Reviews

Thermodynamics of the LiCl + H₂O System

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Literature data for the solubility of lithium chloride salts (anhydrous LiCl, LiCl·H₂O, LiCl·2H₂O, LiCl·3H₂O, and LiCl·5H₂O) in pure water have been compiled and critically evaluated. These data have been represented by empirical temperature−molality expressions from which the coordinates of the eutectics and of the peritectics have been calculated. The thermodynamic properties of the LiCl salts have been calculated from their solubilities in pure water using two different models of aqueous LiCl solutions (Pitzer's ion interaction model and the mean spherical approximation model) which allow the calculation of the activity of water and of the LiCl(aq) activity coefficient to very low temperatures (199 K) and/or very high concentrations (up to 30 M), characteristic of the LiCl + H₂O system. The water−ice equilibrium constant has been determined to 199 K. Results of the Pitzer−Holmes−Mesmer ion interaction model are reliable only for LiCl molalities below 11 M. At higher molalities (corresponding to the solubilities of LiCl·2H₂O(s), of LiCl·H₂O(s), and of anhydrous LiCl for temperatures between 273 and 433 K), the mean spherical approximation model has been used. Entropies and standard enthalpies of formation of the various solids have been retrieved from fits of their solubility products with respect to temperature. Our values are in good agreement with the NBS values. There is a linear correlation between the entropies and standard enthalpies of formation and the number of water molecules in the LiCl hydrates, as already reported for MgCl₂·nH₂O, MgSO₄·nH₂O, and Na₂CO₃·nH₂O.

1. Introduction

Besides anhydrous LiCl, there exist four solid lithium chloride hydrates, with respectively 1, 2, 3, and 5 water molecules (Figure 1). These salts are extremely soluble in water. For example, the solubility of the monohydrate LiCl·H₂O is about 20 mol/kg of H₂O in pure water at 273 K. At the eutectic temperature of the LiCl + H₂O system (199 K), which is one of the lowest of all alkali + water or alkaline earth + water systems, the stable solid is the pentahydrate LiCl·5H₂O. Despite this very low temperature, the concentration of the saturated solutions is very high, 7.86 mol/kg of H₂O[1,2] at the eutectic. The calculation of the thermodynamic properties of the lithium chloride salts from their solubilities is a challenge to aqueous solution modeling. In the present work, existing solubility data of the LiCl salts in pure water were compiled and critically evaluated. Aqueous solution models based on Pitzer's ion interaction formalism[3] and the mean spherical approximation (MSA)[4] were used to calculate the properties of the saturated LiCl solutions (activity of water and activity coefficient of aqueous LiCl), and from there the solubility products of the lithium chloride salts. Standard
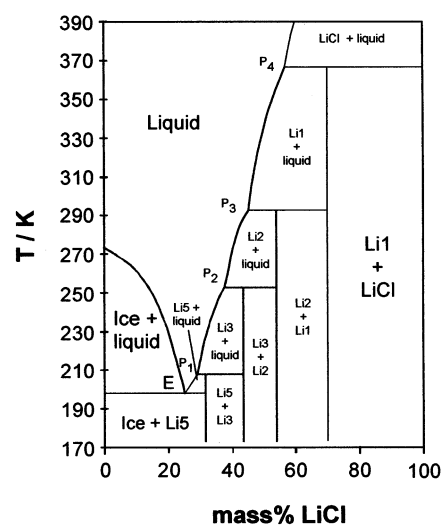

Figure 1. Schematic phase diagram for the LiCl + H₂O system (modified from ref 31). Li*n* refers to the hydrate including *n* water molecules.

enthalpies and entropies of solid lithium chloride salts, obtained from a regression of the solubility products versus temperature, were compared to literature values, which mainly come from calorimetry.[5] We also use empirical correlations between the thermodynamic properties of solid

