOH.H₂O(cr) from compilations of Linke (1965), Zdanovskii and others (1973), from 273.15 to 373.15 K. Triangles represent phase transition (382.05 K: LiOH.H₂O(cr) to LiOH(cr)) point of Kirgintsev and others (1972). Gray diamonds represent high temperature (423.15 K and 473.15 K) LiOH(cr) solubility given by Itkina and others (1967). Circles represent LiOH.H₂O(cr) solubility at 273.15 K (Zdanovskii and others, 1973) (not included in parameterization).

pure phases control the dissolved species concentrations (no double salt). For each temperature, we can identify an invariant point that defines the coexistence of a pure Li-bearing chloride with a pure K-bearing chloride (for example sylvite). However, two sets of data, at 303.15 and 313.15 K (Blidin, 1953) are inconsistent with such behavior and are therefore not used for parameterization. Four other data points (at 273.15, 283.15, 298.15, and 323.15 *K)* are also removed because of inconsistency with the rest of the dataset.

Experimental solubility data show that regardless of the temperature, increasing the LiCl content in a KCl aqueous solution decreases the solubility of sylvite down to a minimum, which decreases as the temperature decreases. Thereafter, a further increase in the dissolved LiCl content destabilizes sylvite once again. Conversely, an increase in the KCl content in a LiCl aqueous solution does not significantly modify or only slightly increases the solubility of the LiCl.nH₂O salts (n = 0, 1, or 2 depending on the temperature).

Model parameterization.—After the parameters for the LiCl-H₂O and KCl-H₂O binary systems have been determined, the ternary interaction parameters (namely, λ_{K-LiCl}, $\zeta_{K-Cl-LiCl}$, θ_{Li-K} and $\psi_{Li-K-Cl}$) for the LiCl-KCl-H₂O system can be fitted. The θ_{Li-K} interaction parameter is common to the two ternary systems of interest involving K (namely LiCl-KCl-H₂O and LiOH-KOH-H₂O). We preferred fitting it from the LiCl-KCl-
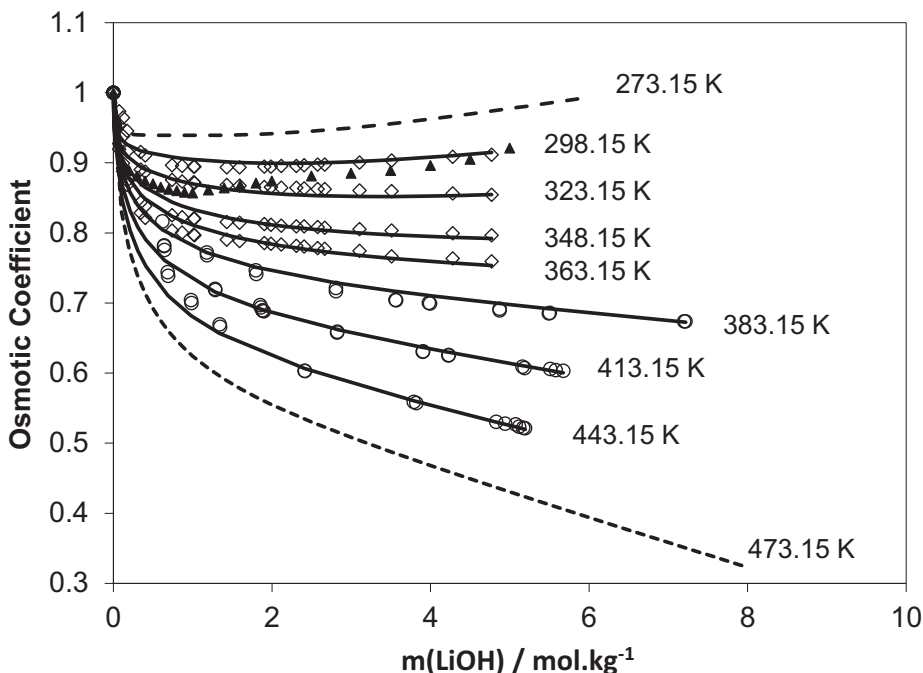
Fig. 10. The calculated (lines) and experimental (symbols) osmotic coefficients (φ) of LiOH-H$_2$O vs. molality *m* of LiOH, at various temperatures. Closed triangles represent the smoothed data of Mikulin (1968) at 298.15 K; open diamonds are data from Nasirzadeh and others (2005), at 298.15, 323.15, 348.15, and 363.15 K; open circles are data from Holmes and Mesmer (1998a) at 383.15, 413.15 and 443.15 K. The dashed lines show extrapolations of the model to lower (273.15 K) and higher (473.15 K) temperatures.

H$_2$O system, for which data are more abundant. Interaction parameters resulting from the fitting procedure (table 8) were plotted (fig. 21). As experimental solubility data are limited to temperatures below 373.15 K, a particular effort was made to obtain smooth functions with respect to temperature in order to be able to extrapolate above 373.15 K with relative confidence. The solubility product of sylvite is taken from Greenberg and Møller (1989), but the parameters have been adjusted (table 3) in order to be consistent with equation (6).

The hygroscopic data for activity of water measured by El Guendouzi and others (2003) provided useful additional constraints at 298.15 K and moderate salinity in the mixed solution (fig. 19). Both the overall σ value (table 1) and the results for mineral solubility (fig. 20) indicate that calculated solubility is in good agreement with experimental data. The position of the LiCl.2H$_2$O(cr)-KCl(cr) and LiCl.H$_2$O(cr)-KCl(cr) invariant points, in particular, are correctly predicted (figs. 20A and 20B). At 373.15 K, however, there is a significant discrepancy between the predicted and the experimental LiCl(cr)-KCl(cr) invariant point (fig. 20C). Indeed, the calculated molality of dissolved KCl at this point is 4.96 mol/kg, whereas the measured value is 4.52 mol/kg. On the other hand, the calculated molality of dissolved LiCl is 31.40 mol/kg for a measured value of 31.49 mol/kg.

The discrepancy obtained for the KCl concentration at the invariant point at 373.15 K is due to the fact that the interaction parameters for the binary KCl-H$_2$O system are taken from Greenberg and Møller (1989), who fitted the relevant specific interaction parameters using the isopiestic experimental data from Holmes and others
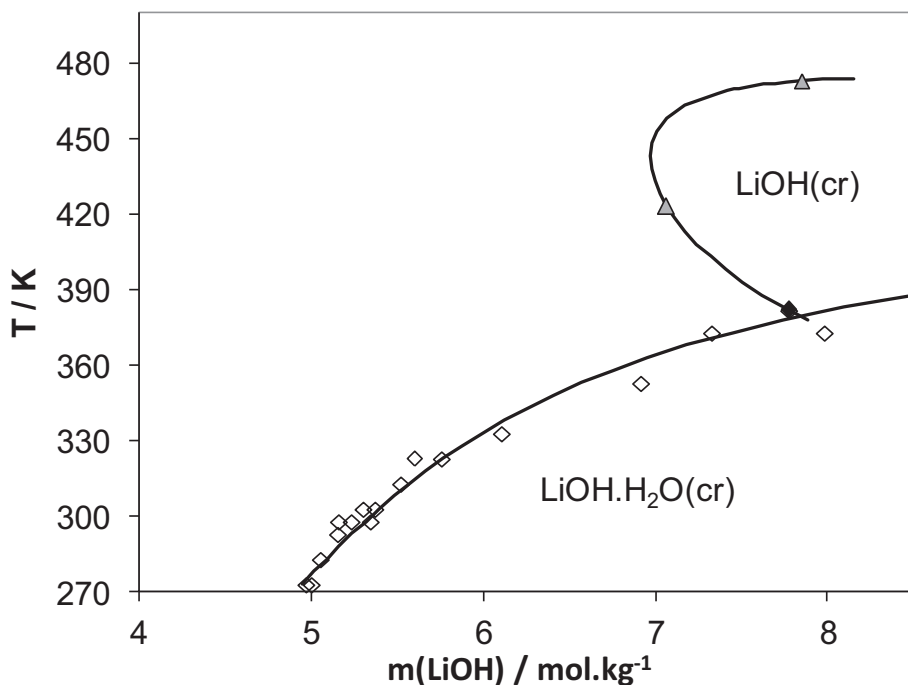
Fig. 11. Experimental (symbols) and calculated (solid lines) solubility of LiOH(cr) and LiOH.H₂O(cr) minerals vs. temperature in the LiOH-H₂O binary system. Experimental data—see figure 9 caption.

(1978) and Holmes and Mesmer (1983). In these studies, KCl molalities were comprised between 0.005 and 8.5 mol/kg, that is up to saturation for sylvite at high temperature. Greenberg and Møller (1989) showed that their model is valid up to a KCl molality of 11 mol/kg at 473.15 K. However, the ionic strength at the LiCl(cr)-KCl(cr) invariant point reaches 23.0 eq/kg at 373.15 K, which is much higher than the validated domain of application of the Greenberg and Møller (1989) model. Our results show, however, that the parameterization of these authors for the KCl-H₂O binary system is stable enough so that its use can be reasonably extended to highly saline ternary systems.

Ternary LiCl-NaCl-H₂O System

Selection of experimental data.—Similar to the LiCl-KCl-H₂O system, few solution property data exist for the ternary LiCl-NaCl-H₂O system. Osmotic coefficients were measured by El Guendouzi and others (2004) using the hygroscopic method, at 298.15 K with total Cl molalities in experimental aqueous solutions ranging between 0.3 and 6 mol/kg for Li/K ratios of 1/2, 1/1, and 2/1 (fig. 22). Solubility measurements describing mixtures of LiCl and NaCl electrolytes from 0 to 100 percent for temperatures between 273.15 and 373.15 K were compiled by Zdanovskii and others (1973). For our parameterizations we selected experimental data from Akopov (1963) at 273.15 K, and from Khy (1960) at 298.15, 323.15, 363.15, and 373.15 K (fig. 23). The selected data show that pure phases control the concentrations of dissolved species (no double salt). For each temperature, we can identify an invariant point that defines the coexistence of a pure Li-bearing chloride with a pure Na-bearing chloride (namely,
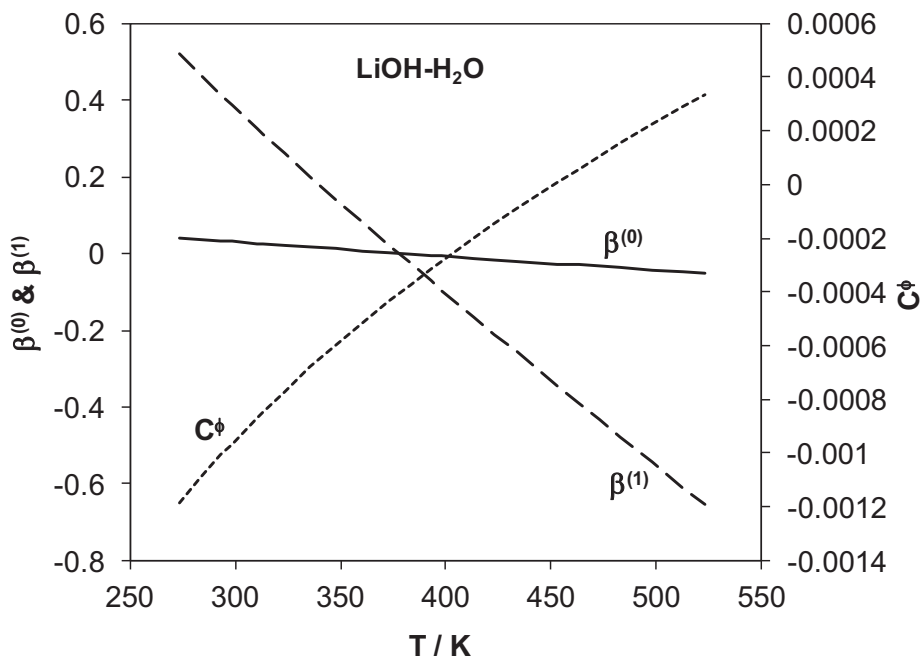
Fig. 12. Estimated $\beta^{(0)}(Li^+, OH^-)$ (solid line), $\beta^{(1)}(Li^+, OH^-)$ (long-dashed line), and $C^\varphi(Li^+, OH^-)$ (short-dashed line) pure electrolyte parameters for the LiOH-H$_2$O binary system from 273.15 to 523.15 K.

halite, NaCl). However, several sets of data, at 298.15, 313.15, 323.15, and 363.15 K (Smits and others, 1924; Blidin, 1953; Kindyakov and others, 1958) are inconsistent with such a behavior and are therefore not used for parameterization. One data point (from Khy, 1960, at 323.15 K) was not used because of inconsistency with the rest of the dataset.

As in the LiCl-KCl-H$_2$O system, experimental solubility data show that regardless of the temperature, increasing the LiCl content in a NaCl aqueous solution decreases halite solubility. The difference here is that the minimum solubility of halite (<0.4 *m* NaCl at 373.15 K) is much lower than that of sylvite (>1.5 *m* KCl at 373.15 K). Moreover, a further increase in the dissolved LiCl content does not further destabilize halite, or only very slightly. An increase in the NaCl content in a LiCl aqueous solution does not modify the solubility of the LiCl.*n*H$_2$O(cr) salts (*n* = 0, 1, or 2 depending on the temperature) until the invariant point is reached.

