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Short review

Thermodynamic consistency of solubility and vapor pressure of a binary saturated salt + water system II. $\text{CaCl}_2 + \text{H}_2\text{O}$

Dewen Zeng^{a,*}, Hongyan Zhou^a, Wolfgang Voigt^b

^a College of Chemistry and Chemical Engineering, Hunan University, 410082 Changsha, PR China

^b Institut für Anorganische Chemie, TU Bergakademie Freiberg, Leipziger Strasse 29, D-09596 Freiberg, Germany

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Abstract

Solubility data of $\text{CaCl}_2 \cdot n\text{H}_2\text{O}$ ($n=2, 4, 6$) were predicted and evaluated by a Stokes and Robinson's adjusted BET-model using the vapor pressures of saturated solution as criteria. Prior to the prediction, the BET model was parameterized with the most recently reported experimental osmotic coefficients. The comparison with other models showed that, despite of fewer model parameters, the BET model could represent the activities in the system $\text{CaCl}_2 + \text{H}_2\text{O}$ as good as the Pitzer model in a large temperature range from 298.15 to 523.15 K. Meanwhile, experimental vapor pressure data of the saturated CaCl_2 solution were critically evaluated and some of them are selected as criteria for solubility prediction. In principle, the predicted solubility has higher accuracy than an average set of various experimental data and therefore is recommended for use in relevant cases.

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Keywords: Solubility; Calcium chloride; Water activity; Modeling; Vapor pressure

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1. Introduction

A large number of experimental data of solubility for the binary system $\text{CaCl}_2 + \text{H}_2\text{O}$ have been determined so far. However, experimental data reported by different authors at different time usually do not agree with each other, and the differences

* Corresponding author. Fax: +86 731 8713642.
E-mail address: dewen_zeng@hotmail.com (D. Zeng).

between them are even larger than 2 mass percent at some temperatures. In this case, Linke and Seidell [1] and Smith-Magovan et al. [2] compiled different sets of solubility values of this system from a large number of experimental data, respectively. Linke and Seidell's data are averages read from a plot of the different experimental results, while Smith-Magovan et al. has given most emphasis on the more recently published experimental data [3–9] in their evaluation. It seems that Smith-Magovan et al. preferred the lower solubility data determined by a visual method. However, large differences still exist among the experimental data determined by a visual method.

In our previous work [10], we have evaluated the solubility data of the system $\text{LiCl-H}_2\text{O}$ with the Stokes and Robinson's modified BET model [11] using experimental vapor pressures of saturated solutions as criteria. The philosophy of the method is concluded as the following: A solubility datum and a vapor pressure above the corresponding salt-saturated aqueous solution must show internal consistency. Because that vapor pressures above concentrated saturated salt solutions can be determined more accurate than chemical composition analysis, thus, with a thermodynamic model, more accurate solubility data can be derived from corresponding vapor pressure measurements.

In this paper the same method will be used to treat the $\text{CaCl}_2\text{-H}_2\text{O}$ system. At first, we will discuss prediction ability of various thermodynamic models and choose suitable one to treat the most recently published experimental osmotic coefficients. Then, the vapor pressure above the saturated solutions will be critically evaluated. After that, a set of solubility data and their limits of uncertainty will be predicted applying the BET model and the vapor pressures above the saturated solutions. At last, the predicted solubility data will be compared with various experimental data and causes for differences will be discussed.

2. Models for the system $\text{CaCl}_2 + \text{H}_2\text{O}$ and their parameterization

Accurate experimental data of water activities used for the parameterization is a prerequisite for an accurate model prediction. Rard and Clegg [12] have critically evaluated the osmotic coefficients of this system recently, their data are considered as the most reliable ones at 298.15 K with uncertainties not exceeding 0.01 for the osmotic coefficient. Unfortunately, reliable water activity data at very high molalities above 298.15 K are scarce. Thus, many researchers [13–17] tried to extrapolate the properties of this system with various versions of Pitzer models relying on the known experimental data in the low molality region. Most recently, Gruskiewicz and Simonson [17] compared the extrapolation effects of various Pitzer models and found large differences among them. In view of the lack of accurate vapor pressure data for concentrated $\text{CaCl}_{2(\text{aq})}$ solutions at elevated temperatures, they undertook simultaneous isopiestic (relative) measurements of water activity and direct (absolute) measurements of vapor pressure of this system at several temperatures between (380.15 and 523.15 K). Their measurements were conducted in the range of water activities between 0.85 and 0.2, approaching, but not reaching the solubility limit of CaCl_2 . Depending on their experimental data and

other data they found consistent with their data, Gruskiewicz and Simonson [17] have determined an entire set of parameters of a new Pitzer model, covering the entire concentration range from infinite dilute solution to solubility limit and the temperature range $T = 298.15\text{--}573.15\text{ K}$. Despite that Gruskiewicz and Simonson's experimental data are believed to be quite accurate, we would rather not use their Pitzer model parameters to judge the thermodynamic consistency of the solubilities and the vapor pressures of the $\text{CaCl}_{2(\text{aq})}$ solution, since some saturated-solution data [18–20] (solubility and vapor pressure of the corresponding saturated solution) are also included in their database for the model parameter determination and different combinations of a solubility data and the vapor pressures above the saturated solution will lead to different osmotic coefficients.

Strong prediction ability of selected thermodynamic model, namely, the model parameters determined by fitting to component activity in unsaturated solution still work up to saturated solution, is another prerequisite for the purpose of this work. As mentioned by Gruskiewicz and Simonson [17], the peculiar behavior of osmotic coefficient for the very concentrated $\text{CaCl}_{2(\text{aq})}$ solution, namely the osmotic coefficient changing flatly at very high molalities, is rather difficult to predict by an extended Pitzer equation with no ionic-strength dependency beyond the second virial [13,15] or by a molality polynomials [14].

In the past 20 years, various primitive and non-primitive MSA-based models have attracted extensive attentions in representing component activities of single and mixing electrolyte solution; however, these models are not accurate enough at extreme high concentration. For example, Simonin et al. [21] have applied primitive MSA to represent the osmotic coefficient of LiCl aqueous solution with an average relative accuracy of 0.5%, but the maximal absolute deviation in osmotic coefficient at concentration above 10 mol kg^{-1} is high up to 0.06. Our previous work [10] showed that the maximal absolute deviation of BET model values from experimental values [22] is below 0.02 in osmotic coefficient at salt concentration above 10 mol kg^{-1} . When a new equation of state based on electrolyte perturbation theory, mean spherical approximation and statistical associating fluid theory are applied to represent the activity coefficient of CaCl_2 aqueous solution, the average relative deviation is already up to 3.876% at salt concentrations below 3 mol kg^{-1} [23].

On the other hand, Stokes and Robinson's modified BET equation [11] has been proved to be quite suitable for highly soluble salt aqueous systems especially in concentrated solution and showed an excellent extrapolation ability in the direction of saturated solution in the system $\text{LiCl} + \text{H}_2\text{O}$ [10]. This equation is given by Eq. (1):

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

where a_w is the water activity referenced to pure water at the temperature in question, $c = \exp(-\Delta E/RT)$, $\Delta E = (U - U_L)$, U is the negative energy of mono-layer adsorption of water onto the solute (CaCl_2), and U_L is the internal energy of liquefaction of pure water. For example, with parameters obtained by fitted to water activity at LiCl concentrations $<20\text{ mol kg}^{-1}$, the

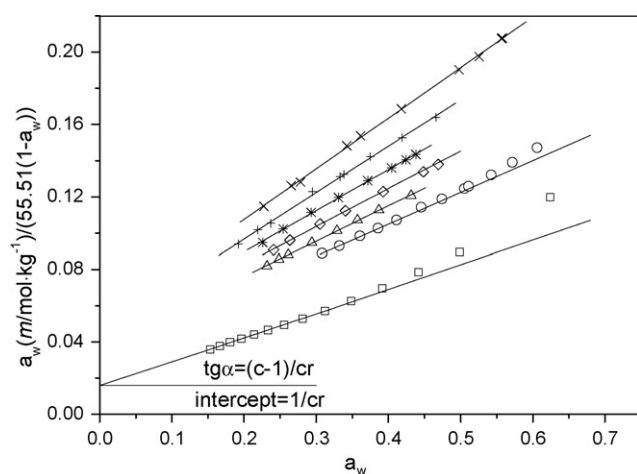


Fig. 1. BET relation of water activity a_w and salt concentration m , mol kg⁻¹ in the system CaCl₂ + H₂O. (—) BET model fitted to the experimental data: (□) $T=298.15$ K [12]; (○) $T=413.15$ K; (△) $T=433.15$ K; (◇) $T=453.15$ K; (*) $T=473.15$ K; (+) $T=498.15$ K; (×) $T=523.15$ K [17].

