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Authors

Phutela, R.C.

Pitzer, K.S.

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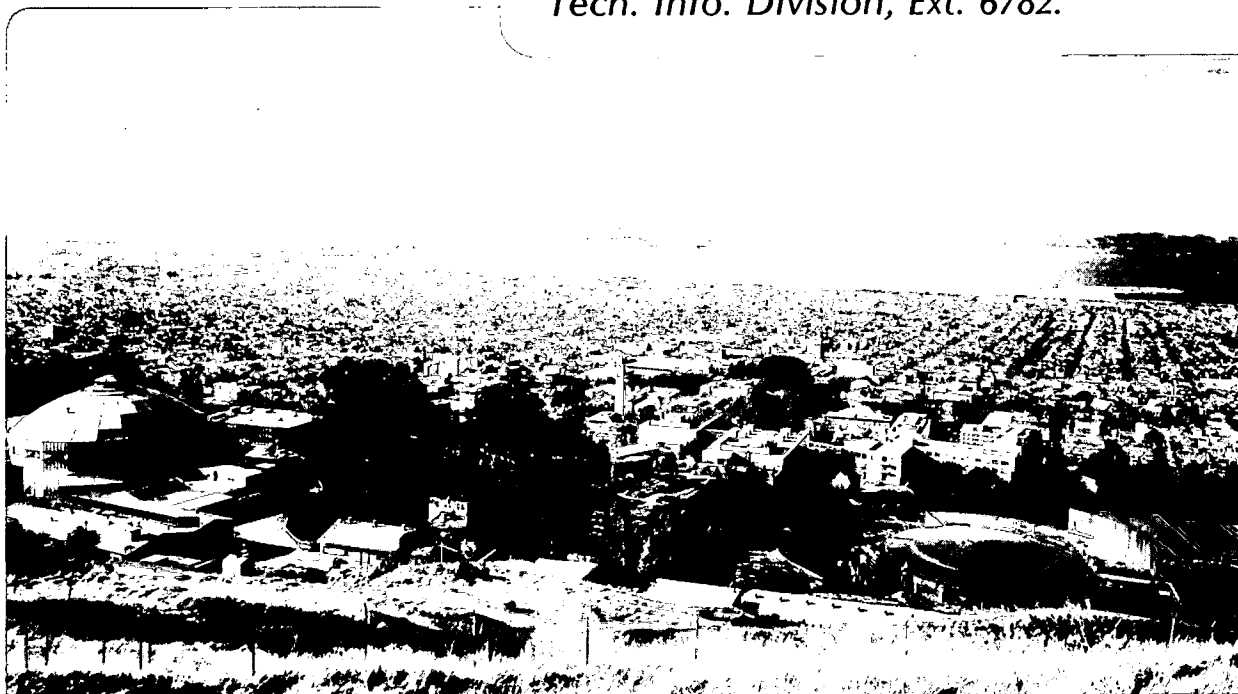
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R. C. Phutela and Kenneth S. Pitzer

November 1982

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Thermodynamics of Aqueous Calcium Chloride

R. C. Phutela and Kenneth S. Pitzer

Department of Chemistry and Lawrence Berkeley Laboratory
University of California, Berkeley, CA 94720

(Abstract)

Various published measurements of the osmotic coefficient and the apparent molal enthalpy of aqueous CaCl_2 are examined and correlated. It is found that CaCl_2 shows an anomalous behavior near 5 molal. Below that molality the various properties are well represented by the usual ion-interaction equation with simple temperature dependent expressions for the second and third virial parameters. Information from neutron diffraction and crystal structure is considered in discussing the anomalous behavior at high molality.

1. Introduction

Calcium chloride is an important component of many natural waters and of aqueous fluids in industrial processes. Hence it is important to have accurate expressions for the thermodynamic properties, not only of pure aqueous CaCl_2 , but also of mixed solutions containing that salt. The general success of ion interaction (Pitzer) equations^(1,2) for mixtures at relatively high ionic strength makes it most desirable to have the appropriate parameters for CaCl_2 on a basis valid to as high concentration as is feasible. In the original fitting of ion interaction equations to many electrolytes, Pitzer and Mayorga⁽³⁾ limited their fit for CaCl_2 to molality 2.5 ($I = 7.5$) whereas their fits of MgCl_2 and SrCl_2 were satisfactory to molality 4 mol kg^{-1} or higher. Additional isopiestic measurements at 25°C have now been published^(4,5) for CaCl_2 , hence it seemed desirable to consider these new data and to attempt to obtain a good representation to at least 4 mol kg^{-1} with the standard form of equation including only the second and third virial coefficients as well as the Debye-Hückel term.

