# Correlation of Thermodynamic Data for Aqueous Electrolyte Solutions to Very High Ionic Strength using INSIGHT: Vapor Saturated Water Activity in the system $CaCl_2 - H_2O$ to 250°C and Solid Saturation[1]

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# ABSTRACT

Osmotic coefficients for the $CaCl_2 - H_2O$ system between 25 and 250°C and from the dilute region to solid saturation or beyond (i.e., to $\approx 12$ at the lowest temperature and $\approx 32 mCaCl_2$ at the highest) have been correlated using the following permutations and modifications of the basic Pitzer ion-interaction equation: 1) the basic Pitzer [1] equation; 2) the Pitzer equation augmented by an ionic strength dependent third virial contribution [2]; 3) the Pitzer equation together with equilibria involving the formation of $CaCl^+$ and $CaCl_2^0$; and 4) the simultaneous combination of all of the above. The effectiveness, accuracy and practicality of each approach will be reviewed.



KEY WORDS: aqueous, calcium chloride, electrolyte, thermodynamics


# 1 INTRODUCTION AND BACKGROUND

While a number of analytical equations of state are available for representing the thermophysical properties of aqueous electrolyte solutions in the dilute to moderate ionic strength region [1], [3], [4], such equations by themselves generally prove inadequate on extension to high ionic strength (or high temperature) due to an increase in the degree of association of the electrolyte components. In some cases, moderate amounts of association can be treated implicitly by including special terms (e.g., the $\beta^2$ term in the Pitzer formalism [5], [6]), or higher order terms in the compositional power series representing the Gibbs energy of the system [7]. Solution properties at high ionic strength can also be treated using expressions valid only in this region, and then these equations can be used in conjunction with equations valid for more dilute solutions in order to correlate/predict properties over the entire composition range. Finally, thermodynamic properties of aqueous electrolyte solutions can be treated over extended compositional ranges by the *explicit* inclusion of associated aqueous species.

While each of these approaches is valid in principle, it is worthwhile to establish a general framework for the continuous correlation of solution properties, at or near

the level of experimental uncertainty, over the entire range from infinite dilution to the extreme ionic strengths characteristic of highly soluble salts. Toward this end, we explore the correlation of water activity data to very high ionic strengths in the system $CaCl_2 - H_2O$ using four different models: 1) the basic Pitzer [1] equation; 2) the Pitzer equation augmented by an ionic strength dependent third virial contribution [2]; 3) the Pitzer equation together with equilibria involving the formation of $CaCl^+$ and $CaCl_2^0$; and 4) the simultaneous combination of all of the above. The calculations described herein were performed using INSIGHT [8] – a new computer algorithm which facilitates the correlation of large, heterogeneous datasets via nonlinear thermodynamic analysis.

Explicit inclusion of association equilibria (i.e., Models 3 and 4) requires an algorithm for speciation calculations [9], and an expression for the relative Gibbs energy [8]:

$$G^{rel}/w_w RT = \sum_i m_i \left(\ln(m_i) - \ln K_i^0 - 1\right) + G^{EX}/w_w RT \tag{1}$$

The summation in Eq. 1 is over all solute species $i$, $w_w$ is the mass of water in kg and $G^{EX}/w_w RT$ represents the difference between the relative Gibbs energy of the solution and that of an ideal solution (as defined on a molality basis) at the same conditions. $\ln K_i^0$ refer to the thermodynamic equilibrium constants for the following reactions: $Ca^{2+} + Cl^- \Longleftrightarrow CaCl^+$, $\ln K^0_{CaCl^+}$; $Ca^{2+} + 2Cl^- \Longleftrightarrow CaCl_2^0$, $\ln K^0_{CaCl_2^0}$.

