THE INTERACTION OF ELECTROLYTES WITH NON-ELECTROLYTES

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It seems almost impossible, now that another point of view has been presented, that the electrolytic dissociation theory, coming after the work of Faraday, Kohlrausch and Hittorf on the properties of electrically conducting systems, and basing its quantitative calculations on these properties, could have been developed with complete disregard of the fact that ions differ from other molecules in being electrically charged. Eight years after the classical papers of Arrhenius and Van't Hoff, Van Laar (1895) did suggest that the electrical forces have an effect on the properties of electrolyte solutions.[2] Twelve years later Sutherland (1907), followed by Bjerrum (1909) claimed that strong electrolytes are completely dissociated. Quantitative calculations were given by Van Laar (1900), Milner (1912) and Ghosh (1917). Ghosh's attempt was voted down almost unanimously, partly because it was wrong in theory. The others were almost completely ignored. This action can be only partially justified by the plea that the earlier works were either vague or complicated. Six years after Ghosh, Debye and Hückel (1923) published a simple and sound treatment which has met with general recognition, and which has in the last three years revolutionized the study of electrolyte solutions.

The Debye picture is essentially that, since the ions are charged particles, the electrostatic forces must be taken into account.

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[1] Lecture, expanded in parts, delivered at the Rockefeller Institute for Medical Research, April 23, 1926.

[2] This brief historical introduction does not pretend to be complete. References are given only to those papers which have a direct bearing on the present work.

Consideration of these forces, using elementary electrical theory, shows that there are two effects of ionic charges on free energies or activities. The first is proportional to the square root of the ion concentration in dilute solutions, but approaches constancy as the concentration increases. It is the result of the interaction of one ion with another. The second is proportional to the first power of the concentration. It is the result of the interaction of an ion with any other particle,—with an uncharged molecule or with another ion. In the case of two ions each takes the parts both of an ion and of a neutral molecule.

The study of the first effect is what is generally known as the Debye or Debye-Hückel theory of electrolytes.[3] The second was presented by Debye and McAulay[4] and extended somewhat by me[5] for the case of an ion and a non-electrolyte, and by Hückel[6] for the case of two ions. It has received much less attention than the first, perhaps because the existence of any such effect was denied by the classical theory of electrolytic dissociation and its study is not a part of standard courses in physical chemistry. It seems to me that it may be at least as important, as the first, particularly in biological systems, and it is this second effect which I shall discuss today.

GENERAL SOLUTION THEORY

It will be convenient to outline at this point the thermodynamic and solution theory which is to be used later. Consider a system containing n_1 mols of solvent, n_2 mols of a non-electrolyte solute, and n_3 mols of an electrolyte, each molecule of which dissociates into ν ions of valence z_+ and z_-.[7] The subscript $_j$ indicates any specified component. The composition of the system will be expressed by three different systems: the mol fraction, $x_j = n_j/(n_1 + n_2 + \nu n_3)$; the molality, $m_j = n_j/w_1 n_1$; and the molal

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[3] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

[4] Debye and McAulay, *ibid.*, **26**, 22 (1925).

[5] Scatchard, *J. Amer. Chem. Soc.*, **47**, 2098 (1925).

[6] Hückel, *Physik. Z.*, **26**, 93 (1925).

[7] The symbols used in this paper, with their definitions are collected on page 402.

concentration, $c_j = n_j/V$. w_1 is one thousandth the molecular weight of the solvent, V is the volume in liters of the system. The ionic strength, μ and a similar quantity, Γ, related to the molal concentration, are defined by the equation:

$$\mu/m_3 = \Gamma/c_3 = (\nu_+z_+^2 + \nu_-z_-^2)/2 = \nu z_+z_-/2.^{8}$$

Let F be the free energy of the system, F_I the free energy of the same amount of an ideal solution of the same concentration, a_j the activity of the component in question, and F_j the free energy of one mol of the pure component in the liquid state, R the molal gas constant, and T the absolute temperature. Equations 1 and 2 define an ideal solution and activity. We will

$$RT \ln x_j = \partial F_I/\partial n_j + F_j \tag{1}$$

$$RT \ln a_j = \partial F/\partial n_j + K_j \tag{2}$$

$$f_j = a_j/x_j \tag{3}$$

define an activity coefficient, f, by equation 3. Combining equations 1, 2 and 3 gives equation 4.[9] K_j is an arbitrary constant depending on the reference state of unit activity coefficient. If this is the pure component $K_j - F_j$ is zero. Although this condition will not generally be met with in our equations, we will omit K_j and F_j and will define for each equation the state in which the activity coefficient is unity.