In addition to the new measurements at 25°C , Holmes, Bayes, and Mesmer,⁽⁶⁾ have reported isopiestic data up to 200°C for aqueous CaCl_2 and fitted these results to the ion interaction equation. Thus it is now possible to combine these high-temperature parameters with the revised values for 25°C and with the results of a new calculation for the enthalpy of dilution to obtain a comprehensive set of equations for aqueous CaCl_2 up to about 4 mol kg^{-1} .

The solubility of CaCl_2 extends much higher to about 9 mol kg^{-1} . We discuss the nature of these very concentrated solutions, and note that Rogers⁽⁷⁾ has developed an ion interaction equation valid for the entire range. Her equation, which extends through the sixth virial

coefficient, is very valuable when required, but the simpler equation presented here will be more convenient yet adequate for many applications.

2. Data and Equations

The ion interaction equations in the formulation of Pitzer and his associates have been presented for the general valence type in various publications. (1,8) For convenient reference, the forms simplified for a pure 2-1 salt and for the quantities of immediate interest are given below.

$$\begin{aligned} \phi-1 = & -2A_{\phi} [I^{1/2}/(1+bI^{1/2})] + (4m/3) [\beta^{(0)} + \beta^{(1)} \exp(-\alpha I^{1/2})] \\ & + 2^{5/2} m^2 C^{\phi}/3 \end{aligned} \quad (1)$$

$$\begin{aligned} \ln \gamma_{\pm} = & -2A_{\phi} [I^{1/2}/(1+bI^{1/2}) + (2/b) \ln(1+bI^{1/2})] \\ & + (4m/3) \{ 2\beta^{(0)} + (2\beta^{(1)}/\alpha^2 I) [1-(1+\alpha I^{1/2} - \alpha^2 I/2) \exp(-\alpha I^{1/2})] \} \\ & + 2^{3/2} m^2 C^{\phi} \end{aligned} \quad (2)$$

$$\phi^L = (3A_H/b) \ln(1+bI^{1/2}) - 4RT^2 (mB^L + 2m^2 C^L) \quad (3a)$$

$$B^L = \beta^{(0)L} + 2\beta^{(1)L} [1-(1+\alpha I^{1/2}) \exp(-\alpha I^{1/2})]/\alpha^2 I \quad (3b)$$

$$C^L = C^{\phi L}/2^{3/2} \quad (3c)$$

where ϕ and γ are the osmotic and activity coefficients, ϕ^L is the apparent molal enthalpy, A_{ϕ} and A_H are the appropriate Debye-Hückel parameters, (9) b and α are general parameters equal to $1.2 \text{ kg}^{1/2} \text{ mol}^{-1/2}$ and $2.0 \text{ kg}^{1/2} \text{ mol}^{-1/2}$, respectively, $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} are the specific ion interaction parameters for CaCl_2 while $\beta^{(0)L}$, $\beta^{(1)L}$, and $C^{\phi L}$ are their temperature derivatives which appear in the equation for the enthalpy. We seek expressions for $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} as functions of temperature which agree with various experimental measurements of the

osmotic or activity coefficient. Also the temperature derivatives at 25°C must agree with the experimental information on the heat of dilution.

There are two recent, comprehensive reviews of the osmotic and activity coefficient measurements of CaCl_2 at 25°C, one by Staples and Nuttall,⁽¹⁰⁾ the other by Rard, Habenschuss, and Spedding.⁽¹¹⁾ In each case they presented complex empirical equations fitting the data to 9 mol kg^{-1} or above. We chose to fit the original isopiestic data of Robinson,⁽¹²⁾ of Stokes,⁽¹³⁾ of Spedding, *et al.*,⁽⁴⁾ and of Rard and Spedding⁽⁵⁾ as slightly refined with respect to reference information by Staples and Nuttall.⁽¹⁰⁾ This array appeared to include the best and most pertinent information all of which is in internal agreement within experimental uncertainty. The Rard and Spedding⁽⁵⁾ measurements extend to very high molality; we made several calculations terminating this series of data at various points in the range 4 to 6 mol kg^{-1} . The final, least-squares fit was based on the data through 4.457 mol kg^{-1} .

For the apparent molal enthalpy at 25°C we used the smoothed NBS values⁽¹⁴⁾ through 5.0 mol kg^{-1} .

The osmotic coefficient measurements at higher temperatures were fitted to these same equations by the original authors,⁽⁶⁾ and we used their values of $\beta^{(0)}$, $\beta^{(1)}$, C^ϕ at each temperature without further examination.