Model parameterization.—The ternary interaction parameters to be determined here are $\lambda_{Na\text{-}LiCl}$, $\zeta_{Na\text{-}Cl\text{-}LiCl}$, $\theta_{Li\text{-}Na}$ and $\psi_{Li\text{-}Na\text{-}Cl}$. The $\theta_{Li\text{-}Na}$ interaction parameter is common to the two ternary systems, LiCl-NaCl-H$_2$O and LiOH-NaOH-H$_2$O. We preferred fitting it from the LiCl-NaCl-H$_2$O system for which data are more abundant. Interaction parameters resulting from the fitting procedure (table 8) were plotted (fig. 24). As experimental solubility data are limited up to a temperature of 373.15 K, an effort was made to obtain smooth functions with respect to temperature to enable extrapolation above 373.15 K with relative confidence. In particular, $\lambda_{Na\text{-}LiCl}$ and $\psi_{Li\text{-}Na\text{-}Cl}$ vary linearly with temperature. The solubility product of halite (table 3) is taken from Thermoddem (Blanc and others, 2012) after the standard enthalpy and entropy suggested by Chase (1998) and the heat capacity given by Helgeson and others (1978).
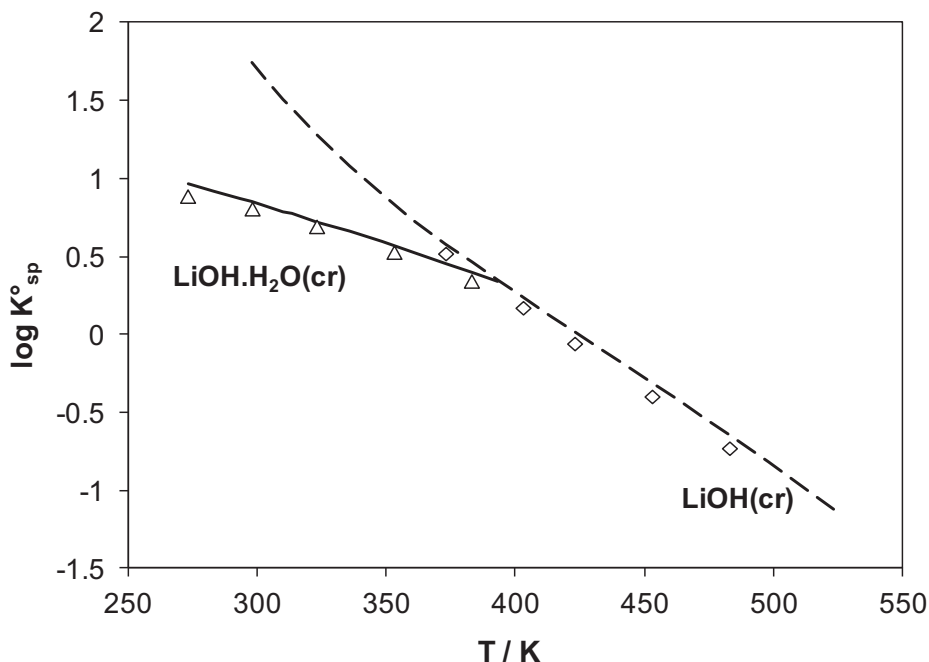
Fig. 13. Comparison of the thermodynamic solubility product (as log K^o_{sp}) of lithium hydroxide solids determined for LiOH.H₂O(cr) (solid line) and LiOH(cr) (dashed line) with recommended values (symbols) from 273.15 to 523.15 K. Triangles and diamonds represent log K^o_{sp} recommendations of Monnin and Dubois (2005) for LiOH.H₂O(cr) and LiOH(cr), respectively.

Results for osmotic coefficients and minerals solubility were plotted (figs. 22 and 23). Both the overall σ value (table 1) and figure 23 show that calculated solubility is in good agreement with experimental data. In particular, the position of the LiCl.2H₂O(cr)-NaCl(cr), LiCl.H₂O(cr)-NaCl(cr) and LiCl(cr)-NaCl(cr) invariant points are correctly predicted (fig. 23B). For temperatures above 273.15 K and LiCl concentrations below 12 M, the accuracy of our model is comparable to that of the recent Pitzer model of Dubois and others (2010). Nevertheless, thanks to the use of the LiCl⁰(aq) aqueous species, our model is stable enough to allow the description of the behavior of the ternary LiCl-NaCl-H₂O system beyond the limit of 12 M LiCl, up to the solubility of the different crystal hydrates of lithium chloride.

Quaternary LiCl-NaCl-KCl-H₂O System

Yanatieva (1947) and Campbell and Kartzmark (1956) measured the composition of brines in the Li-Na-K-Cl-H₂O system along the halite-sylvite equilibrium line up to the invariant point, corresponding to the additional equilibrium with LiCl.nH₂O(cr), where $n = 2$ at T = 273.15 K and $n = 1$ at T = 298.15 and 323.15 K. For each of these experimentally measured compositions, we calculated the saturation indices of the observed salts. They are plotted on figure 25 as a function of the dissolved Li content relative to the total aqueous Cl content (Li/Cl = 1 represents the binary Li-Cl-H₂O system; Li/Cl = 0 represents the ternary Na-K-Cl-H₂O system). These quantities, which are widely used in geochemical modeling, are convenient for evaluating the gap between the actual state of the system (aqueous solution + mineral) and the theoretical thermodynamic equilibrium since they are defined on an energy basis rather than

Predicted mean activity coefficient ($\gamma_\pm$) of LiOH in binary solutions as a function of molality (mol.kg^{-1}) and temperature

Recommended values of:	t°C	$\gamma_\pm$ (LiOH)						
		0.1 mol.kg^{-1}	0.5 mol.kg^{-1}	1.0 mol.kg^{-1}	2.0 mol.kg^{-1}	3.0 mol.kg^{-1}	4.0 mol.kg^{-1}	5.0 mol.kg^{-1}
This study[1]	0	0.804	0.727	0.697	0.670	0.661	0.661	0.666
Calc. [2]		0.757	0.612	0.551	0.503	0.487	0.487	0.497
This study[1]	25	0.781	0.675	0.629	0.584	0.562	0.551	0.545
Calc. [2]		0.766	0.607	0.548	0.502	0.485	0.481	0.484
Calc. [3]		0.946		0.749	0.697	0.671		
Calc. [4]		0.76	0.617	0.554	0.513	0.494	0.481	
Calc.[5]		0.735	0.579	0.522	0.484	0.469	0.457	0.493
Calc. [6]		0.718	0.583	0.523	0.485	0.467	0.454	0.456
This study[1]	50	0.757	0.625	0.566	0.507	0.476	0.457	0.443
Calc. [2]		0.738	0.586	0.521	0.466	0.440	0.426	0.417
Calc. [3]		0.894		0.675	0.613	0.575		
This study[1]	100	0.705	0.528	0.449	0.374	0.333	0.305	0.285
Calc. [2]		0.705	0.527	0.446	0.370	0.328	0.301	0.280
This study[1]	200	0.585	0.349	0.257	0.181	0.143	0.118	0.101
Calc. [2]		0.607	0.384	0.289	0.203	0.159	0.133	0.115
This study[1]	250	0.514	0.265	0.179	0.113	0.083	0.065	0.053
Calc. [2]		0.534	0.301	0.211	0.1357	0.101	0.081	0.069

[1] Predictions of the model presented here.
[2] Predictions of the model of Holmes and Mesmer (1998a).
[3] Recommended values of the model of Nasirzadeh and others (2005) at (0.124, 1.01, 1.99, and 3.106) m.
[4] Recommended values of Robinson and Stokes (1949).
[5] Recommended values of Hamer and Wu (1972).
[6] Recommended values of Mikulin (1968).

on a concentration basis. Indeed, given the dissolution reaction of a mineral, the saturation index of the mineral is defined, in log units, by the ratio of the ion activity product versus the solubility product. The ion activity product represents the actual state of the aqueous solution while the solubility product is the expected value of the ion activity product at equilibrium. Moreover saturation indices can help identify the chemical sub-system(s) for which the model should be improved. Null saturation indices indicate that the aqueous solution and the mineral under consideration are at thermodynamic equilibrium. The saturation indices show that, in agreement with experimental observations, halite and sylvite are close to equilibrium with the brines (fig. 25). However, there are significant discrepancies for some compositions. This concerns mostly halite near or at the invariant point, regardless of the temperature. It is difficult here to clearly identify whether these discrepancies are caused by experimental errors or are inherent to the model but, in any case, these results are satisfactory and confirm that our model can be applied to complex systems.

Ternary LiOH-KOH-H$_2$O System

Selection of experimental data.—Literature data for this ternary system, in the temperature and concentration ranges of interest, are scarcer than for the LiCl-KCl-H$_2$O system. They are limited to solubility data measured at 323.15, 373.15, and 423.15 K (Itkina and others, 1967, 1968), and describe mixtures of LiOH and KOH electrolytes ranging from 0 to 100 percent (figs. 26A and 26B). These experimental
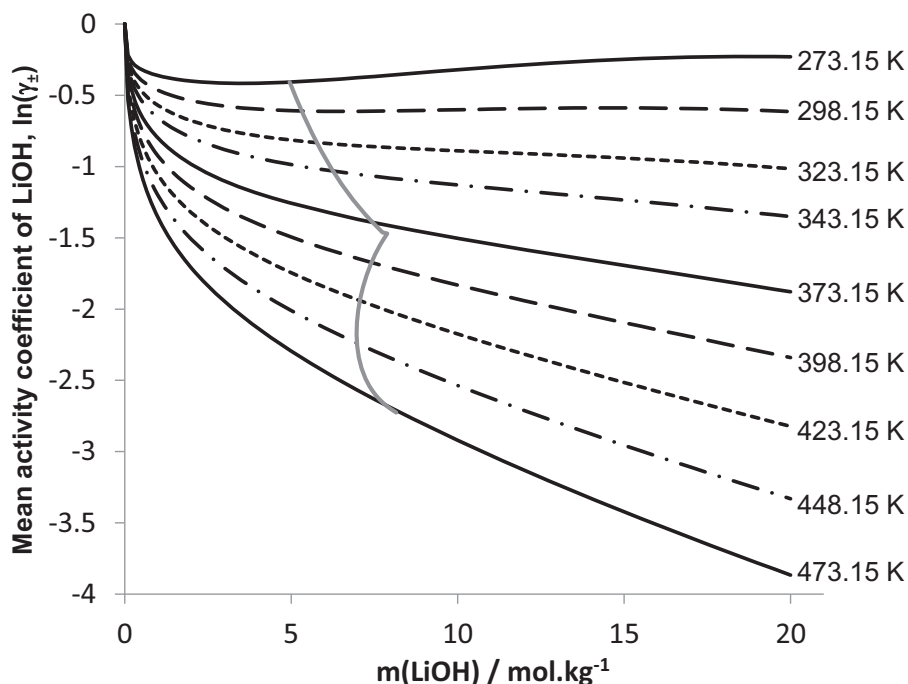
Fig. 14. Calculated mean LiOH activity coefficients in LiOH-H$_2$O solutions vs. molality, from 273.15 to 473.15 K. The gray solid line represents the solubility of LiOH.nH$_2$O (n = 0 or 1) solids (see fig. 11).

data suggest that pure phases control the dissolved species concentrations, and invariant points can be identified, defining conditions of coexistence of two pure phases at equilibrium with the aqueous solution. It also seems that there is no stability domain for mixed crystals or double salts in the systems under consideration in this study.

Model parameterization.—To describe the behavior of the mixed LiOH-KOH-H$_2$O system, the θ_{Li-K} and $\psi_{Li-K-OH}$ specific interaction parameters are required, in addition to parameters and solubility products determined for the binary LiOH-H$_2$O and KOH-H$_2$O systems. The θ_{Li-K} cation-cation interaction parameter was fitted previously for the LiCl-KCl-H$_2$O mixed system (see *Ternary LiCl-KCl-H$_2$O System* section above). Therefore, there is only one temperature-dependent parameter to be fitted in this section: $\psi_{Li-K-OH}$. The equilibrium constant of the KOH.H$_2$O(cr) mineral phase is also needed here and is adapted from Christov and Møller (2004b).

Resulting mineral-solution equilibrium functions compare relatively well with experimental data (figs. 26A and 26B). The overall absolute deviation is 0.0964 for 18 data. This indicates that the θ_{Li-K} parameter determined previously (see *Ternary LiCl-KCl-H$_2$O System* section above) is also well suited here. The temperature function for the $\psi_{Li-K-OH}$ interaction parameter (table 8) was plotted (fig. 27).