$$RT \ln f_j = RT \ln a_j - RT \ln x_j = \partial F/\partial n_j - \partial F_I/\partial n_j + K_j - F_j \tag{4}$$

Since, at the same temperature, the activity of a component is the same in all solutions in equilibrium with the solid or liquid phase of that component, its gaseous phase at some definite

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[8] The second equality sign follows from the equations $\nu_+ + \nu_- = \nu$ and $\nu_+z_+ = \nu_-z_-$.

[9] T, p and the quantity of the other components are held constant during the differentiation, so $\partial F/\partial n_j$ is the μ of Gibbs. If a function Δ_j were defined by the equation $-\Delta_j = \partial F/\partial n_j - RT \ln x_j - F_j$, the equations of this article could be developed a little more simply by adhering more closely to Gibbs. The present treatment is adopted because the concepts of activity and activity coefficient appear less abstract to those not mathematically inclined than the functions μ (Gibbs) and Δ_j.

pressure, or its solution in an immiscible solvent at some definite concentration, the ratio of the solubilities, s' and s'', in two solutions, expressed as mol fractions, is given by equation 5.

$$RT \ln s'_j/s''_j = RT \ln f''_j/f'_j \qquad (5)$$

If the process in an electrical cell is the transfer of the electrolyte from one solution to another, the electromotive force of the cell is given by equation 6, in which q is the quantity of electricity passing through the cell while one mol of electrolyte is transferred.

$$E = E' - E'' = \frac{RT}{q} \ln \frac{a''_j}{a'_j} = \frac{RT}{q} \ln \frac{f''_j}{f'_j} + \frac{RT}{q} \ln \frac{x''_j}{x'_j} \qquad (6)$$

It is obviously convenient to consider solutions of the same mol fraction and to extrapolate to zero concentration of electrolyte. In such a case the electromotive force will be designated by E_x.

For equilibria involving the distribution of the solvent we will use some equations which are exact only at infinite dilution, but which hold approximately in dilute solutions. The subscript $_{n+s}$ will be used later to designate the system, $n_1 + n_2 + n_3$; $_n$

$$\partial F_I/\partial n_1 = \partial F_n/\partial n_1 + \partial F_s/\partial n_1 \qquad (7)$$

$$\partial F/\partial n_1 = - Pv_0 = - Pw_1/d_0 \qquad (8)$$

$$\partial F/\partial n_1 = - Q_0\Theta/T_0 \qquad (9)$$

designates the system in which n_2/n_1 is unchanged but n_3 is zero; and $_s$ designates the system in which n_3/n_1 is unchanged and n_2 is zero. v_0 is the volume of one mol of pure solvent, d_0 its density, T_0 its freezing point, and Q its molal heat of fusion. P is the osmotic pressure of the solution, and Θ its freezing point depression.

ELECTRICAL THEORY

An ion may be represented by a charge of electricity uniformly distributed over the surface of a sphere. We will assume that the radius of this sphere—the equivalent radius of the ion—is a property of the ion itself and independent of the medium. This assumption is probably not strictly accurate because part of the electrical energy of the ion lies in the surrounding medium, so that the equivalent radius is somewhat larger than any mechanical radius of the ion, and it might well vary with the medium. We will restrict our calculations to electrolyte concentrations so small that the interaction between the ions is negligible, that is n_3 shall be very small relative to $n_1 + n_2$. In our computations we will use the Debye-Hückel theory to extrapolate from electrolyte concentrations beyond these limits.

Granting these assumptions the potential at the surface of an ion is given by Coulomb's law, equation 10, and the work of charging the ion reversibly follows as in equation 11 from the definition of potential.

$$\Phi = \frac{e}{Db} \tag{10}$$

$$w_e = \int_0^{z\epsilon} \Phi de = \int_0^{z\epsilon} \frac{ede}{Db} = \frac{z^2\epsilon^2}{2Db} \tag{11}$$

