J. Chem. Eng. Data **2006,** *51,* 315−321 **315**

Thermodynamic Consistency of the Solubility and Vapor Pressure of a Binary Saturated Salt + Water System. 1. LiCl + H_2O

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Solubility data of $LiCl\cdot nH_2O$ ($n = 0, 1, 2$) was evaluated by checking the consistency of evaluated vapor pressures with the experimental data. This process includes the following: (1) A series of vapor pressure data above the $LiCl\cdot nH_2O$ saturated solution were evaluated, and reliable data were selected as "standard" data. (2) A BET model was selected to fit the selected experimental data of water activity at salt concentrations below 20 $mol\cdot kg^{-1}$ and at temperatures ranging from 273.15 K to 428.65 K. (3) Vapor pressures for the solubility data given by different authors were calculated with the BET model and further compared with the standard data. (4) Those solubility data at which vapor pressures calculated with the BET model obviously deviate from the standard data were considered to be unreliable.

Introduction

A large number of experimental solubility data for the binary system LiCl + H_2O have been determined so far.[1−4] However, experimental data reported by different authors at different times usually do not agree with each other, and the differences are quite large at certain temperatures. To determine a reliable set of solubility values of this system from a large number of experimental data, researchers have used different evaluation methods. Link and Seidell[1] took the average values of many experimental data; however, Monnin et al.[5] developed an evaluation approach by plotting experimental points in composition−temperature diagrams, where values outside the general trend were rejected. Cohen-Adad[4] compiled the solubility data of this system, but as pointed out by Monnin et al., the criteria that Cohen-Adad retained for the data selection are not clear. However, the vapor pressures of the $LiCl\cdot nH_2O$ saturated solution have been measured by many chemists,[6−10] and more reliable data[11−16] have been reported. Thermodynamically, if an experimental date of solubility (composition and temperature) is correct, then the vapor pressure of the corresponding saturated solution (composition and temperature) should also be correct. As long as a thermodynamic model can accurately describe the thermodynamic properties of a system, including water activity and solubility, one can calculate the water activity at a given solubility point and therefore the vapor pressure. Furthermore, by comparing the reliable vapor pressures with the calculated ones for the given experimental solubility data, one could evaluate the correctness of experimental solubility data.

Among the thermodynamic models[17,19−23] for concentrated electrolyte solution, we select the Pitzer−Simonson−Clegg model[17−19] and the modified BET model[20] to describe and predict the water activity of the LiCl + H_2O system. Emphasis will be placed on the check of the prediction ability of the models of the salt concentration range near a saturated solution. Then, the vapor pressure data above the $LiCl\cdot nH_2O$ saturated solution will be compiled and evaluated; among them, reliable data will be selected as "standard" data. After that, the vapor pressures of the $LiCl\cdot nH_2O$ saturated solution at given solubility points (components and temperatures) will be calculated and compared with the standard data. Those solubility data at which the calculated vapor pressures deviate obviously from the standard data will be considered to be unreliable. In this approach, the reliability of a series of solubility data will be evaluated.

Models for Concentrated Electrolyte Solution

Pitzer−Simonson−Clegg Model. The Pitzer−Simonson−Clegg model[17−19] expresses the excess Gibbs energy of an aqueous electrolyte system with a long-range electrostatic term and a short-range Margules expansion, as described by eq 14 in ref 19.

For a binary MX + H_2O system, they derived the expression of the water activity coefficient f_1 as

$$\ln f_1 = \frac{2A_x I_x^{3/2}}{1 + \rho I_x^{1/2}} - x_M x_X B_{MX} \exp(-\alpha I_x^{1/2}) + x_I^2(W_{1,MX} + (x_I - x_1)U_{1,MX} + x_1 x_I^2(2 - 3x_1)V_{1,MX}) \quad (1)$$

where $\rho = 2150(d_1/DT)^{1/2}$; $x_I = x_M + x_X = 1 - x_1$; A_x and I_x are the Debye−Hückel parameter and ionic strength based on the mole fraction; x_a, x_c, d_1, D, and T are the mole fractions of the anion and cation, the density of the solvent water, the dielectric constant of the solvent, and the thermodynamic temperature, respectively. B_{MX}, $W_{1,MX}$, $U_{U,MX}$ and $V_{1,MX}$ are model parameters.

Setting $\alpha = 13$, we fit the model parameters in eq 1 to the experimental water activity[24] at 373.15 K and at LiCl concentrations below 18.585 $mol\cdot kg^{-1}$ and obtained the model parameter values in Table 1. The dashed line in Figure 1 shows that the Clegg−Pitzer model can represent the water activity at LiCl concentrations below 18.58 $mol\cdot kg^{-1}$ very well.