Significant discrepancies can however be observed concerning the location of the invariant points at 323.15 and 373.15 K (figs. 26A and 26B). At 323.15 K, the calculated LiOH(cr)-LiOH.H$_2$O(cr) invariant point is located at m(KOH) = 12.44 mol/kg and m(LiOH) = 1.49 mol/kg. For comparison, the experimental point is located at m(KOH) = 14.38 mol/kg and m(LiOH) = 0.98 mol/kg. The cal-
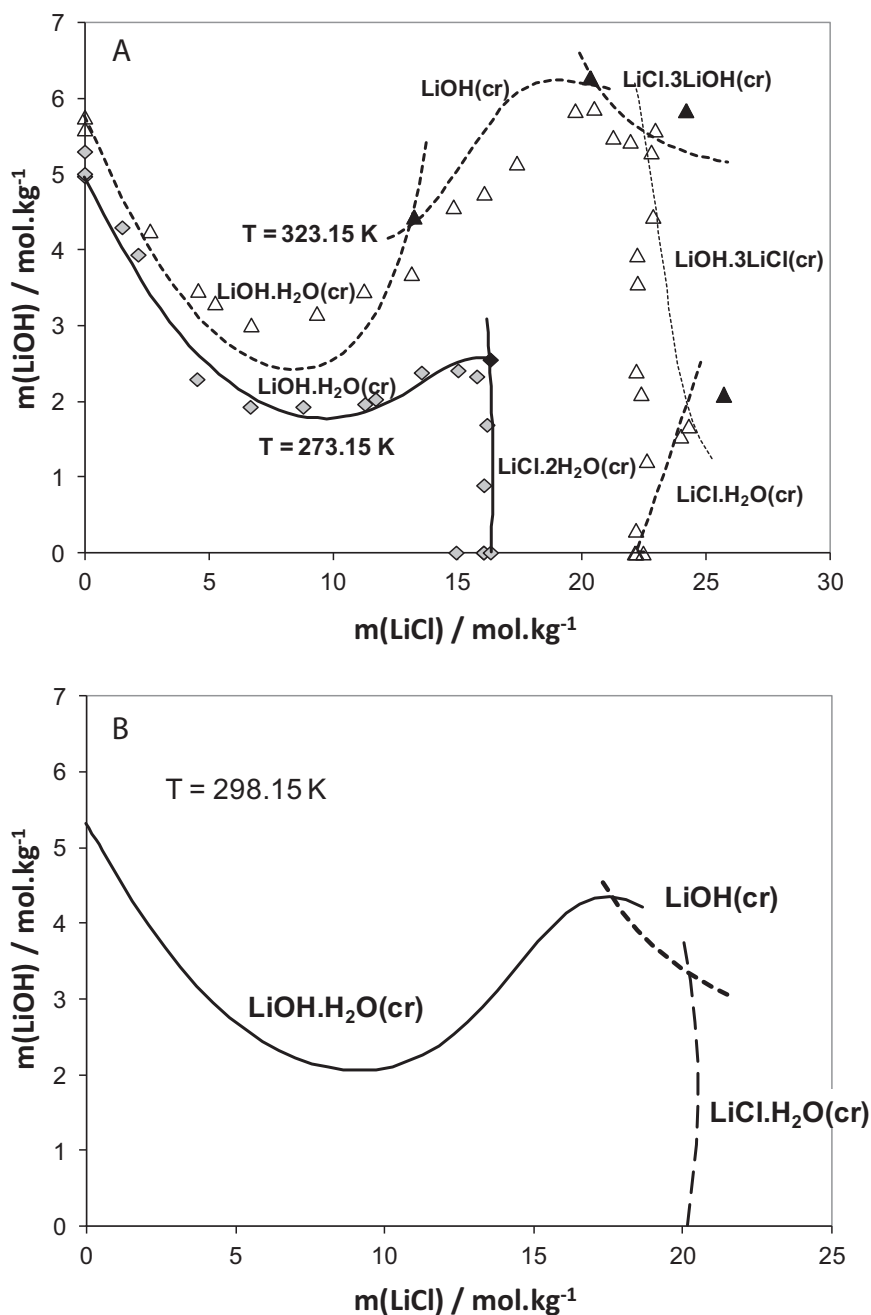
Fig. 15. Experimental (symbols) and calculated (solid lines) solubility data for the LiCl-LiOH-H$_2$O mixed system: (A) at 273.15 and 323.15 K; (B) model prediction at 298.15 K. On figure (A), diamonds are experimental data at 273.15 K and triangles are data at 323.15 K. Gray and black symbols are experimental invariant points. The solubility data are from Chernyh and others (1987). Experiments at 323.15 K show that a solid phase LiCl.LiOH(cr) precipitates from saturated mixed solutions, while the calculated stable phase diagram consists in a field of LiOH:3LiCl(cr) precipitation.
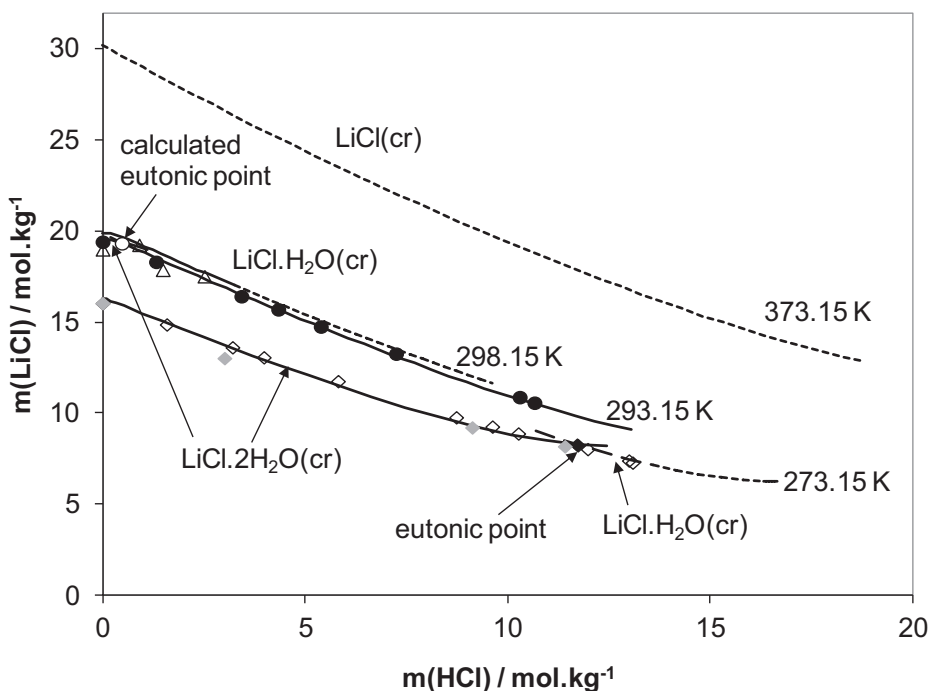
Fig. 16. Experimental (symbols) and calculated (lines) solubility of LiCl.2H₂O(cr) and LiCl.H₂O(cr) minerals at 273.15, 293.15 and 298.15 K in the LiCl-HCl-H₂O ternary system. Experimental data are from Chu and Zai (1965) (white diamonds) and Engel (1888) (gray diamonds) at 273.15 K; from Li and others (2000) (black circles) at 293.15 K; from Herz (1912) (white triangles) at 298.15 K. The experimental eutonic point at 273.15 K (Chu and Zai, 1965) is indicated by the black diamond. The calculated eutonic point at 293.15 K is indicated by the white circle. Calculated solubility is extrapolated up to 373.15 K for LiCl(cr).

culated LiOH(cr)-KOH.H₂O(cr) invariant point is located at m(KOH) = 25.9 mol/kg and m(LiOH) = 0.36 mol/kg, whereas the experimental equivalent is located at m(KOH) = 25.09 mol/kg and m(LiOH) = 0.70 mol/kg. At 373.15 K, the calculated LiOH(cr)-LiOH.H₂O(cr) invariant point is located at m(KOH) = 3.2 mol/kg and m(LiOH) = 5.23 mol/kg, whereas the experimental equivalent is located at m(KOH) = 4.42 mol/kg and m(LiOH) = 4.12 mol/kg. The calculated LiOH(cr)-KOH.H₂O(cr) invariant point is located at m(KOH) = 30.33 mol/kg and m(LiOH) = 0.47 mol/kg whereas the experimental equivalent is located at m(KOH) = 36.99 mol/kg and m(LiOH) = 1.39 mol/kg. As we did for the K⁺-Cl⁻ binary interactions parameters in the LiCl-KCl-H₂O mixed system, we determined the Li⁺-OH⁻ binary interaction parameters using experimental data of the binary LiOH-H₂O system up to the solubility of the related minerals, namely up to a maximum ionic strength of 8 eq/kg. The ionic strengths encountered in the LiOH-KOH-H₂O mixed system are much higher. Therefore, the Li⁺-OH⁻ binary interaction parameters may not be fully optimized to deal with the LiOH-KOH-H₂O mixed system. However, two reasons prevent us from trying to improve our parameterization. Firstly, the scarcity of experimental data would impose too few constraints on the fitting procedure, and secondly, interaction parameters for the KOH-H₂O binary system given by Christov and Møller (2004b) are validated for temperatures between 273.15 and 443.15 K based on experimental aqueous data up to a KOH molality of 5 mol/kg (Holmes and Mesmer, 1998a), and the solubility of the KOH.H₂O(cr) mineral phase up to 343.15 K.
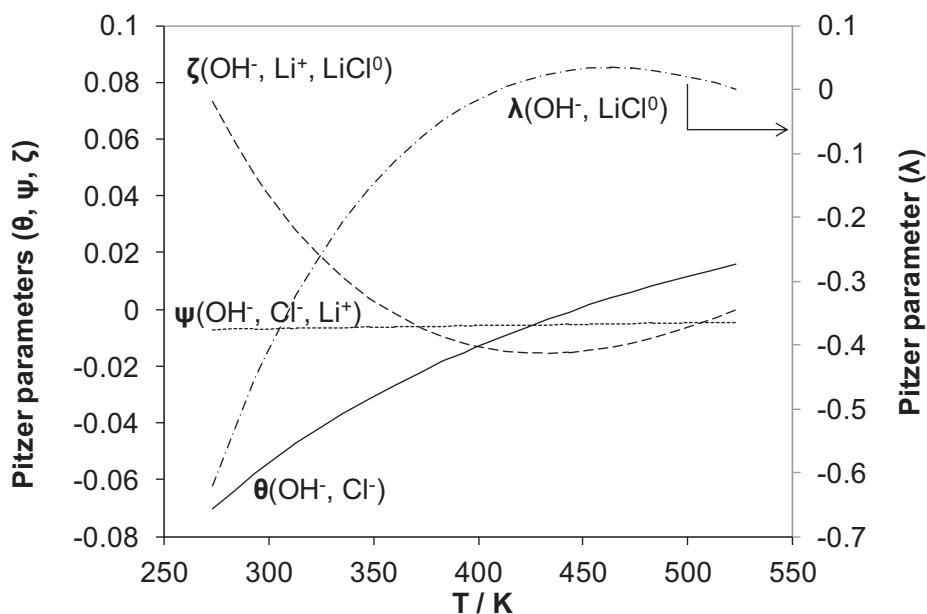
Fig. 17. The estimated ternary interaction parameters $\lambda(OH^-, LiCl^0)$ (dot-dashed line), $\psi(Li^+, OH^-, Cl^-)$ (short-dashed line) and $\zeta(Li^+, OH^-, LiCl^0)$ (long-dashed line) in the electrolytic aqueous mixture LiCl-LiOH-H_2O, from 273.15 to 473.15 K, and extrapolated up to 523.15 K. The ternary interaction parameter $\theta(OH^-, Cl^-)$ (solid line) is from Christov and Møller (2004b).
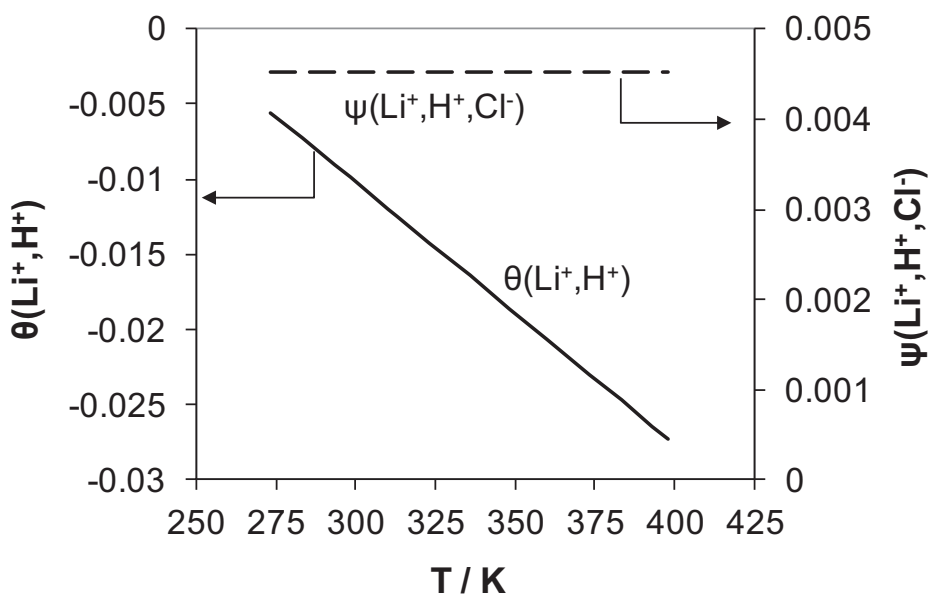

Fig. 18. The estimated ternary interaction parameters $\theta(Li^+, H^+)$ (solid line) and $\psi(Li^+, H^+, Cl^-)$ (long-dashed line) in the electrolytic aqueous mixture LiCl-HCl-H_2O, from 273.15 to 298.15 K, and extrapolated up to 373.15 K.

TABLE 8

Fitting constant values (eq 2) for the ternary solution interaction parameters[a]

Parameters	T range (°C) [a]	Constants [b,c] (T in degrees Kelvin)						
		$a_1(-)$	$a_2(T)\times10^3$	$a_3(T^2)\times10^6$	$a_5(1/T)$	$a_6(\ln(T))$	$a_7(1/(T-263))$	$a_8(1/(680-T))$
$\theta_{Li,K}$	0-150	-1.397383255	-1.08356	0.0172043	0	0.302809885	-0.085261601	0.714329411
$\theta_{Li,Na}$	0-150	-2.304375225	9.185919	-11.382562	195.8054794	0	0	0
$\theta_{Li,H}$	0-25	0.0419639	-0.174	0	0	0	0	0
$\psi_{Li,K,Cl}$	0-100	0.388539791	1.38012743	-1.3143039236	0	-0.1229797915	0.0280301705	0
$\psi_{Li,K,OH}$	0-150	-0.21771139	0.334108	0	32.32936105	0	0	0
$\psi_{Li,Na,Cl}$	0-100	-0.03575475	0.065000	0	0	0	0	0
$\psi_{Li,Na,OH}$	0-150	-0.03498363	0.0741667	0	0	0	0	0
$\psi_{Li,H,Cl}$	0-25	0.00453	0	0	0	0	0	0
$\psi_{Li,OH,Cl}$	0-50	-0.009968981	0.0106	0	0	0	0	0
$\lambda_{Li,LiCl}$	0-250	0	0	0	0	0	0	0
$\lambda_{K,LiCl}$	0-100	-2.879993582	-1.996147	0	0	0.590495613	0.016767927	0
$\lambda_{Na,LiCl}$	0-100	-0.112759482	0.0394693	0	0	0	0	0
$\lambda_{Cl,LiCl}$	0-250	0	0	0	0	0	0	0
$\lambda_{H,LiCl}$	0-250	0	0	0	0	0	0	0
$\lambda_{OH,LiCl}$	0-50	4.625549817	-4.956048	0	-1063.455752	0	0	0
$\zeta_{Li,Cl,LiCl}$	0-250	0	0	0	0	0	0	0
$\zeta_{Li,OH,LiCl}$	0-50	-0.847394851	0.963794	0	179.5378293	0	0	0
$\zeta_{H,Cl,LiCl}$	0-250	0	0	0	0	0	0	0
$\zeta_{K,Cl,LiCl}$	0-100	1.277846484	0.769448	0	0	-0.262633421	0.068191388	0
$\zeta_{Na,Cl,LiCl}$	0-100	0.257865049	-1.495326	2.22	0	0	0	0

[a] The temperature range listed for each parameter is the temperature range of the experimental data used in model parameterization and/or validation.
[b] The constant a_4 in equation (7) is zero for all of the above parameters.
[c] The ternary parameters have been estimated only for model 2 of the LiCl-H$_2$O binary system (that is when the LiCl⁰(aq) species is included).
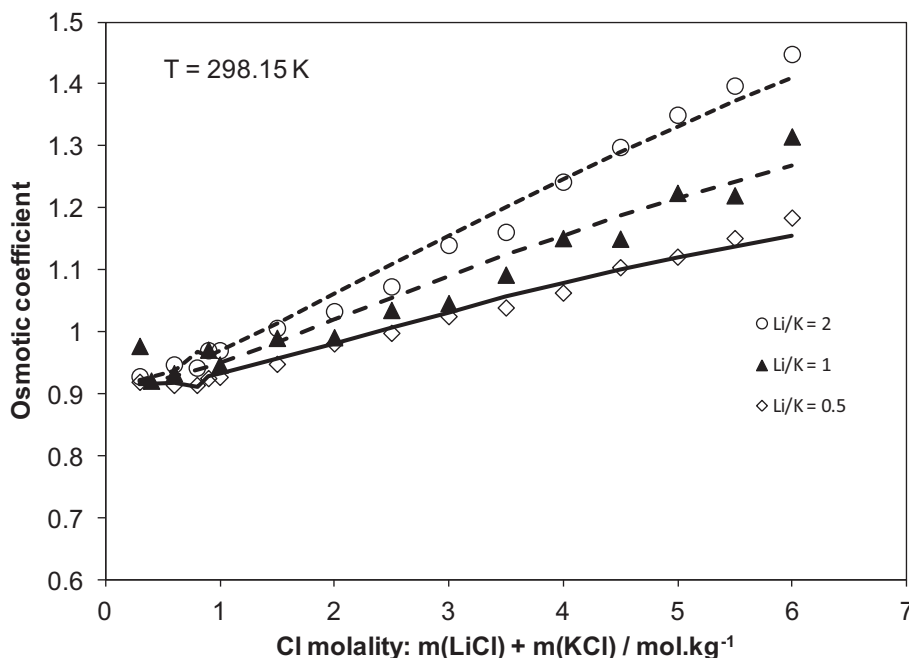
Fig. 19. Osmotic coefficient, φ, for the LiCl-KCl-H₂O ternary system vs. total molality (mLiCl + mKCl) at 298.15 K for three different Li/K ratios. Symbols represent experimental data from El Guendouzi and others (2003): Li/K = 0.5(white diamonds); Li/K = 1 (black triangles); Li/K = 2 (white circles). Lines represent calculated values for the same Li/K ratios: Li/K = 0.5 (solid line); Li/K = 1 (long-dashed line); Li/K = 2 (short-dashed line).