BET model can predict the properties of saturated LiCl aqueous solution (about 30 mol kg⁻¹) at 373.15 K [10]. Therefore, the modified BET model are selected to extrapolate the properties of the CaCl_{2(aq)} solution up to saturated solution.

Previously, Ally [24] treated Rard and Clegg's data for the CaCl_{2(aq)} solution at 298.15 K and showed that the BET linear relation holds quite well for this system in a wide molality range 7 mol kg⁻¹ < m < 11 mol kg⁻¹ (Fig. 3 in Ref. [24]). Nevertheless, some of their recalculated osmotic coefficients deviate from the experimental data even up to 0.03. Thus, we fitted the BET parameter again (Fig. 1) to the experimental data with water activities below 0.2959 and obtained almost the same BET parameter values ($c=9.306$ and $r=6.766$) as Ally. Our recalculated osmotic coefficients are presented in Fig. 2 and Table 1, also plotted are the experimental data of Rard and Clegg [12] and the recalculated data of Ally for comparison. Probably some slight numerical errors appeared in the calculations of Ally with

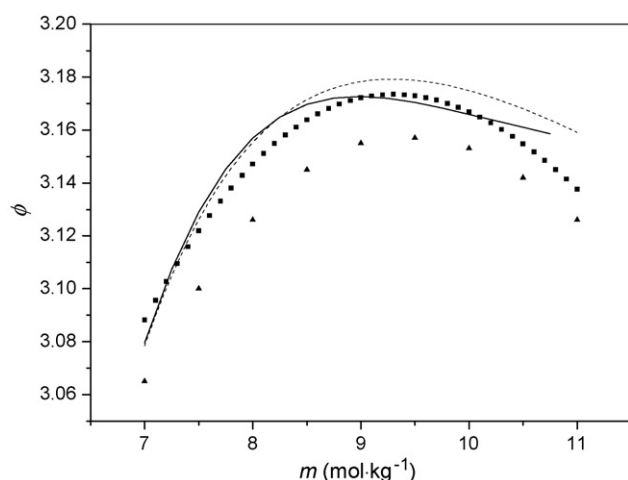


Fig. 2. Comparison of the osmotic coefficient of the CaCl_{2(aq)} solution at 298.15 K. (—) Rard and Clegg's recommended value [12]; (---) Gruskiewicz and Simonson's model value [17]; (▲) Ally's BET model values [24]; (■) BET model values in this work.

Table 1

Experimental and calculated water activities in the system CaCl₂ + H₂O at 298.15 K

m (mol kg ⁻¹)	Exp. [12]		BET [24]		BET, this work	
	a_w	ϕ	a_w	ϕ	a_w	ϕ
7	0.3119	3.0796	0.3136	3.065	0.3109	3.0882
7.5	0.2813	3.1291	0.2846	3.100	0.2821	3.122
8	0.2554	3.157	0.2587	3.126	0.2564	3.147
8.5	0.2331	3.1697	0.2358	3.145	0.2338	3.164
9	0.2137	3.1727	0.2155	3.155	0.2137	3.172
9.5	0.1964	3.1704	0.1977	3.157	0.1952	3.172
10	0.1807	3.1659	0.1819	3.153	0.1806	3.167
10.5	0.1663	3.161	0.1681	3.142	0.1669	3.155

the Eq. (1), for their BET parameters are correct. Our recalculated osmotic coefficients deviate from the experimental data above 7 mol kg⁻¹ by 0.01 in maximum.

As discussed by Gruskiewicz and Simonson [17], a serious defect of calcium chloride arising from the substantial decrease of the solubility product of CaCO₃ in the CaCl_{2(aq)} solution at temperatures above 423 K may bring a remarkable uncertainty into the experimental data. At first, we fit the BET model to their experimental data at 413.15 K (see Fig. 1). Because no vapor pressure data were determined at high molalities (>7 mol kg⁻¹) between 298.15 and 413.15 K, thus, we assume that the BET model parameters r and ΔE change linearly with the temperature and obtain the temperature function of the BET parameters shown in Table 2 and Figs. 3 and 4.

The osmotic coefficients and water activities predicted with the BET parameters are presented in Figs. 5 and 6, respectively. For comparison, the Pitzer-model values given by Gruskiewicz and Simonson, Hoffmann and Voigt, Pitzer and Oakes, are also plotted in these figures. One can see that the BET predicted values coincide quite well with the Gruskiewicz and Simonson's Pitzer-model data [17] in a large molality range and differ from other values essentially. As mentioned by Gruskiewicz and Simonson, the extended Pitzer equation with no ionic-strength

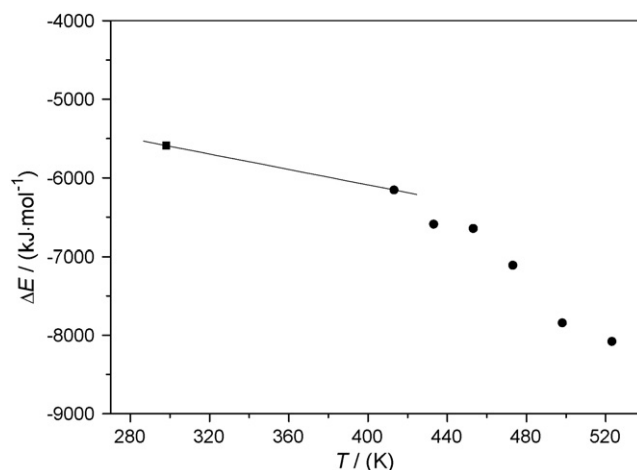


Fig. 3. BET parameter ΔE vs. temperature in the system CaCl₂ + H₂O. (—) Line fitted to the values at 298.15 and 413.15 K; (■) BET parameter fitted to Rard and Clegg's osmotic coefficients [12]; (●) BET parameter fitted to Gruskiewicz and Simonson's experimental values [17].

Table 2
BET model parameter for the system $\text{CaCl}_2 + \text{H}_2\text{O}$

BET parameters ^a				Temperature range of fitting (K)	Exp. data for the parameterization
r		ΔE (J mol ^{−1})			
a	b	a	b		
11.954	−0.0174	−3904.9	−5.4487	298.15–413.15	[12,17]
11.862	−0.0173	−184.06	−14.535	413.15–473.15	[17]

^a $r = a + b(T, \text{K})$, and $\Delta E, \text{J mol}^{-1} = a + b(T, \text{K})$.

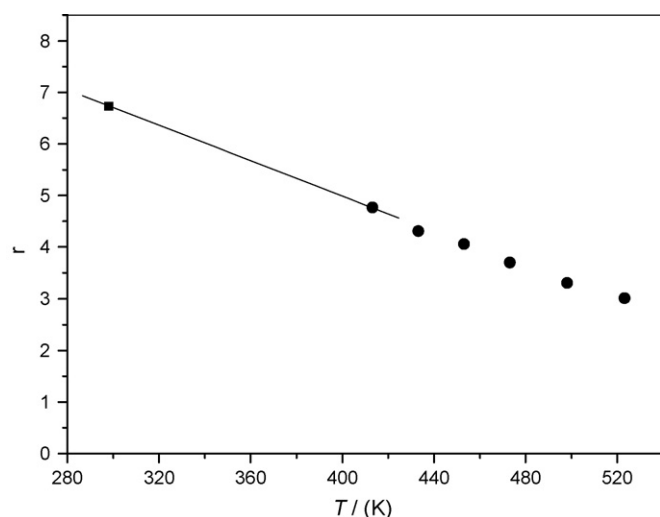


Fig. 4. BET parameter r vs. temperature in the system $\text{CaCl}_2 + \text{H}_2\text{O}$. (—) Line fitted to the values at 298.15 and 413.15 K; (■) BET parameter fitted to Rard and Clegg's osmotic coefficients [12]; (●) BET parameter fitted to Gruskiewicz and Simonson's experimental values [17].

dependency beyond the second virial, used by Ananthaswamy and Atkinson [13] and Hoffmann and Voigt [15], was not adequate for a wide range of temperature and molality of this system, neither Pitzer and Oakes's molality polynomials [14].