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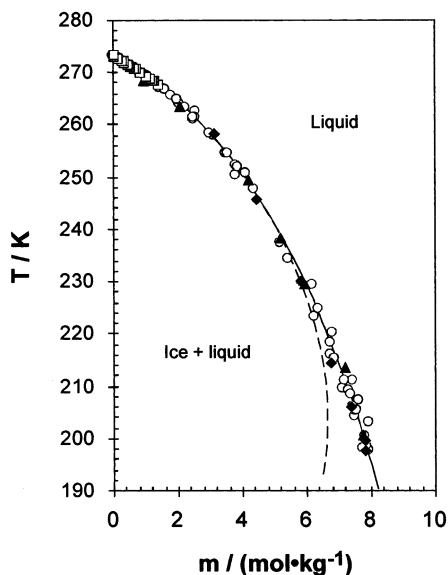§ CNRS/Université Pierre et Marie Curie.

Figure 2. Water—ice equilibrium curve for the LiCl + H_2O system. Data are those compiled by Cohen-Adad[6] with additional points from Gibbard and Fawaz,[24] Garrett and Woodruff,[23] and Moran Jr.[1] (PHMS = Pitzer—Holmes—Mesmer—Spencer model; modified PHMS = PHMS model with the water—ice equilibrium constant fitted to the data): ○, data listed by Cohen-Adad;[6] ▲, Garrett and Woodruff;[23] ◆, Moran Jr.;[1] □, Gibbard and Fawaz;[24] dashed line, PHMS model; plain line, PHMS model with the modified expression of $\ln(K_{sp})$ of the water—ice equilibrium.

hydrates and their number of water molecules as a check of the consistency of our results.

2. Compilation of Literature Data

There exist numerous data (more than 450 experimental points) for the solubility of lithium chloride hydrates in pure water as a function of temperature. Most of these data have been compiled by Cohen-Adad.[6] The criteria retained by Cohen-Adad[6] for the data selection are unclear. So we have carried out our own data evaluation, which turns out to be in accordance with that of Cohen-Adad for all salts but the pentahydrate. Our data evaluation is based on plots of experimental points in composition—temperature diagrams, from which values outside the general trend were rejected.

Literature data for the melting of ice and for the solubility of the various LiCl hydrates are represented in Figures 2—6. The rejected data are indicated by a question mark in these figures. Data have been represented by the empirical mathematical expressions given in Table 1. The data for LiCl·$5H_2O$ are very scattered. The relationship given in Table 1 is only meant to indicate the order of magnitude of the pentahydrate solubility in pure water.

The coordinates of the eutectic and of the various peritectics have been calculated from the expressions reported in Table 1. Values derived this way are in good agreement with those determined experimentally (Table 2).

3. Models of Aqueous LiCl Solutions

Pitzer's Ion Interaction Approach. The thermodynamic properties of aqueous lithium chloride solutions have been extensively investigated by Holmes and Mesmer,[7] who used Pitzer's ion interaction model to correlate calorimetric (heat capacities, enthalpies of dilution, etc.) and free energy (emf, isopiestic, vapor pressure, freezing point depression, etc.) measurements. The data that Holmes and Mesmer
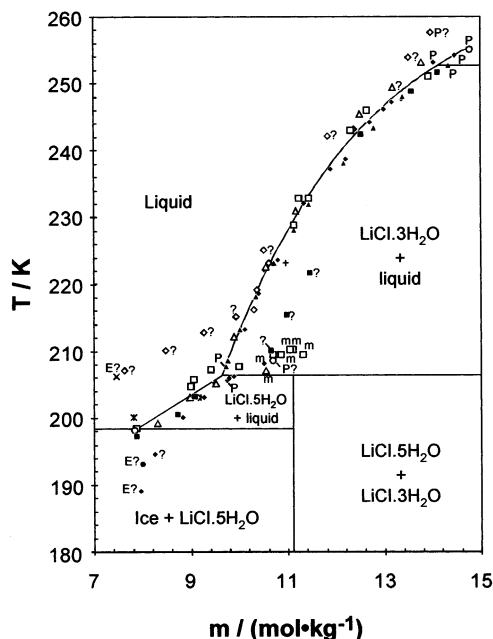