Revisiting the parameterization of this last binary chemical system is beyond the scope of our study.

Phase diagrams of the LiOH-KOH-H₂O system have, nevertheless, been extrapolated to 273.15, 298.15 and 473.15 K (fig. 26C). Results suggest that the two LiOH.H₂O(cr)-LiOH(cr) and LiOH(cr)-KOH(cr) invariant points may still exist at 298.15 K. At 273.15 K, the LiOH(cr) stability domain would no longer exist in favor of the LiOH.H₂O(cr) and KOH.H₂O(cr) minerals, the coexistence of which would define a new invariant point. At 473.15 K, calculations suggest that, in agreement with experimental observations (Itkina and others, 1967), only the LiOH(cr) mineral phase could be at equilibrium with the aqueous solution, at least up to a KOH molality of 25 mol/kg. This is also the case at 423.15 K (fig. 26B).

Ternary LiOH-NaOH-H₂O System

Selection of experimental data.—Literature data for this ternary system are much scarcer than for the other ternary systems considered here. They are exclusively solubility data that have been measured at 303.15 (Evteeva, 1965) and 423.15 K (Itkina and others, 1968) (figs. 28A and 28B). These experimental data suggest that pure phases control the concentrations of dissolved species in the range of concentrations where experimental data are available. Invariant points are not clearly defined, and it seems that there is no stability domain for mixed crystals or double salts. Additional experimental solubility data are also shown (figs. 28A and 28B) for the binary LiOH-H₂O (Linke, 1965) and NaOH-H₂O (see data selection of Christov and Møller, 2004b) systems.
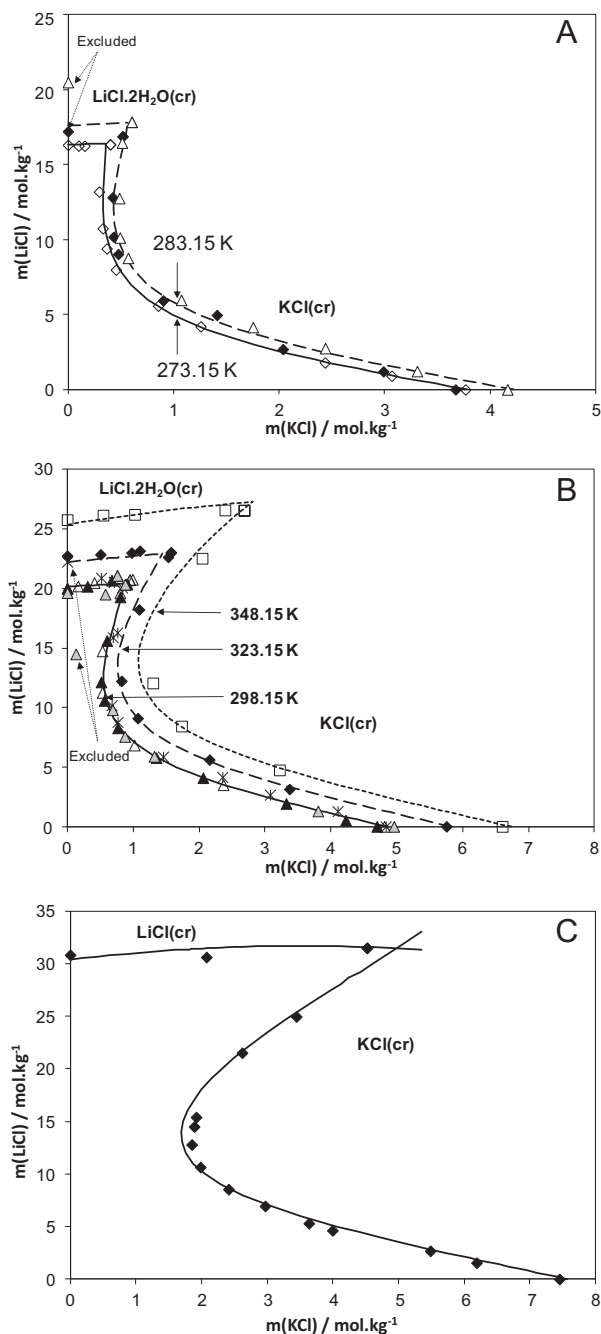
Fig. 20. Experimental (symbols) and calculated (lines) solubility data for the LiCl-KCl-H$_2$O mixed system: (A) at 273.15 and 283.15 K for LiCl.2H$_2$O(cr) and sylvite, (B) at 298.15, 323.15, and 348.15 K for LiCl.H$_2$O(cr) and sylvite, and (C) at 373.15 K for LiCl(cr) and sylvite. Experimental data are from the compilation of Zdanovskii and others (1973): on (A), from Plyushchev and others (1959) (white diamonds) and Akopov (1962) (black diamonds) at 273.15 K, and from Akopov (1962) (white triangles) at 283.15 K; on (B), from Campbell and Kartzmark (1956) (gray triangles), Zatloukal and others (1959) (white triangles), Akopov (1962) (stars), and Plyushchev and others (1959) (black triangles) at 298.15 K, and from Plyushchev and others (1959) at 323.15 K (black diamonds) and 348.15 K (white squares); on (C), data are from Yanko and Goldanel (1964).
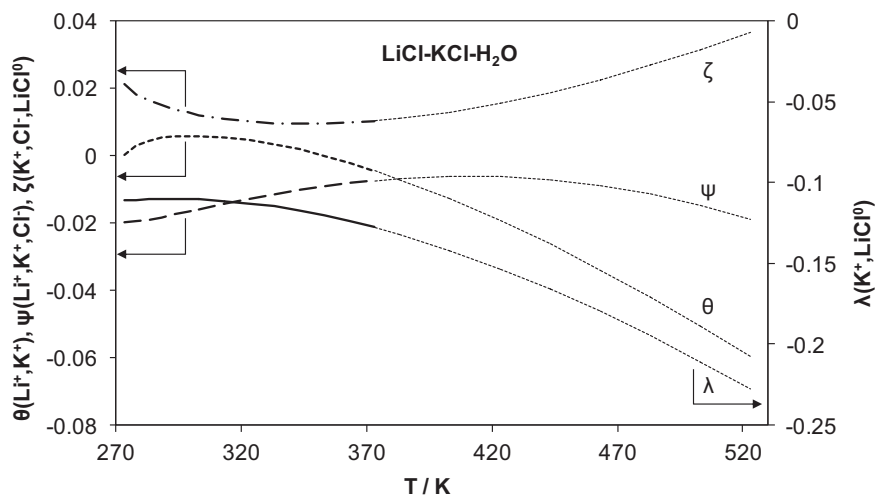
Fig. 21. Estimated ion-interaction $\theta(Li^+,K^+)$ (short-dashed line) and $\psi(Li^+,K^+,Cl^-)$ (long-dashed line) mixing parameters, and neutral specie-ion interaction $\lambda(K^+,LiCl^0)$ (solid line) and $\zeta(K^+,Cl^-,LiCl^0)$ (dot-dashed line) for the $LiCl$-KCl-H_2O system from 273.15 to 523.15 K. Smaller short-dashed lines represent temperature extrapolation of the mixed $LiCl$-KCl-H_2O model at T > 373.15 K.
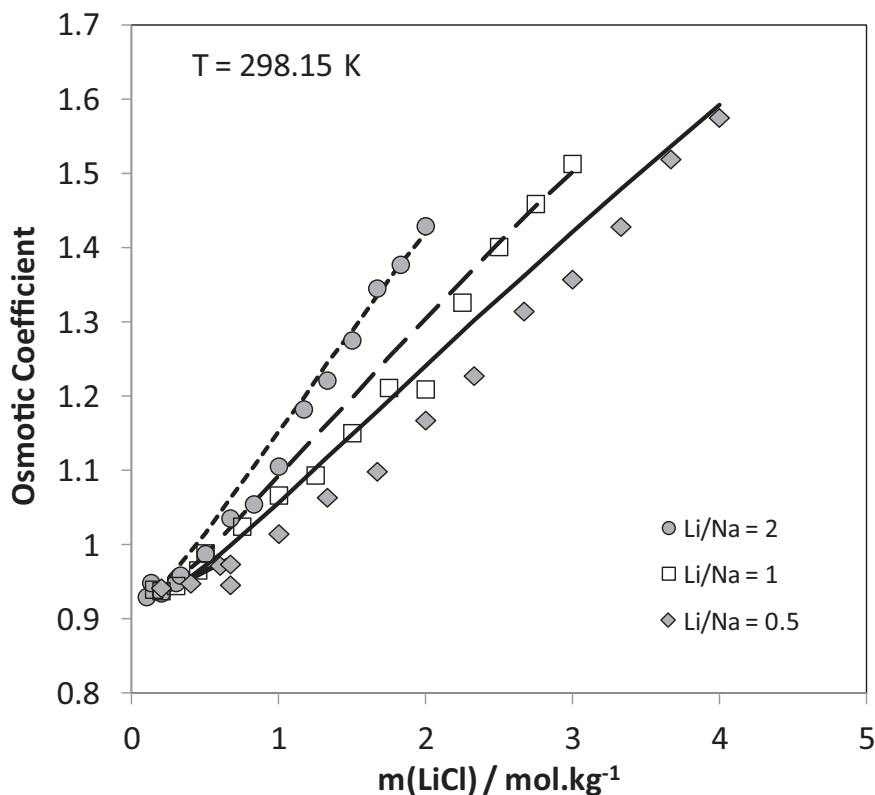
Fig. 22. Osmotic coefficient, φ, for the $LiCl$-$NaCl$-H_2O ternary system vs. $LiCl$ molality at 298.15 K for three different Li/Na ratios. Symbols represent experimental data from El Guendouzi and others (2004): closed gray diamonds, Li/Na = 0.5; open squares, Li/Na = 1; closed gray circles, Li/Na = 2. Lines represent calculated values for the same Li/Na ratios: solid line, Li/Na = 0.5; long-dashed line, Li/Na = 1; short-dashed line, Li/Na = 2.
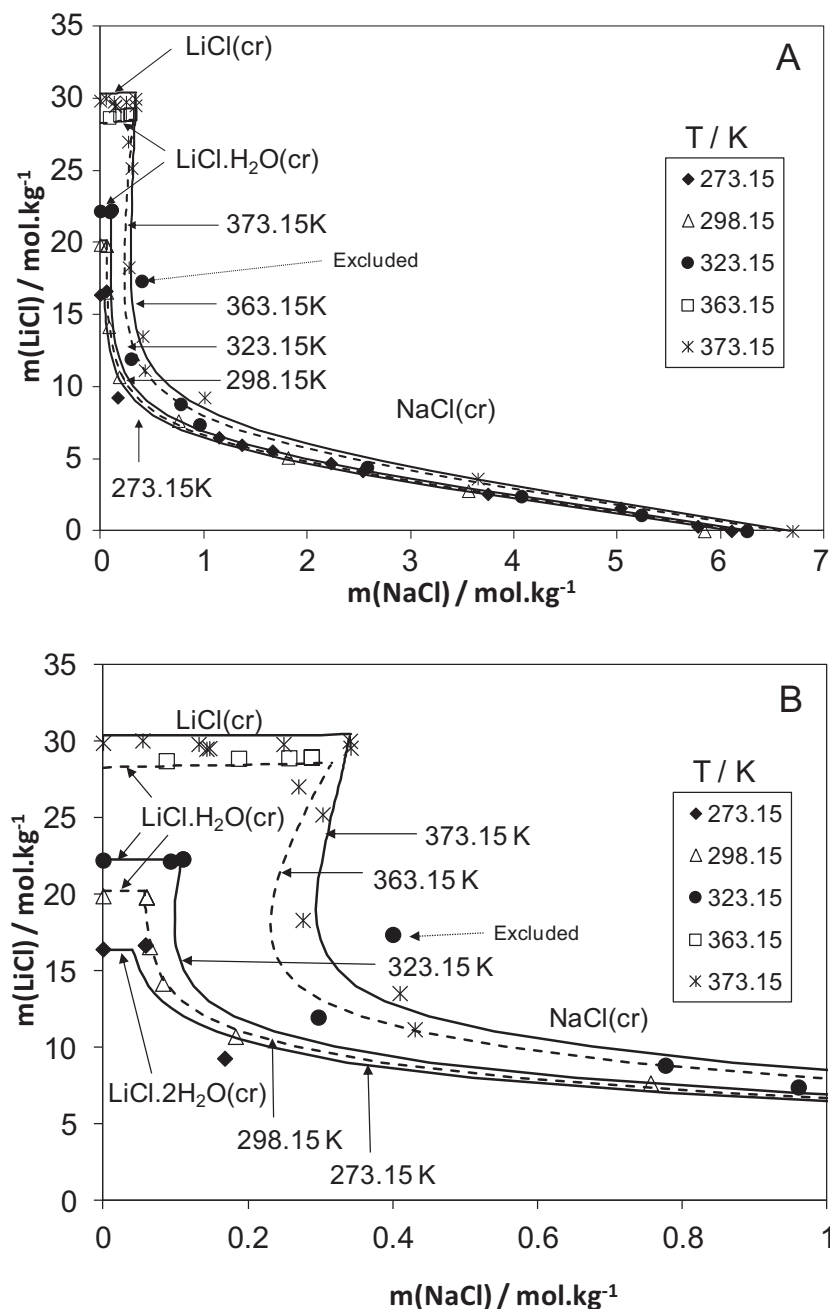
Fig. 23. Experimental (symbols) and calculated (lines) solubility data for the LiCl-NaCl-H$_2$O mixed system at 273.15 K for LiCl.2H$_2$O(cr) and halite; at 298.15, 323.15, and 363.15 K for LiCl.H$_2$O(cr) and halite; and at 373.15 K for LiCl(cr) and halite. (A) In the full range of dissolved NaCl molality; (B) detail in the 0 to 1 molal of dissolved NaCl. Experimental data (see the compilation of Zdanovskii and others, 1973) are from Akopov (1963) at 273.15 K, and from Khy (1960) at 298.15, 323.15, 363.15 and 373.15 K.
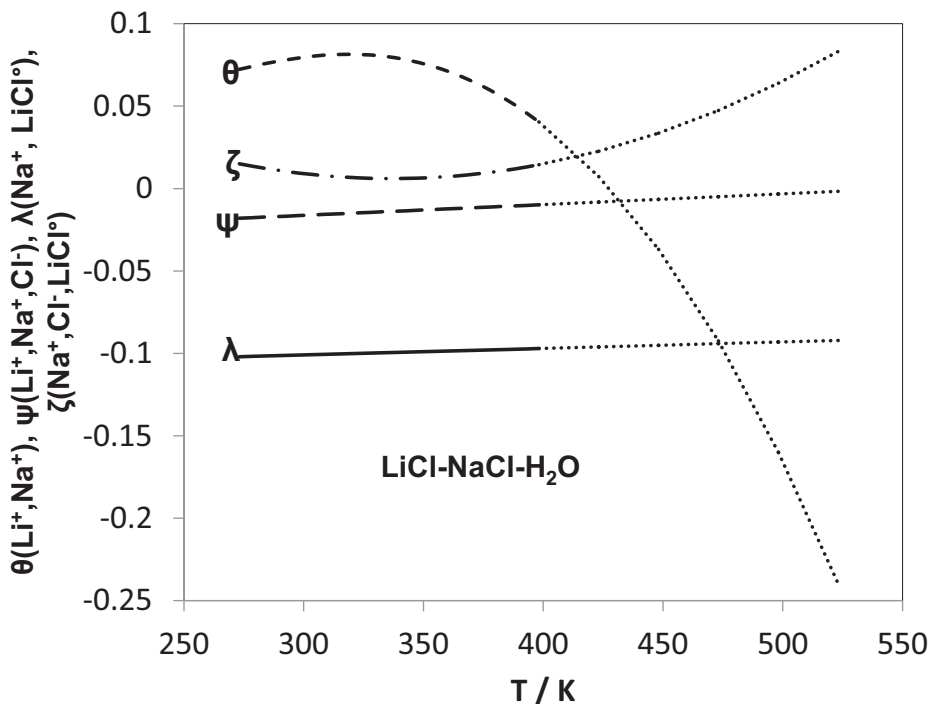
Fig. 24. Estimated ion-interaction θ(Li$^+$,Na$^+$) (short-dashed line) and ψ(Li$^+$,Na$^+$,Cl$^-$) (long-dashed line) mixing parameters, and neutral specie-ion interaction λ(Na$^+$,LiCl^0) (solid line) and ζ(Na$^+$,Cl$^-$,LiCl^0) (dot-dashed line) for LiCl-NaCl-H$_2$O from 273.15 to 523.15 K. Smaller short-dashed lines represent temperature extrapolation of the mixed LiCl-NaCl-H$_2$O model at T > 373.15 K.

