Solute and Solvent Activities of $CaCl_2$(aq) Solutions from the Adsorption Isotherm Treatment

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The values of the two Brunauer−Emmett−Teller (BET) parameters calculated by Stokes and Robinson (1948) are reevaluated using recent experimental data on the activity coefficients of $CaCl_2$(aq) reported by Rard and Clegg (1997). At the 95% confidence level, no significant statistical differences are observed in the values of the BET parameters reported in this work and those reported by Stokes and Robinson (1948). The water activities a_w, osmotic coefficients ϕ, and mean ionic activity coefficients, $\gamma_\pm$ of $CaCl_2$(aq) are then calculated from saturation to dilute solution. Since the standard state of the solute in the BET model is the anhydrous liquid electrolyte rather than the infinitely dilute solution, the technique of Ally and Braunstein (1996) is utilized to obtain the mean ionic activity coefficients of $CaCl_2$(aq) over the entire concentration range. The differences between the chemical potentials of the solute in the infinitely dilute solution standard state (hypothetical) and the anhydrous liquid electrolyte standard state (hypothetical) are shown to remain constant, as must be, since the standard states are fixed at a given temperature. The ability of the model to predict a_w, ϕ, and $\gamma_\pm$ with only two parameters is reported.

Introduction

Concentrated solutions of $CaCl_2$(aq) are of interest in geochemistry because of its presence in dolomite, sphalerites, and some highly concentrated brines. Recently, $CaCl_2$(aq) was used to control the humidity (water activity) for storage of the fungus *Cronartium ribicola*, which causes white pine blister rust disease of Eastern White pine (Zambino, 1998). $CaCl_2$(aq) has good properties to control humidity (Stokes and Robinson, 1949) and provide a favorable environment for developing and storing pure genotype cultures (Zambino, 1998). It is of practical interest to be able to predict the nonideal behavior of concentrated $CaCl_2$(aq) solutions over wide ranges of concentration.

Strong experimental evidence supports the Stokes−Robinson application of the BET model for aqueous electrolytes first embodied as a relationship between water activity and molality for concentrated electrolytes (Stokes and Robinson, 1948). Many investigators have used Stokes and Robinson's model to show good agreement between experimental and calculated water activities even for ternary and quatenary reciprocal aqueous electrolytes, if the system is treated as a pseudobinary. Ally and Braunstein (1993) and Abraham and Abraham (1997) showed that partial, excess, and integral thermodynamic properties of solutions containing 1:1 and 2:1 electrolytes could be predicted with the same model, and fundamentally there is no limitation that restricts the Stokes−Robinson model to a single electrolyte (Ally and Braunstein, 1998).

The accuracy of the thermodynamic properties predicted by the model depends on the accuracy of the two BET parameters. In principle, isothermal vapor pressure measurements at two discrete solute concentrations where the water activities are less than about 0.3 are sufficient to evaluate the two BET parameters. In reality, due to random errors in measurements, confidence in the accuracy of the parameters from only two measurements would be low. Hence, a finite number of data points are required to reduce the uncertainty in the calculated parameters.

This paper determines whether significant adjustments are warranted in the BET parameters for $CaCl_2$(aq) reported by Stokes and Robinson (1948), in light of the recent data of Rard and Clegg (1997). The 95% confidence level is used as the criteria for deciding whether a significant difference exists or not. Since the standard state of the solute in the BET model is taken as the anhydrous liquid salt (hypothetical) at the temperature in question (298.15 K), and the standard state to which the experimental data are referenced is the infinite dilute solution, a procedure to convert from one to the other is presented. To demonstrate the predictive quality of the BET model, water activities, osmotic coefficients, and solute mean ionic activity coefficients are compared with smoothed experimental data for concentrations far beyond the region used to evaluate the two BET parameters.