With the parameters in Table 1, the water activity is calculated up to the LiCl saturated solution, as shown by the dashed line

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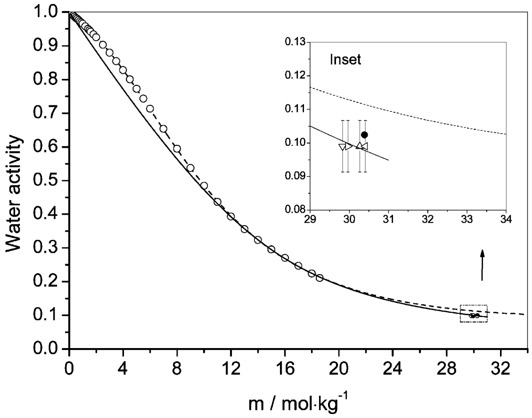

Figure 1. Water activity of the system LiCl + H_2O at 373.15 K: - - -, results recalculated with the Pitzer−Simonson−Clegg model parameters in Table 1; −, results recalculated with the BET model; ○, $T = 373.15$ K, ref 23. Other symbols, water activity converted from Greenspan[16] and solubility data from the literature: △, ref 1; right-facing triangle, ref 3; ▽, ref 4; left-facing triangle, ref 5; I, uncertainty; ●, data interpolated from Applebey et al.[11]

Table 1. Clegg−Pitzer Model Parameters of the System LiCl + H_2O at 373.15 K

solute	maximal molality	α	B_{MX}	$W_{1,MX}$	$U_{1,MX}$	$V_{1,MX}$
LiCl	18.585	13	−47.092	−2.083	14.5	−15.7479

in Figure 1. Until now, no water activity of the LiCl saturated solution has been directly measured at 373.15 K; however, the vapor pressures and solubility of the LiCl saturated solution were measured by Applebey et al.[11] over a wide temperature range. Interpolating their data yields the vapor pressure of the LiCl saturated solution at 373.15 K (10.2 kPa) and the solubility data (30.39 mol·kg^{-1}). Furthermore, the vapor pressure p is converted to water activity a_w according to eq 2[27−29]

$$\ln a_w = \ln\left(\frac{p}{p_0}\right) + \frac{B_T(P - P_0)}{RT} \qquad (2)$$

where p_0 is the vapor pressure of pure water at temperature T, $R = 8.314$ Pa·m^3·mol^{-1}·K^{-1}, and B_T is the second virial coefficient taken from ref 30 at different temperatures. The analyzed water activity and solubility data are presented in Figure 1. Greenspan reported that the relative humidity (P/P_0) over LiCl saturated solution is (9.90 ± 0.77) % at 373.15 K, from which the analyzed a_w with eq 2 and the solubility data[1,3−5] are also presented in Figure 1.

One can see in Figure 1 that the predicted water activity at the saturated point with the Pitzer−Simonson−Clegg model parameters deviates from various analyzed data by about 0.01. That means that the prediction ability of the model is good but its prediction accuracy is not high enough to give a proper judgment of the correctness of different experimental data.

BET Model. Again, we fit the BET model[20] to the literature data of water activity at 373.15 K at salt concentration below 18.585 mol·kg^{-1}. As shown in Figure 2, the linear relation of the BET equation (eq 3) holds at water activities below 0.4,

$$\frac{a_w m}{55.51(1 - a_w)} = \frac{1}{cr} + \frac{(c - 1)a_w}{cr} \qquad (3)$$

where a_w and m are the water activity and salt concentration in mol·kg^{-1} and r and c are model parameters. The calculation of the slope $(c - 1)/cr$ and intercept $1/cr$ of the line yields the parameter values $r = 3.278$ and $c = 9.329$. With the BET parameters, we predict the water activity of the system up to the saturated solution (solid line in Figure 1). The predicted water activity of LiCl saturated solution deviates from different experimental data by less than 0.003. Thus, the BET model seems to have a stronger prediction ability than the former in very concentrated solution. Consequently, in the following work, we will select the BET model to simulate the properties of the LiCl + H_2O system in unsaturated solution and evaluate its properties in saturated solution.

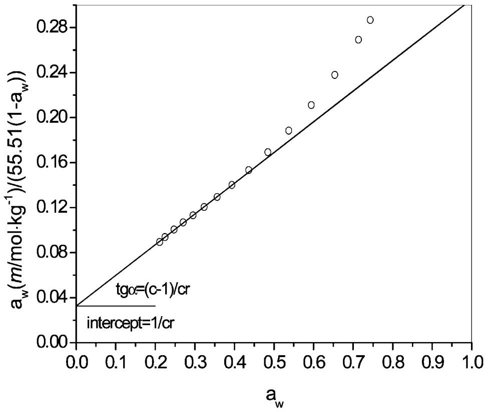

Figure 2. BET relation in the system LiCl + H_2O at 373.15 K: ○, converted values from the literature data;[24] −, fitted line at water activities below 0.4.

