

Aqueous Solutions of Calcium Ions: Hydration Numbers and the Effect of Temperature

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Hydration numbers of calcium ions are determined from extensive measurements of colligative properties of water solutions of calcium salts. The hydration numbers reported refer to the average number of water molecules that are bound sufficiently strongly to calcium ions so as to be removed from the solvent and become part of the solute. Contrary to common descriptions of deviations from ideal behavior for concentrated solutions, ideal behavior is demonstrated when mole fractions are calculated by taking account of such bound water. Measurements over wide concentration and temperature ranges are used to obtain the effect of temperature on the average hydration number of Ca^{2+} . Freezing point depression measurements yield a hydration number of 12.0 ± 0.8 . Boiling point elevations yield 6.7 ± 0.6 . Consistent with this, vapor pressure measurements from 0 to 200 °C show a gradual decrease in hydration number with increasing temperature, with a value of 5.0 at 200 °C.

Introduction

Because of its importance in biological processes there has been extensive literature pertaining to the hydration number of calcium ions in water solutions. Calcium is the most abundant cation in the human body and is the fifth most abundant element in the earth's crust. Results from various techniques are not always in agreement partially because of the lack of a commonly accepted definition of the terms solvation number, hydration number, and coordination number. For example, Taube's definition as the number of water molecules that are distinguishable in some way from those of bulk water is too broad.¹ It is dependent on the analytical technique used and even on the sensitivity of different instruments of the same technique. Reviews relevant to the topic² enumerate various techniques used including transference (transport number), conductance, electromotive force, diffusion, thermodynamic measurements, spectroscopic and other optical methods (generally infrared), isotopic exchange, sound velocity-compressibility, effective volume, dielectric properties, diffraction methods (X-ray, neutron, electron, Extended X-ray Absorption Fine Structure), ¹H NMR, and theoretical calculations (molecular dynamics and Monte Carlo simulations). To these must be added mass spectroscopy of gas-phase ion–water clusters and ab initio calculations. As a result, "solvation is in a state of confusion because the solvation number depends on the method of measurement"^{2a} and "a clear and consistent picture of Ca^{2+} hydration has yet to emerge, with widely different results being reported for the average water coordination number".³ For example, diffraction measurements (neutron, X-ray) for Ca^{2+} have yielded numbers between 5.5 and 10.⁴ Active research is currently continuing regarding properties of aqueous solutions of calcium ions, their interaction with biomolecules, and their hydration numbers.^{3–5} For example, the hydration of calcium and magnesium ions affects their binding to adenosine triphosphate ions and this affects the thermodynamic properties of the hydrolysis of ATP.

Notably absent from the above list of measurements and techniques are colligative properties such as freezing point depression, vapor pressure lowering, and boiling point elevation. We have examined colligative properties of water solutions in an effort to understand their deviations from ideal behavior. Debye–Hückel theory is commonly cited in this respect, but it is only applicable to extremely dilute solutions. We have demonstrated that deviations from ideal behavior of aqueous concentrated solutions of nonelectrolytes and of a large variety of strong electrolytes of metal chlorides, bromides, and iodides can be understood and eliminated if the number of water molecules removed from the bulk solvent by strong binding with the solute is taken into account.⁶ Strong binding was estimated as a binding energy of approximately 13.3 kcal mol^{−1} or greater and water molecules so bound in dynamic equilibria become part of the solute. In this way it was demonstrated that deviations from ideal behavior of colligative properties of NaCl solutions, up to the limit of solubility as one example, disappear when the number of water molecules removed from the bulk solvent is taken into account. It was also shown that measurements of colligative properties of water solutions of metal chlorides, bromides, and iodides yield essentially the same hydration numbers. This was taken as evidence that only the cation binds water molecules sufficiently strongly to remove them from the bulk solvent. These anions are certainly solvated but they do not bind to water sufficiently strongly to remove it from the bulk solvent. Their binding energies from water cluster measurements and theoretical calculations bear this out, being less than 13.3 kcal mol^{−1} for the attachment of the first water molecule to these anions.⁶

The hydration number of Ca^{2+} as affected by temperature does not appear to have been examined systematically and in a self-consistent fashion. Many measurements of colligative properties of concentrated aqueous calcium chloride, bromide, and iodide solutions exist at various temperatures, but until recently there was no way of extracting hydration numbers from them.⁶ In this work we examine in detail colligative properties of vapor pressure lowering, freezing point depression, and