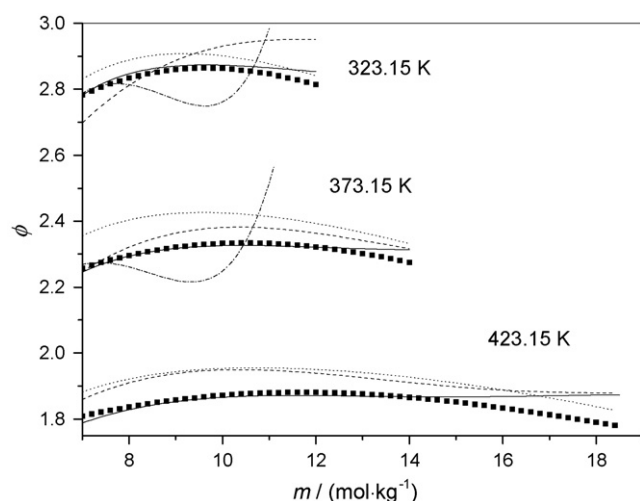


Fig. 5. Comparison of osmotic coefficient of the $\text{CaCl}_{2(\text{aq})}$ solution at 323.15, 373.15 and 423.15 K. (—) Gruskiewicz and Simonson's model values [17]; (···) Pitzer and Oakes's model values [14]; (---) Hoffmann and Voigt's Pitzer-model values [15]; (- · - · -) Ananthaswamy and Atkinson's Pitzer-model values [13]; (■) BET model in this work.

We note also that, at higher molality end approaching the saturation points of each temperature, the BET predicted osmotic coefficients are systematically lower than the Gruskiewicz and Simonson's model values [17] and the deviation gets larger with increasing temperature. As mentioned above, some saturated solution data [18–20] were included in Gruskiewicz and Simonson's database for their Pitzer model parameterization, and these data, which are to be evaluated objects, were not used in the BET parameter determination of this work. In fact, Gruskiewicz and Simonson [17] measured the vapor pressures of the $\text{CaCl}_{2(\text{aq})}$ solution over a molality range up to $11.076 \text{ mol kg}^{-1}$ at 413.15 K, and the saturation concentration of CaCl_2 at this temperature is about $16.7\text{--}17.2 \text{ mol kg}^{-1}$. The extrapolation of the water activity to over 6 mol kg^{-1} far away from the known experimental data is a serious challenge for any thermodynamic models. In our previous work [10] it has been shown that the BET model relationship Eq. (1) holds for the $\text{LiCl}_{(\text{aq})}$ solution at 373.15 K over a large molality range of $12\text{--}30 \text{ mol kg}^{-1}$. In the case for the $\text{CaCl}_{2(\text{aq})}$ solution, assuming that the BET relation holds from high salt concentration up to the saturated solution could be also reasonable.

In view of the small osmotic coefficient difference (about 0.01 in Figs. 2 and 5) between the BET predicted values in this work and the extended Pitzer model values reported by Rard

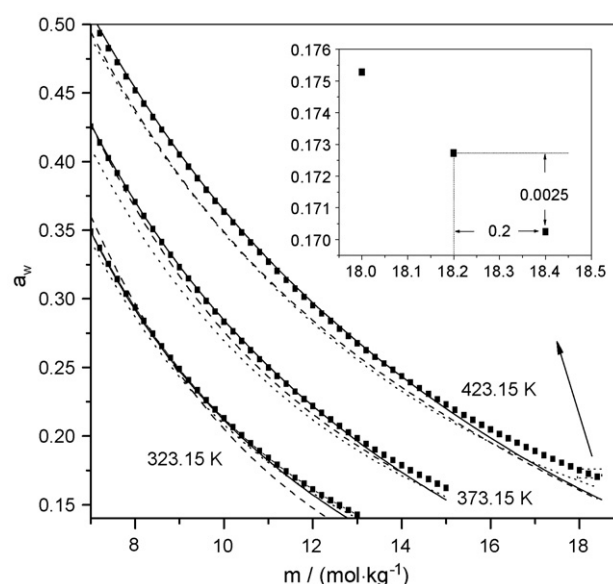


Fig. 6. Comparison of water activity of the $\text{CaCl}_{2(\text{aq})}$ solution at 323.15, 373.15 and 423.15 K. (—) Gruskiewicz and Simonson [17]; (···) Pitzer and Oakes [14]; (---) Hoffmann and Voigt [15]; (■) BET model in this work.

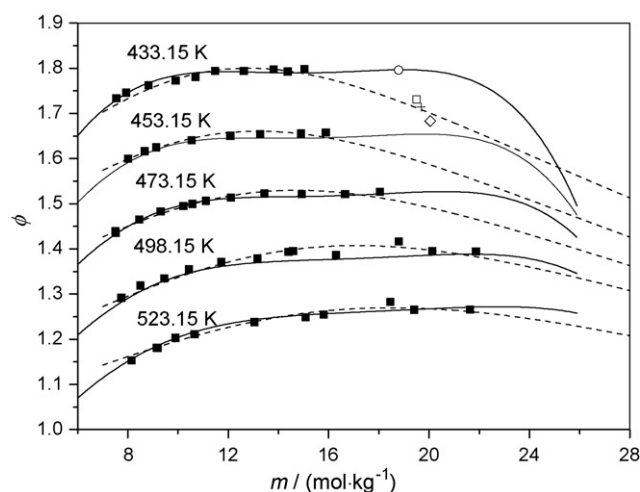


Fig. 7. Comparison of osmotic coefficient of the $\text{CaCl}_2(\text{aq})$ solution at 433.15, 453.15, 473.15, 498.15, and 523.15 K. (■) Gruskiewicz and Simonson's experimental data [12]; (—) Gruskiewicz and Simonson's Pitzer-model data [17]; (---) BET model in this work; other symbols are the calculated values with the vapor pressure [20] above the CaCl_2 saturated solution at 433.15 K combining various solubility data: (○) Clyne and Potter [25]; (□) Smith-Magowan et al. [2]; (+) Sinke et al. [7]; (◇) Roozeboom [18].

and Clegg [12] (298.15 K) and by Gruskiewicz and Simonson [17] (323.15–423.15 K) over a wide molality range above 7 mol kg^{-1} , and the maximal experimental uncertainty 0.025 in osmotic coefficient reported by Gruskiewicz and Simonson for their experimental data at 413.15 K, which have been used for the BET parameter determination in this work, it can be reasonably assumed that the predicted values of the BET model in this work possess an accuracy of 0.025 for the osmotic coefficient or 0.0025 for water activity. This accuracy equals also to, as shown by the insert in Fig. 6, a solubility uncertainty of 0.2 mol kg^{-1} at 423.15 K.

Meanwhile, we treat Gruskiewicz and Simonson's experimental data at temperatures higher than 413.15 K and get quite good BET linear relations at each temperature, as shown in Fig. 1. However, the temperature dependence of the BET parameter ΔE , as shown in Fig. 3, is quite different in the two temperature ranges of lower and higher than 413.15 K. That the BET parameter ΔE changes more sharply above 413.15 K may indicate some unknown structure change of the salt solution. We note also in Fig. 3 that the BET parameters ΔE are some scattered at different temperatures. To obtain a relatively accurate set of parameter, we fit the BET model to the experimental data above 413.15 K again and obtain another set of BET parameter (in Table 2).