The Pitzer equation, as used here in Models 2 and 4, differs from that originally described by Pitzer [1], [10] in that an ionic strength dependence has been incorporated into the third virial coefficient between two species of opposite charge [2], [11]. Thus, while other quantities are as given in Pitzer [1], for the excess Gibbs energy we have:

$$C_{MX} = C_{MX}^{(0)} + C_{MX}^{(1)} h(\alpha_3 I^{1/2}) \tag{2}$$

$$h(x) = 4\left[6 - (6 + 6x + 3x^2 + x^3)\exp(-x)\right]/x^4 \tag{3}$$

Osmotic and activity forms for $C_{MX}$ and $h(x)$ can be found in Sterner et al. [12]. The temperature dependencies for each electrolyte model parameter: $\beta^0_{MX}$, $\beta^1_{MX}$, $C^0_{MX}$,

$C^1_{MX}$, $\ln K^0_{\mathrm{CaCl}^+}$ and $\ln K^0_{\mathrm{CaCl}^0_2}$ were described using the following expansion:

$$\Omega_1(T) \quad = \quad a_1/T_r + a_2 + a_3 T_r \tag{4}$$

where $T_r = T/298.15$ ($T$ in Kelvin). Each of these parameters is independent of pressure. The Debye-Hückel parameter, $A_\phi$, was calculated at $T$ and pressures along the saturation curve of pure water using expressions given by Archer and Wang [13].

# 2 DATA AND ANALYSIS

Osmotic coefficients for the $\mathrm{CaCl_2} - \mathrm{H_2O}$ system from 0.01 to 4.5 molal and between 25 and 250°C predicted using the equation of Holmes et al. [14] together with values predicted from the treatment of Pitzer and Oakes [15] extending from 5.0 molal to solid saturation over this same temperature range, and three additional experimental observations in the super-saturated region at 25°C (Rard, pers. comm.) form the database used in the present work. Uncertainties are estimated at $\sigma_\phi \approx 0.005$ at all temperatures where $\mathrm{mCaCl_2} \leq 5.0$ and at 25°C for all concentrations; $\sigma_\phi \approx 0.01 - 0.02$ or worse elsewhere. The data were analysed using the four models summarized in Table 1 and the results are displayed graphically in later sections. Numerical coefficients describing the temperature dependence of parameters (Eq. 4) for each model are given in Table 2.

The Pitzer ion-interaction equation was chosen as the foundation for the present work because the basic Pitzer formalism is capable of accurately representing solution properties over a broader compositional range than other available electrolyte models. For many aqueous systems, this region of validity extends to very high concentrations (see compilations in [10]), while for others, accurate representation of solution properties using the basic equation is restricted to the lower ionic strength region. As discussed by Phutela and Pitzer [16], the $\mathrm{CaCl_2} - \mathrm{H_2O}$ system falls into this latter category, which taken together with the availability of data over an extensive ionic strength-temperature range makes this system an ideal choice for the present demonstration.

Table 1: Essential Model Elements

| Element | Model 1 | Model 2 | Model 3 | Model 4 |
|---|---|---|---|---|
| Std. Pitzer[1] | $X$ | $X$ | $X$ | $X$ |
| Archer term[2] | | $X$ | | $X$ |
| Expl. Assoc.[3] | | | $X$ | $X$ |
| $\chi^{2\,\dagger}$ | 1.25 | 0.37 | 0.08 | 0.03 |

[1] Conventional "Pitzer Ion-Interaction Model" [1]
[2] Ionic strength dependent $3^{rd}$ virial term [2])
[3] Ion Association – Gibbs energy minimization [9])
$^\dagger$ "chi-square": $\chi^2 = \sum_{i=1}^{N} \left(\frac{\phi^{obs}-\phi^{calc}}{\sigma_\phi}\right)^2$; $N = 131$; $\sigma_\phi \equiv 1$ for all data

Difficulties encountered in treating the $CaCl_2 - H_2O$ system over the entire range of solution compositions to solid saturation using a single equation were considered by Phutela and Pitzer [16] to arise from a shift from a dominantly $H_2O$ inner shell around $Ca^{2+}$ below $\approx 5$ molal to a mixed $Cl^-$ and $H_2O$ shell at higher molality. While systems displaying such features are difficult to describe accurately using fully dissociated electrolyte models, they are readily handled using more complex treatments that explicitly account for ion association [17] as will be demonstrated.