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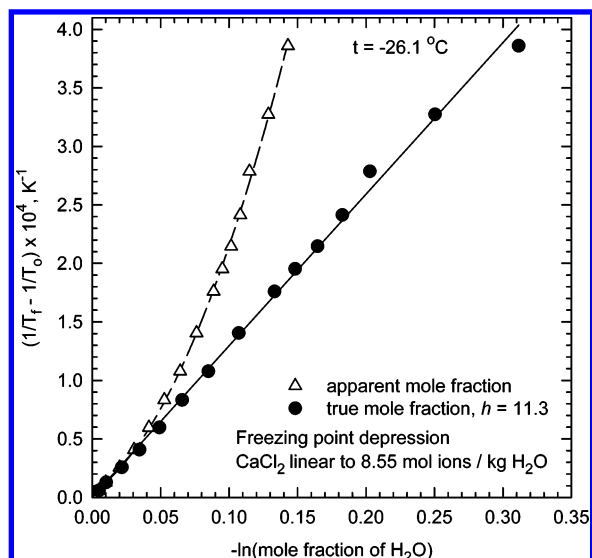


Figure 1. Plot of freezing point depression measurements for CaCl_2 to $-26.1\text{ }^\circ\text{C}$ and 2.85 mol of salt per 1000 g of H_2O . Triangles are points calculated conventionally by eq 1. Solid circles are calculated by eq 2 with a hydration number of 11.3.

boiling point elevation to obtain hydration numbers of Ca^{2+} at different temperatures.

Results and Discussion

Several sets of freezing point depression measurements for calcium chloride and bromide are available. Ideal behavior requires that plots of $1/T_f - 1/T_0$ vs $\ln(1 - x)$ be linear. T_f is the freezing point of the solution (in K), T_0 is the freezing point of water, and $(1 - x)$ is the molar fraction of water, x being the molar fraction of solute particles assuming 100% dissociation for the salts ($3 \times$ moles of CaCl_2). Diffraction studies have shown that chloride does not form contact ions pairs with calcium ions in up to 6 *m* solutions (6 mol per 1000 g of H_2O).^{5c} The conventional calculation of mole fraction of solute is by eq 1.

$$x = \frac{(\text{mol of solute particles})}{(\text{mol of } \text{H}_2\text{O} + \text{mol of solute particles})} \quad (1)$$

Plots of the experimental measurements using eq 1 and shown by the triangles in Figure 1 show large curvatures, commonly described as indicating deviations from ideal behavior. In fact, the measurements plotted in Figure 1 do not indicate deviations from ideality. Instead, the equation used to calculate mole fractions is incorrect. Equation 1 does not allow for the possibility that some water may be removed from the bulk or “free” solvent by strong binding to solute. If the binding is sufficiently strong, the “bound” water becomes part of the solute without increasing the number of solute particles, but decreasing the number of “free” solvent molecules. Mole fraction of solute then must be calculated by eq 2, where the value of h is the number of water molecules removed from the bulk solvent by strong binding with each Ca^{2+} .

$$x = \frac{(\text{mol of solute particles})}{[(\text{mol of } \text{H}_2\text{O}) + (\text{mol of solute particles}) - (h \times \text{mol of } \text{Ca}^{2+})]} \quad (2)$$

If eq 2 is the correct way of calculating mole fractions, then a value of h must exist that fulfills two requirements *simultaneously*. It must produce linear plots and the resulting straight line must pass through the origin. The filled circles of Figure 1