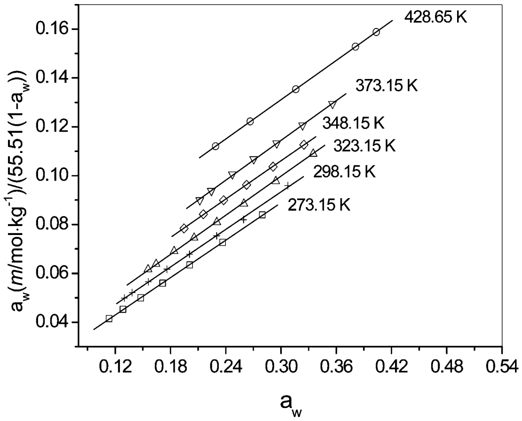

Figure 3. BET relation in the system LiCl + H_2O: −, fitted to the reference data; □, +, △, ◇, ▽, ref 24; ○, ref 31.

With the same method shown in Figure 2, we fitted the BET equation (eq 3) to the literature data[24] of water activity at 273.15 K, 298.15 K, 323.15 K, and 373.15 K and the literature data[31] at 428.65 K and obtained BET parameters r and ΔE as a function of temperature T (Figure 3, Figure 4, and Figure 5): $r = 4.7323 - 0.00378(T/\text{K})$, $\Delta E/\text{J·mol}^{-1} = R(T/\text{K}) \ln c = -8166.6 + 3.526(T/\text{K})$. With increasing temperature, the maximal hydration sites get slightly smaller, as well as the absolute value of the energy change $|\Delta E|$ accompanying the movement of 1 mol of water molecules from pure water onto the hydration sites of the LiCl salt. The predicted water activities with the above BET parameters are presented in Figure 6 and agree quite well with literature data[3,4,9,24,31] in concentrated solution over a wide temperature range from 323.15 K to 428.65 K.

If we assume that the BET linear relation (eq 3) holds over the whole concentration range of LiCl solution up to its saturated solution, then the prediction accuracy of the model should depend on the accuracy of the water activity data selected for the parameter fitting. Gibbard and Scatchard's data[24] deviate

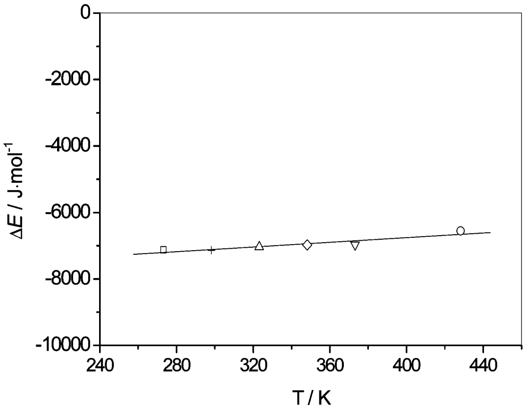

Figure 4. BET parameter ΔE vs temperature in the system LiCl + H_2O: −, fitted line; □, +, △, ◇, ▽, ref 24; ○, ref 31.

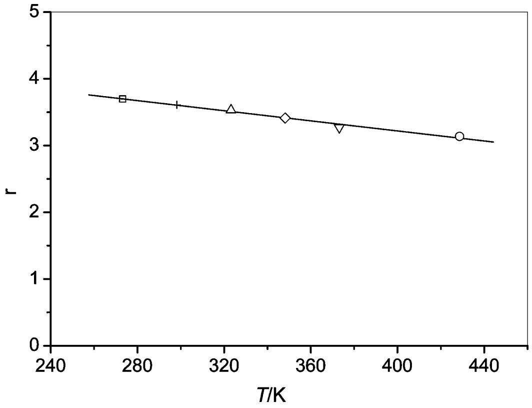

Figure 5. BET parameter *r* vs temperature in the system LiCl + H_2O: −, fitted line; □, +, △, ◇, ▽, ref 24; ○, ref 31.

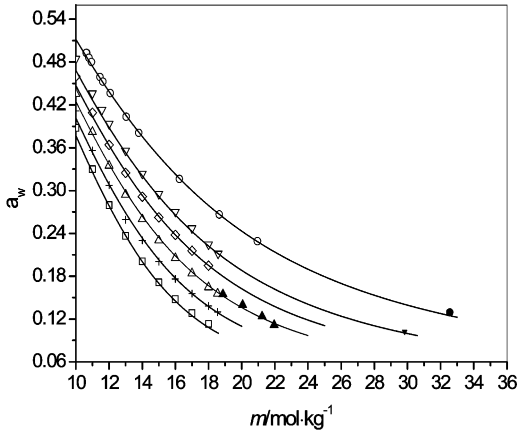

Figure 6. Water activity vs salt concentration in the system LiCl + H_2O: −, recalculated values with the BET model. Symbols represent literature data: □, $T = 273.15$ K, ref 24; +, $T = 298.15$ K, ref 24; △, $T = 323.15$ K, ref 24; ◇, $T = 348.15$ K ref 24; ▽, $T = 373.15$ K, ref 24; ○, $T = 428.65$ K, ref 31. The following data are not used for parameter fitting: ▲, $T = 323.15$ K, ref 9; ▼, $T = 373.15$ K, salt concentration taken from the solubility data[4] and water activity converted with eq 2 according to vapor pressure data;[11] ●, $T = 428.65$ K, salt concentration taken from the solubility data[3] and water activity converted with eq 2 according to vapor pressure data.[11]