BET Parameters from Isopiestic Vapor-Pressure Data

The set of 57 smoothed, critically assessed values from Rard and Clegg (1997) are plotted in Figure 1, and the values corresponding to the linear portion of the graph are tabulated in Table 1. The last column in Table 1 represents the values of the ordinate in the Stokes−Robinson application of the BET model (Stokes and Robinson, 1948),

$$\frac{m a_w}{55.5084(1 - a_w)} = \frac{1}{cr} + \frac{(c - 1)a_w}{cr} \qquad (1)$$

where a_w is the thermodynamic activity of water referenced to pure water at the temperature in question, $c = \exp(-\epsilon/\boldsymbol{RT})$, $\epsilon = (\boldsymbol{U} - \boldsymbol{U}_L)$, $\boldsymbol{U}$ is the negative energy (internal) of monolayer adsorption of water onto the solute ($CaCl_2$), and U_L is the internal energy of liquefaction of pure water. Since U and U_L are both negative, and $|U| > |U_L|$, ϵ is negative for monolayer adsorption and zero for adsorp-

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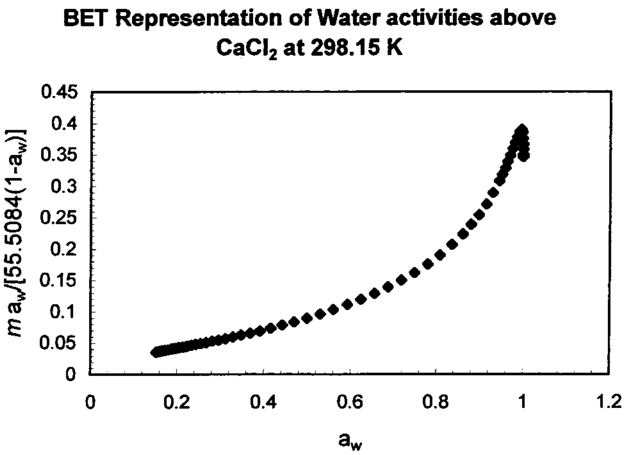

Figure 1. BET plot of water activities above $CaCl_2$(aq) at 298.15 K (Rard and Clegg, 1997). Only the linear portion of the curve is suitable for extracting the two BET parameters *c* and *r* (see eq 1 in text).

Table 1. Smoothed Values of Water Activities a_w and Mean Molal Activity Coefficients $\gamma_\pm$ at 298.15 K (Rard and Clegg, 1997)

m ($CaCl_2$)/ (mol·kg^{-1})	a_w	$\gamma_\pm$	$ma_w/55.51(1 - a_w)$
7.25	0.2959	20.276	0.054 89
7.5	0.2813	22.263	0.052 88
7.75	0.2678	24.27	0.051 07
8	0.2554	26.291	0.049 43
8.25	0.2439	28.321	0.047 94
8.5	0.2331	30.36	0.046 54
8.75	0.2231	32.411	0.045 27
9	0.2137	34.477	0.044 07
9.25	0.2048	36.566	0.042 92
9.5	0.1964	38.685	0.041 83
9.75	0.1883	40.841	0.040 75
10	0.1807	43.042	0.039 73
10.25	0.1733	45.292	0.038 71
10.5	0.1663	47.598	0.037 73
10.75	0.1596	49.96	0.036 78
11.00[a]	0.1531[a]	52.377[a]	0.035 82

[a] These values are extrapolated slightly above the range of experimental data (Rard and Clegg, 1997).

tion of water beyond the first layer. Thus, eq 1 represents a two-state model with water molecules either on a salt sorption site or in contact with other water molecules only (Ally and Braunstein, 1998). The moles of adsorption sites offered per mole of solute are represented by *r*.

The two BET parameters *c* and *r* are evaluated by fitting eq 1 to the data in Table 1 for $a_w < 0.3$, that is, where the relationship between $ma_w/55.5084(1 - a_w)$ (ordinate) and a_w (abscissa) is linear. Two cases are considered. First, the set of 11 data points where $0.1531 < a_w < 0.2331$ and, second, all 16 data points where $0.1531 < a_w < 0.2959$.

BET Parameters when $0.1531 \leq a_w \leq 0.2331$

The arithmetic mean $\bar{x}$ of $n = 11$ consecutive data points of a_w (designated *x*) is 0.1902 with a standard deviation (SD(*x*)) of 0.02643 and a sum of squares $S_{xx} = 6.990 \times 10^{-3}$ where $S_{xx} = (n - 1)(\mathrm{SD}(x))^2$. Likewise, the arithmetic average $\bar{y}$ of the 11 corresponding points on the ordinate, $ma_w/55.5084(1 - a_w)$ (designated *y*) is 4.092×10^{-2}, with a SD(*y*) of 3.533×10^{-3} and a sum of squares $S_{yy} = 1.248 \times 10^{-4}$. The sum of the cross products of the abscissa ($x = a_w$) and the ordinate ($y = ma_w/55.5084(1 - a_w)$) is $S_{xy} = 9.339 \times 10^{-4}$. The slope ($S_{xy}/S_{xx}$) and intercept $b = \bar{y} - (S_{xy}/S_{yy})\bar{x}$ of the BET fit are 1.336×10^{-1} and 1.550×10^{-2}, respectively. Linear regression of the data (Figure 2) yields