TABLE 1: Hydration Numbers of Ca^{2+} Solutions with Mole Fractions Calculated by Eq 2

salt	temp, $^\circ\text{C}$	colligative property ^a	linear to m^b	hydration no., h^c	correlation coefficient ^d	ref
CaCl_2	-31.3	FP	9.74	10.2	0.9995	9
CaCl_2	-26.1	FP	8.55	11.3	0.9985	10
CaCl_2	-21.7	FP	7.62	12.3	0.9992	11
CaCl_2	-15.4	FP	6.00	13.5	1.0000	12
CaBr_2	-1.6	FP	0.90	12.3	0.9995	12
CaBr_2	-0.8	FP	0.46	12.3	1.0000	10
CaCl_2	0.0	VP	10.50	9.6	0.9985	13
CaCl_2	0.0	VP	9.01	10.1	0.9998	10
$\text{Ca}(\text{ClO}_4)_2$	0.0	VP	8.37	12.6	0.9995	10
CaCl_2	10.0	VP	9.01	9.8	0.9999	10
CaCl_2	20.0	VP	9.01	9.5	1.0000	10
CaCl_2	30.0	VP	9.01	9.2	0.9998	10
CaCl_2	30.0	VP	9.05	9.3	0.9993	14
CaI_2	30.0	VP	9.66	9.4	0.9982	14
CaCl_2	40.0	VP	9.01	9.1	0.9998	10
CaCl_2	40.0	VP	9.00	9.6	0.9993	13
CaCl_2	40.0	VP	9.05	9.2	0.9996	14
CaCl_2	50.0	VP	9.01	8.8	0.9997	10
CaCl_2	50.0	VP	9.05	9.0	0.9996	14
CaI_2	50.0	VP	8.75	9.1	0.9979	14
CaCl_2	60.0	VP	9.01	8.5	0.9995	10
CaCl_2	60.0	VP	8.75	8.7	0.9996	14
CaCl_2	70.0	VP	9.01	8.2	0.9993	10
CaCl_2	70.0	VP	9.00	8.6	0.9996	13
CaCl_2	70.0	VP	9.05	8.5	0.9996	14
CaI_2	70.0	VP	9.66	8.8	0.9980	14
CaCl_2	80.0	VP	11.58	7.8	0.9994	10
CaCl_2	90.0	VP	11.58	7.5	0.9994	10
CaCl_2	90.0	VP	9.00	8.1	0.9992	13
CaCl_2	100.0	VP	11.58	7.2	0.9992	10
CaCl_2	100.0	VP	9.00	7.9	0.9991	13
CaCl_2	100.0	VP	12.00	7.6	0.9995	11
CaBr_2	104.31	BP	8.44	5.8	0.9992	10
CaCl_2	106.72	BP	8.54	7.2	0.9993	10
CaBr_2	107.77	BP	15.00	6.4	0.9997	13
CaCl_2	115.12	BP	15.00	7.5	1.0000	13
CaCl_2	150.0	VP	11.58	6.7	0.9998	10
CaCl_2	200.0	VP	14.55	5.0	0.9994	10

^a FP = freezing point depression; VP = vapor pressure lowering; BP = boiling point elevation. ^b Linear to indicated molality of ions or maximum concentration measured. ^c Average number of water molecules “bound” to Ca^{2+} . ^d Correlation coefficient of linear regression.

show that a value of $h = 11.3$ does exist that fulfills both stringent requirements simultaneously. There is no deviation from ideal behavior over wide concentration ranges when the experimental measurements are plotted correctly. In searching for the value of h for use with eq 2, we selected the passing through the origin to be the criterion because there can be no argument that at zero solute there will be no effect on the colligative property. Simultaneously, the correlation coefficient of the resulting linear regression is very near unity, greater than 0.99.

The set of measurements plotted in Figure 1 were selected from among five available to illustrate experimental scatter giving the poorest correlation coefficient (0.9985). Over the very wide concentration ranges treated here, simultaneous satisfaction of both criteria, linearity and zero intercept, guarantees that the value of h obtained cannot be fortuitous and that it has the physical meaning attributed to it by eq 2, i.e., it is the hydration number of Ca^{2+} .

Additional measurements of freezing point depressions are listed in Table 1. The values of h obtained from each set of measurements show some variation, the average being 12.0 with