Model parameterization.—To describe the behavior of the mixed LiOH-NaOH-H$_2$O system, the θ$_{Li-Na}$ and ψ$_{Li-Na-OH}$ specific interaction parameters are required in addition to the parameters and solubility products determined for the binary LiOH-H$_2$O and NaOH-H$_2$O systems. The θ$_{Li-Na}$ cation-cation interaction parameter was fitted for the LiCl-NaCl-H$_2$O mixed system (see the *Ternary LiCl-NaCl-H₂O System* section above). Therefore, there is only one temperature-dependent parameter to be fitted in this section: ψ$_{Li-Na-OH}$. The equilibrium constants of the NaOH.H$_2$O(cr) and NaOH.4H$_2$O(cr) mineral phases are also needed here. They are taken from Christov and Møller (2004b).

The resulting mineral-solution equilibrium functions (figs. 28A and 28B) compare relatively well with experimental data. The overall absolute deviation is 0.1081 for 22 data. This indicates that the θ$_{Li-Na}$ parameter determined in the *Ternary LiCl-NaCl-H₂O System* section discussed above is relatively well suited here. The temperature function for the ψ$_{Li-Na-OH}$ interaction parameter (table 8) was plotted (fig. 27). The model is limited by minerals solubility at temperatures lower than 323.15 K, and to NaOH molalities of 20 *m* above this temperature.

SUMMARY AND RECOMMENDATIONS

A parameterization procedure for models based on Pitzer formalism for binary electrolyte systems with at least one univalent ion was developed in order to select those best suited for binary systems. This involves developing models as simple as possible, and then increasing their complexity while seeking accuracy. The suitability of the
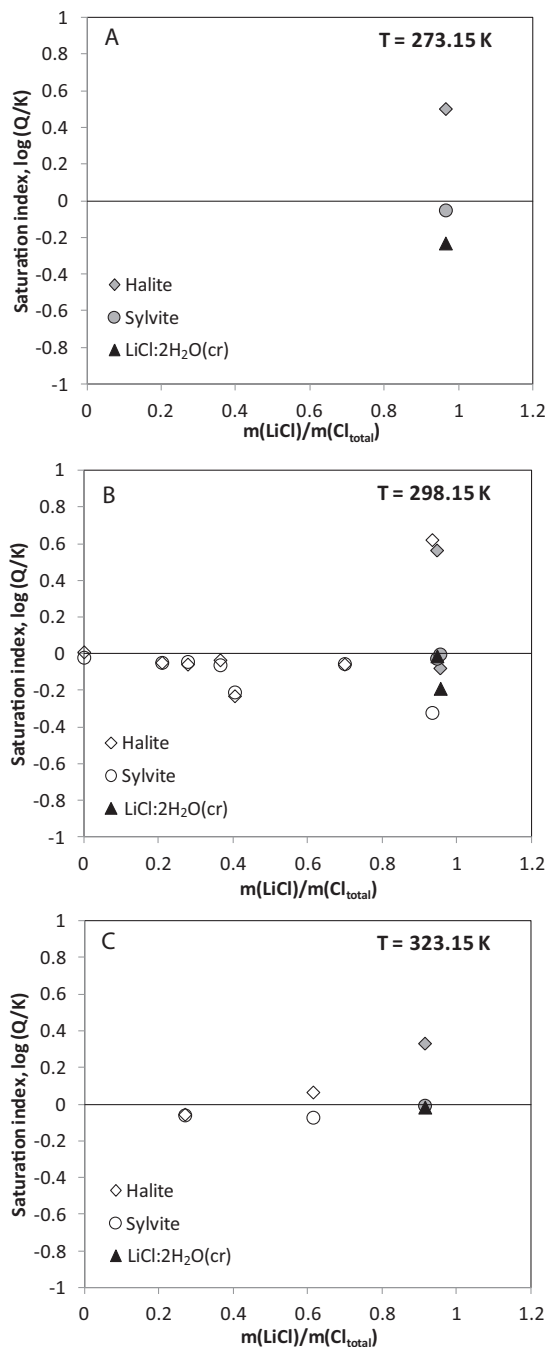
Fig. 25. Calculated saturation index [log (IAP/K$_{sp}^{\circ}$)] of halite (diamonds), sylvite (circles), LiCl.2H$_2$O, and LiCl.H$_2$O (black triangles) for experimentally measured aqueous compositions on the halite-sylvite equilibrium line vs. Li concentration relative to total Cl concentration, (A) at 273.15 K, (B) at 298.15 K, and (C) at 323.15 K. Gray symbols represent saturation indices calculated at the invariant points, where halite, sylvite and LiCl.nH$_2$O (n = 1 or 2) are observed simultaneously. Experimental data are from Yanatieva (1947) at 273.15, 298.15, and 323.15 K, and from Campbell and Kartzmark (1956) at 298.15 K (see also the compilation of Zdanovskii and others, 1975).
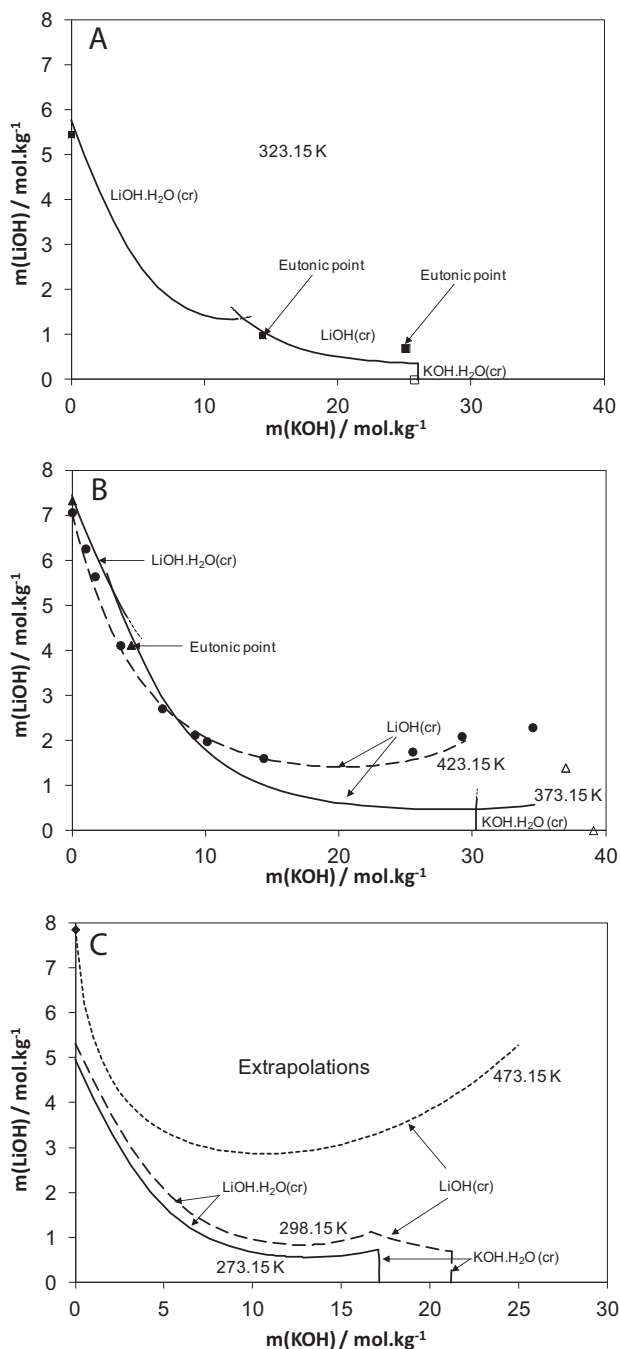
Fig. 26. Experimental (symbols) and calculated (lines) solubility data for the LiOH-KOH-H$_2$O mixed system, that is for LiOH.H$_2$O(cr), LiOH(cr) and KOH.H$_2$O(cr), (A) at 323.15 K, (B) at 373.15 and 423.15 K, and (C) extrapolated solubilities at low (273.15 and 298.15 K) and high (473.15 K) temperatures. Experimental data (see the compilation of Zdanovskii and others, 1973) are from Itkina and others (1967) at 323.15 K and 373.15 K, and from Itkina and others (1968) at 423.15 K.
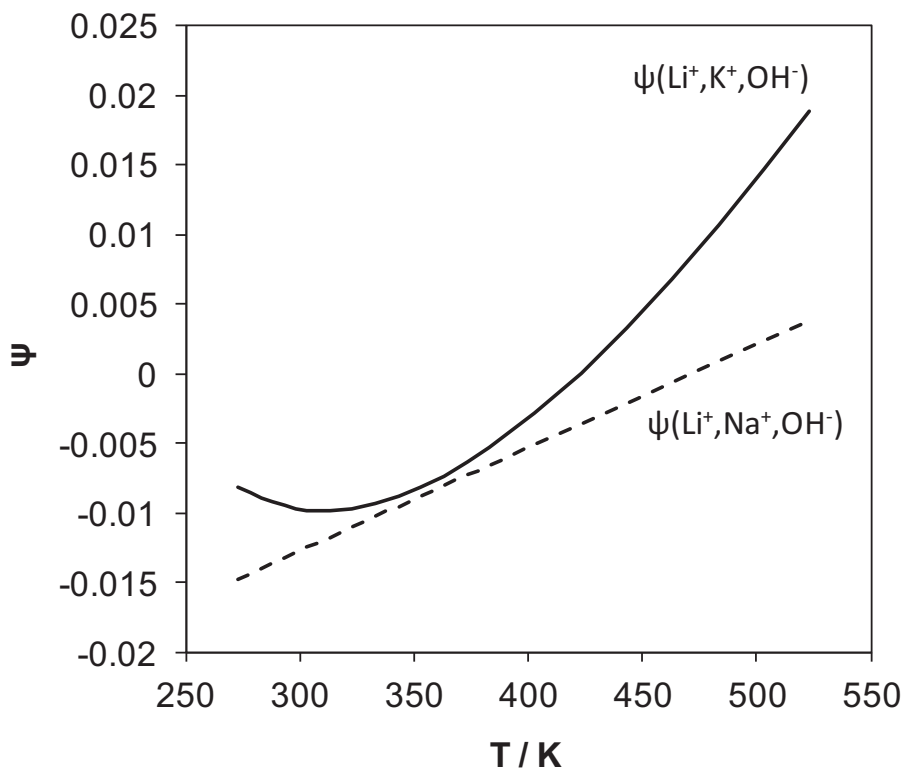
Fig. 27. Estimated ion-interaction $\psi(Li^+,K^+,OH^-)$ (solid line) and $\psi(Li^+,Na^+,OH^-)$ (dashed line) mixing parameters from 273.15 to 423.15 K, extrapolated up to 523.15 K.

models accepted for binary systems is then confirmed by the development of accurate models for higher order mixed systems.