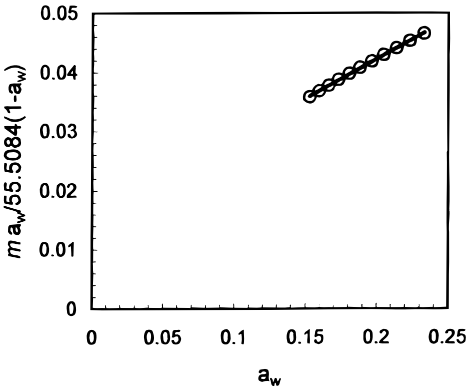

Figure 2. Linear regression of the BET equation to water activities a_w above $CaCl_2$(aq) at 298.15 K where $0.1532 < a_w < 0.2331$. The correlation coefficient $R^2 = 0.9995$.

$$y = 0.1336(x) + 0.01550 \qquad (2)$$

with the correlation coefficient $R^2 = 0.9995$, where $y = ma_w/[55.5084(1 - a_w)]$ and $x = a_w$.

The residual sum of squares (RSS) is calculated as 6.036×10^{-8} where $\mathrm{RSS} = S_{yy} - b^2S_{xx}$. The residual standard deviation (RSD), an estimate of the precision of the linear fit, is 8.189×10^{-5}, where $\mathrm{RSD} = [\mathrm{RSS}/(n - 2)]^{0.5}$. Due to the nature of random errors in the data, the slope and intercept in eq 2 will exhibit variability. The degree of confidence that is ascribed to the slope and intercept in eq 2 can be estimated statistically. A 95% confidence interval (CI) for the true slope (Caulcutt and Boddy, 1991) is estimated as $\mathrm{CI}(95\%) = b \pm t(\mathrm{RSD})/(S_{xx})^{0.5}$, where *t* is the two-sided student's t-test with $(n - 2)$ degrees of freedom (df). The value of t from statistical tables for df = 9 (Caulcutt and Boddy, 1991) is 2.26. Thus, CI(95%) for the true slope is 0.1336 ± 0.002213.

The 95% CI for the true intercept is (Caulcutt and Boddy, 1991)

$$y|_{x=0} \pm t(\mathrm{RSD})\sqrt{\left(\frac{1}{n} + \frac{\bar{x}^2}{S_{xx}}\right)} = 0.0155 \pm 0.00041 \qquad (3)$$

Equating the estimates of the true slopes and intercepts with the appropriate coefficients in eq 1 yields

$$\frac{1}{cr} = 0.0155 \pm 0.00041 \qquad (4)$$

$$\frac{(c - 1)}{cr} = 0.1336 \pm 0.0022 \qquad (5)$$

Solving eqs 4 and 5 simultaneously yields

$$c = 9.615 \pm 0.2675 \qquad (6)$$
$$r = 6.706 \pm 0.2564$$

where *c* and *r* should be retained to three significant figures because the student's t-test is tabulated to three digits.

BET Parameters where $0.1531 \leq a_w \leq 0.2959$

Following the same procedure as above, the linear regression of the 16 data points (Figure 3) yields

$$y = 0.1319x + 0.01588 \qquad (7)$$

with the correlation coefficient $R^2 = 0.9998$. The BET

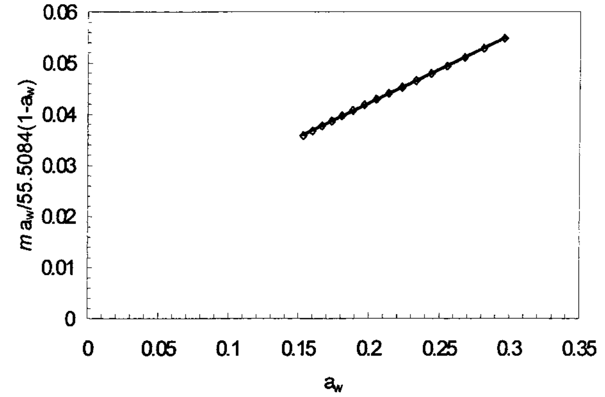

Figure 3. Linear regression of the BET equation to water activities a_w above $CaCl_2$(aq) at 298.15 K where $0.1532 < a_w < 0.2959$. The correlation coefficient $R^2 = 0.9998$.