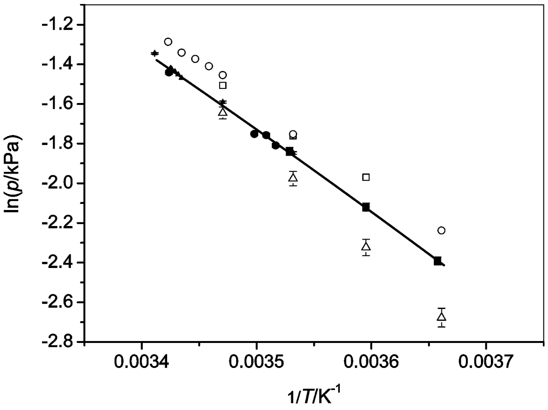

Figure 7. Vapor pressures of LiCl·$2H_2O$ saturated solution vs temperature: ●, ref 12; ▲, ref 13; ■, ref 15; □, ref 8; ○, ref 10; △, ref 16; I, uncertainty; −, standard line fitted only to the reference data.[12,13,15]

markedly from that of Pearce and Nelson;[7] the latter were obtained by a dynamic method with lower accuracy. However, Gibbard and Scatchard's data[24] agree very well with Robinson and Stokes' data[26] at 298.15 K and differ from Kangro and Groeneveld's osmotic coefficient[25] at 298.15 K by only ±0.02. The osmotic coefficients determined by Kangro and Groeneveld, according to their statement, have an accuracy of ±0.001, thus it is reasonable to believe that the osmotic coefficient data reported by Gibbard and Scatchard[24] have an accuracy of ±0.02. This accuracy can be interpreted as water activity equal to 0.130 ± 0.002 for a 18.542 mol·kg^{-1} LiCl solution at 298.15 K or as the mass percent LiCl solubility (40.8 ± 0.1) % at 298.15 K. With such accuracy, the BET model can be used to judge the reliability of solubility data from different sources; for example, the mass percent LiCl solubility reported by Woskresenskaya and Yanatieva[39] is 38.7 % at 273.15 K, which is 2 % lower than the 40.87 % data given by Friend and Colley.[37]

Evaluation of Experimental Data of the Vapor Pressure above Saturated Electrolyte Solutions

Before evaluating different solubility data, one must first determine a "correct" set of vapor pressure data of the LiCl·$2H_2O$ saturated solution. So far, many vapor pressures or relative humidity data of the LiCl·$2H_2O$ saturated solution have been reported[6,8,10,12,15,16] (Figure 7). Among them, the data given by Hüttig and Reuscher[6] at low temperatures are obviously not accurate; for example, they obtained the same vapor pressure value of 0.10665 kPa above the LiCl·$2H_2O$ saturated solution at 273.15 K and 278.15 K and the same vapor pressure value of 0.2666 kPa at 285.65 K and 288.15 K. The absolute accuracy of the relative humidity data of the LiCl saturated solution cited by Rockland[8] is only 1 %. Greenspan[16] accumulated experimental data from various researchers and calculated "best" values of relative humidity, but his analyzed data differ remarkably from the experimental data given by Hedlin[12] and Acheson[13] (Figure 7). Hedlin et al.[12] stated that the experimental uncertainty in their relative humidity is only ±0.1 %,[12] and Acheson[13] reported that their vapor pressure data above the LiCl saturated solution is very accurate with an absolute uncertainty of only 1 Pa. Thirty-four years later, Morillon et al.[15] determined the vapor pressures of the LiCl·$2H_2O$ saturated solution again; these data have an uncertainty of 2 % and agree with the data of Hedlin[12] quite well. Therefore, the experimental data of Hedlin et al.,[12] Acheson,[13] and Morillon et al.[15] are believed to be more reliable in this work and are consequently fitted with a temperature function of the vapor pressure above the LiCl·$2H_2O$ saturated solution:

$$p/\text{kPa} = \exp(a + b/(T/\text{K}) + c\ln(T/\text{K})) \tag{4}$$

Equation 4 was derived by assuming that the heat of vaporization of water in the solution depends linearly on temperature.[32] Parameter values *a*, *b*, and *c* are tabulated in Table 2.