The recalculated osmotic coefficients with the BET model and their comparison with the Gruskiewicz and Simonson's original experimental data and their Pitzer model values above 413.15 K are presented in Fig. 7. One can see that all data are in good agreement in the experimental concentration range. Beyond this range, however, the BET model and Pitzer model predict quite different results. When the Pitzer model predicts a plateau and then an abrupt descent of the osmotic coefficient with the increasing molality, the BET model predicts a gradual fall after the maximum. Combining the vapor pressure

data [19] above the $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ saturated solution with various solubility data [2,7,18,25] at 433.15 K, one can obtain various osmotic coefficients, as shown in Fig. 7. It can be seen that the Gruskiewicz and Simonson's Pitzer model reproduces the solubility data of Clyne and Potter [25] and the BET model those of Sinke et al. [7]. As mentioned above, some solubility data have already been used for the parameterization of the Pitzer model.

3. Evaluation of experimental data of vapor pressure above saturated electrolyte solutions

As the solubility, the vapor pressures above the saturated solution of this system have been widely measured. Among all the vapor pressure data [18–20,26–29] measured for the $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ saturated solution (Fig. 8), the data reported by Acheson [27], and Lannung [29] have a stated absolute uncertainty of about 1.3 Pa, corresponding to a relative error of 0.5%. Morillon et al.'s data [28] have a stated relative error of 2%. However, the data of Roozeboom [18] and Collins and Menzies [20] are less accurate in the low vapor pressure range, for example, Collins and Menzies's reported absolute differences of 26 Pa for a duplicate samples at 298.15 K corresponds to a relative error of 2.8%. It is noteworthy that the three sets of data [27–29] determined at different times by different authors agree to 2% with each other. Thus, the vapor pressure data of Acheson [27], Lannung [29] are selected as the 'standard' values for the $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ solubility prediction.

The vapor pressures of the $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\alpha, \beta, \gamma)$ saturated solution from various sources are plotted in Figs. 9–11, respectively. As Collins and Menzies [20] reported, the quality of their data improves with increasing temperature and pressure. The relative deviations of their data for the $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\alpha)$ saturated solution from other data [18,19,27,29] are generally smaller than

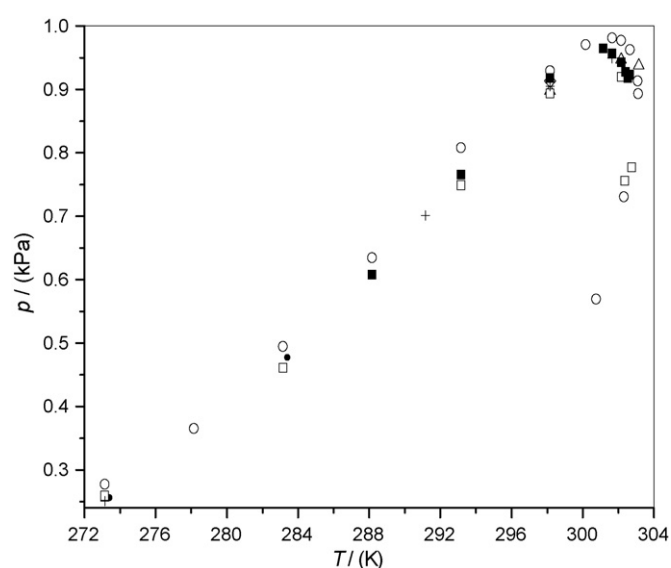


Fig. 8. Vapor pressures of the $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ saturated solution vs. temperatures. (□) Roozeboom [18]; (○) International Critical Tables [19]; (△) Collins and Menzies [20]; (◇) Richardson and Malthus [26]; (■) Acheson [27]; (●) Morillon et al. [28]; (+) Lannung [29].

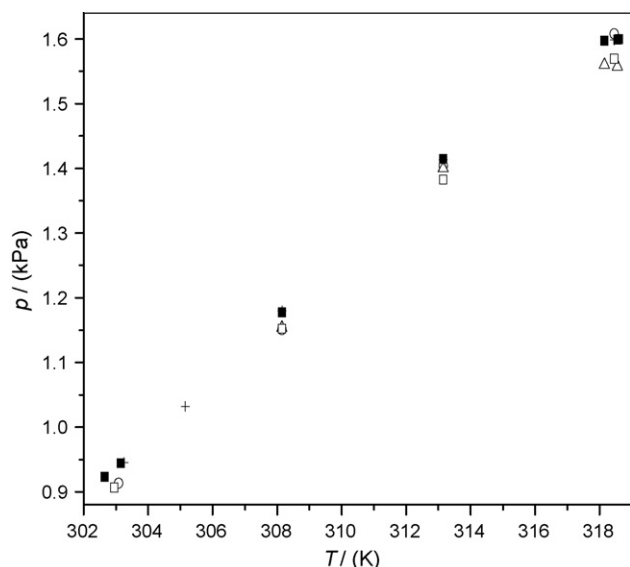


Fig. 9. Vapor pressures of the $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\alpha)$ saturated solution vs. temperatures. (□) Roozeboom [18]; (○) International Critical Tables [19]; (△) Collins and Menzies [20]; (■) Acheson [27]; (+) Lannung [29].

2.5%, while the agreement of Acheson's [27] and Lannung's [29] data within 0.5% is better. As the stated absolute uncertainty of Acheson's and Lannung's data is only 1.3 Pa, their data are selected as the 'standard' values in the present work. The differences of the vapor pressure of the $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\beta)$ saturated solution from different sources [19,29] are quite large, as shown in Fig. 10. One notes that the structure types of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\beta)$ and $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\gamma)$ were even not clear until 1933, when Bassett et al. [30] found a new solubility line lying between that of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\alpha)$ and $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\beta)$ assigned by Roozeboom [18] in 1889, thus, Bassett et al. assigned Roozeboom's $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\beta)$ as $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\gamma)$ and their themselves new curve for $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\beta)$. The data in the

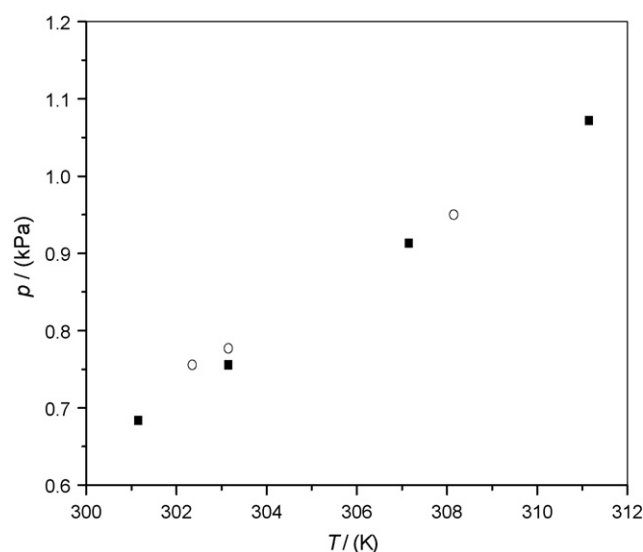


Fig. 11. Vapor pressures of the $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\gamma)$ saturated solution vs. temperatures. (○) Roozeboom [18]; (■) Lannung [29].

International Critical Tables [19] in 1928 for $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\beta)$ could be for $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\gamma)$, consequently, the Lannung's data [29] for $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\beta)$ are taken as the 'standard' values. The disagreement of Lannung's [29] and Roozeboom's data for $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\gamma)$ is within 3% (Fig. 10). Since the stated precision of Lannung is higher, their data are selected as the 'standard' values (Fig. 12).