Table 2. Comparison of BET Parameters for $CaCl_2$(aq) at 298.15 K

r	c	ϵ/kJ·mol^{-1}
6.73[a]	9.50 [a]	5.58[a]
6.71 ± 0.256[b]	9.61 ± 0.267[b]	5.61 ± 0.070[b]

[a] Stokes and Robinson, 1948. [b] This work.

constants c and r are

$$c = 9.33 \pm 0.671 \qquad (8)$$
$$r = 6.77 \pm 0.514$$

The BET parameters in eq 8 estimated from 16 data points where $a_w \leq 0.2959$ show greater variability than the same parameters estimated from 11 data points where $a_w \leq 0.2331$. Strictly speaking, the BET model is valid at low water activities. Hence, the parameters of eq 6 are accepted.

Substituting the estimated value of c from eq 6 in $c = \exp(\epsilon/RT)$ yields $\epsilon = -5.61 \pm 0.070$ kJ·mol^{-1}. The values of $\epsilon = -5.61$ kJ·mol^{-1} and $r = 6.70$ are accepted for subsequent calculations.

A summary of the parameters evaluated in this work compared with those reported by Stokes and Robinson (1948) is given in Table 2.

Comparison of BET Parameters

Comparison between the BET parameters of Stokes and Robinson (1948) and this work can be made on a statistical basis. From Table 2, the results of this work indicate that, with 95% confidence, the true values of c and r lie between 9.61 ± 0.267 and 6.71 ± 0.256, respectively. These intervals also include the respective values of c (9.50) and r (6.73) reported by Stokes and Robinson (1948). Therefore, it is concluded that no evidence of bias, at the 95% confidence level, exists in the BET parameters reported by Stokes and Robinson (1948) and those reported in this work using the results of Rard and Clegg (1997).

Activities and Osmotic Coefficients from the BET Model

The chemical potential of the solute $CaCl_2$(aq) in the BET model may be written as

$$\mu_s^{BET}(x_s,T) = \mu_s^{*liq}(x_s = 1,T) + RT \ln \frac{a_s(x_s,T)}{a^{*liq}{}_s(x_s = 1,T)} \qquad (9)$$

where $\mu_s^{BET}(x_s,T)$, is the chemical potential of the solute in solution at temperature T, containing x_s stoichiometric mole fraction of solute, $\mu_s^{*liq}(x_s = 1,T)$ is taken as the chemical potential of pure liquid solute in the standard state (hypothetical), and $a_s^{*liq}(x_s = 1,T)$ is the solute activity in the standard state, whose value is 1. The BET model gives the solute activity as

Table 3. Values of $\delta = [\mu_s^\theta(m_\pm^\theta,T) - \mu_s^{*,liq}(x_s = 1,T)]/RT$ for $CaCl_2$ at 298.15 K

m($CaCl_2$)/(mol·kg^{-1})	$\gamma_\pm$	$a_s^{BET}(\times 10^4)$	δ ($\times 10^{12}$)
11.0	52.377	11.275	1.4738
10.50	47.598	7.6095	1.5236
10.00	43.042	4.9354	1.5473
9.50	38.685	3.0650	1.54373
9.0	34.477	1.8146	1.5185
8.5	30.360	1.0201	1.4840

$$a_s(x_s,T) = \lambda^r \qquad (10)$$

where λ in the BET model (Abraham, 1981) is given by

$$\frac{\lambda(1 - x_s)}{(1 - \lambda)x_s} = \frac{r}{c} + \frac{r(1 - c)}{c}\lambda \qquad (11)$$

The parameters c and r retain the same definitions as in eq 1.

For experimental data on the molality scale, the chemical potential of the solute is represented as

$$\mu_s(m,T) = \mu_s^\theta(m_\pm^\theta,T) + RT \ln(\gamma_\pm)^\nu + RT \ln (m_\pm)^\nu \qquad (12)$$

where $\mu_s(m,T)$ is the chemical potential of solute in solution whose molality m corresponds to the stoichiometric mole fraction of salt x_s and $\mu_s^\theta(m_\pm^\theta,T)$ is the chemical potential of solute in the standard state (hypothetical ideal solution at $m_\pm = 1$). ($\gamma_\pm$ is the usual mean ionic activity coefficient, $m_\pm$ is the mean ionic molality of solute defined as $m_\pm = [(\nu_+^{\nu+}\nu_-^{\nu-})^{1/\nu}]m$, ν_+ and ν_- are the stoichiometric numbers of cations and anions, assuming complete dissociation of solute, and $\nu = \nu_+ + \nu_-$.