Figure 3. Solubility of the LiCl penta- and trihydrates in pure water versus temperature. Because our data selection for the pentahydrate differs from that of Cohen-Adad,[6] all retained points refer to the original papers: △, Steudemann;[32] ●, Hüttig and Steudemann;[25] ◇, Voskressienskaïa and Yanatieva;[33] *, Garrett and Woodruff;[23] ◆, Schimmel;[26] □, Kessis;[34] ▲, Vuillard and Kessis;[2] ○, Akopov;[35] ×, Ennan and Lapshin;[36] ■, Moran Jr.;[1] +, Claudy et al.;[37] ?, discarded data; E, eutectic point; P, peritectic point; m, metastable.
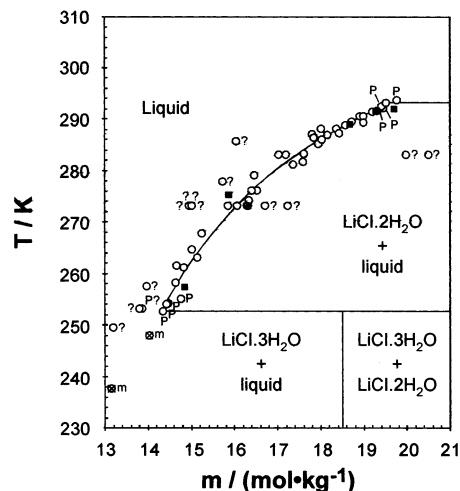

Figure 4. Solubility of the LiCl dihydrate in pure water versus temperature. We retained data selected by Cohen-Adad,[6] with the exception of two points from Schimmel[26] and Steudemann[32] that we considered metastable: ○, data listed by Cohen-Adad;[6] ⊗, data rejected from Cohen-Adad.[6] Additional data from Bassett and Sanderson[38] (▲), Benrath[39] (◆), and Moran Jr.[1] (■) are taken into account. ?, discarded data; P, peritectic point; E, eutectic point; m, metastable data.

used in the calculation of Pitzer model parameters cover LiCl concentrations up to 3.9 M for temperatures between (251 and 273) K and concentrations up to 9.4 M for temperatures to 523 K. They found that the Pitzer interaction parameters for LiCl vary almost linearly with temperature in the temperature range they considered in their study. We have retained these parameters for calculations down to the eutectic temperature of the LiCl + H_2O system.

Table 1. Solubility−Temperature Relationships for Ice and for the Solid Lithium Chloride Salts[a]

phase	expression of $m/\mathrm{mol\cdot kg^{-1}}$	temp range of fit/K	N/N_t
ice	$m = 8.445\,792 \times 10^4 + 76.87556(T/\mathrm{K}) - (5.740\,467 \times 10^{-2})(T/\mathrm{K})^2 - [(1.281\,748 \times 10^6)/(T/\mathrm{K})] - 1.719\,797 \times 10^4 \ln(T/\mathrm{K})$	197−273	160/176
pentahydrate	$m = 0.187\,668(T/\mathrm{K}) - 29.1690$	197−207	18/36
trihydrate	$m = 0.001\,448\,828(T/\mathrm{K})^2 - 0.572\,436(T/\mathrm{K}) + 66.2148$	205−255	47/56
dihydrate	$m = (5.351\,75 \times 10^{-5})(T/\mathrm{K})^3 - 0.041\,600\,3(T/\mathrm{K})^2 + 10.8571(T/\mathrm{K}) - 936.363\,58$	237−293	52/68
monohydrate	$m = 0.001\,193\,2(T/\mathrm{K})^2 - 0.651\,544(T/\mathrm{K}) + 108.036$	291−371	102/112
anhydrous LiCl	$m = (1.676\,76 \times 10^{-4})(T/\mathrm{K})^2 - (8.143\,54 \times 10^{-2})(T/\mathrm{K}) + 37.4487$	368−573	28/37