For the temperature dependence of each parameter a quadratic expression was used. Both the value and derivative at 25°C were given relatively high weight in the least-squares evaluation. This did not significantly degrade the fit at higher temperature, and it assured that the final values at 25°C for the enthalpy parameters (the temperature derivatives) were essentially the same as those evaluated directly

from the enthalpy measurements. In other words, there was no conflict between parameters from different sources and the quadratic expression was adequate for the present range and precision of the data.

3. Results

The results are presented as the following equations:

$$\beta_{\text{CaCl}}^{(0)} = 0.11614 + 0.0011642 T - 1.7764 \times 10^{-6} T^2 \quad (4)$$

$$\beta_{\text{CaCl}}^{(1)} = 3.4787 - 0.015417 T + 3.1791 \times 10^{-5} T^2 \quad (5)$$

$$C_{\text{CaCl}}^{\phi} = 0.082585 - 3.8310 \times 10^{-4} T + 3.801 \times 10^{-7} T^2 \quad (6)$$

The dimensions are kg mol^{-1} for $\beta^{(0)}$ and $\beta^{(1)}$ and $\text{kg}^2 \text{mol}^{-2}$ for C^{ϕ} .

The resulting values for 298.15 K are given in Table I for both the parent functions and the temperature derivatives.

The standard deviation of fit for the osmotic coefficient at 25°C was 0.0026 with all points equally weighted. Actually the uncertainty increases considerably for points below 1 mol kg^{-1} and a deweighting of those points would decrease somewhat the weighted standard deviation without much change in the final parameters. Nevertheless, we preferred to obtain as good a fit as possible in the dilute range and there appeared to be no significant distortion of the fit at higher molality.

The deviation for the final point at $4.457 \text{ mol kg}^{-1}$ was 0.0057 but for the next point at $4.256 \text{ mol kg}^{-1}$ it was only 0.0017. Hence, one can state the range of validity at 25°C as 4.3 mol kg^{-1} for full accuracy. The highest molality of the higher temperature measurements ranged from 3.23 at 414 K to 3.96 at 474 K. Since there appears to be no significant degradation of the fit at these upper limits of

measurement, some extrapolation to higher molality is probably possible without serious error. For the apparent molal enthalpy the agreement is satisfactory to 5 mol kg^{-1} .

4. Behavior at Very High Molality

It is interesting to compare the properties of CaCl_2 with those of MgCl_2 in the range above 4 molal. For this purpose we calculate a deviation function based on the osmotic coefficient and defined by eq (7a).

$$g \equiv \left[\phi - 1 + \frac{2A_\phi I^{1/2}}{1+bI^{1/2}} \right] / m - \frac{4}{3} \beta^{(1)} e^{-\alpha I^{1/2}} \quad (7a)$$

$$= 4\beta^{(0)}/3 + m(2^{5/2} C^\phi/3). \quad (7b)$$

If this type of equation fits the data, a plot of the quantity g against m will yield a straight line with slope $2^{5/2} C^\phi/3$ and intercept $4\beta^{(0)}/3$. Figure 1 shows such a plot for CaCl_2 and MgCl_2 . For the latter the line represents the equation of Pitzer and Mayorga⁽³⁾ and the points the originally fitted data of Robinson and Stokes⁽¹⁵⁾ together with a few points at high molality from the recent measurements of Rard and Miller.⁽¹⁶⁾ The equation of the latter authors and other data from their work would yield essentially the same result although there are small differences. For CaCl_2 the line represents the present equation while the points are calculated from the smoothed values of Staples and Nuttall.⁽¹⁰⁾

The change in slope near 5 molal for CaCl_2 is remarkably sudden. It must represent some change in structure involving substantial numbers of ions and molecules in order to occur so abruptly. It is very difficult to represent this behavior by a power series, but Rogers⁽⁷⁾ has succeeded with an extension of the present type of equation through the sixth

virial coefficient. However, the second and third virial parameters are greatly changed from our values and the higher terms make a substantial contribution throughout the 2-4 molal range. Since the actual behavior in this range is very simple and well described by the equation with only second and third virial coefficients, it appears that the complicating behavior does not become significant until molalities greater than 4.

In contrast to CaCl_2 , the behavior of MgCl_2 seems quite simple, although its solubility is more limited. In the range 5 to 6 molal where CaCl_2 is showing a marked anomaly, the points for MgCl_2 fall close to an extrapolation of the equation fitted to data below 4 molal.