Table 2: Electrolyte Model Parameters

| Parameter | Model 1 | Model 2 | Model 3 | Model 4 |
|---|---|---|---|---|
| $\beta^0_{Ca^{2+}-Cl^-}$ | | | | |
| $a_1$ : | $7.9447982D-01$ | $2.4347874D+00$ | $2.6221215D-01$ | $1.2140386D+00$ |
| $a_2$ : | $-3.8821422D-01$ | $-2.5666223D+00$ | $-6.4836385D-02$ | $-1.3462339D+00$ |
| $a_3$ : | $3.4518985D-02$ | $7.1262758D-01$ | $1.0644625D-01$ | $3.8173261D-01$ |
| $\beta^1_{Ca^{2+}-Cl^-}$ | | | | |
| $a_1$ : | $-1.0993707D+01$ | $-1.1628250D+00$ | $-4.9748424D-01$ | $-4.5065579D-01$ |
| $a_2$ : | $1.0240638D+01$ | $-1.6299060D+00$ | $6.9090298D-01$ | $3.1133093D-01$ |
| $a_3$ : | $7.0946637D-01$ | $3.3966263D+00$ | $1.5080112D+00$ | $1.9068443D+00$ |
| $C^0_{Ca^{2+}-Cl^-}$ | | | | |
| $a_1$ : | $-1.8378208D-02$ | $-4.1719258D-02$ | $-8.3831553D-03$ | $-5.4085694D-02$ |
| $a_2$ : | $1.6034217D-02$ | $4.6857261D-02$ | $1.9806151D-02$ | $8.5017135D-02$ |
| $a_3$ : | $-3.6094024D-03$ | $-1.3339735D-02$ | $-1.0247146D-02$ | $-2.7650366D-02$ |
| $C^1_{Ca^{2+}-Cl^-}$ | | | | |
| $a_1$ : | $--$ | $-3.2545826D+00$ | $--$ | $-2.3188620D+00$ |
| $a_2$ : | $--$ | $4.2345609D+00$ | $--$ | $3.2538131D+00$ |
| $a_3$ : | $--$ | $-1.2389857D+00$ | $--$ | $-8.2582648D-01$ |
| $\alpha_3$ | $--$ | $1.0009559D+00$ | $--$ | $1.2943630D+00$ |
| $\beta^0_{CaCl^+-Cl^-}$ | | | | |
| $a_1$ : | $--$ | $--$ | $7.4989440D-02$ | $3.4443239D-01$ |
| $a_2$ : | $--$ | $--$ | $5.3201716D-01$ | $-6.4454201D-02$ |
| $a_3$ : | $--$ | $--$ | $-2.5016608D-01$ | $1.6166716D-02$ |
| $\beta^1_{CaCl^+-Cl^-}$ | | | | |
| $a_1$ : | $--$ | $--$ | $1.2964259D+01$ | $-4.8427817D+00$ |
| $a_2$ : | $--$ | $--$ | $-1.1501094D+01$ | $1.7977861D+01$ |
| $a_3$ : | $--$ | $--$ | $3.3491862D+00$ | $-7.7946527D+00$ |
| $C^0_{CaCl^+-Cl^-}$ | | | | |
| $a_1$ : | $--$ | $--$ | $-4.7376089D-03$ | $-1.0740975D-02$ |
| $a_2$ : | $--$ | $--$ | $-6.3766606D-03$ | $8.5546752D-03$ |
| $a_3$ : | $--$ | $--$ | $4.3433887D-03$ | $-2.6306117D-03$ |
| $\lambda_{CaCl^0_2-CaCl^0_2}$ | | | | |
| $a_1$ : | $--$ | $--$ | $1.8398851D+01$ | $3.0698322D+01$ |
| $a_2$ : | $--$ | $--$ | $-2.0623575D+01$ | $-3.3473186D+01$ |
| $a_3$ : | $--$ | $--$ | $5.9341234D+00$ | $9.2782779D+00$ |
| $\ln K^0_{CaCl^+}$ | | | | |
| $a_1$ : | $--$ | $--$ | $1.2614317D+01$ | $-6.2161585D+00$ |
| $a_2$ : | $--$ | $--$ | $-2.8714079D+01$ | $4.5506169D-01$ |
| $a_3$ : | $--$ | $--$ | $1.4336246D+01$ | $3.7689272D+00$ |
| $\ln K^0_{CaCl^0_2}$ | | | | |
| $a_1$ : | $--$ | $--$ | $-1.1645809D+02$ | $-1.1972489D+02$ |
| $a_2$ : | $--$ | $--$ | $9.7885936D+01$ | $1.0292433D+02$ |
| $a_3$ : | $--$ | $--$ | $-1.9346055D+01$ | $-1.9857105D+01$ |