[a] m = LiCl molality (mol/kg of H_2O). N = number of data retained in the fit. N_t = total number of experimental data points.
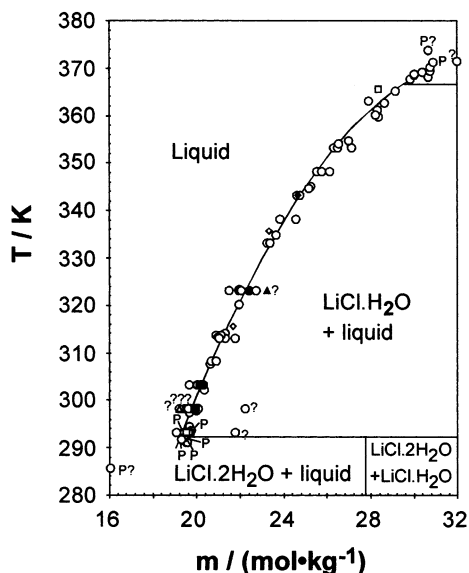

Figure 5. Solubility of the LiCl monohydrate in pure water versus temperature. Data from Demassieux[40] (▲), Pearce and Nelson[41] (△), Birnthaler and Lange[42] (■), Benrath[39] (□), Johnson Jr. and Molstad[43] (◆), and Moran[1] (◇) are added to those retained by Cohen-Adad[6] (○): ?, discarded data; P, peritectic point.
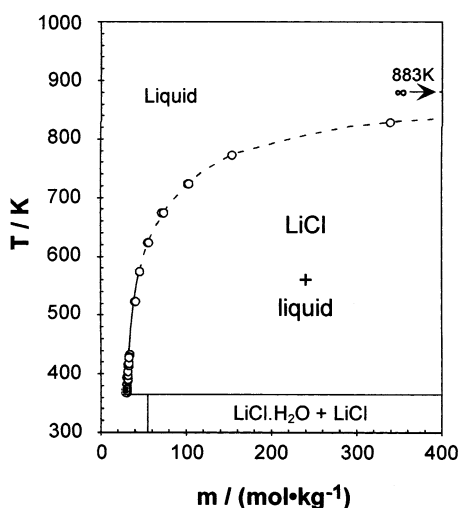

Figure 6. Solubility of anhydrous LiCl in pure water versus temperature. Data are those compiled by Cohen-Adad[6] (○), along with that from Benrath[39] (■). The plain curve represents the data fitted in this work (up to 573 K). The dashed curve is for visual support of the high-temperature data.

Holmes and Mesmer used values of the Debye−Hückel slope A_ϕ strictly valid for temperatures above 273 K, but they have successfully treated data down to 252 K.[7] Alternatively, in their low-temperature model of the Na−K−Ca−Mg−Cl−SO₄−H₂O system, Spencer et al.[8] have

Table 2. LiCl Molality and Temperature of the Eutectic and the Peritectics of the LiCl + H₂O System

	experimental		calc (this work)	
	m_{LiCl}	T	m_{LiCl}	T
	$\mathrm{mol\cdot kg^{-1}}$	K	$\mathrm{mol\cdot kg^{-1}}$	K
eutectic	7.86[1,2]	198.4[1,2]	7.87	197.3
	7.74[23]	198.15[35]		
5−3 peritectic	9.71[2]	207.75[2,34,35]	9.82	207.8
	9.78[35]	207.55 ± 0.1[1]		
3−2 peritectic	14.34[2]	252.65[2,34,35]	14.60	255.89
	14.46[26]			
2−1 peritectic	19.42[34]	292.55[34]	19.57	293.94
	19.52[44]	292.2 ± 0.1[1]		
		292.2 ± 0.25[26]		
		292.25 ± 0.25[45]		
		292.22 ± 0.02[46]		
1−anhyd peritectic	29.88[47]	366.65 ± 0.5[46,47]	30.26	369.74
		366.66 ± 0.03[46]		