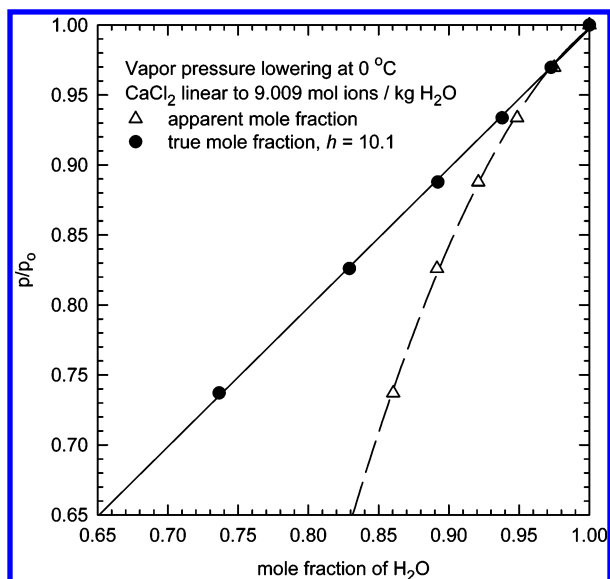


Figure 2. Plot of vapor pressure lowering measurements for CaCl_2 to 3.003 mol of salt per 1000 g of H_2O at 0 °C. Open triangles are points calculated conventionally by eq 1. Solid circles are calculated by eq 2 with a hydration number of 10.1. Slope = 0.9937, intercept = 0.003, correlation coefficient of linear regression = 0.9998.

an average deviation of 0.8. The temperature shown in Table 1 for each set of freezing point depression measurements is the lowest for which linearity holds or for which experimental measurements are available. Correlation coefficients of the linear regressions obtained are generally greater than 0.999.

Linearity obtained by using eq 2 does not always extend to the full range of available data. CaCl_2 solutions have a eutectic at 4.325 *m*, at which point what crystallizes out of solution is no longer water-ice but also hydrates of the salt. Assuming a constant value of $h = 12.0$ to the eutectic, 51.9 mol of water would be “bound”, or 93% of the total. As “free” water becomes unavailable, the value of h must decrease. In the case of the highest concentration included in Figure 1 (2.85 mol of CaCl_2 per 1000 g of H_2O , 8.55 *m* ions), 32.2 mol of total water is bound to the cation. Between 2.85 and 4.325 mol of CaCl_2 , the average hydration number begins to decrease. At the eutectic ($T_f = 273.15 - 50.99$ K) the actual hydration number can be calculated and is 9.5, binding 41.3 mol of water, or 74.4% of the total water.⁷ As available “free” water becomes scarce, the anions start forming “solvent-shared” ion pairs causing the onset of curvature. It has been observed that thermodynamic data show a structural transition around 4.5 *m* CaCl_2 ,⁸ a concentration value near that of the eutectic.

Measurements of vapor pressure lowering are available for temperatures ranging from 0 to 350 °C. For ideal behavior, plots of the ratio of vapor pressure of solution to the vapor pressure of pure water (p/p_0) vs molar fraction of water should be linear with zero intercept and a slope of unity, Raoult’s law. Figure 2 shows a typical plot at 0 °C. Significant curvature is obtained when mole fractions are calculated conventionally by eq 1. With eq 2, a value of h exists that *simultaneously* produces a straight line with a correlation coefficient greater than 0.99 and zero intercept *and* a slope of 1.00 over a wide range of concentrations. Additional typical results are shown in Table 1.

For all vapor pressure measurements of Table 1 a value of h exists that satisfies simultaneously all three requirements of ideal behavior: linearity, zero intercept, and unity slope. Correlation coefficients of the linear regressions obtained are generally greater than 0.999 and the resulting slopes are all well within 1% of unity. Vapor pressure measurements are available for

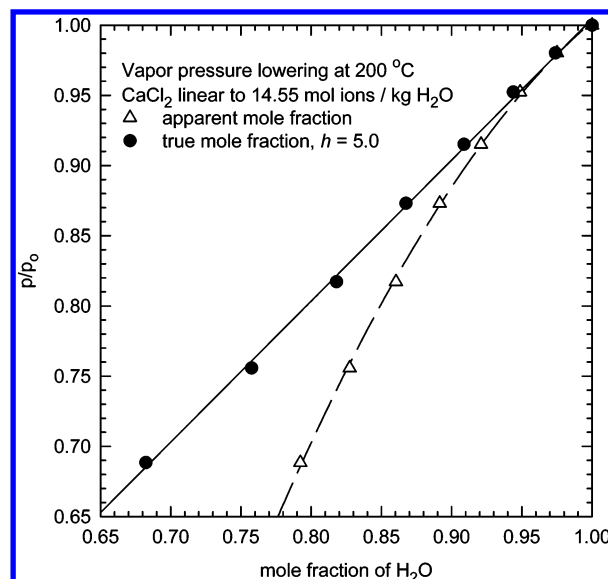


Figure 3. Plot of vapor pressure lowering measurements for CaCl_2 to 4.851 mol of salt per 1000 g of H_2O , 14.55 *m* ions, at 200 °C. Open triangles are points calculated conventionally by eq 1. Solid circles are calculated by eq 2 with a hydration number of 5.0. Slope = 1.007, intercept = 0.002, correlation coefficient of linear regression = 0.9994.