Unfortunately, the quite accurate Lannung's vapor pressure data [29] for the $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ saturated solution is only up to 323.15 K and Acheson's data [27] to 328.15 K. The relevant data in the International Critical Tables in 1928 [19] and in Collins and Menzies's work [20], however, are up to 449 K. Fortunately, all the data [19,20,27,29] agree well to 2% in the temperature

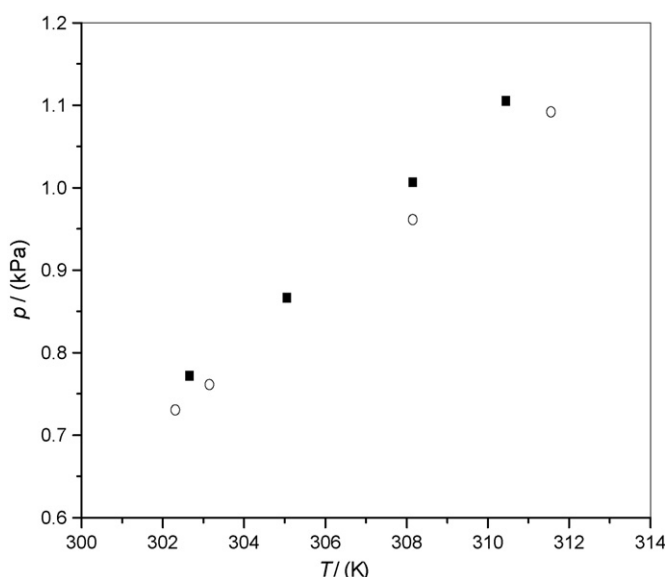


Fig. 10. Vapor pressures of the $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\beta)$ saturated solution vs. temperatures. (○) International Critical Tables [19]; (■) Lannung [29].

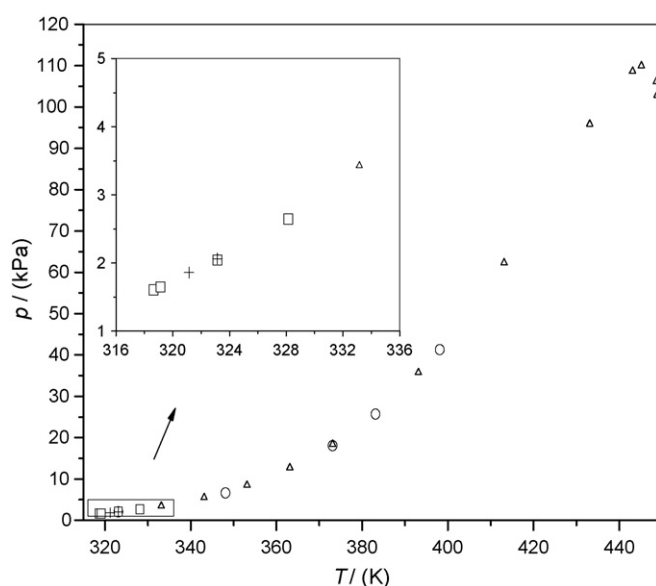


Fig. 12. Vapor pressures of the $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ saturated solution vs. temperatures. (△) International Critical Tables [19]; (○) Collins and Menzies [20]; (□) Acheson [27]; (+) Lannung [29].

range $T=318\text{--}328\text{ K}$. It seems that the data of International Critical Tables [19] and Collins and Menzies's [20] are more accurate at higher temperatures. Thus, it could be reasonably assumed that all the vapor pressure data [19,20,27,29] above $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ saturated solution possess an accuracy of 2% in the temperature range $T=318\text{--}449\text{ K}$, and will be used for the solubility prediction in this work.

To summarize, we believe, the uncertainty of all the vapor pressure data of the saturated solutions selected in this work is within 2%, from which the uncertainty of predicted solubility will be discussed later.

4. Solubility prediction of the system $\text{CaCl}_2 + \text{H}_2\text{O}$

The selected vapor pressures p above the $\text{CaCl}_2 \cdot n\text{H}_2\text{O}$ saturated solution are converted to water activities a_w according to Eq. (2) [12]:

$$\ln a_w = \ln \left(\frac{p}{p_0} \right) + \frac{B_T(p - p_0)}{RT} + V_w(p - p_0) \quad (2)$$

where p_0 and p are the vapor pressure of pure water and salt solution at temperature T , $R=8.314\text{ J mol}^{-1}\text{ K}^{-1}$, V_w the partial molar volume of water in the solution and approximately taken the value of pure water in this work, B_T the second virial coefficient taken from literature [31] at various temperatures. The uncertainty arising from the approximation for V_w can be negligible, compared with the experimental error of the vapor pressure p . Applying the water activities converted from the vapor pressures above saturated solution as criteria, we predict the solubility of the $\text{CaCl}_2 + \text{H}_2\text{O}$ system with the BET model parameters listed in Table 2. The predicted solubility data are presented in Fig. 13. Furthermore, we fit the solubility products $\ln k_{\text{CaCl}_2 \cdot n\text{H}_2\text{O}}$ of each hydrate phase to the predicted solubility points by calculating the salt activity a_{CaCl_2} and the water activity a_w according to Eq. (3), where the salt activity is calculated

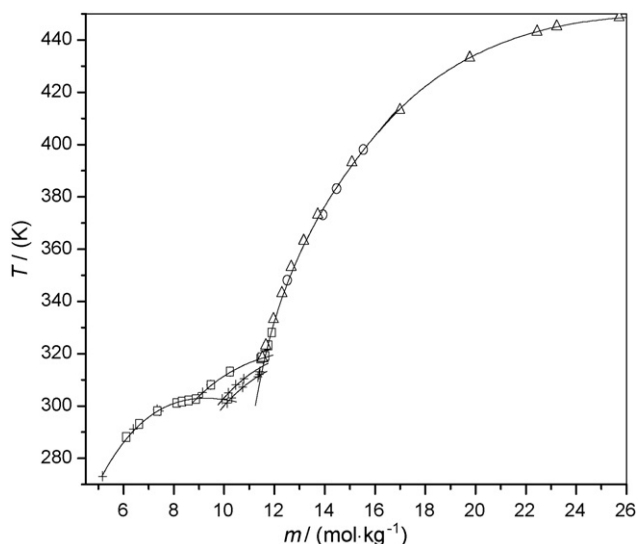


Fig. 13. Predicted phase diagram of the system $\text{CaCl}_2 + \text{H}_2\text{O}$ using the vapor pressures above saturated solution as criteria. (Δ) International Critical Tables [19]; (\circ) Collins and Menzies [20]; (\square) Acheson [27]; (+) Lannung [29].

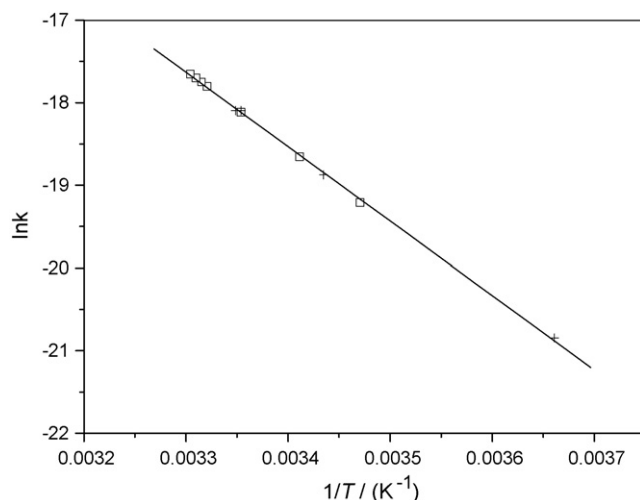


Fig. 14. Temperature dependence of the solubility product $\ln k$ of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. (\square) Acheson [27]; (+) Lannung [29].

with the expression derived by Voigt [32]:



$$\ln k_{\text{CaCl}_2 \cdot n\text{H}_2\text{O}} = \ln a_{\text{CaCl}_2} + n \ln a_w \quad (3)$$

As shown in Figs. 14 and 15, the temperature dependence of $\ln k_{\text{CaCl}_2 \cdot n\text{H}_2\text{O}}$ for $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\alpha)$, $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\beta)$ and $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\gamma)$ can be sufficiently expressed by a linear relationship: $\ln k_{\text{CaCl}_2 \cdot n\text{H}_2\text{O}} = (a_1 + a_2)/(T, \text{ K})$. The $\ln k_{\text{CaCl}_2 \cdot n\text{H}_2\text{O}}$ values for $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ are somewhat complicated and were fitted in two separated temperature ranges of higher and lower than 413 K (Fig. 16). All the fitted parameters of $\ln k_{\text{CaCl}_2 \cdot n\text{H}_2\text{O}}$ are listed in Table 3. The solubility diagram predicted with the BET parameters in Tables 2 and 3 is plotted in Fig. 13. For convenient use, the equilibrium temperatures of each hydrate are fitted as polynomials of their saturation concentration and all the parameters of the expressions are provided in Table 4.