Table 3. Parameters of the Expression (Eq 1) Giving the Variation of the Debye−Hückel Slope for the Osmotic Coefficient[8]

	A_ϕ
a_1	86.683 649 8
a_2	0.084 879 594 2
a_3	$-8.888\,785\,150 \times 10^{-5}$
a_4	$4.880\,963\,93 \times 10^{-8}$
a_5	$-1327.314\,77$
a_6	$-17.646\,017\,2$

treated A_ϕ as an adjustable parameter and determined the following expression that allows its calculation down to 218 K:

$$A_\phi = a_1 + a_2(T/\mathrm{K}) + a_3(T/\mathrm{K})^2 + a_4(T/\mathrm{K})^3 + \frac{a_5}{(T/\mathrm{K})} + a_6 \ln(T/\mathrm{K}) \quad (1)$$

The values of the a_i parameters are given in Table 3. In our work on the CsCl + H₂O system,[9] we have checked that the discrepancy in the calculated CsCl osmotic coefficient using the two sets of values for A_ϕ does not exceed 0.002. This meets the conclusions of Clegg and Brimblecombe,[10] who noted in their work on sulfuric acid that the choice of the Debye−Hückel slopes is not critical for calculations involving highly concentrated solutions at subfreezing temperatures. In the present work, we have retained the A_ϕ expression given by Spencer et al.[8] and used it throughout the whole temperature range considered in this study.

Mean Spherical Approximation. The mean spherical approximation was first introduced[11,12] to account for the effect of volume exclusion in the thermodynamic description of molecular fluids. This theory has been subsequently applied to ionic solutions.[13,14] For aqueous electrolytes, the MSA is equivalent to the Debye−Hückel (DH) theory at very low salt concentration. It yields good results at high concentration because it takes into account the finite size

of the ions.[4] Unlike Pitzer's model, parameters of the MSA model (ion size, solvent permittivity) have a simple physical meaning. In the present work, we have used a version of the MSA model that has been recently applied to the description of the thermodynamic properties of aqueous ionic solutions.[15–18] An electrolyte solution is described as being composed of charged hard spheres (ions) distributed in a continuum (the solvent) characterized by its sole dielectric permittivity ϵ. At 298 K, an accurate representation of the thermodynamic properties can be obtained to very high concentrations by allowing some parameters to vary with the solute concentration. We assumed that, for a binary solution, the size of the cation, σ_+, and the inverse of the solvent dielectric permittivity ϵ^{-1} vary linearly with the concentration:

$$\sigma_+ = \sigma_+^{(0)} + \sigma_+^{(1)} C$$

$$\epsilon^{-1} = \epsilon_W^{-1}(1 + \alpha C) \qquad (2)$$

where C is the salt concentration, ϵ_W is the permittivity of pure water, and $\sigma_+^{(0)}$ is the ion size at infinite dilution. $\sigma_+^{(1)}$ and α are adjustable parameters. Notice that $\sigma_+^{(0)}$ is a constant characteristic of a given cation.[16] The size of anions (in the present case aqueous chloride) is taken as a constant (crystallographic, or "optimum", size). In all cases, the fitted parameter $\sigma_+^{(0)}$ was found to be greater or equal to the corresponding crystallographic value, which may be interpreted as a consequence of hydration.

In the present work, this MSA model has been extended to temperatures ranging from (273 to 473) K, by assuming that the parameters appearing in eq 2 have the following simple linear temperature dependence:

$$\sigma_+(C,T) = \sigma_+^{(0)} + \sigma'_+^{(0)}\Delta T + (\sigma_+^{(1)} + \sigma'_+^{(1)}\Delta T)C$$

$$\epsilon^{-1}(C,T) = \epsilon_W^{-1}[1 + (\alpha + \alpha'\Delta T)C] \qquad (3)$$

with $\Delta T = T - 298.15$ K. This assumption involves three new adjustable parameters: $\sigma'_+^{(0)}$, $\sigma'_+^{(1)}$, and α'.