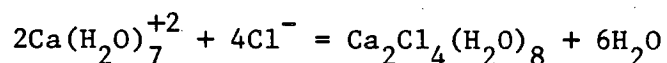
Hewish, et al. ⁽¹⁷⁾ have made neutron diffraction measurements on aqueous CaCl_2 at 1.0, 2.8, and 4.5 molal and find that the number of water molecules coordinated to Ca^{++} decreases from 10 to 7 to 6.4 for these solutions. This shift in coordination number does not yield any thermodynamic anomaly in the 1 to 4.5 molal range. But it may indicate a weakness in the hydrating nature of Ca^{++} which is related to the anomaly at higher concentration. Presumably the smaller Mg^{++} ion coordinates 6 water molecules.

Hewish, et al., find no substantial population of Cl^- in the inner hydration shell at the molalities they studied. It seems likely, however, that it is a shift of Cl^- into the inner shell that is occurring above 5 molal.

The crystal structures ⁽¹⁸⁾ of the three forms of the tetrahydrate of CaCl_2 are interesting in this connection. All show some mixture of Cl^- and H_2O in the inner shell around the Ca^{++} ions, but the detailed patterns differ remarkably. The β form has one third of the Ca^{++} as

CaCl_6 and the other two thirds as $\text{CaCl}_2(\text{H}_2\text{O})_6$ with some of the Cl and H_2O in bridging positions. In contrast the α form has $\text{Ca}_2\text{Cl}_4(\text{H}_2\text{O})_8$ units with two Cl in bridging locations while the γ form has simple $\text{CaCl}_2(\text{H}_2\text{O})_4$ units with many hydrogen bonds but no bridging by either Cl or O.

This complex variability indicates an almost exactly equal Gibbs energy for various structural patterns. It also suggests that no single species dominates the concentrated CaCl_2 solutions and therefore that no single equilibrium dominates the anomalous shift in the region 5 to 6 molal. A possible contributing reaction is



where the species on the right is that appearing in the α tetrahydrate. With 4 Cl^- on the left and 6 H_2O on the right of this equation, a small increase in the activity of Cl^- relative to that of H_2O would rapidly shift the equilibrium from left to right. Presumably several reactions of this type occur in the range above 5 molal for CaCl_2 . But with several species involved, it seems doubtful that a speciation model would represent the properties through 9 molal any more simply than the virial series equations of Rogers⁽⁷⁾ (6 parameters adjusted for CaCl_2) or those of Staples and Nuttall⁽¹⁰⁾ (8 parameters) or Rard, et al.,⁽¹¹⁾ (8 parameters).

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REFERENCES

- (1) K. S. Pitzer and J. J. Kim, *J. Am. Chem. Soc.*, 96, 5701 (1974).
- (2) C. E. Harvie and J. H. Weare, *Geochim. Cosmochim. Acta*, 44, 981 (1980).
- (3) K. S. Pitzer and G. Mayorga, *J. Phys. Chem.*, 77, 2300 (1973).
- (4) J. A. Rard, A. Habenschuss, and F. H. Spedding, *J. Chem. Eng. Data*, 21, 374 (1976).
- (5) J. A. Rard and F. H. Spedding, *J. Chem. Eng. Data*, 22, 56 (1977).
- (6) H. F. Holmes, C. F. Bayes, Jr., and R. E. Mesmer, *J. Chem. Thermo.*, 10, 983 (1978).
- (7) P. S. Z. Rogers, to be submitted for publication.
- (8) K. S. Pitzer, Chapter 7 in "Activity Coefficients in Electrolyte Solutions", R. M. Pytkowicz Ed., CRC Press, Inc., Boca Raton, FL., 1979.
- (9) D. J. Bradley and K. S. Pitzer, *J. Phys. Chem.*, 83, 1599 (1979).
- (10) B. R. Staples and R. L. Nuttall, *J. Phys. Chem. Ref. Data*, 6, 385 (1977).
- (11) J. A. Rard, A. Habenschuss, and F. H. Spedding, *J. Chem. Eng. Data*, 22, 180 (1977).
- (12) R. A. Robinson, *Trans. Faraday Soc.*, 36, 735 (1940).
- (13) R. H. Stokes, *Trans. Faraday Soc.*, 41, 637 (1945).
- (14) V. B. Parker, D. D. Wagman, and W. H. Evans, NBS Technical Note 270-6, U. S. Gov. Printing Office, Washington, DC, 1971.
- (15) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", 2nd ed., revised, Butterworths, London, 1965.
- (16) J. A. Rard and D. G. Miller, *J. Chem. Eng. Data*, 26, 38 (1981).
- (17) N. A. Hewish, G. W. Neilson, and J. E. Enderby, *Nature*, 297, 138 (1982).
- (18) "Structure Reports", J. Trotter, ed., 46A, 168 (1980); 45A, 162 (1979); 44A, 151 (1978).