## 2.1 Model 1

Phutela and Pitzer [16] have shown that the Pitzer model can accurately represent the thermochemical behavior in the $CaCl_2 - H_2O$ system up to $\approx 4$ molal. That the basic equation [1] or slight modifications thereof (i.e., [5], [14]) cannot satisfactorily account for the observed osmotic behavior over the extensive compositional range considered here, was noted by these authors. Nevertheless, to form a basis for comparison with models presented in later sections, we have applied the basic Pitzer equation to the entire $CaCl_2 - H_2O$ osmotic dataset described above with the result shown in Fig. 1.

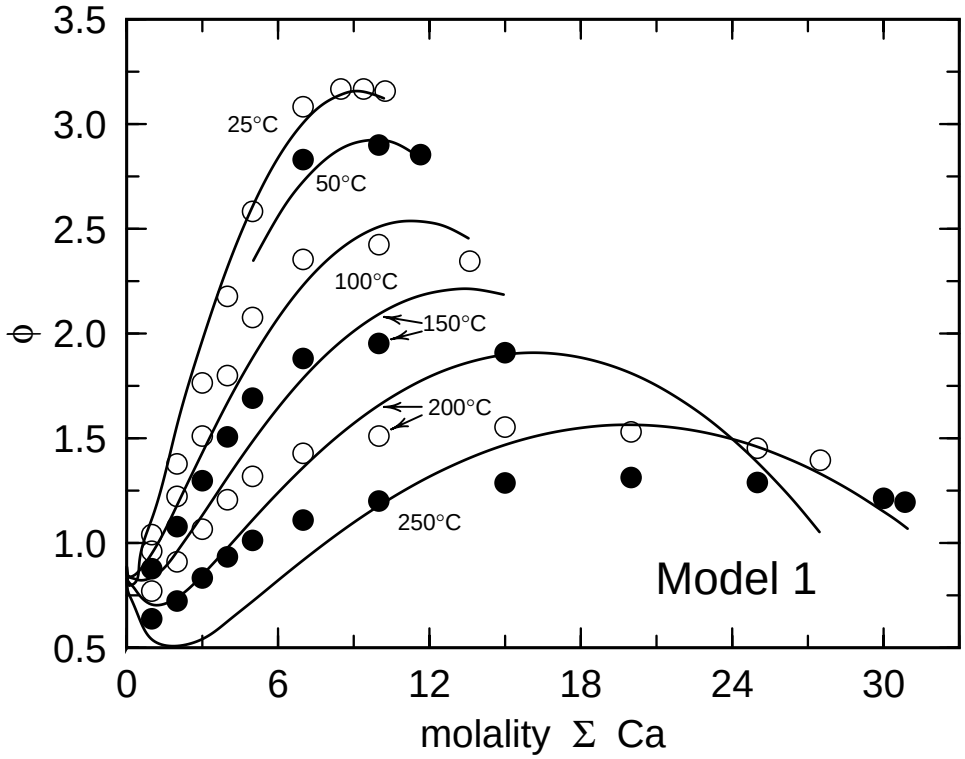


Figure 1: Model 1 predictions for $CaCl_2 - H_2O$ osmotic coefficients. For clarity, alternate temperature data are indicated using different symbols.