These parameters have been determined by a least-squares fit of the osmotic coefficients for LiCl solutions using empirical formulas for ϵ_W between (0 and 100) °C[19] and between (100 and 200) °C[20] to molalities of about 19 mol/kg below 100 °C. The relative deviation of the fit was 0.6%. The values for $\sigma_+^{(0)}$, $\sigma_+^{(1)}$, and α have been taken from previous work,[16] that is, $\sigma_+^{(0)} = 5.430$ Å, $\sigma_+^{(1)} = -9.147 \times 10^{-2}$ Å·mol⁻¹·L, and $\alpha = 0.1545$ mol⁻¹·L. The optimum values found for the parameters are $\sigma'_+^{(0)} = -2.191 \times 10^{-3}$ Å·K⁻¹, $\sigma'_+^{(1)} = 3.369 \times 10^{-5}$ Å·mol⁻¹·L·K⁻¹, and $\alpha' = -2.855 \times 10^{-4}$ mol⁻¹·L·K⁻¹. Note that the effective size of Li⁺ decreases with increasing temperature at constant concentration, as indicated by the negative value of $\sigma'_+^{(0)}$. For this adjustment, the parameters of the model have been fitted to osmotic coefficient data for LiCl solutions[21,22] to a typical molality of 19 mol/kg below 100 °C. The resulting global average relative deviation was 0.6%.

In Figure 7 we have plotted osmotic coefficients of LiCl solutions at 25 °C. It is not possible to fit the data over the whole concentration range with Pitzer's model within experimental accuracy. It can only be used to reproduce the osmotic coefficient data to about 11 mol/kg of H₂O, the molality at which the variation of the osmotic coefficient of LiCl solutions with concentration starts leveling off. On the contrary, the MSA model can reproduce the data over the full concentration range with the same number of adjustable parameters (three) as Pitzer's model. We have
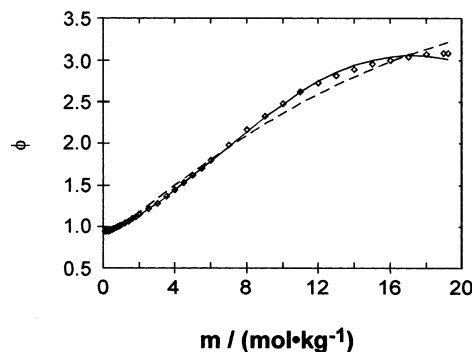

Figure 7. Osmotic coefficient of LiCl aqueous solutions at 298 K: symbols, experimental data;[5] dashed curve, Pitzer–Holmes–Mesmer model; plain curve, MSA.

been able to fit the data between (273 and 473) K with the MSA model.

4. Ice Melting Curve of the LiCl + H₂O System

The equilibrium constant of the liquid water–ice reaction has been determined by Spencer et al.[8] as a function of temperature (eq 1). Figure 2 compares the freezing point depression calculated using the Pitzer–Holmes–Mesmer model[7] for the aqueous phase and the water–ice equilibrium constant of Spencer et al., to the literature experimental data for LiCl. In Figure 2, we have retained 140 points also selected by Cohen-Adad, to which we have added the data of Garrett and Woodruff,[23] Moran Jr.,[1] and Gibbard and Fawaz.[24] Contrarily to Cohen-Adad, data for the eutectic given by Hüttig and Steudemann[25] and Schimmel[26] were not included in the data set.

One can see that the model results deviate from the experimental data for temperatures below about 230 K (Figure 2). The discrepancy can be corrected by a slight adjustment of the C_{LiCl}^{Φ} parameter in the Pitzer–Holmes–Mesmer model, but such a correction induces a marked change at 230 K in the variation of C_{LiCl}^{Φ} with temperature. Such a modification would not be in accordance with the results of Holmes and Mesmer,[7] who found that Pitzer's parameters $\beta_{\text{LiCl}}^{(0)}$, $\beta_{\text{LiCl}}^{(1)}$, and C_{LiCl}^{Φ} vary (almost) linearly with temperature. So there is no reason C_{LiCl}^{Φ} would suddenly change at 230 K. On another hand, the water + ice equilibrium constant given by Spencer et al.[8] has been determined to temperatures of about 227 K. Adjusting this equilibrium constant to the data is enough for the model to agree with the experimental data (Figure 2). The following expression can describe the variation of the water–ice equilibrium constant down to 199 K:

$$\ln K_{\text{sp}} = A + \frac{B}{(T/\text{K})} + C\ln(T/\text{K}) \qquad (4)$$

The water + ice equilibrium constant given by eq 4 deviates by 6% at 200 K from the value recently calculated by Marion[27] and by Clegg and Brimblecombe[10] from data for sulfuric acid. From the parameters of the above expression (Table 4), we calculate a value of (5.887 ± 0.04) J·mol⁻¹ for the ice enthalpy of fusion at 273 K, in good agreement with the accepted value of 5.998 J·mol⁻¹.[8]

5. Calculation of the LiCl·nH₂O Solubility Products from Solubility Data

The solubility products of the five LiCl salts have been calculated for each temperature, from the aqueous LiCl molality and from the aqueous LiCl activity coefficient and the activity of water given either by the Pitzer–Holmes–

Table 4. Parameters of Eq 4 for Ice and the LiCl Salts

	A	B	C	temp range of fit/K	no. of points
ice	-21.041 ± 0.05	268.52 ± 5.0	3.575 ± 0.01	199–273	160
LiCl anhydrous	252.06 ± 0.6	-7442.90 ± 35.0	-37.393 ± 0.09	368–429	25
LiCl·H$_2$O	397.15 ± 0.4	-15416.6 ± 20.0	-58.53 ± 0.06	293–368	63
LiCl·2H$_2$O	8.482 ± 0.02	436.17 ± 5.5	0	273–291	24
LiCl·3H$_2$O	11.586 ± 0.015	-721.0 ± 3.1	0	205–233	25
LiCl·5H$_2$O[a]	13.935 n.a.[a]	-1684.85 n.a.[a]	0	198–208	2

[a] n.a.: not available. Because of the scatter in the solubility data, the thermodynamic parameters for the pentahydrate have been calculated from the temperatures and molalities of the eutectics and of the pentatrihydrate peritectics.

Mesmer model or by the MSA model. As shown above, only the MSA is able to accurately calculate the thermodynamic properties of LiCl solutions above molalities of about 11 M. The MSA model was therefore used to calculate the solubility products of the most soluble LiCl salts, that is, LiCl(s), LiCl·H$_2$O(s), and LiCl·2H$_2$O(s) for temperatures above 273 K. Unlike the MSA, Pitzer's model can be used for temperatures below 273 K, but because of the concentration limit to which it is valid, solubility data for LiCl·2H$_2$O(s) between (255 and 273) K (which extends from about (13 to 15) M) could not be taken into account. Similarly, solubility data for LiCl·3H$_2$O(s) between (235 and 250) K (corresponding to molalities between (12 and 14) M) have not been considered in the present calculations. Because of the scatter in the solubility data for the pentahydrate, its solubility product has been tentatively calculated from the coordinates of the eutectic and of the peritectic assuming a linear change of ln K_{sp} versus the inverse of temperature (corresponding to a zero heat capacity of reaction).

Equation 4 has been fitted to the calculated solubility products. The parameters A, B, and C are reported in Table 4. A curvature in the Arrhenius plots was found only for anhydrous LiCl and for the monohydrate.

6. Thermodynamic Properties of the Solid LiCl Hydrates

The standard entropy, the standard enthalpy, and the standard heat capacity (298 K, 1 bar) of the dissolution reactions of the lithium chloride hydrates can be calculated from the A, B, and C parameters of eq 4. Holmes and Mesmer[7] give the heat capacity of LiCl aqueous solutions, but no heat capacity data are available for the lithium chloride hydrates. So we have supposed that the heat capacities of the dissolution reactions do not vary with temperature.