Generally, the uncertainty of the predicted solubility mainly comes from three parts: (1) Δm , the uncertainty $\Delta \phi$ of the

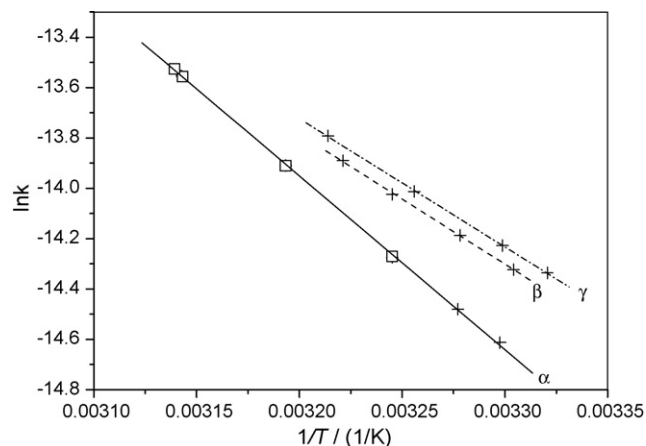


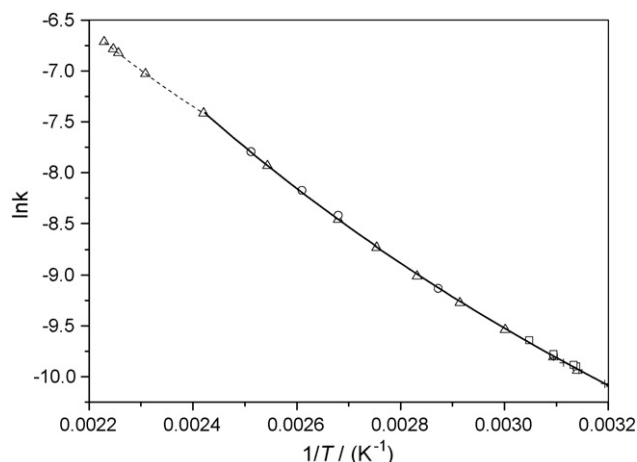
Fig. 15. Temperature dependence of the solubility product $\ln k$ of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\alpha, \beta, \gamma)$. Lines, fitted values; (\square) Acheson [27]; (+) Lannung [29].

Table 3

Temperature dependence of $\ln k_{\text{CaCl}_2 \cdot n\text{H}_2\text{O}}$ ^a

	A	B	C	D ($\times 10^{-4}$)	E	Temperature range of fitting (K)	No. of points
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	11.699	−8867.4	0	0	0	273–303	11
$\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\alpha)$	7.7869	−6775.9	0	0	0	302–318	9
$\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\beta)$	2.4406	−5053.5	0	0	0	302–311	4
$\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\gamma)$	2.1956	−4958.8	0	0	0	298–311	5
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	2799.8743	−57917.15	1.643064	8.11447077	−532.46122	418–413	22
	−179.1829	7336.188	0	0	25.56691	413–449	4

^a $\ln k_{\text{CaCl}_2 \cdot n\text{H}_2\text{O}} = A + B/(T, \text{K}) + C(T, \text{K}) + D(T, \text{K})^2 + E \ln(T, \text{K})$.

Fig. 16. Temperature dependence of the solubility product $\ln k$ of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. (Δ) International Critical Tables [19]; (○) Collins and Menzies [20]; (□) Achen-son [27]; (+) Lannung [29].

experimental osmotic coefficients of under-saturated solutions, to which the BET model parameters are fitted; (2) Δm_2 , the uncertainty of the experimental vapor pressures of saturated solution used as criteria in the solubility prediction; (3) Δm_3 , the uncertainty of the BET model extrapolation values. Since the water activity a_w , the osmotic coefficient ϕ and the saturation salt concentration m_s are related by the relation: $\ln a = -3\phi(m_s, \text{kg mol}^{-1})/55.51$, for a given water activity criteria, the uncertainty of the osmotic coefficient $\Delta\phi$ will result in a saturation salt concentration uncertainty $\Delta m_1 = \Delta\phi m_s / \phi$. The maximal value $\Delta\phi$ is taken as 0.01 and 0.025 at 298.15 K [13] and 413.15 K [21], respectively. The value $\Delta\phi$ is assumed to change linearly with the temperature: $\Delta\phi = 0.01 + 0.025 - 0.01((T, \text{K}) - 298.15)/(413.15 - 298.15)$ between 298.15 and 413.15 K and keeps constant 0.01 and 0.025 at temperatures lower than

298.15 K and higher than 413.15 K, respectively. The estimated uncertainty Δm_1 are shown in Fig. 18. As discussed above, the relative uncertainty $\Delta p/p$ of the experimental vapor pressures p above the saturated solution is less than 2% on the whole temperature range considered, thus, it can be reasonably considered that the uncertainty Δa_w of the water activity converted by the Eq. (2) is approximately equal to $0.02 a_w$. This term will cause an uncertainty of the predicted solubility $\Delta m_2 = (dm_s/da_w) \times \Delta a_w = (dm_s/da_w) \times a_w \times 0.02$. To obtain the dm_s/da_w values, the water activities are first calculated near the saturation concentration at various temperatures, as shown in Fig. 17, from which one can derive the values

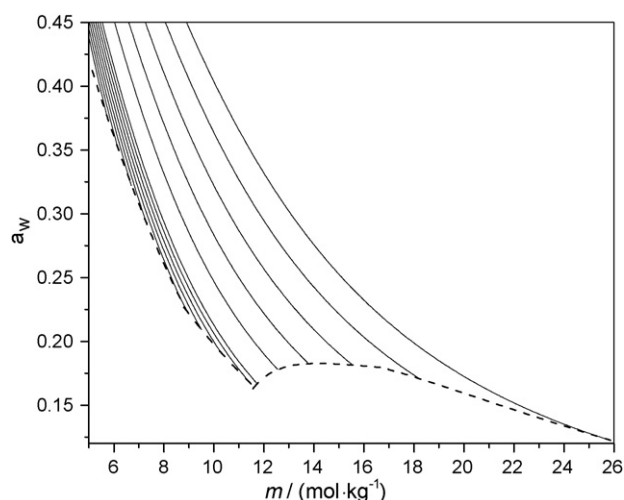
Fig. 17. Temperature and concentration independence of water activity a_w in the $\text{CaCl}_{2(\text{aq})}$ solution. (—) Calculated isotherms at $T = 283.15, 288.15, 293.15, 298.15, 303.15, 308.15, 313.15, 318.15, 323.15, 348.15, 373.15, 398.15, 423.15, 443.15$ K; (---) calculated water activity at solubility limits.

Table 4

Predicted solubility–temperature relationships for the calcium chloride hydrates

Phase	Solubility–temperature expression
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	$(T, \text{K}) = 73.0333 + 65.1280(m, \text{kg mol}^{-1}) - 6.01768(m, \text{kg mol}^{-1})^2 + 0.179901(m, \text{kg mol}^{-1})^3$
$\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\alpha)$	$(T, \text{K}) = 8.41362 + 65.16704(m, \text{kg mol}^{-1}) - 4.56768(m, \text{kg mol}^{-1})^2 + 0.108171(m, \text{kg mol}^{-1})^3$
$\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\beta)$	$(T, \text{K}) = -133.584 + 88.8759(m, \text{kg mol}^{-1}) - 5.75112(m, \text{kg mol}^{-1})^2 + 0.123091(m, \text{kg mol}^{-1})^3$
$\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\gamma)$	$(T, \text{K}) = -142.799 + 90.2415(m, \text{kg mol}^{-1}) - 5.85015(m, \text{kg mol}^{-1})^2 + 0.125553(m, \text{kg mol}^{-1})^3$
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	$(T, \text{K}) = -6148.7259 + 1942.1821(m, \text{kg mol}^{-1}) - 244.44948(m, \text{kg mol}^{-1})^2 + 16.509484(m, \text{kg mol}^{-1})^3$ $- 0.62500492(m, \text{kg mol}^{-1})^4 + 0.012523065(m, \text{kg mol}^{-1})^5 - (1.0359118 \times 10^{-4})(m, \text{kg mol}^{-1})^6$

