

THE VAPOUR PRESSURES OF
CONCENTRATED SOLUTIONS
OF SILVER NITRATE AT
VARIOUS TEMPERATURES.

By

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Abstract.

The vapour pressures of solutions of silver nitrate from zero concentration to eighty-five weight percent were determined over a range of temperature from 30° to about 100°C. (for solutions up to seventy percent) and over a more narrow range for the more concentrated solutions. A differential manometer and an absolute barometric apparatus were used to measure the vapour pressures.

By an application of the Clausius-Clapeyron equation it was hoped to detect evidence of layer hydration of ions as postulated by Stokes and Robinson. Within the limits of experimental error no evidence of hydration was found and it was concluded that the Clausius-Clapeyron equation as applied in this research was not suitable for the estimation of the extent of ionic hydration. Water activities, osmotic pressures, and osmotic coefficients were also calculated.

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THEORETICAL INTRODUCTION.

THEORETICAL INTRODUCTION

Ionic Solvation:

The concept of ionic solvation has become an important part of the theory of electrolytic solutions. Ions in solution in polar solvents are thought of as being coordinated with a certain number of solvent molecules. The number varies from ion to ion and is referred to as the solvation number of the ion, but, in spite of much experimental work, the significance of the term "solvation number" has remained in doubt. The various experimental methods used to estimate the solvation number give large differences in numerical values. Thus, partly because of the unreliability of the experimental methods, the meaning of the term "solvation number" remains indefinite.

In order to get around the difficulty of assigning a solvation number to an ion more recent workers on ionic solvation have attacked the problem from a different direction. In this regard efforts have been directed principally to the calculation of heats of solvation or solvation energies because this quantity infers a total interaction and is open to less ambiguity than are the solvation numbers.

A more accurate knowledge of ion-solvent interaction is of great importance in several ways, firstly, to further the model of an ionic solution, secondly in the development of the theory of concentrated electrolytic solutions and lastly, the calculation of solvation

numbers as an aid in the theory of reactions in solution.

Early in the development of the idea of ionic solvation the ions were regarded as being chemically bound to the water molecules. The observations of S. Aschkenazi (1) seemed to support this concept. He quoted sudden changes in conductivity, cryoscopic constants, etc. with solution composition which he thought corresponded to the formation and composition of various definite hydrates. There was difficulty, however, in confirming the existence of definite hydrates in solution. Therefore consideration of the polarizability of water molecules and the field about the ion led K. Fajans (19) to the conclusion that the interaction energy in solvation was entirely coulombic and did not involve covalent linkages. The water molecules did not adhere to the ion at all times but rather it was believed that the molecules in the hydration sheath were continually interchanging with those in the bulk of the solution.

This picture of ionic hydration was substantiated by M. Born (8) who showed that the solvation energy arising from a very simple interpretation of Fajans concept was in close agreement with experiment for univalent electrolytes. When the existence of a definite structure for liquids was realized it became apparent that the steric properties of the ion became important in determining its solvation. This accounts for the different ionic velocities found for a series of ions in various solvents since ions having a radius greater than some critical value would have difficulty "fitting in" to the structure of

certain solvents.

It would seem that the electrostatic theory of solvation energy applies as long as the simpler ions of groups IA and IIA of the Periodic Table and the halogens are considered. This type of ion-solvent interaction is almost entirely coulombic, other types of interaction being unimportant in this connection.

This conclusion cannot be assumed for certain in the case of the more complicated ions e.g. for those of group VIII where strong coordinating power tends to favor covalent attachment between ion and solvent. For many of these ions there exists little quantitative evidence of solvation.

If we are willing to accept the Fajans-Born concept of simple coulombic interaction it follows logically that a certain number of solvent molecules would be attached firmly to the ion and further ion-dipole interaction would involve other solvent molecules outside the inner solvation sheath. It has been suggested (6) that the term primary hydration or more generally primary solvation be used when referring to the attachment of solvent molecules to those ions in solution for which (i) the ion and its attachment of solvent molecules move together as one entity during electrolytic transport and (ii) the solvent ions have completely lost their own separate translational degrees of freedom.