Two binary and six ternary systems were studied using this procedure within the framework of the Pitzer formalism: LiCl-H₂O, LiOH-H₂O, LiCl-LiOH-H₂O, LiCl-HCl-H₂O, LiCl-KCl-H₂O, LiCl-NaCl-H₂O, LiOH-KOH-H₂O, LiOH-NaOH-H₂O systems. We propose a new Pitzer parameterization that enables us to describe the excess properties of aqueous solutions (osmotic coefficient, activity of water, activity coefficients) and minerals solubility for a wide range of concentrations and temperatures. Our study, like others (Christov and Møller, 2004b; Lassin and others, 2009), clearly shows that the standard Pitzer formalism (using the $\beta^{(0)}$, $\beta^{(1)}$, and C^{φ} interaction parameters) is able to describe mineral-solution systems up to very high salinities (40 mol/kg, for the binary LiCl-H₂O system) and temperatures (523.15 K). For this binary system, however, the neutral ion pair $LiCl^0$(aq) must be added to cover the entire range of concentrations and temperatures of interest. A four-interaction parameter Pitzer model (using an additional $\beta^{(2)}$ parameter) is also proposed. Using constant α_1 and α_2 parameters, the range of application of this model is limited to temperatures and salinities lower than 485 K and 37 mol/kg of LiCl, respectively.

Whereas Christov and Møller (2004b) have already well described the complex H-Na-K-Cl-OH-H₂O system up to mineral solubility and high temperatures, our work makes it possible to extend the application to the **H-Li-Na-K-Cl-OH-H₂O** system, including mineral-solution equilibria, up to high salinities and high temperatures.
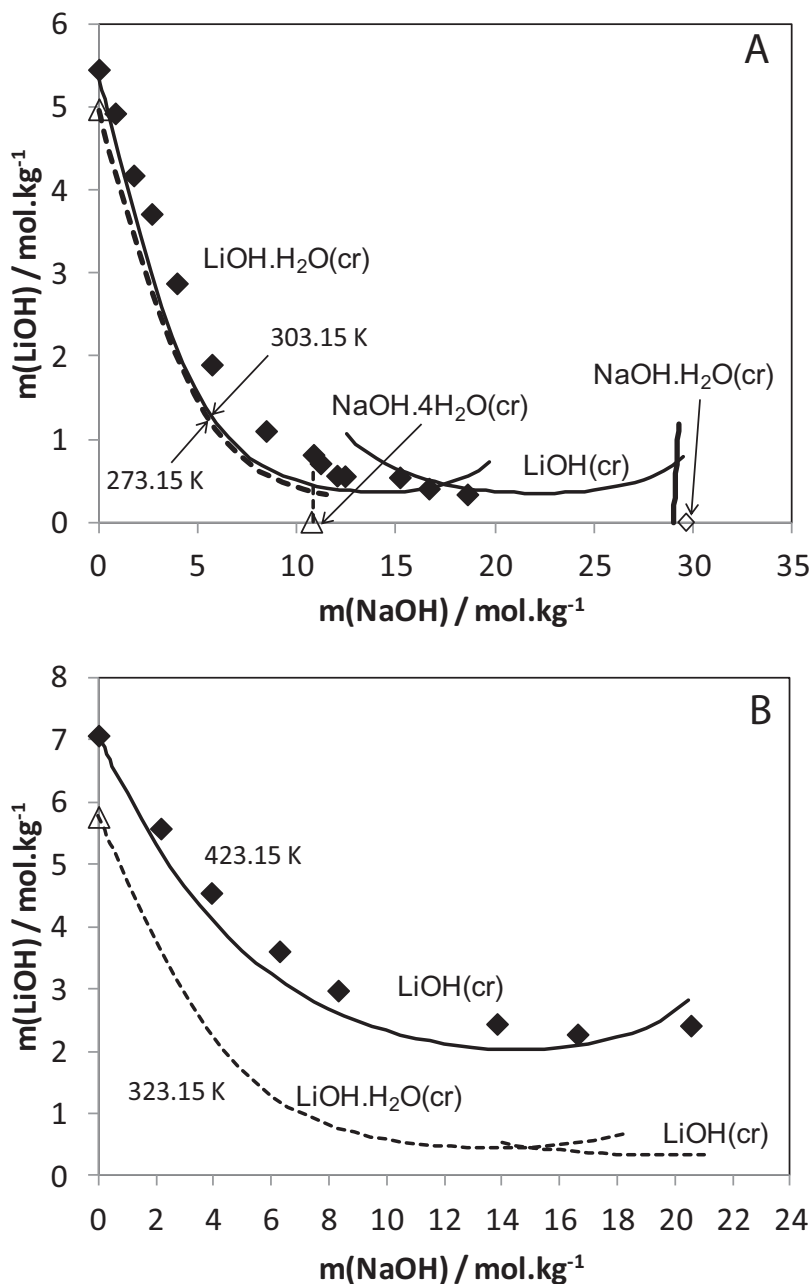
Fig. 28. Experimental (symbols) and calculated (lines) LiOH.H$_2$O(cr), LiOH(cr) and NaOH.H$_2$O(cr) solubility in the LiOH-NaOH-H$_2$O mixed system: (A) at 273.15 and 303.15 K, (B) at 323.15 and 423.15 K. Experimental data are from Evteeva (1965) at 303.15 K, and from Itkina and others (1968) at 423.15 K (see also the compilation of Zdanovskii and others, 1973). The white symbols on the x-axis indicate the NaOH.nH$_2$O(cr) (n = 1 or 4) solubility in the binary NaOH-H$_2$O system (Rollet and Cohen-Adad, 1964, and Christov and Møller, 2004b).

The salinity and temperature limits for the application of this model will depend on the chemical elements actually present. However, this is primarily due to the lack of experimental data that are needed to better constrain the model under extreme conditions in order to improve and/or extend its domain of validity. In particular, it would be of interest to include additional commonly occurring cations such as magnesium and calcium, and anions such as sulfates in the model.

This work is the essential first step to tentatively describing lithium behavior in saline natural environments, and highlights a real need for additional experimental data.

REFERENCES

Akopov, E. K., 1962, Polytherms of solubility in the system LiCl-KCl-H₂O: Zhurnal Neorganicheskoi khimii (Russian Journal of Inorganic Chemistry), v. 7, p. 385–389.
—— 1963, Solubility polytherms of the ternary system LiCl-NaCl-H2O: Zhurnal Fizicheskoi Khimii (Russian Journal of Physical Chemistry), v. 36, p. 1918.
Applebey, M., and Cook, R., 1938, The transition temperatures of lithium chloride hydrates: Journal of the Chemical Society, p. 547.
Benrath, H., 1934, Die Polytherme des ternären Systems: MnCl₂-(LiCl)₂-H₂O: Zeitschrift für anorganische und allgemeine Chemie, v. 220, n. 2, p. 145–153, http://dx.doi.org/10.1002/zaac.19342200204
Blanc, P., Lassin, A., Piantone, P., Azaroual, M., Jacquemet, N., Fabbri, A., and Gaucher, E. C., 2012, Thermoddem: A geochemical database focused on low temperature water/rock interactions and waste materials: Applied Geochemistry, v. 27, n. 10, p. 2107–2116, http://dx.doi.org/10.1016/j.apgeochem.2012.06.002
Blidin, V. P., 1953, Ternary soluility diagrams for the systems LiCl-NaCl-H₂O and LiCl-KCl-H₂O: Doklady Akademii Nauk S.S.S.R., v. 88, p. 459.
Bradley, D. J., and Pitzer, K. S., 1979, Thermodynamics of electrolytes. 12. Dielectric properties of water and Debye-Hueckel parameters to 350.degree.C and 1 kbar: The Journal of Physical Chemistry, v. 83, n. 12, p. 1599–1603, http://dx.doi.org/10.1021/j100475a009
Brendler, V., and Voigt, W., 1994, Isopiestic measurements at high temperatures. I. Aqueous solutions of LiCl, CsCl, and CaCl₂ at 155 °C: Journal of Solution Chemistry, v. 23, n. 10, p. 1061–1072, http://dx.doi.org/10.1007/BF00976256
Campbell, A. N., and Kartzmark, E. M., 1956, The System LiCl–NaCl–KCl–H₂O at 25 °C: Canadian Journal of Chemistry, v. 34, p. 672–678.
Chase, M. W. J., 1998, NIST-JANAF Thermochemical tables, Fourth Edition.: Journal of Physical and Chemical Reference Data, v. Monograph 9, p. 1–1951.
Chernyh, L., Smirnova, T., and Morozova, E., 1987, Solubility in the LiCl-LiOH-H₂O system at 0 and 50°C: Zhurnal Neorganicheskoi kamii (Russian Journal of Inorganic Chemistry), v. 32, n. 5, p. 1226–1227 (in Russian). (In Zdanovskii and others, 2003, p. 4142).
Christov, C., 1994, Thermodynamic study of (b_1RbCl + b_2MeCl₂)(aq), where b denotes molality and Me denotes Mn, Co, Ni, or Cu, at the temperature 298.15 K, on the basis of Pitzer's model: The Journal of Chemical Thermodynamics, v. 26, n. 10, p. 1071–1080, http://dx.doi.org/10.1006/jcht.1994.1125
—— 1995, Thermodynamic study of (b_1LiBr +b_2MgBr₂)(aq), where b denotes molality, at the temperature 348.15K: The Journal of Chemical Thermodynamics, v. 27, n. 11, p. 1267–1273, http://dx.doi.org/10.1006/jcht.1995.0133
—— 1998, Thermodynamic study of the KCl-K₂SO₄-K₂Cr₂O₇-H₂O system at the temperature 298.15 K: Calphad, v. 22, n. 4, p. 449–457, http://dx.doi.org/10.1016/S0364-5916(99)00004-8
—— 2001a, Thermodynamic study of the K–Mg–Al–Cl–SO₄–H₂O system at the temperature 298.15 K: Calphad, v. 25, n. 3, p. 445–454, http://dx.doi.org/10.1016/S0364-5916(01)00063-3
—— 2001b, Thermodynamic study of the NaCl—Na₂SO₄—Na₂Cr₂O₇—H₂O system at the temperature 298.15 K: Calphad, v. 25, n. 1, p. 11–17, http://dx.doi.org/10.1016/S0364-5916(01)00025-6
—— 2004, Pitzer ion-interaction parameters for Fe(II) and Fe(III) in the quinary {Na + K + Mg + Cl +

SO$_4$ + H$_2$O} system at T = 298.15 K.: Journal of Chemical Thermodynamics, v. 36, n. 3, p. 223–235, http://dx.doi.org/10.1016/j.jct.2003.11.010

—— 2005, Thermodynamics of formation of double salts and mixed crystals from aqueous solutions: The Journal of Chemical Thermodynamics, v. 37, n. 10, p. 1036–1060, http://dx.doi.org/10.1016/j.jct.2005.01.008

—— 2009, Chemical Equilibrium Model of Solution Behavior and Bishofite (MgCl$_2$·6H$_2$O(cr)) and Hydrogen-Carnallite (HCl·MgCl$_2$ ·7H$_2$O(cr)) Solubility in the MgCl$_2$ + H$_2$O and HCl-MgCl$_2$ + H$_2$O Systems to High Acid Concentration at (0 to 100) °C: Journal of Chemical & Engineering Data, v. 54, n. 9, p. 2599–2608, http://dx.doi.org/10.1021/je900135w

—— 2012, Temperature variable chemical model of bromide–sulfate solution interaction parameters and solid–liquid equilibria in the Na–K–Ca–Br–SO$_4$–H$_2$O system: Calphad, v. 36, p. 71–81, http://dx.doi.org/10.1016/j.calphad.2011.11.003

Christov, C., and Møller, N., 2004a, A chemical equilibrium model of solution behavior and solubility in the H-Na-K-Ca-OH-Cl-HSO$_4$-SO$_4$-H$_2$O system to high concentration and temperature: Geochimica et Cosmochimica Acta, v. 68, n. 18, p. 3717–3739, http://dx.doi.org/10.1016/j.gca.2004.03.006

—— 2004b, Chemical equilibrium model of solution behavior and solubility in the H-Na-K-OH-Cl-HSO$_4$-SO$_4$-H$_2$O system to high concentration and temperature: Geochimica et Cosmochimica Acta, v. 68, n. 6, p. 1309–1331, http://dx.doi.org/10.1016/j.gca.2003.08.017

Christov, C., Balarew, C., Petrenko, S., and Valyashko, V., 1994, Investigation of the aqueous lithium and magnesium halide systems: Journal of Solution Chemistry, v. 23, n. 5, p. 595–604, http://dx.doi.org/10.1007/BF00972747

Christov, C., Velikova, S., Ivanova, K., and Tanev, S., 1999, Thermodynamic Study of Na$_2$Cr$_2$O$_7$(aq) at 25 °C: Collection of Czechoslovak Chemical Communications, v. 64, n. 4, p. 595–599, http://dx.doi.org/10.1135/cccc19990595

Christov, C., Velikova, S., and Ivanova, K., 2000, Study of (m_1LiX + m_2CaX$_2$)(aq) where m_i denotes molality and X denotes Cl, or Br at the temperature 298.15 K: The Journal of Chemical Thermodynamics, v. 32, n. 11, p. 1505–1512, http://dx.doi.org/10.1006/jcht.2000.0688

Christov, C., Dickson, A. G., and Møller, N., 2007, 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$_2$O System from 0 to 100 °C: Journal of Solution Chemistry, v. 36, n. 11–12, p. 1495–1523, http://dx.doi.org/10.1007/s10953-007-9191-9

Chu, K.-J., and Zai, W.-T., 1965, Study of phase equilibria in the quaternary aqueous salt SYSTEM H$^+$, Li$^+$, Mg^{2+}//Cl-H$_2$O for O °C: Acta Chimica Sinica, v. 31, p. 192 (in Chinese with Russian abstract).

CODATA, 1978, CODATA recommended key values for thermodynamics, 1977 Report of the CODATA Task Group on key values for thermodynamics, 1977: The Journal of Chemical Thermodynamics, v. 10, n. 10, p. 903–906, http://dx.doi.org/10.1016/0021-9614(78)90050-2

Cohen-Adad, R., 1991, Lithium Chloride, *in* Cohen-Adad, R., and Lorimer, J. W., editors, Alkali Metal and Ammonium Chlorides in Water and Heavy Water (Binary Systems): Amsterdam, Pergamon, p. 1–63.