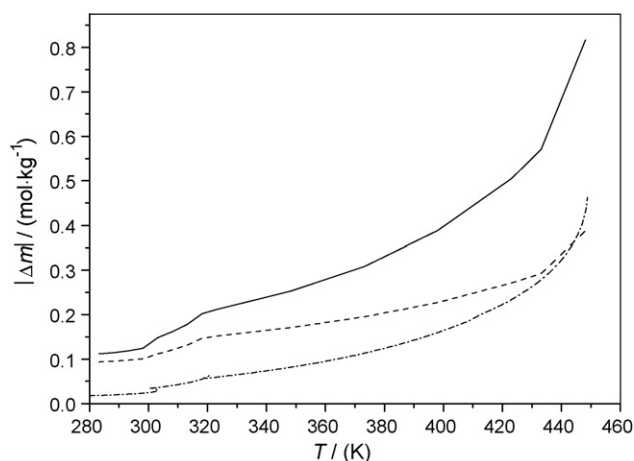


Fig. 18. Uncertainty of the predicted solubility at various temperatures. (---) Δm_1 , estimated solubility uncertainty arising from the uncertainty of the experimental osmotic coefficients [12,17]; (-.-) Δm_2 , estimated solubility uncertainty arising from the uncertainty of the experimental vapor pressures of saturated solution; (—) $\Delta m_1 + \Delta m_2$, total uncertainty of estimated solubility.

dm_s/da_w and thereby Δm_2 (see Fig. 18). Furthermore, we assume that the BET relation of Eq. (1) is valid for the $\text{CaCl}_2(\text{aq})$ solution from concentrated solution up to its solubility limit at each temperatures, then the above mentioned uncertainty Δm_3 will be negligible. Thus, the total estimated uncertainty of the predicted solubility becomes $\Delta m_1 + \Delta m_2$, as shown by the solid line in Fig. 18.

5. Evaluation of various experimental solubility data

Deviations of various experimental data from the predicted solubility in this work are shown in Figs. 19–23.

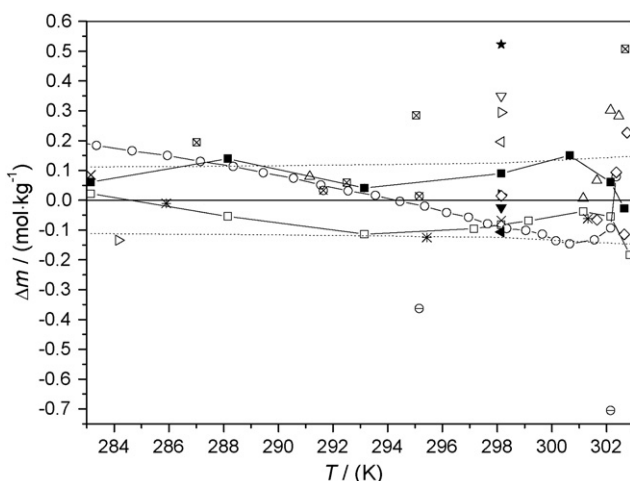


Fig. 19. Differences between experimental and predicted solubility of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ at various temperatures. (Δ) Assarsson and Balder [33]; (∇) blidin [34]; (\triangleleft) Cameron et al. [35]; (\triangleright) Carli [36]; (\blacktriangle) Druzhinin and Shepelev [5]; (\blacktriangledown) Ehret [38]; (\blacktriangleleft) Filippov and Mihelbison [39]; (\blacktriangleright) Lee and Egerton [40]; (+) Mazzetti [41]; (\times) Millikan [42]; (*) Potter and Clynne [3]; (*): Pelling and Roberson [43]; (\diamond) Roozeboom [18]; (\boxtimes) Hammerl [44]; (\otimes) Yanatieva [4]; (\ominus) Etard [45]; (\circ) Conde [37]; (\square) Smith-Magovan et al. [2]; (\blacksquare) Linke and Seidel [1]; (---) estimated maximal uncertainty of the predicted solubility.

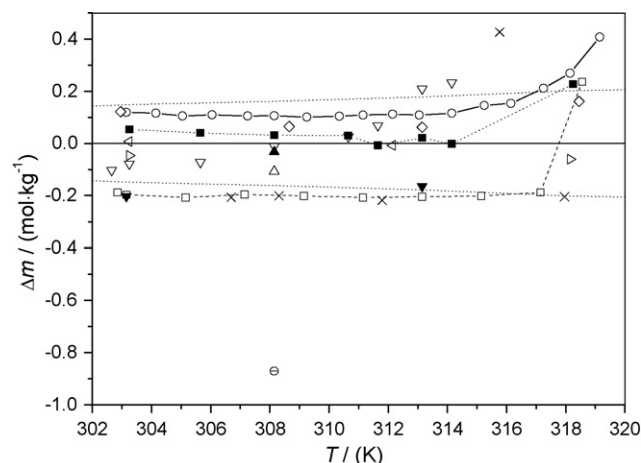


Fig. 20. Differences between experimental and predicted solubility of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\alpha)$ at various temperatures. (Δ) Filippov and Mihelbison [39]; (∇) Assarsson and Balder [33]; (\triangleleft) Bassett et al. [8]; (\triangleright) Druzhinin and Shepelev [5]; (\blacktriangle) Lightfoot and Prutton [47]; (\blacktriangledown) Makarov and Vol'nov [48]; (\times) Potter and Clynne [3]; (\diamond) Roozeboom [18]; (\ominus) Etard [45]; (\circ) Conde [37]; (\square) Smith-Magovan et al. [2]; (\blacksquare) Linke and Seidel [1]; (---) estimated maximal uncertainty of the predicted solubility.

5.1. On the solubility data of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$

As shown in Fig. 19, the predicted solubility data agree quite well within the estimated uncertainty with the experimental data of Potter and Clynne [3], Druzhinin and Shepelev [5], Ehret [38], Filippov and Mihelbison [39], Lee and Egerton [40], Mazzetti [41], Millikan [42] and most points of Yanatieva [4], Roozeboom [19] and Assarsson and Balder [33], while deviating from the data of blidin [34], Cameron et al. [35], Carli [36], Pelling and Roberson [43], Hammerl [44] and Etard [45] obviously. Since Smith-Magovan et al. [2] and Linke and Seidel's [1] data mainly come from the work of Potter and Clynne [3], Yanatieva [4], and therefore are in reasonable agreement with the predicted values. The data of Linke and Seidel [1] are generally $0.1\text{--}0.2\text{ kg mol}^{-1}$.

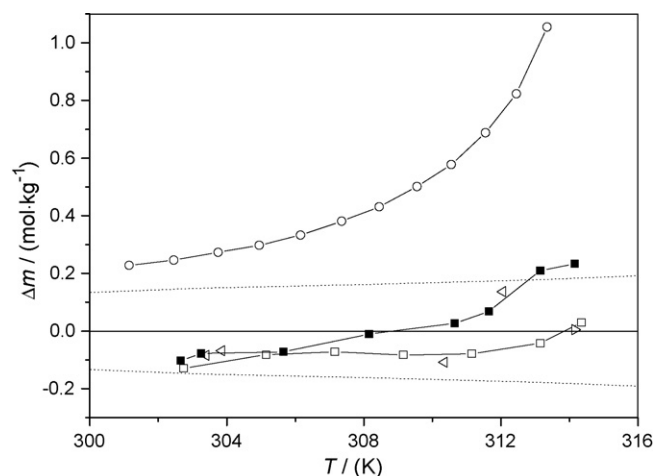


Fig. 21. Differences between experimental and predicted solubility of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\beta)$ at various temperatures. (\triangleleft) Bassett et al. [8]; (\triangleright) Druzhinin and Shepelev [5]; (\circ) Conde [37]; (\square) Smith-Magovan et al. [2]; (\blacksquare) Linke and Seidel [1]; (---) estimated uncertainty of the predicted solubility.