"Secondary solvation" then involves all interactions which are not included in the definition of primary solvation. The term

total solvation would therefore be the sum of these two types. It may be said here that the measurement of solvation energies involves the estimation of the energies involved in the total effect.

Investigations (4) into the structure of water have been a great aid in accounting for the properties of ionic solutions especially those relating to solvation. Since the internal field of water is determined by the electrostatic field of the dipoles the introduction of charged ions will obviously modify the field considerably. This effect on the basis of coulombic forces will be roughly proportional to the polarizing power of the ion, that is, its charge divided by the ionic radius. It follows that large monovalent ions will have comparably small polarizing power because of their low charge density. Small, highly charged ions on the other hand will have a much greater effect. According to J. D. Bernal and R. H. Fowler (4) the hydration of an ion will occur when the potential energy of a water molecule forming part of the coordination shell about an ion is less than that of a molecule in free water. The charge of the ion would be expected to attract the two H-nuclei or the two vacant spaces in the water molecule symmetrically, that is, from the point of view of further coordination to occupy them both. Therefore it follows in free water every molecule has four neighbors and a single molecule coordinated to an ion has three, the ion and two water molecules on either side. On this basis it would seem that except for F^- and OH^- the potential energy of coordination is so small

that there is no true hydration of anions.

F. A. Lindemann (30) has proposed a different theory of ionic solvation. He suggests that there is no permanent hydration sheath existing in solution. The observed solvent transport during movement of an ion is caused by the transfer of momentum from ion to solvent molecules on collision. Smaller ions, on the basis of this theory, would be expected to transfer more momentum than the larger ions. Also the theory explains the dependence of the temperature coefficient of conductance on ion size, but this theory suffers from lack of evidence and will not be considered further.

R. H. Stokes and R. A. Robinson (39) have advanced a hydration model for concentrated solutions from studies made on the highly concentrated solutions and gels of calcium nitrate. They picture the system as an adsorbent (calcium nitrate) - adsorbate (water) system. At high concentrations it is their belief that ion-solvent forces are the dominant factor and they develop a treatment which to a first approximation ignores ion-ion forces or rather assumes that they are little affected by concentration in this range. The concentrated solutions contain ions in different stages of hydration, some with complete monomolecular layers, some incomplete and others with more than one layer. The outer layer of solvent molecules would be held much less firmly than the innermost solvation sheath. This hydration model bears a close resemblance to the adsorption isotherm of Brunauer, Emmett and Teller (12) with the result that Stokes and

Robinson presented their equation as

$$\frac{m a_w}{55.51 (1-a_w)} = \frac{1}{Cr} \left/ \frac{C-1}{Cr} a_w \right. \quad (1)$$

where a_w = the activity of water,

m = the molality,

r = the number of water molecules in a monomolecular hydration sheath when complete.

C = a constant related to the heat of adsorption E of the molecules in the layer by the approximate relation

$C = \exp. (E - E_L) RT$, E_L being the heat of liquifaction of pure water.

On the whole this theory seems to be one of the best advanced to date although until more theoretical and practical work is done on the basis of this theory no really reliable estimate of its possibilities can be stipulated.

Since a great deal of the more recent work on the problem of solvation has to do with solvation energies rather than with solvation numbers a closer examination of the pertinent theory regarding energies of solvation is in order.

On the basis of the theory of salt dissolution it is argued that the large solubility of many salts in suitable solvents, in which the essential steps are the breaking down of the crystal lattice and the creation of free ions can only be explained if some special process occurs upon dissolution of a crystal which produces an amount of energy of the same order as that of the crystal lattice. Since the

lattice energies are of considerable magnitude even for salts containing univalent ions it follows that the amount of energy required in the process must also be considerable. This process is termed the solvation or in aqueous solution the hydration of ions and signifies the attachment of solvent molecules to ions in solution, caused principally by the coulombic attraction forces of the ions for the polar molecules of the solvent. If the heat change which occurs during solvation (the heat of solvation) is sufficiently exothermic, it compensates for the energy used in breaking up the lattice and the salt dissolves. As a consequence of the first law of thermodynamics the algebraic sum of the heats of solvation and the lattice energy is the heat of solution thus:

$$\Delta H = -U + (Q_+ + Q_-)$$

where ΔH = the heat of solution,

U = the lattice energy,

$(Q_+ + Q_-)$ = the heat of solvation.