Not surprisingly, considering that equal emphasis was given to all data, extensive deviations are noted over the entire range of compositions and temperatures. Nevertheless, this simplistic treatment (i.e., considering only $Ca^{2+}$ and $Cl^-$) is at least qualitatively correct over the extensive range of solution compositions and temperatures considered.

## 2.2 Model 2

Model 2 combines an ionic strength dependent third virial contribution [2] with the basic Pitzer equation. Results are shown in Fig. 2. Although the accuracy of Model 2

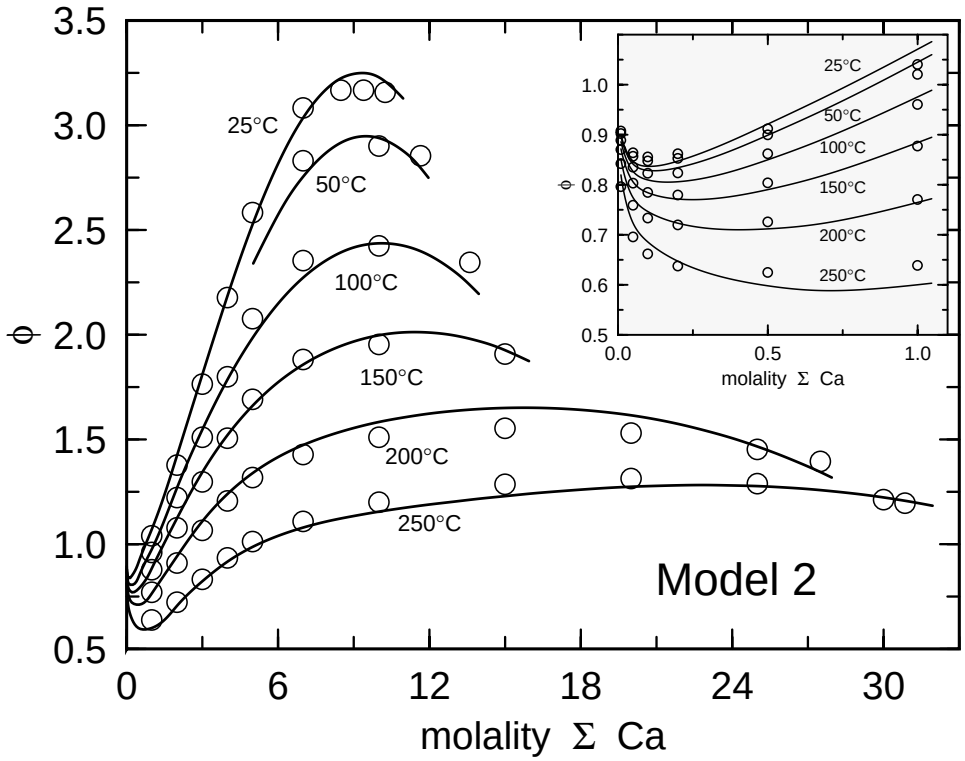


Figure 2: Model 2 predictions for $CaCl_2 - H_2O$ osmotic coefficients.

is still well outside the estimated experimental uncertainties, addition of the new term results in substantial quantitative improvement over the fit obtained using Model 1, while maintaining nearly the same level of computational simplicity.