calcium perchlorate at 0 °C and they are included in Table 1. Studies by ^1H NMR have shown that perchlorate anion is not hydrated and results for CaCl_2 and for $\text{Ca}(\text{ClO}_4)_2$ were found to be essentially the same at equivalent concentrations.¹⁵ ClO_4^- is known not to coordinate with Ca^{2+} .^{5c} The three sets of data at 0 °C show a hydration number of 10.7 ± 1.2 . The entries of Table 1 demonstrate that hydration numbers from vapor pressure measurements show a gradual decline with increasing temperature. The three sets of measurements at 100 °C show a hydration number of 7.6 with an average deviation of 0.3. At 150 °C the hydration number decreases to 6.7. Figure 3 shows a plot of vapor pressure measurements at 200 °C. The open triangles show the usual curvature obtained by use of eq 1 for the calculation of mole fractions. The filled circles are obtained by use of eq 2 with $h = 5.0$ and are consistent with ideal behavior of a linear plot with slope of unity and zero intercept.

Vapor pressure measurements of calcium chloride solutions at 250 °C cannot be treated satisfactorily by eq 2. The value of $h = 3.1$ that yields a zero intercept does not fully remove the curvature of the resulting points (filled circles), as shown in Figure 4. The correlation coefficient of linear regression is lower than any from Table 1. Alternatively, the value of $h = 5.8$ that yields the highest linear correlation coefficient, 0.9997, yields unacceptable values of slope = 0.767 and intercept = 0.229. A similar situation is found for calcium chloride measurements at 300 and 350 °C. One likely explanation is that the large decrease of the dielectric constant of water at high temperatures leads to ion association and formation of ion pairs, invalidating the assumption of 100% dissociation. The dielectric constant of water drops from 88 at 0 °C to 35 at 200 °C and to only 27 at 250 °C.

Four sets of boiling point elevation measurements are included in Table 1, covering various temperature ranges and showing linearity with eq 2 up to 115.12 °C for a 5.0 *m* solution of CaCl_2 . The average hydration number obtained from these four sets is 6.7 ± 0.6 , appropriately a somewhat lower value compared to vapor pressure lowering at 100 °C. Figure 5 shows one set of boiling point elevation measurements. Ideal behavior requires linearity of plots of $1/T_b - 1/(T_b + \Delta T)$ vs $\ln(\text{mol fraction of } \text{H}_2\text{O})$. T_b is the boiling point of water (in K) and ΔT

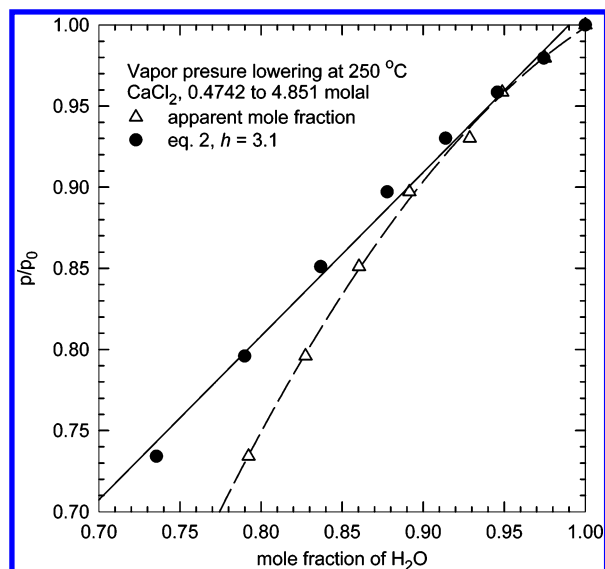


Figure 4. Plot of vapor pressure lowering measurements for CaCl_2 to 14.55 m ions, at 250 °C. Open triangles are points calculated conventionally by eq 1. Solid circles are calculated by eq 2 with a hydration number of 3.1 to yield zero intercept. Slope = 1.009, intercept = 0.001, correlation coefficient of linear regression = 0.9966. Curvature is evident in the filled circles.