The heat of solvation therefore can be calculated by this equation it being borne in mind that the value found contains both the interaction energy of the ion and dipole and the work of breaking up the solvent (hole formation) caused by the dissolution of the ion.

Table I shows the heats of hydration of the alkali halides calculated from lattice energies and heats of solution in water.

TABLE I.

Lattice Energies, Initial Heats of Solution, and Heats of Hydration of the Alkali Halides in Kilocalcs.

Salt	U T = 291°K	ΔH T = 291°K	$Q_f \neq Q_-$ T = 291°K
LiF	- 247.0	1.1	- 245.9
LiA	- 202.7	- 8.6	- 211.3
LiBr	- 191.4	-11.1	- 202.5
LiI	- 177.6	-14.8	- 192.4
NaF	- 218.2	0.6	- 217.6
NaCl	- 185.5	1.3	- 184.2
NaBr	- 177.8	0.2	- 177.6
NaI	- 165.6	- 1.4	- 167.0
KF	- 194.7	- 4.1	- 198.8
KCl	- 169.6	4.4	- 165.2
KBr	- 162.8	5.1	- 157.7
KI	- 153.9	5.1	- 148.8
RbF	- 184.9	- 5.8	- 190.7
RbCl	- 163.4	4.5	- 158.9
RbBr	- 157.4	6.4	- 151.0
RbI	- 149.2	6.5	- 142.7

The problem of obtaining values for hydration energies of individual ions is frequently encountered but generally it is very difficult to solve. These individual values cannot be obtained directly from experimental results without resorting to the use of some non-thermodynamic facts such as the properties of the ions and solvent.

The best known attempt to calculate the heats of hydration from the properties of ion and solvent is that of Born (8) who regarded the heat of hydration of an ion as the difference in its electrostatic energy in vacuo and that in a medium of dielectric constant ϵ .

The energy of an ion regarded as a sphere of radius a in vacuo is

$$\frac{Z_i^2 e_o^2}{2a}$$

where Z_i = the valence of the ion,

e_o = the electronic charge.

If the medium of dielectric constant ϵ is considered as a continuum the corresponding energy in it is $\frac{1}{\epsilon}$ times that in a vacuum. Therefore the change in free energy per mol accompanying the transfer of the ion from vacuo into a medium of dielectric constant ϵ is

$$\begin{aligned} F &= -N_A \left[\frac{Z_i^2 e_o^2}{2a} - \frac{Z_i^2 e_o^2}{2\epsilon a} \right] \\ &= \frac{-N_A Z_i^2 e_o^2}{2a} \left[1 - \frac{1}{\epsilon} \right] \end{aligned} \quad (2)$$

The heat of hydration Q_i can be obtained from the Gibbs Helmholtz equation as

$$Q_i = \Delta F - T \left(\frac{\partial \Delta F}{\partial T} \right)_P$$

from which

$$Q_i = \frac{-N_A Z_i^2 e_o^2}{2a} \left[1 - \frac{1}{\epsilon} - \frac{T}{\epsilon^2} \left(\frac{\partial \epsilon}{\partial T} \right)_P \right] \quad (3)$$

Two main difficulties are immediately confronted in the application of this equation. Firstly there is the difficulty of ascertaining the radius of the ion. X-ray measurements of crystals give internuclear distances in the crystal on the assumption that the cation and anion are in close contact in the crystal. The main ambiguity is encountered in the division of these internuclear distances into the individual ionic radii. Also it is not certain that the ionic radii of the crystal are the same as that in the solvent medium. Secondly the Born equation infers that the heat of solvation of a monovalent ion should depend only on the dielectric constant of the medium and the temperature, apart from the ionic radius. This would mean that all ions whether cation or anion of the same radius would yield the same solvation energy. The use of the macroscopic dielectric constant is also in serious error since near the vicinity of the ion, at least, the dielectric constant is considerably reduced, due to the influence of the field of the ion.