Table 2. Fitted Standard Curve of the Vapor Pressure of the $LiCl\cdot nH_2O$ Saturated Solution with the Temperature

phase	vapor pressure of saturated solution, p/kPa	temperature range, T/K	source of data, refs
$LiCl\cdot 2H_2O(s)$	$\ln(p/kPa) = 133.6116 - 9278.12/(T/K) - 18.19053 \ln(T/K)$	273−293	12, 15, 16
$LiCl\cdot H_2O(s)$	$\ln(p/kPa) = 149.41106 - 11419.74114/(T/K) - 19.68268 \ln(T/K)$	293−268	11, 16
$LiCl(s)$	$\ln(p/kPa) = 70.83197 - 8611.23808/(T/K) - 7.66919 \ln(T/K)$	368−453	11

The vapor pressure data above or the water activity of the $LiCl\cdot H_2O$ saturated solution has been reported by different researchers.[6−9,11,12,16,33] The data reported by Hüttig et al.[6] and Applebey et al.[11] are slightly scattered. As mentioned above, Pearce and Nelson's data[7] are less reliable. The data cited by Rockland[8] are not very accurate. The data from Hedlin et al.,[12] Acheson,[13] and Greenspan[16] agree with each other quite well in their stated uncertainty ranges. These data, along with Applebey et al.'s data above 350 K,[11] are selected to fit the standard curve with eq 4, as shown in Figure 8.

Unfortunately, the data for the vapor pressure above the LiCl(s) saturated solution is available only from Applebey et al.[11] The uncertainty of their data is unknown. These data are fitted with eq 4, as shown in Figure 9.

Comparison of Vapor Pressure and Evaluation of Solubility Data

As introduced above, various solubility data of $LiCl\cdot nH_2O$ have been published. Linke and Seidell[1] compiled all of the existing solubility data before 1965 and gave one set of average values of the experimental data. After that, Clynne and Potter[3] measured the solubility data of this system again, claiming that their data have an average precision of ±0.09 %. Recently, Cohend-Adad[4] and Monnin et al.[5] evaluated all published solubility data again and gave results different from those given by Linke and Seidell[1] and by Clynne and Potter.[3] To evaluate their solubility data and other older data, we will calculate the water activity at each solubility data point with the BET model and then convert the water activity data to vapor pressure data with eq 2. The calculated vapor pressures will be compared with the standard curve.

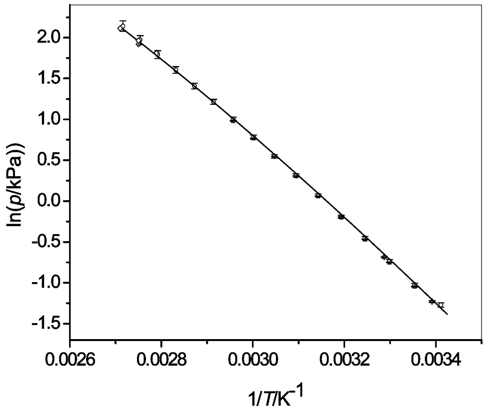

Figure 8. Vapor pressures of $LiCl\cdot H_2O$ saturated solution vs temperature: □, ref 13; △, ref 12; ○, ref 16; ◇, ref 11; I, uncertainty; literature data; −, fitted standard line.

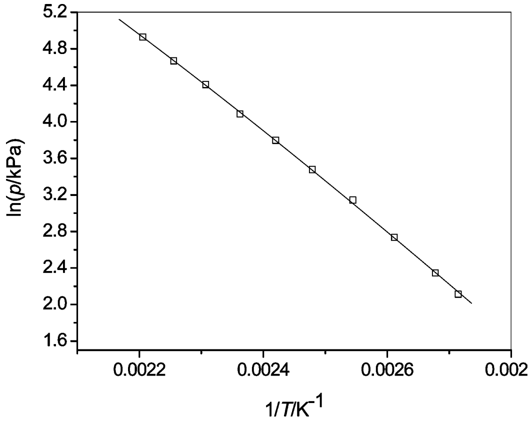

Figure 9. Vapor pressures of LiCl saturated solution vs temperature: ○, ref 11; −, fitted standard line.

On the Solubility Data of $LiCl\cdot 2H_2O$. The vapor pressures calculated for the typical solubility data of Linke and Seidell[1], Clynne and Potter,[3] and Monnin et al.[5] are presented in Figure 10. Also presented in this Figure are the standard curve and the BET model uncertainty arising from that of the experimental data,[24] namely, ±0.02 for the osmotic coefficient. One can see that most of the vapor pressures calculated for the solubility data[1,3,5] fall in the estimated uncertainty range of the standard line, except for two points at 278.15 K and 273.15 K.[1]

Furthermore, the vapor pressures of the $LiCl\cdot 2H_2O$ saturated solution are calculated for solubility data given by other authors, and the comparison with the standard value is presented in Figure 11. It is surprising that most of the evaluated vapor pressures for the solubility data[35,36,38,39,40,42] fall outside the uncertainty range of the standard values. The vapor pressures calculated for the solubility data[38,40] are smaller than the standard values, whereas those for other solubility data[35,36,39,42] are larger. An obvious positive deviation of the vapor pressure from the standard curve appears for the solubility data.[35,39,42] The International Critical Tables[42] in 1928 reported that the eutectic temperature of $LiCl\cdot 2H_2O + LiCl\cdot H_2O$ lies at 285.65 K, at which the evaluated vapor pressure deviates markedly from the standard value (Figure 11 and Table 3). At the invariant points reported by other researchers[1,5,34] the vapor pressures are also calculated. All of the calculated data and their differences from the standard curve are tabulated in Table 3.