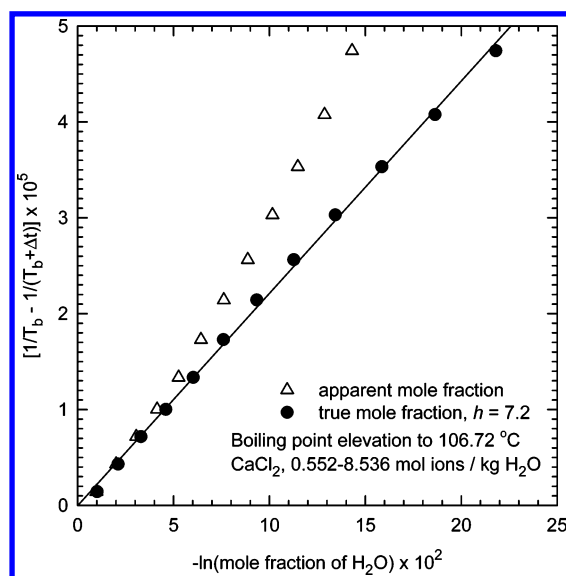


Figure 5. Plot of boiling point elevation measurements of all available data for CaCl_2 to 106.72 °C and 2.8452 mol of salt per 1000 g of H_2O . Triangles are points calculated conventionally by eq 1. Solid circles are calculated by eq 2 with a hydration number of 7.2. Correlation coefficient of the linear regression = 0.9993.

is the number of degrees of the boiling point elevation. Figure 5 shows curvature when mole fractions are calculated conventionally by eq 1, open triangles. Consistent with ideal behavior, the curvature disappears and a straight line through the origin is obtained with eq 2 and $h = 7.2$.

The hydration number obtained from colligative properties is both unequivocal and straightforward as defined by eq 2. For example, as shown from vapor pressure measurements, no h values other than those listed in Table 1 will simultaneously produce linear correlations with zero intercept and unity slope as required for ideal behavior.

The results of Table 1 are shown graphically in Figure 6. The scatter of the points appears due to a combination of factors: experimental uncertainties in the reported measurements from many different laboratories for four different calcium salts

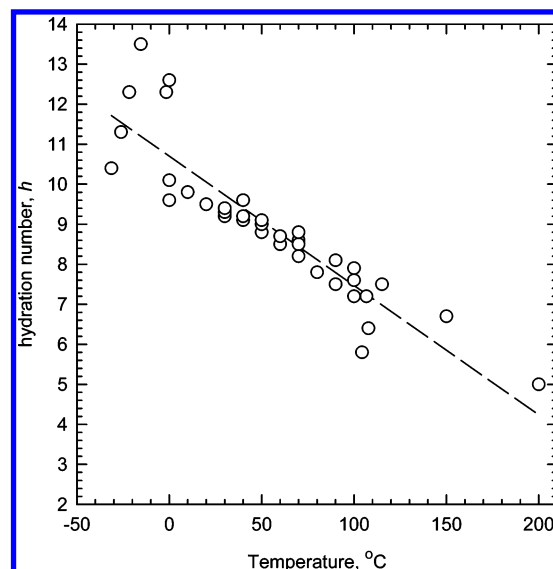


Figure 6. Plot of hydration numbers from Table 1 vs temperature (°C). The dashed line is a linear regression through the points.

and possible uncertainties in interpolations and extrapolations of experimental measurements.¹⁰ The heuristic approach via eq 2 has an uncertainty of only $h = \pm 0.1$, the step size we used.