Doherty, J., 2004, PEST. Model-independent parameter estimation. User manual: 5th Edition, Watermark Numerical Computing, http://www.pesthomepage.org

Dubois, M., Monnin, C., Castelain, T., Coquinot, Y., Gouy, S., Gauthier, A., and Goffé, B., 2010, Investigation of the H$_2$O-NaCl-LiCl System: A Synthetic Fluid Inclusion Study and Thermodynamic Modeling from −50° to +100 °C and up to 12 mol/kg: Economic Geology, v. 105, n. 2, p. 329–338, http://dx.doi.org/10.2113/gsecongeo.105.2.329

Ebensperger, A., Maxwell, P., and Moscoso, C., 2005, The lithium industry: Its recent evolution and future prospects: Resources Policy, v. 30, n. 3, p. 218–231, http://dx.doi.org/10.1016/j.resourpol.2005.09.001

Egorov, A. V., Komolkin, A. V., Chizhik, V. I., Yushmanov, P. V., Lyubartsev, A. P., and Laaksonen, A., 2003, Temperature and concentration effects on Li$^+$-ion hydration. A molecular dynamics simulation study: Journal of Physical Chemistry B, v. 107, n. 14, p. 3234–3242, http://dx.doi.org/10.1021/jp026677l

El Guendouzi, M., Dinane, A., and Mounir, A., 2001, Water activities, osmotic and activity coefficients in aqueous chloride solutions at T=298.15 K by the hygrometric method: The Journal of Chemical Thermodynamics, v. 33, n. 9, p. 1059–1072, http://dx.doi.org/10.1006/jcht.2000.0815

El Guendouzi, M., Benbiyi, A., Dinane, A., and Azougen, R., 2003, The thermodynamic study of the system LiCl-KCl-H$_2$O at the temperature 298.15 K: Calphad, v. 27, n. 2, p. 213–219, http://dx.doi.org/10.1016/j.calphad.2003.08.001

—— 2004, Thermodynamic properties of multicomponent NaCl-LiCl-H$_2$O aqueous solutions at temperature 298.15 K: Calphad, v. 28, n. 1, p. 97–103, http://dx.doi.org/10.1016/j.calphad.2004.05.004

Engel, R., 1888, Torisiéme Mémoire, Solubilité des chlorures en présence de l'acide chlorhydrique: Annales de Chimie et de Physique, v. 13, p. 385.

Evteeva, O. G., 1965: Izvestiya Sibirskogo otdeleniya Akademii nauk SSSR. Seriya khimicheskikh nauk, v. 7, p. 144 (In Zdanovskii and others, 1973, pp. 111–112).

Farelo, F., Fernandes, C., and Avelino, A., 2005, Solubilities for Six Ternary Systems: NaCl + NH$_4$Cl + H$_2$O, KCl + NH$_4$Cl + H$_2$O, NaCl + LiCl + H$_2$O, KCl + LiCl + H$_2$O, NaCl + AlCl$_3$ + H$_2$O, and KCl + AlCl$_3$ + H$_2$O at T = (298 to 333) K: Journal of Chemical & Engineering Data, v. 50, n. 4, p. 1470–1477, http://dx.doi.org/10.1021/je050111j

Felmy, A. R., Cho, H., Rustad, J. R., and Mason, M. J., 2001, An aqueous thermodynamic model for polymerized silica species to high ionic strength: Journal of Solution Chemistry, v. 30, n. 6, p. 509–525, http://dx.doi.org/10.1023/A:1010382701742

Felmy, A. R., and Weare, J. H., 1986, The prediction of borate mineral equilibria in natural waters: Application to Searles Lake, California: Geochimica et Cosmochimica Acta, v. 50, n.12, p. 2771–2783, http://dx.doi.org/10.1016/0016-7037(86)90226-7

Garrett, D. E., 2004, Handbook of lithium and natural calcium chloride. Their deposits, processing, uses and properties: Amsterdam, The Netherlands, Elsevier Academic Press, 476 p.

Gibbard, H. F., Jr., and Scatchard, G., 1973, Liquid-vapor equilibrium of aqueous lithium chloride, from 25 to 100.deg. and from 1.0 to 18.5 molal, and related properties: Journal of Chemical & Engineering Data, v. 18, p. 293–298, http://dx.doi.org/10.1021/je60058a011

Greenberg, J. P., and Møller, N., 1989, The prediction of mineral solubilities in natural waters: A chemical equilibrium model for the Na-K-Ca-Cl-SO₄-H₂O system to high concentration from 0 to 250 °C: Geochimica et Cosmochimica Acta, v. 53, n. 10, p. 2503–2518, http://dx.doi.org/10.1016/0016-7037(89)90124-5

Grosjean, C., Miranda, P. H., Perrin, M., and Poggi, P., 2012, Assessment of world lithium resources and consequences of their geographic distribution on the expected development of the electric vehicle industry: Renewable and Sustainable Energy Reviews, v. 16, n. 3, p. 1735–1744, http://dx.doi.org/10.1016/j.rser.2011.11.023

Gruber, P. W., Medina, P. A., Keoleian, G. A., Kesler, S. E., Everson, M. P., and Wallington, T. J., 2011, Global Lithium Availability: Journal of Industrial Ecology, v. 15, n. 5, p. 760–775, http://dx.doi.org/10.1111/j.1530-9290.2011.00359.x

Gruszkiewicz, M. S., and Simonson, J. M., 2005, Vapor pressures and isopiestic molalities of concentrated CaCl₂(aq), CaBr₂(aq), and NaCl(aq) to $T = 523$ K: The Journal of Chemical Thermodynamics, v. 37, n. 9, p. 906–930, http://dx.doi.org/10.1016/j.jct.2004.12.009

Gueddari, M., Monnin, C., Perret, D., Fritz, B., and Tardy, Y., 1983, Geochemistry of Brines of the Chott-El-Jerid in Southern Tunisia—Application of Pitzers Equations: Chemical Geology, v. 39, n. 1–2, p. 165–178, http://dx.doi.org/10.1016/0009-2541(83)90078-5

Hamer, W. J., and Wu, Y.-C., 1972, Osmotic Coefficients and Mean Activity Coefficients of Uni-univalent Electrolytes in Water at 25 °C: Journal of Physical and Chemical Reference Data, v. 1, p. 1047–1099, http://dx.doi.org/10.1063/1.3253108

Harsányi, I., Bopp, P. A., Vrhovšek, A., and Pusztai, L., 2011, On the hydration structure of LiCl aqueous solutions: A Reverse Monte Carlo based combination of diffraction data and Molecular Dynamics simulations: Journal of Molecular Liquids, v. 158, n. 1, p. 61–67, http://dx.doi.org/10.1016/j.molliq.2010.10.010

Harvie, C. E., and Weare, J. H., 1980, The prediction of mineral solubilities in natural waters: the Na–K–Mg–Ca–Cl–SO₄–H₂O system from zero to high concentration at 25 °C: Geochimica et Cosmochimica Acta, v. 44, n. 7, p. 981–997, http://dx.doi.org/10.1016/0016-7037(80)90287-2

Harvie, C. E., Møller, N., and Weare, J. H., 1984, The prediction of mineral solubilities in natural waters: The Na-K-Mg-Ca-H-Cl-SO₄-OH-HCO₃-CO₃-CO₂-H₂O system to high ionic strengths at 25 °C: Geochimica et Cosmochimica Acta, v. 48, n. 4, p. 723–751, http://dx.doi.org/10.1016/0016-7037(84)90098-X

Helgeson, H. C., Delany, J. M., Nesbitt, H. W., and Bird, D. K., 1978, Summary and critique of the thermodynamic properties of rock-forming minerals.: American Journal of Science, v. 278-A, p. 229.

Hellams, K. L., Paterson, C. S., Prentice, B. H., III, and Taylor, M. J., 1965, Osmotic Properties of Some Aqueous Solutions at 45 °C: Journal of Chemical & Engineering Data, v. 10, n. 4, p. 323–325, http://dx.doi.org/10.1021/je60027a006

Herz, W., 1912, Die Löslichkeit von Alkalimetallsalzen in den dazu gehörigen Säuren: Zeitschrift für anorganische und allgemeine Chemie, v. 73, p. 274, http://dx.doi.org/10.1002/zaac.19110730115

Holmes, H. F., and Mesmer, R. E., 1981, Isopiestic studies of aqueous solutions at elevated temperatures VI. LiCl and CsCl: The Journal of Chemical Thermodynamics, v. 13, n. 11, p. 1035–1046, http://dx.doi.org/10.1016/0021-9614(81)90003-3

—— 1983, Thermodynamic Properties of Aqueous Solutions of the Alkali Metal Chlorides to 250 °C: The Journal of Physical Chemistry, v. 87, pn. 7, . 1242–1255, http://dx.doi.org/10.1021/j100230a030

—— 1998a, Isopiestic molalities for aqueous solutions of the alkali metal hydroxides at elevated temperatures: The Journal of Chemical Thermodynamics, v. 30, n. 3, p. 311–326, http://dx.doi.org/10.1006/jcht.1997.0301

—— 1998b, An isopiestic study of aqueous solutions of the alkali metal bromides at elevated temperatures: The Journal of Chemical Thermodynamics, v. 30, n. 6, p. 723–741, http://dx.doi.org/10.1006/jcht.1997.0377

Holmes, H. F., Baes, C. F., Jr., and Mesmer, R. E., 1978, Isopiestic studies of aqueous solutions at elevated temperatures I. KCl, CaCl₂, and MgCl₂: The Journal of Chemical Thermodynamics, v. 10, n. 10, p. 983–996, http://dx.doi.org/10.1016/0021-9614(78)90060-5

Itkina, L., Chaplighina, N., and Portnova, S., 1967: Zhurnal Neorganicheskoi kamii (Russian Journal of Inorganic Chemistry), v. 12, p. 547 (in Zdanovskii and others, 1973, p. 124).

Itkina, L., Portnova, S., and Chaplighina, N., 1968: Zhurnal Neorganicheskoi kamii (Russian Journal of Inorganic Chemistry), v. 13, p. 1415 (In Zdanovskii and others, 1973, p. 114).

Kangro, W., and Groeneveld, A., 1962, Konzentrierte wäßrige Lösungen, I: Zeitschrift für Physikalische Chemie Neue Folge, v. 32, p. 110–126, http://dx.doi.org/10.1524/zpch.1962.32.1_2.110

Kessis, J. J., 1961, Système eau-chlorure de lithium (suite) - Mesures de solubilité entre −65 et + 60 °C: Bulletin de la Société Chimique de France, p. 1503–1504.

Khy, K.-Y., 1960: Zhurnal Fizicheskoi Khimii (Russian Journal of Physical Chemistry), v. 5, p. 190–192 (in Zdanovskii and others, 1973, p. 43).

Kim, H. T., and Frederick, W. J., 1988a, Evaluation of Pitzer ion interaction parameters of aqueous electrolytes at 25 °C. 1. Single salt parameters: Journal of Chemical & Engineering Data, v. 33, n. 2, p. 177–184, http://dx.doi.org/10.1021/je00052a035

Kim, H. T., and Frederick, W. J., Jr., 1988b, Evaluation of Pitzer ion interaction parameters of aqueous mixed electrolyte solutions at 25 °C. 2. Ternary mixing parameters: Journal of Chemical & Engineering Data, v. 33, p. 278–283, http://dx.doi.org/10.1021/je00053a017

Kindyakov, P. S., Kychtymova, E. A., and Rogova, S. T., 1958: Trudy Moskovskiĭ institut tonkoĭ khimicheskoĭ tekhnologii imeni M. V. Lomonosov (Proceedings of the Moscow Institute of Fine Chemical Technology, named after M. V. Lomonosova), v. 7, p. 25, 28, 30 (in Zdanovskii and others, 1973, p. 42).

Kirgintsev, A. N., Trushnikova, L. N., and Lavrent'eva, V. G., 1972, Solubility of inorganic substances in water: St. Petersburg, Khimia, UDK, 541 p.

Kushnir, D., and Sandén, B. A., 2012, The time dimension and lithium resource constraints for electric vehicles: Resources Policy, v. 37, n. 1, p. 93–103, http://dx.doi.org/10.1016/j.resourpol.2011.11.003

Lassin, A., Kervevan, C., Andre, L., and Azaroual, M., 2009, Pitzer parametrization constrained by density: application to natural and industrial systems, 19th Annual VM Goldschmidt Conference: Davos, Switzerland: Geochimica et Cosmochimica Acta, v. 73, n. 13, Supplement, p. A724-A724.

Li, Y., Song, P., Xia, S., and Gao, S., 2000, Prediction of the component solubility in the ternary systems HCl-LiCl-H_2O, HCl-$MgCl_2$-H_2O and LiCl-$MgCl_2$-H_2O at 0 °C and 20 °C using the ion-interaction model: Calphad, v. 24, n. 3, p. 295–308, http://dx.doi.org/10.1016/S0364-5916(01)00006-2

Linke, W., 1965, Solubilities of inorganic and metal-organic compounds, 4th Edition: Washington, D. C., American Chemical society, v. 1 and 2.

Marion, G. M., Catling, D. C., and Kargel, J. S., 2003, Modeling aqueous ferrous iron chemistry at low temperatures with application to Mars.: Geochimica and Cosmochimica Acta, v. 67, n. 22, p. 4251–4266, http://dx.doi.org/10.1016/S0016-7037(03)00372-7

Mikulin, G., 1968, Voprosy Fizicheskoi Khimii Electrolytov: St. Petersburg, Izd. Khimiya.

Møller, N., 1988, The prediction of mineral solubilities in natural waters: A chemical equilibrium model for the Na-Ca-Cl-SO_4 system, to high temperature and concentration: Geochimica et Cosmochimica Acta, v. 52, n. 4, p. 821–837, http://dx.doi.org/10.1016/0016-7037(88)90354-7

Møller, N., Christov, C., and Weare, J. H., 2005, Models of subsurface rock water chemical processes affecting fluid flow: Stanford University, Stanford, California, USA., Stanford University, 30th Proceedings, Thirtieth Workshop on Geothermal Reservoir Engineering, 7 p.

—— 2006, Thermodynamic models of aluminium silicate mineral solubility for application to enhanced geothermal systems: Stanford, California, Stanford University, Proceedings, 31st Workshop on Geothermal Reservoir Engineering, 8 p.