On the Solubility Data of $LiCl\cdot H_2O$. The vapor pressures calculated for the $LiCl\cdot H_2O$ solubility data[1,3,5,43] and their comparison with the standard curve are presented in Figure 12.

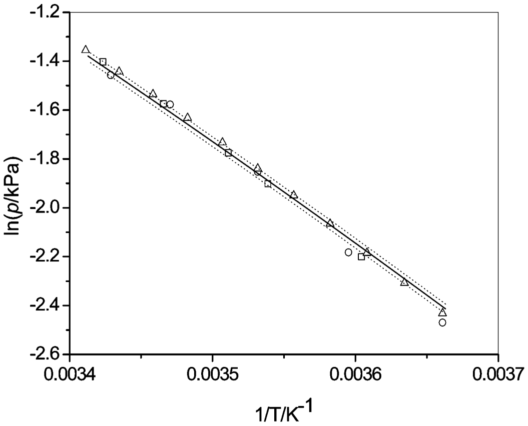

Figure 10. Vapor pressures of the $LiCl\cdot 2H_2O$ saturated solution vs temperature: −, standard values; ..., model uncertainty based on the standard values; ○, ref 1; □, ref 3; △, ref 5. All symbols are BET model values evaluated for the solubility data of the reference literature.

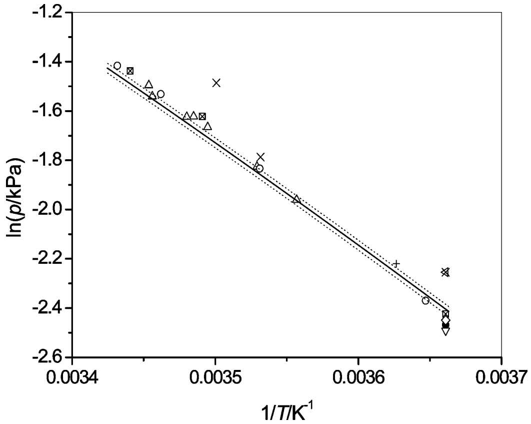

Figure 11. Vapor pressures of $LiCl·2H_2O$ saturated solution vs temperature: −, standard values; ..., model uncertainty basing on the standard values; ○, ref 11; □ containing ×, ref 35; +, ref 36; △, ref 37; ◇, ref 38; left-facing triangle, ref 39; ▽, ref 40; ●, ref 41; ×, ref 42. All symbols are BET model values evaluated for the solubility data of the reference literature.

Table 3. Vapor Pressures Evaluated at the $LiCl·2H_2O$ + $LiCl·H_2O$ Peritectic Point and Their Comparisons with the Standard Values

literature data of solubility		vapor pressure, kPa		
m_{LiCl}/mol·kg^{-1}	T/K	evaluated	standard	deviation^a, kpa
19.57[1]	291.65[1]	0.233	0.236	0.003
19.42[34]	292.55[34]	0.250	0.246	−0.003
19.57[5]	293.94[5]	0.272	0.263	0.009
17.599[42]	285.65[42]	0.187	0.177	−0.011

[a] Deviation = standard value minus evaluated value.

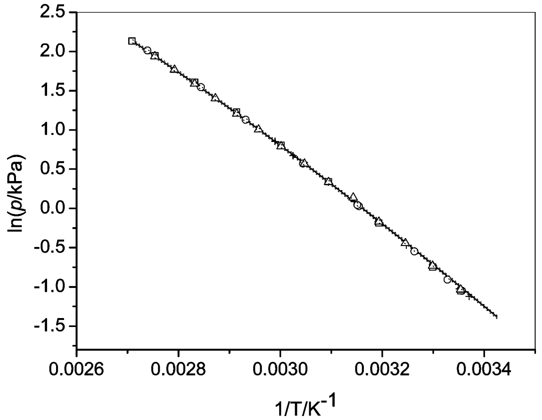

Figure 12. Vapor pressures of the $LiCl·H_2O$ saturated solution vs temperature: −, standard values; ..., model uncertainty based on the standard values; ○, ref 1; □, ref 3; △, ref 5; +, ref 43. All symbols are BET model values evaluated for the solubility data of the reference literature.