Since the chemical potential of a solute in solution at any prescribed concentration must be independent of the choice of units, eqs 9 and 12 can be equated and solved algebraically to yield

$$\ln \frac{a_s^{BET}(x_s,T)}{(Qm)^\nu} = \ln \delta + \ln (\gamma_\pm)^\nu \qquad (13)$$

where $Q = (\nu_+^{\nu+}\nu_-^{\nu-})^{1/\nu}$. For $CaCl_2$, $\nu_+ = 1$, $\nu_- = 2$, $\nu = 3$, and,

$$\delta = \frac{[\mu_s^\theta(m_\pm^\theta,T) - \mu_s^{*,liq}(x_s = 1,T)]}{RT} \qquad (14)$$

Since δ represents the difference in the two standard states (hypothetical), its value should be independent of the solution concentration in the region where the BET model is valid, as long as the temperature remains constant. Slight rearrangement of eq 13 yields

$$\delta = \frac{a_s^{BET}(x_s,T)}{(Qm\gamma_\pm)^\nu} \qquad (15)$$

where δ is an explicit function of the solute activities calculated from the BET model. Table 3 shows values of δ calculated over the molality range 8.5−11.0 mol·kg^{-1} with

Table 4. Experimental and Calculated Water and $CaCl_2$(aq) Activites and Mean Ionic Activity Coefficients at 298.15 K

$m(CaCl_2)$/ $(mol \cdot kg^{-1})$	exp[a]			BET[b]			
	a_w	$\gamma_\pm$	ϕ	a_w	a_s	$\gamma_\pm$	ϕ
0.001	0.999 948	0.8886	0.9623	0.999 88	1.56×10^{-33}	6.37×10^{-5}	2.220
0.005	0.999 749	0.7871	0.9275	0.999 396	7.61×10^{-29}	4.41×10^{-4}	2.236
0.01	0.999 509	0.729	0.9078	0.998 79	7.98×10^{-27}	1.10×10^{-3}	2.240
0.02	0.999 042	0.6651	0.8871	0.997 58	8.38×10^{-25}	2.58×10^{-3}	2.242
0.05	0.997 671	0.5786	0.8628	0.993 96	3.98×10^{-22}	8.07×10^{-3}	2.242
0.10	0.995 402	0.5187	0.8527	0.987 93	4.29×10^{-20}	0.01921	2.247
0.20	0.990 760	0.4716	0.8588	0.975 9	4.74×10^{-18}	0.046	2.257
0.40	0.980 85	0.4476	0.8944	0.951 9	5.68×10^{-16}	0.114	2.280
0.60	0.969 98	0.4527	0.9401	0.928 1	9.84×10^{-15}	0.196	2.301
0.80	0.958 00	0.4721	0.9924	0.904 4	7.74×10^{-14}	0.292	2.324
1.00	0.944 86	0.5021	1.0495	0.880 9	3.95×10^{-13}	0.403	2.346
1.20	0.930 54	0.5411	1.11	0.857 5	1.54×10^{-12}	0.528	2.370
1.40	0.915 05	0.5891	1.1733	0.834 4	4.98×10^{-12}	0.669	2.393
1.60	0.898 4	0.6467	1.2393	0.811 34	1.40×10^{-11}	0.827	2.418
2.00	0.861 5	0.7965	1.3793	0.765 97	8.32×10^{-11}	1.197	2.467
2.50	0.808 9	1.0702	1.5699	0.710 49	5.35×10^{-10}	1.781	2.530
3.00	0.750 1	1.4811	1.7731	0.656 6	2.64×10^{-9}	2.526	2.595
3.50	0.687 9	2.0795	1.9778	0.604 59	1.08×10^{-8}	3.466	2.660
4.00	0.624 3	2.9377	2.1796	0.554 69	3.88×10^{-8}	4.641	2.726
4.50	0.560 4	4.1762	2.3808	0.507 16	1.25×10^{-7}	6.095	2.792
5.00	0.498 8	5.9208	2.5743	0.462 3	3.69×10^{-7}	7.871	2.855
5.50	0.441 8	8.2526	2.7479	0.420 35	1.01×10^{-6}	10.007	2.916
6.00	0.391 5	11.169	2.892	0.381 52	2.58×10^{-6}	12.533	2.972
6.50	0.348 3	14.575	3.0022	0.345 94	6.15×10^{-6}	15.461	3.022
7.00	0.311 9	18.322	3.0796	0.313 66	1.38×10^{-5}	18.779	3.065
7.50	0.281 3	22.263	3.1291	0.284 65	2.90×10^{-5}	22.457	3.100
8.00	0.255 4	26.291	3.157	0.258 78	5.73×10^{-5}	26.436	3.126
8.50	0.233 1	30.360	3.1697	0.235 83	1.07×10^{-4}	30.644	3.145
9.00	0.213 7	34.477	3.1727	0.215 57	1.89×10^{-4}	35.000	3.155
9.50	0.196 4	38.685	3.1704	0.197 71	3.18×10^{-4}	39.420	3.157
10.00	0.180 7	43.042	3.1659	0.181 99	5.10×10^{-4}	43.828	3.153
10.50	0.166 3	47.598	3.161	0.168 14	7.83×10^{-4}	48.156	3.142
11.00	0.153 1	52.377	3.1563	0.155 92	1.16×10^{-3}	52.347	3.126