The simple theory of Born has been extensively improved by taking into account ion-dipole interaction, the orientation and polarization of the water molecules by the ionic fields and the work of disturbing the structure of the solvent caused by the presence of the ions. In Table II the heats of hydration of some individual ions calculated by the Born equation are compared with more recent values corrected in accordance with the factors mentioned above.

TABLE II

Heats of Hydration of Individual Ions in
Kilocals at 291°K.

Ion	Li ⁺	Na ⁺	K ⁺	Rb ⁺	F ⁻	Cl ⁻	Br ⁻	I ⁻
Radius A°	0.68	0.98	1.33	1.48	1.33	1.81	1.96	2.19
Q _i (Born Equation)	240	166	123	110	123	90	83	74
Q _i (Corrected)	131	116	92	87	94	67	63	49

Although a great deal of work has been done on the problem of ionic solvation there is still no acceptable theory at present. All of the theoretical concepts advanced to date have been found to be inadequate to a greater or lesser degree. Much of the difficulty lies in

the lack of knowledge of the type of binding that exists between the ions and the solvent molecules and the dearth of reliable experimental methods available for the measurement of both the solvation numbers and energies of the ions. Until such time as these inadequacies are removed the entire problem of electrolytic solutions will remain unsettled.

Experimental:

A wide range of experimental phenomena have been studied in attempts to determine solvation numbers experimentally. This fact alone would seem to indicate that ion-solvent interactions have a widespread influence on solution behavior. Included among the phenomena studied are: refractivity, freezing and boiling points, vapor pressure, surface tension, density, specific heat, compressibility of ionic solutions, transport numbers of ions, and solubility of non-electrolytes in the presence of electrolytes.

Most of these methods have a common difficulty; the dividing up of the solvation of the salt between its ions. Some workers (34) in the field have assumed that large organic ions such as $C_6H_5NO_3^+$ have zero solvation. Some have extended this to include such ions as NO_3^- (9) and I^- (15). The most sensible method appears to be division in the ratio of the ion sizes based upon some salt such as potassium fluoride where the ionic radii are close to being equal.

One of the first methods used in attempting to estimate ionic hydration is the method of ionic or solvent transport using an inert

reference substance. The reference substance is used to determine if there is a concentration change when the ions move due to an applied difference in potential. If the ions are hydrated water will be transported with the ions and an increase in the concentration of the reference substance should be observed. The fundamental assumption of course is that the reference substance does not move under the influence of the applied field. Buchbock (13) and Washburn (44) were the first to use this method successfully. They used raffinose as their inert reference solute. By referring the changes in the content of water and of the salt to the non-electrolyte as a reference substance a relation between the degrees of hydration of the ions was derived. Using the following equation Washburn was able (as he thought) to calculate the number of moles of water carried per equivalent of cation and anion:

$$\Delta n = \tau_c N_w^c - \tau_a N_w^a \quad (4)$$

where Δn = the change in the number of moles of water in a given electrode portion,

τ_c = the true transference number of the cation,

τ_a = the true transference number of the anion

N_w^c and N_w^a = the number of moles of water carried per equivalent of cation and anion respectively. It is necessary to

assume either N_w^c or N_w^a since both of these quantities are unknown.

P. Z. Fischer and T. E. Koval (20) have since shown that raffinose, the inert reference substance, used by Washburn is transported during electrolysis. Also it has been shown by L. G. Longworth (31) that the non-electrolyte used has an effect on the displacement per Faraday of the ions. Therefore it would seem that this method is open to considerable objection and that the results obtained are quite uncertain.