The calculated vapor pressures for all four sets of solubility data agree with the standard values very well, with the average percent deviation from the standard curve being smaller than 1.1 % (Table 4). It is noteworthy that although these authors used different methods to evaluate and obtain their data they found consistent results. However, the deviations of the vapor pressures calculated for other experimental solubility data[6,9,35,37,42] from the standard values are a little larger (Figure 13 and Table 4), with the average percent deviation being larger than 1.5 %. The vapor pressures calculated for the most recently finished two sets of experimental solubility data[3,43] agree better with the standard values than for the older experimental data.[6,9,35,37,42] On account of the uncertainty (±0.02) in the osmotic coefficient, to which the BET model parameters are fitted, only those sets of solubility data with average deviations larger than 2 % in Table 4 are believed to be unreliable.

Table 4. Deviation of the Vapor Pressures of the $LiCl·H_2O$ Saturated Solution Calculated for Different Solubility Data from the Standard Values

literature of solubility data	temperature range, T/K	number of data, n	average deviation^a
Linke and Seidell[1]	298.15−369.15	9	0.96
Farelo et al.[43]	296.7−334.5	10	0.97
Clynne and Potter[3]	297.95−365.1	9	1.04
Monnin et al.[5]	298.15−363.15	14	1.08
Friend and Colley[37]	291.15−361.15	13	1.49
Benrath[35]	298.15−363.15	5	1.72
Johnson, Jr. and Molstad[9]	303.15, 323.15	2	2.38
Hüttig and Reuscher[6]	303.15−100.5	6	2.65
International Critical Tables[42]	293.15−373.65	10	4.92

[a] Average deviation $= {}^{1}/_{n} \sum_{i=1}^{n} |p_i^{\mathrm{calc}} - p_i^{\mathrm{std}}|/p_i^{\mathrm{std}} \times 100$.

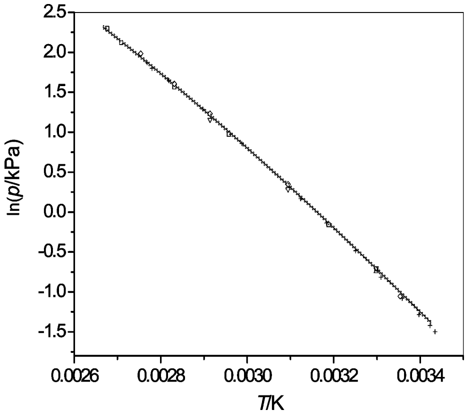

Figure 13. Vapor pressures of the $LiCl·H_2O$ saturated solution vs temperature: −, standard values; ..., model uncertainty based on the standard values; □, ref 6, △, ref 9; ▽, ref 42; ◇, ref 35; +, ref 37. All symbols are BET model values evaluated for the solubility data of the reference literature.

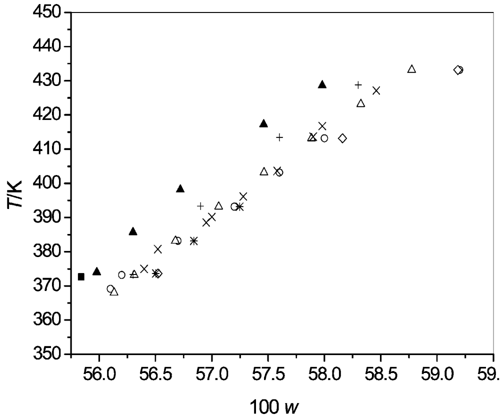

Figure 14. Solubility of the solid-phase LiCl(s) in pure water vs temperature: ○, ref 1; ▲, ref 3; △, ref 5; ◇, ref 6; +, ref 11; ■, ref 35; *, ref 42; ×, ref 44.

On the Solubility Data of LiCl. The solubility data of the solid-phase LiCl given by different authors[1,3,5,6,11,35,42,44] do not agree with each other, as shown in Figure 14. It is also noted that the vapor pressures calculated for these solubility data are generally lower than the standard curve (Figure 15 and Table 5). This result may suggest the uncertainty of the model and/or the standard values of the vapor pressure. On one hand, the standard vapor pressure data are fitted only to the experimental data of Applebey et al.,[11] the uncertainty range of which was not reported. One the other hand, the BET model parameters at 428.65 K are fitted to the experimental data of Brendler and Voigt,[31] who experimentally determined the isopiestic molalities of LiCl solution with a $MgCl_2$ reference solution and calculated the osmotic coefficients with a set of Pitzer model parameters[45]