[a] Rard and Clegg, 1997. [b] This work.

an arithmetic averaged value of 1.51×10^{-12} and a SD(δ) = $\pm 3.03 \times 10^{-14}$. From eq 14, δ is dependent on temperature only and independent of the solute concentration. This is verified by the results in Table 3. δ exhibits very slight deviation from its arithmetic mean and can be considered to remain essentially constant given intrinsic variability in the data. It is essential to calculate δ because it serves as a link (Ally and Braunstein, 1996) between the standard state used in experimental data (infinite dilute solution) and that used in the BET model (molten salt).

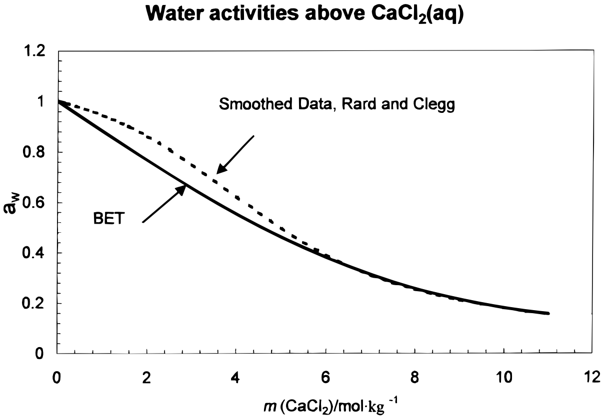

Figure 4. Experimental and predicted water activities above $CaCl_2$(aq) at 298.15 K. The values of the BET parameters are $c = 9.61$ and $r = 6.70$.

Water activities a_w referenced to the pure water standard state are calculated from eq 1. Solute activity coefficients $\gamma_\pm$, referenced to the infinitely dilute solution standard state (hypothetical), are calculated by solving eqs 10, 11, and 15, as in Ally and Braunstein (1996), Ally and Braunstein (1993), Abraham and Abraham (1997), and Abraham (1981). Table 4 directly compares the experimental versus calculated values of water activities a_w, solute mean ionic activity coefficients, and solute activities referenced to the liquid molten salt standard state in the BET model. Good agreement between the experimental and calculated water activities throughout the entire concentration range ($0.001\ mol \cdot kg^{-1} < m < 11\ mol \cdot kg^{-1}$) is observed (Figure 4). It is however inappropriate to conclude, merely on the evidence of this numerical agreement in water activities, that the BET model is valid over the entire molality range in question. Although a linear plot of the experimental and calculated mean ionic activity coefficients versus m in Figure 5a also shows reasonable agreement, the limitations of the BET model become graphic when the logarithm of the mean ionic activity coefficient is plotted versus m, as in Figure 5b. It is pointed out that satisfaction of the Gibbs−Duhem equation is guaranteed in the BET model (Ally and Braunstein, 1998; Braunstein and Ally, 1996). This implies that a_w and $\gamma_\pm$ calculated from the model are thermodynamically consistent. However, satisfaction of the Gibbs−Duhem equation does not automatically guarantee agreement with experimental data. Examination of Figures 4 and 5b shows that excellent agreement between the BET model and experimental data is observed from saturated solution (11 $mol \cdot kg^{-1}$) to about 6 $mol \cdot kg^{-1}$. It signifies that the quasi-ionic lattice view of concentrated aqueous electrolytes is essentially valid as low as 6 $mol \cdot kg^{-1}$. From 2 to 6 $mol \cdot kg^{-1}$, the numerical agreement between calculated and experimental a_w and $\gamma_\pm$ is good, but the argument that the quasi-ionic lattice structure holds in this intermediate concentration range is not as strongly supported as it is in the