The standard thermodynamic data for LiCl(aq) and H$_2$O-(l) from the NBS tables[5] have been used to calculate the absolute entropy, the standard enthalpy of formation, and the heat capacity of the LiCl salts, that are reported in Table 5. The magnitude of the discrepancy between our values of the standard enthalpies and entropies of dissolution of the LiCl salts and those calculated from the NBS tables[5] is similar to what has been found, for example, for sodium carbonates[28] and magnesium chlorides and sulfates.[29]

Finally, it has already been observed for Na$_2$CO$_3$·nH$_2$O,[28] MgCl$_2$·nH$_2$O, and MgSO$_4$·nH$_2$O[29] that the contribution of each water molecule to the absolute entropy or the standard enthalpy of formation of a hydrated solid is approximately constant. This result may be interpreted in terms of group contribution, which states that the thermodynamic properties of a hydrated solid phase are the sum of the contributions of the corresponding quantities for the cation in aqueous solution and of those for the anion and for the water molecules in the crystalline structure (see

Table 5. Standard Thermodynamic Properties of Compounds in the LiCl + H$_2$O System

	$\Delta_f H^\circ$/kJ·mol^{-1}	S°/J·mol^{-1}·K	C_p°/J·mol^{-1}·K
LiCl(aq)	-445.64[a]	69.9[a]	-67.8[a]
H$_2$O(l)	-285.83[a]	69.91[a]	75.291[a]
LiCl(s)	-414.8 ± 3.7[b]	56.5 ± 1.5[b]	243.0 ± 7.0[b]
	-408.61[a]	59.33[a]	
LiCl·H$_2$O(s)	-714.55 ± 0.3[b]	97.18 ± 0.9[b]	494.1 ± 0.5[b]
	-712.58[a]	102.84[a]	
LiCl·2H$_2$O(s)	-1013.7 ± 0.5[b]	139.2 ± 0.2[b]	
	-1012.65[a]		
LiCl·3H$_2$O(s)	-1309.12 ± 0.3[b]	188.30 ± 0.9[b]	
	-1311.30[a]		
LiCl·5H$_2$O(s)	-1889.11[b,c]	302.24[b,c]	

[a] NBS. [b] This work: the uncertainties are those on the reaction properties (derived from the parameters in Table 4) and hence are only estimates of the errors on the standard properties of compounds because they include the uncertainties on the NBS values of the standard properties of LiCl(aq) and of H$_2$O(l). [c] See footnote of Table 4.
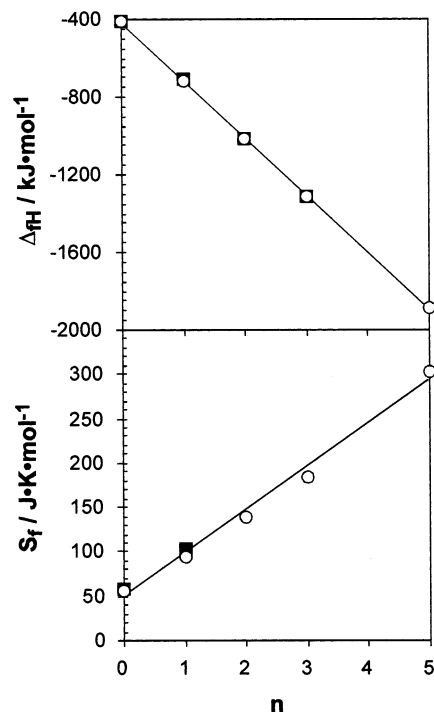

Figure 8. Absolute entropies and standard enthalpies of formation of the solid lithium chloride hydrates versus the number of water molecules in the crystalline structure: circles, this work; squares, NBS[5] (the two sets of values for the enthalpy cannot be distinguished on the plot).

ref 30 for the example of hydrated borates, and references therein). This leads to a linear trend when the standard enthalpy or entropy is plotted versus the number of hydration waters, which is here observed for LiCl·nH$_2$O (Figure 8).

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