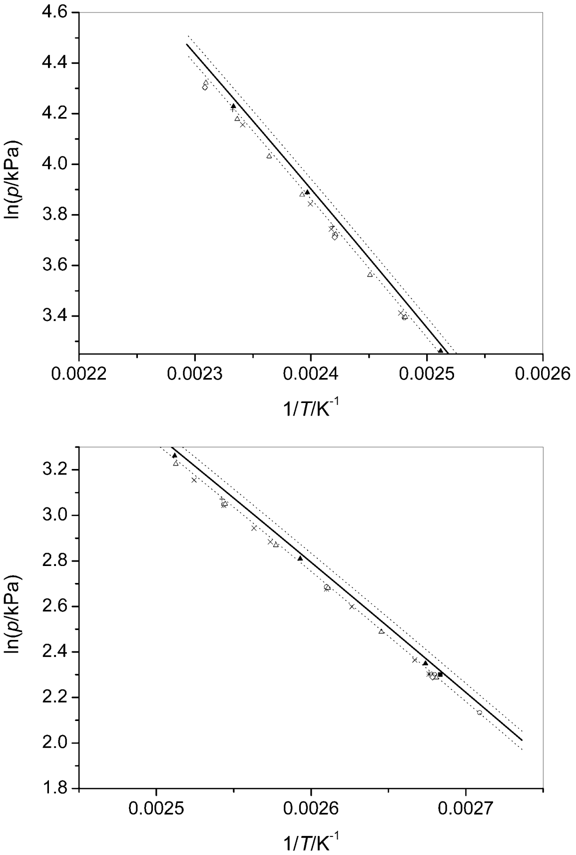

Figure 15. Vapor pressures of the LiCl saturated solution vs temperature: −, standard values; ..., model uncertainty based on the standard values; ○, ref 1; ▲, ref 3; △, ref 5; ◇, ref 6; +, ref 11; ■, ref 35; *, ref 42; ×, ref 44. All symbols are BET model values evaluated for the solubility data of the reference literature.

Table 5. Deviation of the Vapor Pressures *p* of the LiCl Saturated Solution Calculated for Different Solubility Data from the Standard Values

literature of solubility data	temperature range, T/K	number of data, n	average deviation[a]
Clynne and Potter[3]	385.65−428.6	5	2.718
Benrath[35]	372.65	1	1.675
Applebey et al.[11]	373.35−428.75	4	4.577
Monnin et al.[5]	373−433	14	5.672
Friend et al.[44]	374.95−427.15	9	5.697
Linke and Seidell[1]	369.15−433.15	7	5.810
International Critical Tables[42]	373.65−393.15	3	5.945
Hüttig and Reuscher[6]	373.35−433.15	3	7.208

[a] Average deviation $= {}^{1}/_{n} \sum_{i=1}^{n} |p_i^{\text{calc}} - p_i^{\text{std}}|/p_i^{\text{std}} \times 100$.

for the $MgCl_2$ solution. Simultaneously, they also compared the model values with Dittrich's experimental values,[46] yielding an average deviation of ±0.04 for the osmotic coefficient. Thus, it can be reasonably assumed that the osmotic coefficient of LiCl solution determined by the isopiestic method should also have an uncertainty of ±0.04. This uncertainty is drawn in Figure 15 on the basis of the standard curve. Of all of the calculated vapor pressures for the solubility data,[1,3,5,6,11,35,42,44] only those pertaining to the data of Clynne et al.[3] and Benrath[35] fall in the uncertainty range of the standard curve. The exact differences between the calculated and standard values are presented in the last column of Table 5. Although Clynne et al.'s data[3] are different from most of the others, their data should not be discounted when one evaluates the solubility data of LiCl critically. This conclusion can also find support from the visual measurement method of Clynne et al.,[3,47] who suggested that the chemical analysis of the highly viscous saturated solutions gives larger values because of suspended crystallites. Although Friend et al.[37] also employed the visual method, Clynne et al.'s data,[3] with an average precision of 0.09 %, may be more accurate than Friend et al.'s data.

Conclusions

By fitting the BET model parameters to the selected water activity data in the system LiCl + H_2O at salt concentrations below 20 $mol\cdot kg^{-1}$ and in the temperature range from 273.15 K to 428.65 K, the vapor pressures for solubility data given by different authors were calculated and compared with reliable experimental data. By comparing the consistency of calculated and experimental vapor pressures above $LiCl\cdot nH_2O$ saturated solution, the reliability of the solubility data was evaluated. The investigation of this work indicated that the vapor pressures evaluated for the solubility data of $LiCl\cdot 2H_2O$ given by Clynne et al., Monnin et al., Linke and Seidell, except that at two Linke and Seidell points at 273.15 K and 278.15 K, are generally in good agreement with the experimental data within the model estimated error. For all other $LiCl\cdot 2H_2O$ solubility data cited in the work, the calculated vapor pressures are scattered. A comparison of the calculated and experimental vapor pressures also indicated that all of the solubility data for $LiCl\cdot H_2O$ from Linke and Seidell, Clynne and Potter, and Monnin et al. are reliable. However, the calculated vapor pressures above the LiCl saturated solution are systematically lower than the experimental data. Among them, only the vapor pressures calculated using Clynne and Potter's solubility data are consistent with the experimental values in the error range of the model. Consequently, Clynne and Potter's solubility data for LiCl should not be discounted, although their data are different from most of the others' data.

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Received for review August 13, 2005. Accepted December 11, 2005.

JE050322O