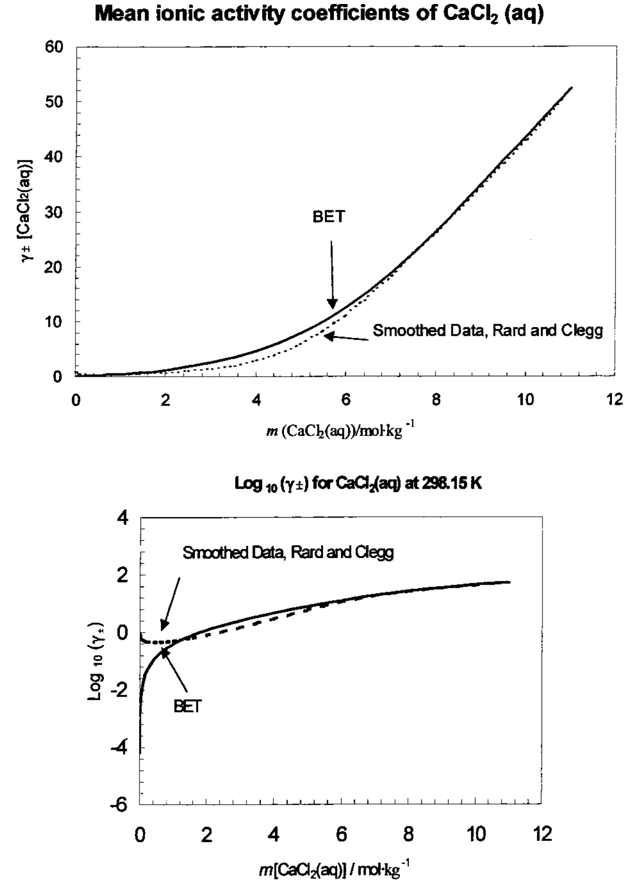

Figure 5. (a, top) Experimental and predicted mean ionic activity coefficients of $CaCl_2$(aq) at 298.15 K. The BET parameters used are $c = 9.61$ and $r = 6.70$. (b, bottom) Comparison of experimental and predicted values of the mean ionic activity coefficients, becoming vivid when $\mathrm{Log}_{10}(\gamma_\pm)$ is plotted against m. Excellent agreement is observed when 6 mol·kg^{-1} < m < 11 mol·kg^{-1}. Good agreement is observed when 2 mol·kg^{-1}<m <6 mol·kg^{-1}. The BET model shows deterioration when m < 2 mol·kg^{-1}.

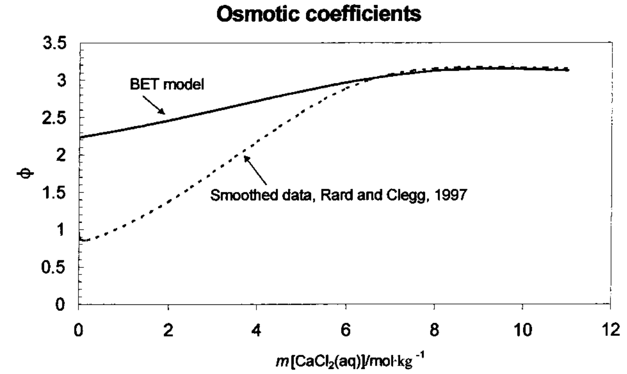

Figure 6. Comparison of osmotic coefficients from the BET model versus the smoothed data of Rard and Clegg (1997). Good agreement is seen when 6 mol·kg^{-1} < m < 11 mol·kg^{-1}. The greater sensitivity of osmotic coefficients relative to mean ionic activity coefficients is a better indicator of agreement between the BET model and data.