## 2.3 Model 3

Figure 3 shows the results of combining the basic Pitzer ion-interaction model together with explicit inclusion of associated aqueous species $CaCl^+$ and $CaCl_2^0$. The overall fit of Model 3 approaches the estimated experimental uncertainties over most of the temperature-composition space considered. Furthermore, the predicted speciation con-

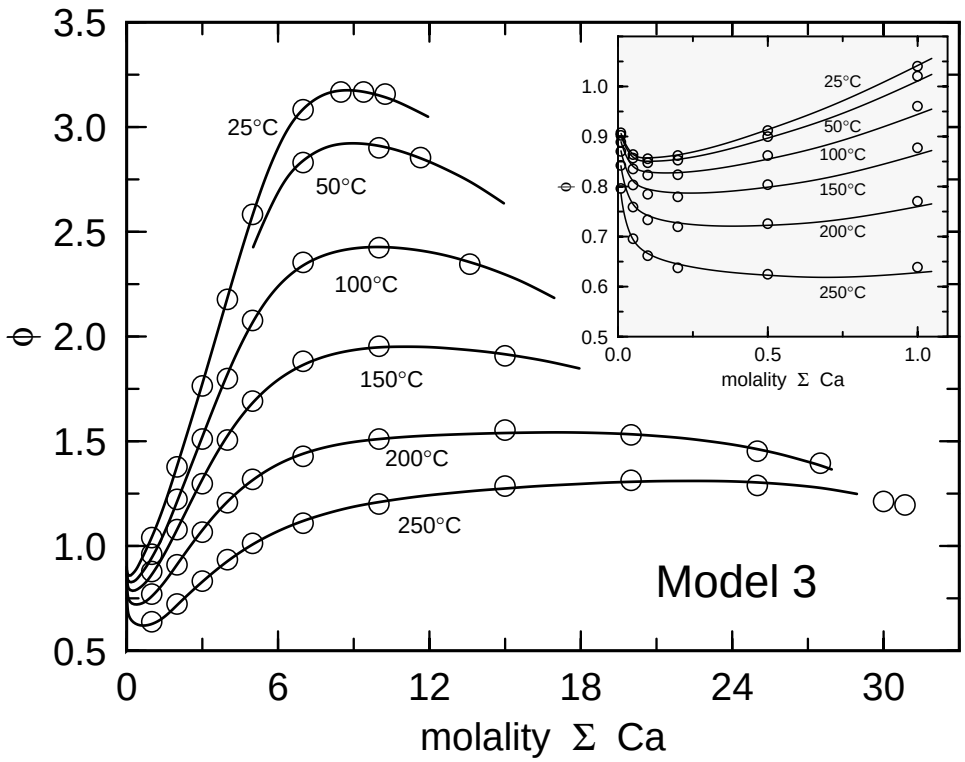


Figure 3: Model 3 predictions for $CaCl_2 - H_2O$ osmotic coefficients.

figuration is reasonable, i.e., basically the same as that predicted by Model 4 discussed in the next section. Explicit inclusion of ion association in Model 3 adds an additional complication not found in Models 1 or 2: the equilibrium distribution of aqueous species must be determined using numerical methods and the inherent complexity of the equations can result in multiple solutions. This situation, discussed in greater detail by Sterner et al. [12], occurs at high ionic strengths and numerical analyses indicate that the problem can be avoided by including an ionic strength dependence in $C_{Ca^{2+}-Cl^-}$ (Eq. 2) as we have done in Model 4.

## 2.4 Model 4

The final model considered combines all the elements of the previous three (Table 1). Results are shown in Fig. 4. Model 4 predictions are approximately within the esti-