Φ is the potential at the surface of the ion sphere, e is the charge on the ion, D is the dielectric constant of the medium, b is the radius of the ion, z its valence, and ϵ is the charge of the hydrogen ion. w_e is the electrostatic contribution to the free energy of the system. If there is no other cause for deviation from the laws of ideal solutions, the sum for all the ions, W_e, is equal to the difference between the free energy of the solution and that of the corresponding ideal solution. This sum is given by equation 12,

$$W_e = F - F_I = \frac{N\epsilon^2 n_3 \nu z_+ z_-}{2Db} \tag{12}$$

in which N is Avogadro's number.[10]

That completes the electrical theory. It only remains to differentiate equation 12 and to combine the result with the

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[10] The equations of Note 8 are used to obtain equation 12 from the summation of equation 11, and b is a mean radius of the two ions of such a nature that $1/b = (z_+/b_+ + z_-/b_-)/(z_+ + z_-)$.

appropriate equation from the last section. The results will be given in terms of the activity coefficients.

$$RT \ln f_3 = \frac{\partial F}{\partial n_3} - \frac{\partial F_{\mathrm{I}}}{\partial n_3} = \frac{N\epsilon^2 \nu z_+ z_-}{2Db} \tag*{(13)[11]}$$

For the non-electrolytes it is possible to give a general equation only if the dielectric constant is known as a function of n_2/n_1. If n_2 is small relative to n_1 the dielectric constant may be represented by equation 14, in which D_0 is the dielectric constant of the pure solvent, and β is a constant characteristic of the two

$$\frac{1}{D} = \frac{1}{D_0}\left(1 + \frac{\beta n_2}{w_1 n_1}\right) \tag{14}$$

non-electrolytes. Combination of equations 12 and 14 gives equation 15.

$$W_e = F - F_{\mathrm{I}} = \frac{N\epsilon^2 n_3 \nu z_+ z_-}{2D_0 b}\left(1 + \frac{\beta n_2}{w_1 n_1}\right) \tag{15}$$

$$RT \ln f_2 = \frac{\partial F}{\partial n^2} - \frac{\partial F_{\mathrm{I}}}{\partial n_2} = \frac{N\epsilon^2 n_3 \nu z_+ z_- \beta}{2D_0 b w_1 n_1} = \frac{N\epsilon^2 \beta \mu}{D_0 b} \tag*{(16)[12]}$$

$$RT \ln f_1 = \frac{\partial F}{\partial n_1} - \frac{\partial F_1}{\partial n_1} = - \frac{N\epsilon^2 n_3 \nu z_+ z_- \beta n_2}{2D_0 b w_1 n_1^2} = - \frac{N\epsilon^2 w_1 \beta \mu m_2}{D_0 b} \tag*{(17)[12]}$$

Combining equation 17 with 7, 8 and 9 gives equations 18 and 19.[13]

$$P_{\mathrm{n+s}} - P_{\mathrm{n}} - P_{\mathrm{s}} = \frac{N\epsilon^2 d_0 \beta \mu m_2}{D_0 b} \tag{18}$$

$$\Theta_{\mathrm{n+s}} - \Theta_{\mathrm{n}} - \Theta_{\mathrm{s}} = \frac{N\epsilon^2 w_1 T_0 \beta \mu m_2}{Q_0 D_0 b} \tag{19}$$

[11] Because of the peculiar definition of the corresponding ideal solution f_3 is unity when D is infinite. In practice an arbitrary factor is included to make f_3 unity in some specified system, generally in pure water.

[12] f_2 and f_1 are unity when n_3 is zero.

[13] Equations 18 and 19, which are derived here on the assumption that there is no deviation from the laws of ideal solutions except that due to the electrostatic forces here discussed, may also be derived with the less sweeping assumption that any other deviation in $\partial F_{\mathrm{n+s}}/\partial n_1$ is equal to the sum of the deviations in $\partial F_{\mathrm{n}}/\partial n_1$ and $\partial F_{\mathrm{s}}/\partial n_1$.

With the above equations it is possible to express the changes with changing composition in equilibria involving the distribution of any component of a mixture of two non-electrolytes and an electrolyte, if the electrolyte concentration is very small, in terms of the properties of the pure components and one property, the dielectric constant, of the mixture of non-electrolytes. One property of the electrolyte, the apparent radius, cannot be determined at present independently of some distribution measurement.