—— 2007, Thermodynamic model for predicting interactions of geothermal brines with hydrothermal aluminum silicate minerals: Stanford, California, Stanford University, Proceedings, 32nd Workshop on Geothermal Reservoir Engineering, 7 p.

Monnin, C., and Dubois, M., 2005, Thermodynamics of the LiOH + H_2O System: Journal of Chemical & Engineering Data, v. 50, n. 4, p. 1109–1113, http://dx.doi.org/10.1021/je0495482

Monnin, C., Dubois, M., Papaiconomou, N., and Simonin, J.-P., 2002, Thermodynamics of the LiCl + H_2O System: Journal of Chemical & Engineering Data, v. 47, n. 6, p. 1331–1336, http://dx.doi.org/10.1021/je0200618

Moore, J. T., Humphries, W. T., and Paterson, C. S., 1972, Isopiestic Studies of Some Aqueous Electrolyte Solutions at 80 °C: Journal of Chemical and Engineering Data, v. 17, n. 2, p. 180–182, http://dx.doi.org/10.1021/je60053a035

Nasirzadeh, K., Neueder, R., and Kunz, W., 2005, Vapor Pressures and Osmotic Coefficients of Aqueous LiOH Solutions at Temperatures Ranging from 298.15 to 363.15 K: Industrial & Engineering Chemistry Research, v. 44, n. 10, p. 3807–3814, http://dx.doi.org/10.1021/ie0489148

Ojkova, T., Christov, C., and Mihov, D., 1998, Investigation of the Aqueous Lithium and Nickel Selenate System: Zeitschrift fur Physikalische Chemie, v. 203, p. 87–93, http://dx.doi.org/10.1524/zpch.1998.203.Part_1_2.087

Pabalan, R. T., and Pitzer, K. S., 1987, 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: Geochimica et Cosmochimica Acta, v. 51, n. 9, p. 2429–2443, http://dx.doi.org/10.1016/0016-7037(87)90295-X

Palmer, D. A., Rard, J. A., and Clegg, S. L., 2002, 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: The Journal of Chemical Thermodynamics, v. 34, n. 1, p. 63–102, http://dx.doi.org/10.1006/jcht.2000.0901

Parkhurst, D. L., and Appelo, C. A. J., 1999, User's guide to PHREEQC (version 2)—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Water-Resources Investigations Report 99-4259, 312 p.

Patil, K. R., Tripathi, A. D., Pathak, G., and Katti, S. S., 1990, Thermodynamic properties of aqueous electrolyte solutions. 1. Vapor pressure of aqueous solutions of lithium chloride, lithium bromide, and lithium iodide: Journal of Chemical & Engineering Data, v. 35, n. 2, p. 166–168, http://dx.doi.org/10.1021/je00060a020

Pauwels, H., Fouillac, C., and Fouillac, A.-M., 1993, Chemistry and Isotopes of Deep Geothermal Saline Fluids in the Upper Rhine Graben—Origin of Compounds and Water-Rock Interactions: Geochimica et Cosmochimica Acta, v. 57, n. 12, p. 2737–2749, http://dx.doi.org/10.1016/0016-7037(93)90387-C

Pauwels, H., Brach, M., and Fouillac, C., 1995, Study of Li^+ adsorption onto polymeric aluminium (III) hydroxide for application in the treatment of geothermal waters: Colloids and Surfaces A: Physicochemical and Engineering Aspects, v. 100, p. 73–82, http://dx.doi.org/10.1016/0927-7757(95)03185-G

Petit, L., Vuilleumier, R., Maldivi, P., and Adamo, C., 2008, Ab Initio Molecular Dynamics Study of a Highly Concentrated LiCl Aqueous Solution: Journal of Chemical Theory and Computation, v. 4, n. 7, p. 1040–1048, http://dx.doi.org/10.1021/ct800007v

Petrenko, S. V., and Pitzer, K. S., 1997, Thermodynamics of aqueous NaOH over the complete composition range and to 523 K and 400 MPa: The Journal of Physical Chemistry B, v. 101, n. 18, p. 3589–3595, http://dx.doi.org/10.1021/jp963707+

Pitzer, K. S., 1973, Thermodynamics of electrolytes. I. Theoretical basis and general equations: The Journal of Physical Chemistry, v. 77, n. 2, p. 268–277, http://dx.doi.org/10.1021/j100621a026

—— 1991, Activity coefficients in electrolyte solutions, 2nd edition: Boca Raton, Florida, USA, CRC Press, 542 p.

Pitzer, K. S., and Kim, J. J., 1974, Thermodynamics of electrolytes. IV. Activity and osmotic coefficients for mixed electrolytes: Journal of the American Chemical Society, v. 96, n. 18, p. 5701–5707, http://dx.doi.org/10.1021/ja00825a004

Pitzer, K. S., and Mayorga, G., 1973, Thermodynamics of electrolytes. II. Activity and osmotic coefficients for strong electrolytes with one or both ions univalent: The Journal of Physical Chemistry, v. 77, n. 19, p. 2300–2308, http://dx.doi.org/10.1021/j100638a009

—— 1974, Thermodynamics of electrolytes. III. Activity and osmotic coefficients for 2–2 electrolytes: Journal of Solution Chemistry, v. 3, n. 7, p. 539–546, http://dx.doi.org/10.1007/BF00648138

Pitzer, K. S., and Silvester, L. F., 1976, Thermodynamics of electrolytes. VI. Weak electrolytes including H_3PO_4: Journal of Solution Chemistry, v. 5, n. 4, p. 269–278, http://dx.doi.org/10.1007/BF00645465

Pitzer, K. S., Peiper, J. C., and Busey, R. H., 1984, Thermodynamic Properties of Aqueous Sodium Chloride Solutions: Journal of Physical and Chemical Reference Data, v. 13, p. 1–102.

Pitzer, K. S., Wang, P., Rard, J. A., and Clegg, S. L., 1999, Thermodynamics ofelectrolytes. 13. Ionic strength dependence of higher-order terms; equations for $CaCl_2$ and $MgCl_2$: Journal of Solution Chemistry, v. 28, n. 4, p. 265–282, http://dx.doi.org/10.1023/A:1022695525943

Plummer, L. N., Parkhurst, D. L., Fleming, G. W., and Dunkle, S. A., 1988, A computer program incorporating Pitzer's equations for calculation of geochemical reactions in brines: USGS Water-Resources Investigations Report 88-4153, p. 193.

Plyushchev, V. E., Kuznetsova, G. P., and Stepina, S. B., 1959, Issledovanie Sistemy LiCl-KCl-H_2O, Zhurnal Neorganicheskoi Khimii (Russian Journal of Inorganic Chemistry), v. 4, n. 6, 1449–1453 (in Russian) (in Zdanovskii and others, 2003, p. 47).

Rard, J. A., and Clegg, S. L., 1997, Critical evaluation of the thermodynamic properties of aqueous calcium chloride. 1. Osmotic and activity coefficients of 0–10.77 mol.kg⁻¹ aqueous calcium chloride solutions at 298.15 K and correlation with extended Pitzer ion-interaction models: Journal of Chemical & Engineering Data, v. 42, n. 5, p. 819–849., http://dx.doi.org/10.1021/je9700582

Reardon, E. J., 1988, Ion interaction parameters for aluminum sulfate and application to the prediction of metal sulfate solubility in binary salt systems: The Journal of Physical Chemistry, v. 92, n. 22, p. 6426–6431, http://dx.doi.org/10.1021/j100333a046

Risacher, F., and Fritz, B., 2009, Origin of Salts and Brine Evolution of Bolivian and Chilean Salars: Aquatic Geochemistry, v. 15, n. 1–2, p. 123–157, http://dx.doi.org/10.1007/s10498-008-9056-x

Robinson, R. A., and Stokes, R. H., 1949, Tables of osmotic and activity coefficients of electrolytes in aqueous solution at 25° C: Transactions of the Faraday Society, v. 45, p. 612–624, http://dx.doi.org/10.1039/tf9494500612

Rollet, A., and Cohen-Adad, R., 1964, Les systèmes "eau-hydroxide alcalin": Revue de Chimie Minérale, v. 1, p. 451.

Rudolph, W., Brooker, M. H., and Pye, C. C., 1995, Hydration of Lithium Ion in Aqueous Solution: The Journal of Physical Chemistry, v. 99, n. 11, p. 3793–3797, http://dx.doi.org/10.1021/j100011a055

Rumyantsev, A. V., Hagemann, S., and Moog, H. C., 2004, Isopiestic Investigation of the Systems $Fe_2(SO_4)_3$–H_2SO_4–H_2O, $FeCl_3$–H_2O, and Fe(III)–(Na, K, Mg, Ca)Cl_n–H_2O at 298.15 K: Zeitschrift für Physikalische Chemie, v. 218, n. 9, p. 1089–1127, http://dx.doi.org/10.1524/zpch.218.9.1089.41670

Shock, E. L., and Helgeson, H. C., 1988, Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Correlation algorithms for ionic species and equation of state predictions to 5kb and 1000 °C: Geochimica et Cosmochimica Acta, v. 52, n. 8, p. 2009–2036, http://dx.doi.org/10.1016/0016-7037(88)90181-0

Smits, A., Elgersma, J., and Hardenberg, M. M. E., 1924, A critical mixing point in the solid phase of the system NaCl-LiCl: Recueil des Travaux Chimiques des Pays-Bas, v. 43, n. 9, p. 671–676, http://dx.doi.org/10.1002/recl.19240430909

Song, P., and Yao, Y., 2001, Thermodynamics and Phase Diagram of the Salt Lake Brine System at 25 °C I. Li^+, K^+, Mg^{2+}/Cl^-, SO_4^{2-}, $-H_2O$ System: Calphad, v. 25, p. 329–341, http://dx.doi.org/10.1016/S0364-5916(01)00053-0

—— 2003, Thermodynamics and phase diagram of the salt lake brine system at 298.15 K: V. Model for the system Li^+, Na^+, K^+, Mg^{2+}/Cl^-, SO_4^{2-}-H_2O and its applications: Calphad, v. 27, n. 4, p. 343–352, http://dx.doi.org/10.1016/j.calphad.2004.02.001

Sterner, S. M., Felmy, A. R., Oakes, C. S., and Pitzer, K. S., 1998, Correlation of thermodynamic data for aqueous electrolyte solutions to very high ionic strength using INSIGHT: Vapor saturated water activity in the system $CaCl_2$-H_2O to 250 °C and solid saturation: Symposium on thermophysical properties: Boulder, CO (United States): International Journal of Thermophysics, p. 761–770.

Sverjensky, D. A., Shock, E. L., and Helgeson, H. C., 1997, Prediction of the thermodynamic properties of aqueous metal complexes to 1000 °C and 5 kb: Geochimica et Cosmochimica Acta, v. 61, n. 7, p. 1359–1412, http://dx.doi.org/10.1016/S0016-7037(97)00009-4

Tanaka, K., Ogita, N., Tamura, Y., Okada, I., Ohtaki, H., Pálinkás, G., Spohr, E., and Heinzinger, K., 1987, A Molecular Dynamics Study of the Structure of an LiCl·3H_2O Solution: Z. Naturforsch., v. 42a, p. 29–34.

Valyashko, V. M., Urusova, M. A., Voigt, W., and Emons, H. H., 1987, Solution properties of $MgCl_2$-H_2O system in a large scale of temperature and concentration: Zhurnal Neorganicheskoi Khimii (Russian Journal of Inorganic Chemistry), v. 33, n. 1, 228–232 (in Russian).

Warren, J. K., 2010, Evaporites through time: Tectonic, climatic and eustatic controls in marine and nonmarine deposits: Earth-Science Reviews, v. 98, n. 3–4, p. 217–268, http://dx.doi.org/10.1016/j.earscirev.2009.11.004

Yanatieva, O. K., 1947, Solubility, viscosity and specific gravities in the quaternary aqueous system consisting of chlorides of the alkaline and alkaline earth metals: Zhurnal Obshchei Khimii, v. 17, n. 6, 1039–1043 (in Russian).

Yanko, A. P., and Goldanel, A. Y., 1964: Izvestiya Fizika–Khimiya v. 6, p. 146, (in Zdanovskii and others, 2003, p. 49).

Zatloukal, J., Jäger, L., Machala, J., and Jerman, Z., 1959: Chemický Průmysl, v. 9, p. 305 (in Zdanovskii and others, 2003, p. 47).

Zdanovskii, A. B., Solov'eva, E. F., Lyakhovskaya, E. I., Shestakov, N. E., Shleimovich, R. E., and Abutkova, L. M., 1973, Experimental solubility data on salt-water systems. Vol. 1, Three component systems, v. 1: Leningrad, "Chemistry" Publishing, 1070 p.

—— 1975, Experimental solubility data on salt-water systems. Vol. 2, four component and more complex systems, v. 2: Leningrad, "Chemistry" Publishing, 1064 p.

Zdanovskii, A., Soloveva, E., Liahovskaia, E., Shestakov, N., Shleimovich, P., Abutkova, L., Cheremnih, L., Kulikova, T., 2003, Experimentalnie dannie po rastvorimosti mnogokomponentnih vodno-solevih system, v. II-1 and v. II-2: St. Petersburg, Russia Khimizdat.

Zeng, D., Liu, H., and Chen, Q., 2007, Simulation and prediction of solubility phase diagram for the separation of $MgCl_2$ from LiCl brine using HCl as a salting-out agent: Hydrometallurgy, v. 89, n. 1–2, p. 21–31, http://dx.doi.org/10.1016/j.hydromet.2007.05.001

Zhang, A.-Y., Yao, Y., Li, L.-J., and Song, P.-S., 2005, Isopiestic determination of the osmotic coefficients and Pitzer model representation for $Li_2B_4O_7$(aq) at T = 298.15 K: The Journal of Chemical Thermodynamics, v. 37, n. 2, p. 101–109, http://dx.doi.org/10.1016/j.jct.2004.07.028

Zhang, X.-Y., Févotte, G., Qian, G., Zhou, X.-G., and Yuan, W.-K., 2011, Solubility prediction of weak electrolyte mixtures, ISIC 18, 18th International Symposium on Industrial Crystallization: Zurich, Switzerland.

Zhou, J., Chen, Q. Y., Li, J., Yin, Z. L., Zhou, X., and Zhang, P. M., 2003, Isopiestic measurement of the osmotic and activity coefficients for the $NaOH-NaAl(OH)_4-H_2O$ system at 313.2 K: Geochimica et Cosmochimica Acta, v. 67, n. 18, p. 3459–3472, http://dx.doi.org/10.1016/S0016-7037(03)00133-9