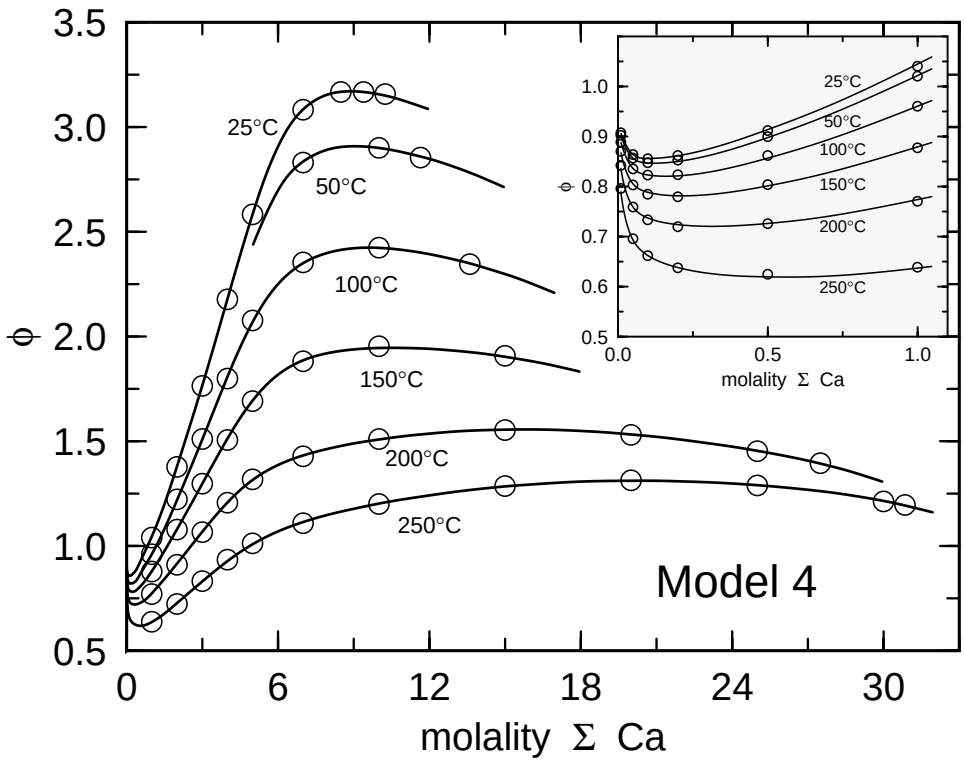


Figure 4: Model 4 predictions for $CaCl_2 - H_2O$ osmotic coefficients.

mated uncertainties of the original data over the entire temperature-composition range. The distribution of aqueous species predicted using Model 4 is shown in Fig. 5. As with Model 3 (not shown), at low temperatures, Model 4 predicts essentially complete dissociation at low ionic strength yielding to comparable amounts of $Ca^{2+}$ and $CaCl^{+}$ near solid saturation; the neutral species becomes important at intermediate and high ionic strengths for $T \geq 100°C$; and at high temperatures, an association/redissociation effect involving $CaCl^{+}$ is noted in the dilute region followed by a preponderance of $CaCl^{+}$ above bulk concentrations of $\approx 12\,mCaCl_2$.

Two distinct association features are predicted by both Models 3 and 4: one, an association/redissociation phenomena, occurs only in the dilute region at high temperature, and the other, a more gradual association, takes place at intermediate to high ionic strengths and is much less temperature dependent. The dilute solution behavior is analogous to that noted in higher valence systems at ambient temperatures and has