In the Remy (35)-Babarovsky (3) method of water transport which overcame the necessity of adding an inert non-electrolyte the liquid is allowed to pass through a thin membrane between cathode and anode compartments and thus indicate the net volume change arising from the different extent of solvation of the cation and anion. This method too is open to adverse criticism. Probably included in the measured water transport is the water which is transported by a transfer of momentum from ions to molecules much in the same way as that suggested by Lindemann. This would result in hydration numbers that were too high. Another objection is the considerable volume change in the anode and cathode compartments caused by reactions at the electrodes. Also, below a concentration of 1 N the effect of electroendosmosis at the membrane is considerable. In conclusion the Remy-Babarovsky method measures some part of the total rather than the primary hydration.

The same conclusions and criticism also holds true for the Jander's diffusion method (26) and the dialysis method of Brintzinger (11).

Ionic mobilities constitute another phenomenon which has been studied as an aid in determining the solvation of ions. In this regard the method of Ulich (41) is probably the best known. This method seems to measure a more definite quantity than the methods so far discussed since it obtains directly the volume of the solvated ions from an application of Stoke's law to ionic mobilities at low concentrations, so that an estimate of primary solvation is obtained. Several objections have been leveled against this method. The non applicability of Stoke's law to some ions in solution (28) seems to be the most serious one. Also the calculation of the molecular volume of the water molecules about the ion is open to doubt. The high pressures in the vicinity of the ions and the inhibition of rotational degrees of freedom of the dipoles attached to the ion tend to constrict the normal molecular volume of the water. Therefore the molecular volume so calculated would be too large and the resulting solvation numbers would be too small, giving therefore a lower limit.

Ulich calculated an upper limit by assuming that the molecular volume was diminished to one half its original value. Ulich's final value is an average taken of the upper and lower solvation limits.

Methods based upon activity determinations such as the cryoscopic, vapor pressure, and salting-out methods all give high results and therefore seem to give a total interaction effect.

The cryoscopic method employed by E. Rouyer, F. Bourion and Hun (10) seems to be open to doubt since the results depend upon the

non-electrolyte employed. In this method the cryoscopic or ebullioscopic constants of a non-electrolyte is measured in an electrolytic solution and in pure water. Using the following relation the hydration of the electrolyte may be found

$$x = \frac{100 (k' - k)}{k'} \quad (5)$$

where x = the per cent of water of hydration of the electrolyte,
 k = the cryoscopic constant of the non-electrolyte in water,
 k' = the cryoscopic constant of the non electrolyte in the electrolytic solution.

These workers used such non-electrolytes as paraldehyde, acetone and resorcinol. The first two act unreasonably while resorcinol appears to be a suitable non-electrolyte. This method suffers to a great extent by the absence of a satisfactory theoretical basis and it would appear that the advancement of an adequate treatment would be extremely difficult.

The measurement of vapor pressures to estimate hydration numbers was carried out by B. H. Van Ruyven (43). He pictures the ion as having a definite number of water molecules bound to it in solution. The strong electrolyte is not considered to be in general wholly ionized but there exists a degree of ionization.

From considerations of the Arrhenius law of electrolytic dissociation and Raoult's law he deduces the expression:

$$\alpha_p = \frac{1000 (S-S_2) - 18 N_w S_2}{18 N_w S_2} \quad (6)$$

where α_p = the degree of ionization calculated from vapor pressures,
 S = the vapor pressure of solvent,
 S_2 = the vapor pressure of the electrolyte,
 N_w = the concentration in gram molecules of solute per 1000 grams of solvent.

The above equation breaks down at higher concentrations because of the lowering of the amount of free water present as a consequence of the binding of water molecules to the ions. He therefore rewrites the equation as:

$$\alpha_{px} = \frac{1000 (S-S_2) - 18 N_w S_2}{18 N_w S_2 + 18x N_w (S-S_2)} \quad (7)$$

where α_{px} = the degree of ionization of the electrolyte binding x molecules of water. By the use of proper values of x in this equation the discrepancies which arise at the higher concentrations are removed and the resulting hydration number assumed correct. Van Ruyven's values are quite high and as a result it would seem that his measurements include more than just the firmly held molecules. Also his theoretical treatment leaves much to be desired.

The salting-out effect (29) has been utilized in an attempt to deduce the hydration number of ions. The solubility of a non-electrolyte decreases upon the addition of an electrolyte and this