The reason for the existence of fractional hydration numbers is that they refer to an average dynamic number of water molecules bound to Ca^{2+} . Gas-phase cluster studies have shown a distribution of $\text{Ca}^{2+}(\text{H}_2\text{O})_n$ species.¹⁶ We have normalized the graphic data reported at 300 K (27 °C) for clusters of $n = 6$ to 14 as follows ($\sum n = 1.000$): $n = 6$, population = 0.000; $n = 7$, population 0.028; $n = 8$, population 0.112; $n = 9$, population 0.348; $n = 10$, population = 0.331; $n = 11$, population = 0.111; $n = 12$, population = 0.056; $n = 13$, population = 0.014; $n = 14$, population = 0.000. The average value thus obtained is $h = 9.4$, consistent with $h = 9.5$ at 20 °C and $h = 9.3 \pm 0.1$ obtained from three sets of vapor pressure measurements at 30 °C (Table 1). This type of agreement between our results from colligative properties of solutions and those from gas-phase clusters lends confidence to the validity of eq 2. For the realistic concentration ranges treated here there is no need to invoke Debye–Hückel theory.

Thermochemical measurements^{5h} of calcium ion–water clusters reported for 298 K showed that the 12th water molecule is held with a binding energy of 13.0 ± 1.0 kcal mol⁻¹, the 11th with 13.3 ± 1.0 , and the 10th with 14.5 ± 1 . On the basis of our estimate that about 13.3 kcal mol⁻¹ of binding energy appears sufficient to remove a water molecule from bulk or “free” water solvent, the above cluster binding energies indicate a hydration number of 10 to 11.

Diffraction studies should provide a fairly accurate estimate of the number of water molecules in the first coordination shell around an ion. Such coordination numbers are not directly comparable to hydration numbers as defined here. For example, large coordination numbers reported^{2c} by scattering studies for Cl^- and I^- refer to the number of water molecules that fit and are ordered around the solvated anion, not the number of water molecules that are bound sufficiently strongly as to be effectively removed from “bulk” solvent. Recent diffraction studies of aqueous solutions have reported Ca^{2+} coordination numbers of 8.1 (EXAFS, 0.2 m CaCl_2),^{5b} of 7.3 ± 0.1 (neutron diffraction with calcium isotope substitution in light and heavy water, NDIS, 4.0 m CaCl_2 at ambient temperature),³ and of 8 (EXAFS and large angle X-ray scattering of solutions of CaCl_2 , CaBr_2 ,

CaI₂, and Ca(ClO₄)₂ at ambient temperature);^{5c} an older study reported a value of 10 (about 1 *m* CaCl₂, NDIS).¹⁷

Theoretical calculations with the Car–Parrinello¹⁸ ab initio (DFT) molecular dynamics simulation around 306 K indicate that Ca²⁺·(H₂O)₇ is more stable with six H₂O in the inner shell and one on the second shell than a structure with seven H₂O in the first shell.¹⁹ For Ca²⁺·(H₂O)₈, again the 6–2 arrangement is more stable than 8–0. These results show that the eighth water molecule is held with a calculated binding energy of 17.9 kcal mol^{−1}, considerably higher than bonding of water molecules with themselves,⁶ and in fair agreement with the experimental value of 16.1 ± 1.^{5h} The calculations indicate a coordination number of 6 for the inner shell, but a hydration number greater than 8 in terms of our definition of *h* and of the energy of 13.3 kcal mol^{−1} as borderline for strong binding. Vapor pressure measurements yield *h* = 9.3 at 30 °C. The hydration numbers obtained from colligative properties encompass more than just the first hydration shell.

The results of this work do not agree with the conclusions recently reported for a monotonic and significant decline of hydration numbers for Ca²⁺ from *h* = 22 in dilute solution to about *h* = 12 at 4.0 *m*, as deduced from isentropic compressibility measurements from 0 to 50 °C.²⁰ The colligative property measurements used in this work showed that the same hydration number is valid for solutions at least up to 3.00 *m* in the same temperature range. The isentropic compressibility was, however, found to decline with increasing temperature, consistent with our findings of declining hydration number with increasing temperature.

Conclusions

Measurements of colligative properties of aqueous solutions of CaCl₂, CaBr₂, CaI₂, and Ca(ClO₄)₂ yield hydration numbers reflecting the number of water molecules bound to Ca²⁺ sufficiently strongly as to be removed from the bulk solvent and become part of the solute. The hydration number declines with increasing temperature, from a high of 12 around −20 °C to a low of 5 at 200 °C. Contrary to common practice of describing colligative properties of aqueous solutions as deviating from ideality for all but very dilute solutions, we show that ideality is exhibited over wide concentration ranges when mole fractions are calculated correctly with eq 2.

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