higher concentration range. From 2 to 0.001 mol·kg^{-1}, the agreement between experimental and calculated $\gamma_\pm$ values is poor, indicating that the quasi-ionic lattice model perhaps shows deterioration around less than 2 mol·kg^{-1}. The greater sensitivity of ϕ over $\gamma_\pm$ provides clearer insight. The osmotic coefficients are calculated from $\phi = [(-55.5084 \ln a_w)/\nu m]$ and are plotted in Figure 6 (also refer to Table 4). The interesting question is, in what ranges of low concentrations can the quasi-ionic lattice model be reasonably applied? Strictly speaking, the osmotic coefficient is a more stringent test of the applicability of the model than $\gamma_\pm$ or a_w. It may be hypothesized that gradual deterioration of the quasi-ionic lattice structure occurs as the solute concentration is diluted more than 6 mol·kg^{-1} and that rapid deterioration occurs near concentrations where the ratio of the number of solute particles (on a dissociated basis) to the number of water particles approaches approximately 1:7. Returning to the region where m varies from 2 to 6 mol·kg^{-1}, it can be conceptualized that some ordered feature of the quasi-ionic lattice model is loosely preserved even at such moderate concentrations. This is a possible explanation for the agreement between experimental and calculated values of a_w and $\gamma_\pm$ in this moderately dilute region.

Discussion

At the 95% confidence level, no significant statistical differences are observed in the two BET parameters c and r reported in this work and by Stokes and Robinson in 1948. The BET model is used to compare experimental and predicted water and solute activities m from 0.001 to 11 mol·kg^{-1}. Excellent agreement with experimental data is seen when 6 mol·kg^{-1} < m < 11 mol·kg^{-1}, and reasonable agreement is seen in the range 2 mol·kg^{-1} < m < 6 mol·kg^{-1}. Below 2 mol·kg^{-1}, the model becomes invalid. The BET model, however, was intended for concentrated solutions, without regard for the behavior of extremely dilute solutions, and it turns out, in fact, that $\lim(a_s^{BET}/(Qm)^\nu$ as $m \rightarrow 0)$ does not exist. It is noteworthy that the model uses only two parameters that are held constant and provides good agreement with experimental data in the concentrated solution range.

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Literature Cited

Abraham, M. Activity of a High Concentration Salt in Pure Water. *J. Chim. Phys.* **1981**, *78*, 57−59.

Abraham, M.-C.; Abraham, M. The Adsorption Theory of Electrolytes and the Volumetric Properties of Some Nitrate-Water Systems. From Fused Salts to Dilute Solutions. *Monatsh. Chem.*, **1997**, *128*, 805−826.

Ally, M. R.; Braunstein, J. BET Model for Calculating Activities of Salts and Water, Molar Enthalpies, Molar Volumes and Liquid−Solid-Phase Behavior in Concentrated Electrolyte Solutions. *Fluid Phase Equilib.* **1993**, *87*, 213−236.

Ally, M. R.; Braunstein, J. A Comparison of Electrolyte Mean Ionic Activity Coefficients in Concentrated Aqueous Solutions as Calculated with Brunauer−Emmett−Teller Model and With Other Models. *Fluid Phase Equilib.* **1996**, *120*, 131−141.

Ally, M. R.; Braunstein, J. Statistical Mechanics of Multilayer Adsorption: Electrolyte and Water Activities in Concentrated Solutions. *J. Chem. Thermodyn.* **1998**, *30*, 49−58.

Braunstein, J.; Ally, M. R. On the Abraham Equation for Salt Activities in Concentrated Solutions. *Monatsh. Chem.* **1996**, *127*, 269−273.

Caulcutt, R.; Boddy, R. *Statistics for Analytical Chemists*; Chapman and Hall: 1991; ISBN 0-412-23730-X.

Rard, J. A.; Clegg, S. L. Critical Evaluation of the Thermodynamic Properties of Aqueous Calcium Chloride. 1. Osmotic and Activity

Coefficients of 0−10.77 mol·kg^{-1} Aqueous Calcium Chloride Solutions at 298.15 K and Correlation with Extended Pitzer Ion-Interaction Models. *J. Chem. Eng. Data* **1997**, *42*, 819−849.

Stokes, R. H.; Robinson, R. A. Ionic Hydration and Activity in Electrolyte Solutions. *J. Am. Chem. Soc.* **1948**, *70*, 1870−1878.

Stokes, R. H.; Robinson, R. A. Standard Solutions for Humidity Control at 25 °C. *Ind. Eng. Chem.* **1949**, *41*, 2013.

Zambino, P. Personal communication, 1998, U.S. Department of Agriculture Forest Service, Forestry Sciences Laboratory, Wisconsin.

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