Table I. Ion Interaction Parameters for CaCl_2 at 25°C

$$\beta^{(0)} = 0.30534 \text{ kg mol}^{-1}$$

$$\beta^{(0)L} = 1.049 \times 10^{-4} \text{ kg mol}^{-1} \text{ K}^{-1}$$

$$\beta^{(1)} = 1.7083 \text{ kg mol}^{-1}$$

$$\beta^{(1)L} = 3.54 \times 10^{-3} \text{ kg mol}^{-1} \text{ K}^{-1}$$

$$C^\phi = 2.153 \times 10^{-3} \text{ kg}^2 \text{ mol}^{-2}$$

$$C^{\phi L} = -1.565 \times 10^{-4} \text{ kg}^2 \text{ mol}^{-2} \text{ K}^{-1}$$

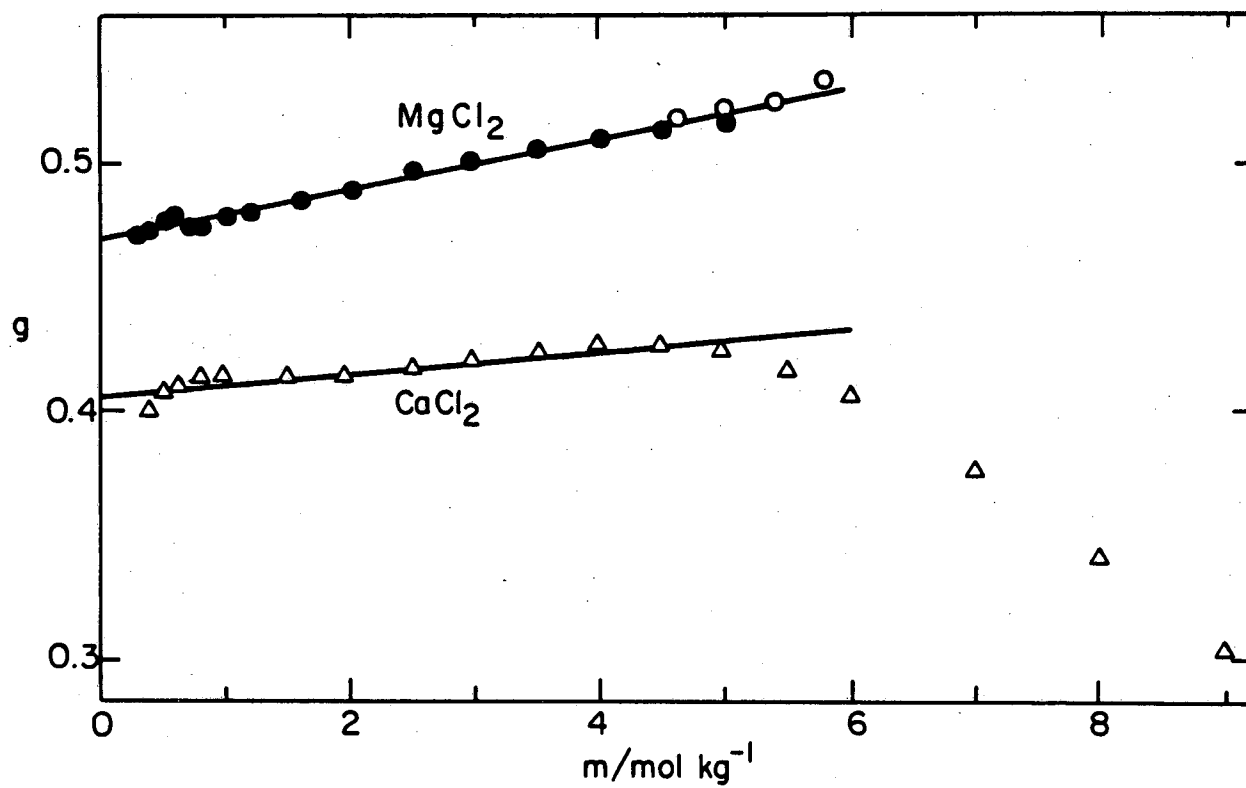


Figure 1. A deviation function based on the osmotic coefficient shows the peculiar behavior of CaCl_2 near 5 mol kg^{-1} in contrast to the simple behavior of MgCl_2 .

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