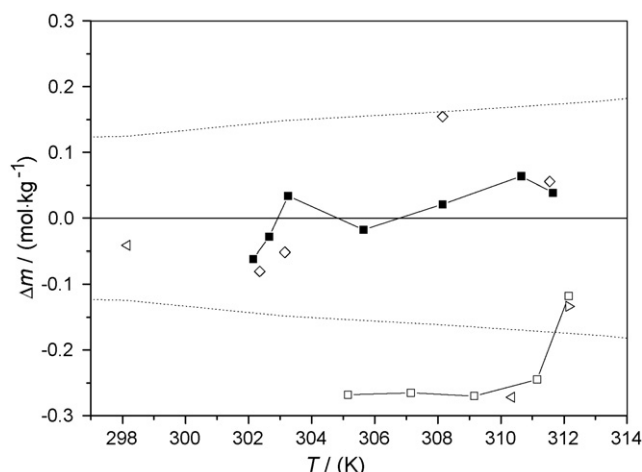


Fig. 22. Differences between experimental and predicted solubility of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\gamma)$ at various temperatures. (\triangleleft) Bassett et al. [8]; (\triangle) Druzhinin and Shepelev [5]; (\diamond) Roozeboom [18]; (\square) Smith-Magovan et al. [2]; (\blacksquare) Linke and Seidel [1]; (\bullet) Conde [37]; (\cdots) estimated maximal uncertainty of the predicted solubility.

higher than of Smith-Magovan et al. [2] and our predicted data fall in between them.

5.2. On the solubility data of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\alpha)$

The predicted solubility agree quite well with the data of Filippov and Mihelbison [39], Bassett et al. [8], Druzhinin and Shepelev [5], Lightfoot and Prutton [47], Roozeboom [18] and most of data of Assarsson and Balder [33] and deviate from the data of Potter and Clynne [3] and Makarov and Vol'nov [48] (Fig. 20). As the data for $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, Etard's data [45] for $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\alpha)$ are also proved to be unreliable. Smith-Magovan et al. [2] selected the data of Potter and Clynne [3] and Makarov and Vol'nov [48] in their compiling and their selection

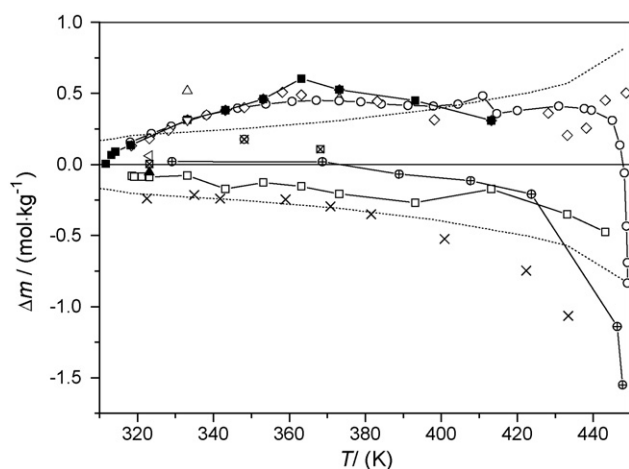


Fig. 23. Differences between experimental and predicted solubility of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ at various temperatures. (\boxtimes) Assarsson [9]; (\triangle) Assarsson and Balder [33]; (\triangleleft) Bassett et al. [49]; (\blacktriangle) Druzhinin and Shepelev [5]; (\odot) Lightfoot and Prutton [47]; (\diamond) Roozeboom [18]; (\times) Clynne and Potter [25]; (\circ) Conde [37]; (\square) Smith-Magovan et al. [2]; (\blacksquare) Linke and Seidel [1]; (\oplus) Sinke et al. [7]; (∇) Tschischikoff [46]; (\cdots) estimated maximal uncertainty of the predicted solubility.

may be questionable. Linke and Seidel's data [1], taken mainly from the data of Bassett et al. [8], Druzhinin and Shepelev [5] and Roozeboom [18], agree also with the prediction. Most of the data Conde [37] for this phase agree with the prediction reasonably.

5.3. On the solubility data of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\beta)$

Except the data of Conde [37], other data from Bassett et al. [8], Druzhinin and Shepelev [5], Smith-Magovan et al. [2] and Linke and Seidel [1] fall in the uncertainty range of the prediction (Fig. 21). Conde [37] may select simply Roozeboom's solubility data for $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\beta)$, which Bassett et al. [8] assigned to be $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\gamma)$ later.

5.4. On the solubility data of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\gamma)$

The experimental solubility data of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\gamma)$ mainly come from the works of Bassett et al. [8], Druzhinin and Shepelev [5] and Roozeboom [18]. Linke and Seidel [1] preferred to the data of Roozeboom [18] while Smith-Magovan et al. [2] preferred to the data of Bassett et al. [8] and Druzhinin and Shepelev [5]. Our prediction is more consistent with the data of Roozeboom [18] and Druzhinin and Shepelev [5] than of Bassett et al. [8] and Smith-Magovan et al. [2] (Fig. 22).

5.5. On the solubility data of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$

The differences of various solubility data for $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ get larger with increasing temperature and molality. Our predicted values agree quite well with the data of Druzhinin and Shepelev [5], Sinke et al. [7], Assarsson [9], Lightfoot and Prutton [47], and Bassett et al. [49]. It seems that Roozeboom's [18] and Assarsson and Balder's [33], Tschischikoff [46], solubility data are too high while Clynne and Potter's data [25] are too low. The different emphases on the experimental solubility data will result in quite different results. Smith-Magovan et al.'s [2] data are the average values of Druzhinin and Shepelev [5], Sinke et al. [7], Assarsson [9] and Clynne and Potter [25] and fall within the uncertainty range of this prediction in the whole temperature range. Linke and Seidel's [1] and Conde's [37] data come mainly from Roozeboom [18], which lie outside the uncertainty range of this prediction in the temperature range $T = 320\text{--}390\text{ K}$.

In summary, solubility measurement methods have meaningful influence on the data quality. The Roozeboom's solubility data [18], obtained by chemical analysis of the equilibrated mixture below 398 K, are usually higher than the data by a visual method [7,25]. However, the solubility data [7,19,25] obtained with a same visual method can be different depending on other experimental factors, for example, the sealing method of samples and agent purity. Our prediction shows that the 'real' solubility of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ may be neither as high as the values of Roozeboom, nor as low as of Clynne and Potter [25], but lie between them, just like the data of Sinke et al., with which our predicted results agree to 0.2 kg mol^{-1} in a large concentration range $T = 329\text{--}423\text{ K}$ (see Fig. 23). The same is true for the solubility data for $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}(\alpha)$.

6. Conclusion

By fitting the BET model parameters to the most recently published accurate water activity data of CaCl_2 solutions in the temperature range from 273.15 to 523.15 K, we obtained the BET model parameters and compared the BET model values with the Pitzer model values. It was shown that the BET model with much fewer parameters could give at least the same good prediction results as the Pitzer model in the concentrated CaCl_2 solution. Meanwhile, the experimental vapor pressures above various CaCl_2 - $n\text{H}_2\text{O}$ saturated solution have been critically evaluated. Those data with high stated accuracy and being consistent with each other are selected as criteria for the solubility prediction of this system. The solubility diagram predicted with the BET model is presented, as well as the estimated uncertainty of the prediction. Furthermore, the predicted values were compared with various experimental data and compiled data. It should be noted that the reliability of the predicted solubility data depends mainly on the following three aspects: (1) the accuracy of the experimental water activity (or osmotic coefficient) in under-saturated $\text{CaCl}_{2(\text{aq})}$ solution; (2) the accuracy of the experimental vapor pressure above CaCl_2 - $n\text{H}_2\text{O}$ saturated solution; (3) the assumption that the BET linear relationship holds in concentrated $\text{CaCl}_{2(\text{aq})}$ solution up to solubility limit at each temperature. Through careful selection and critical evaluation of the available experimental data, we have achieved the highest accuracy as we can in the first two aspects. For the validity range of the BET model, no obvious contradictory case has been encountered for this system at temperatures in question. Anyway, this work adds a more way to the present evaluation methods on the solubility data of the system $\text{CaCl}_2 + \text{H}_2\text{O}$.

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