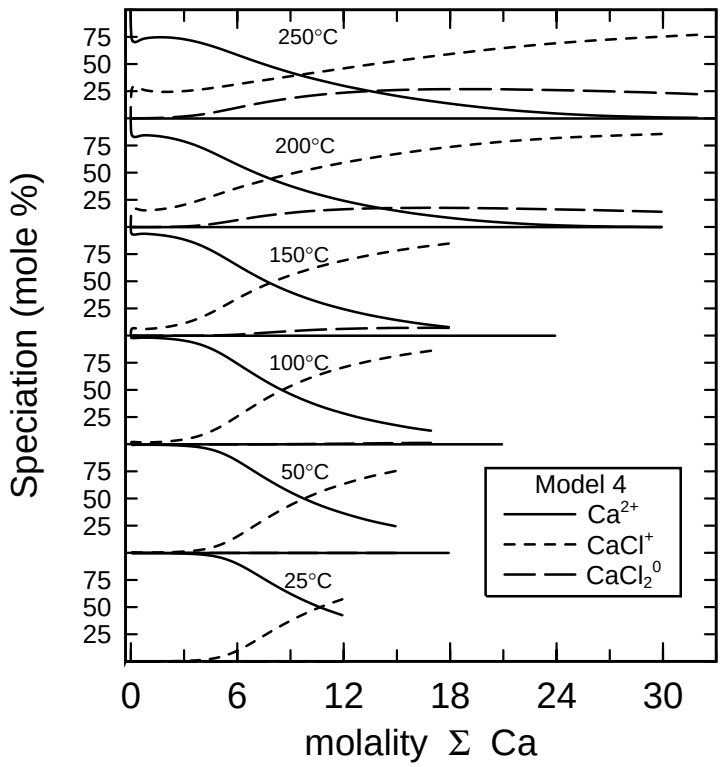


Figure 5: Distribution of aqueous species predicted using Model 4.

been discussed by Pitzer and Silvester [6] and Felmy and Weare [18]. The $\beta^2$ term was introduced into the Pitzer formalism [5] to account for this effect (a slight departure of the excess Gibbs energy from limiting-law behavior in the dilute region) implicitly without the inclusion of ion pairs. Although this feature is generally recognized in connection with more highly-charged particles, it is not surprising that it should also occur in a 2:1 electrolyte system at high temperature as the dielectric constant decreases. Indeed, considerable association in the dilute region of the $CaCl_2 - H_2O$ system is inferred from enthalpy of dilution results at $T \geq 250°C$ [19]. Also, the equation of Holmes et al. [14] used to constrain our models in the dilute region, accounted for this behavior by using a $\beta^2$ term, and as we have not included $\beta^2$ in the present treatment, an amount of explicit association in the dilute region will necessarily be required.

A more gradual association occurs at higher ionic strength. At 25°C, appreciable association occurs above $\approx 4.5$ m$CaCl_2$ and at somewhat lower bulk concentrations with

increasing temperature. A speciation change in this region is consistent with the shift from a dominantly $H_2O$ inner shell around $Ca^{2+}$ below $\approx 5$ molal to a mixed $Cl^-$ and $H_2O$ shell at higher molality postulated by Phutela and Pitzer [16].

No evidence of complex behavior in the Gibbs energy surface was detected for bulk compositions as high as 43 $mCaCl_2$. Thus, inclusion of the ionic strength third virial term appears to have increased the flexibility permitting higher accuracy throughout.

# 3 DISCUSSION

It is indeed possible, at least for $CaCl_2 - H_2O$, to accurately describe water activities from the dilute region to extreme ionic strengths using a single, continuously valid expression – even though the degree of association changes markedly with bulk concentration. However, a few generalizations are in order regarding the precise analytical form of the model used for such a correlation. Within the Pitzer framework, the $\beta^{(2)}$ term with $\alpha_2 = 12$ is intended to substitute for explicit consideration of the corresponding association equilibria, and has been shown to accomplish this task satisfactorily in several systems involving moderate amounts of association in the dilute region. In cases where it becomes necessary to explicitly treat association by the introducion of an appropriate aqueous species (and $\ln K_i^0$), the corresponding $\beta^{(2)}$ can generally be avoided as these terms are largely redundant. Along these lines, two other sources of potential redundancy are worth mentioning. Although not quite so pronounced, there is a partial redundancy between an association constant $\ln K^0_{MX_{aq}}$, and the sum of $\beta^{(0)}_{M-X}$ and $\beta^{(1)}_{M-X}$; also, a similar situation exists between the equilibrium constant for further association $\ln K^0_{M_2X_{aq}}$, the sum of $\beta^{(0)}_{M-MX}$ and $\beta^{(1)}_{M-MX}$, and the $C_{MX}$ term for the three particle interaction between the fully dissociated species.

Lastly, it should be re-emphasized that *explicit* inclusion of ion association can result in very computationally intensive calculations – ones that may preclude the use of such models for certain applications. However, faster computers, parallel processing and

algorithm optimization can be expected to alleviate part of this problem in the future.

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