The relations of these equilibria have been given many explanations, such as hydration, chemical action between the two solutes, or a change in internal pressure. I wish to emphasize the fact that the Debye theory does not deny the existence of any of these factors but merely claims that there must be in addition this electrical effect. Similarly the Debye-Hückel theory does not claim that all electrolytes are completely ionized, or that any specific electrolyte is. It claims only that when there are ions there is an electrical force between them. When this force is taken into account it explains the properties of many salt solutions so exactly that we must conclude with Professor Debye that in these cases, "there are not enough undissociated molecules to show any signs of life." The rest of my talk will be devoted to showing how completely electrical effects will account for the properties of electrolyte-non-electrolyte solutions.

ACTIVITY OF THE ELECTROLYTE

For the treatment of the activity of the electrolyte the Debye-Hückel equation, given in equations 20 and 21, will be needed to extrapolate to zero electrolyte concentration. D in these equations is the dielectric constant of the solution without electrolyte,

$$-\frac{1}{\nu}\ln f_3 = -\ln f_{\pm} = \frac{N\epsilon^2 z_+ z_-}{2DRT}\,\frac{\kappa}{1+\kappa\, a} - B\,\Gamma \qquad (20)^{14}$$

$$\kappa = \left(\frac{8000\,\pi\epsilon\Gamma}{DRT}\right)^{1/2} \qquad (21)$$

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[14] In these equations f_3 and $f_{\pm}$ are unity when $n_3 = 0$ and n_2/n_1 is the same as in the solution under consideration.

π has its usual significance, $f_{\pm}$ is the mean activity coefficient of the ions, a is the mean diameter of their collision spheres, and B, which is a constant for a given electrolyte and given solvent, is an approximation for a complex function of all the variables except the concentrations. a and B have been determined for various electrolytes in aqueous solution, and for hydrogen chloride also in 50 and in 100 mol per cent ethyl alcohol. For hydrogen chloride a appears to be independent of the solvent. For other electrolytes we will assume that this independence is general, and that the ratio of B's for two electrolytes is also independent of the solvent. For solvents other than water-alcohol mixtures we will assume that B is a function of the dielectric constant. Since $B\Gamma$ is generally only a small fraction of the total effect, any error in these assumptions is not very important.

The constants for aqueous sodium chloride at 25° are $D = 78.8$, $a = 2.35\times10^{-8}$, $B = 0.089$; $x_{\pm}$ is 0.0924 and Γ is 5.422 for the saturated solution. From equation 20 we determine that $f_{\pm} = 1.155$, and $a_{\pm} = f_{\pm}x_{\pm} = 0.1067$. With the assumption that $E = 0$ for a solution of unit activity in water, $E = -0.1183 \log a_{\pm}$ for any other solution. Therefore for the saturated solution $E = 0.1150$. This value is the same for the saturated solution in any solvent.

For sodium chloride in anhydrous ethyl alcohol at 25°, $D = 25.2$, $B = 0.0288$; in the saturated solution $x_{\pm} = 0.000713$, and $\Gamma = 0.0122$ By equation 20, $f_{\pm} = 0.540$ and $a_{\pm} = 0.000385$. $E_x = E + 0.1183 \log a_{\pm} = 0.1150 - 0.4039 = -0.2884$. This value is represented by the circle cutting the right margin of Figure 1. The other circles in this figure are determined by similar computations from the solubility measurements in mixed solvents. They do not depend in any way on the theory discussed earlier in this paper.

Applying equations 6 and 13 to E_x for pure alcohol leads to the result, $b = 1.31\times10^{-8}$ cm. for sodium chloride. This is not very different from the mean ionic radius found for the solid salt. With this value of b and the dielectric constants of water-alcohol mixtures, the same equations give the curve of figure 1, which is thus independent of the solubility measurements in mixed solvents. Yet it corresponds very closely to the best smooth curve which could be drawn through the circles. It is nearly a straight line, but the deviations from a straight line would be considerably larger.

Let us consider what might prevent the simple theory from describing the facts so accurately. We have said that *b* might not be independent of the solvent. In computing the mol fraction it has been assumed that the molecular weight of water is eighteen and that of alcohol is forty-six; if there were any polymerization of either species or any compound formation between them this assumption would be inaccurate. If either of the ions reacted with either of the non-electrolytes the shape of the curve would be altered. It is also assumed that, except for the electrical effects, the constant of Henry's law is the same in each solution. No non-electrolyte—even among the noble gases where we should least expect specific actions—behaves so simply. In spite of all this the agreement is as shown. This figure explains better than anything else I know the request Professor Debye made to me when I was preparing this material for publication, "Be sure to tell them that the theory works better than it has any right."

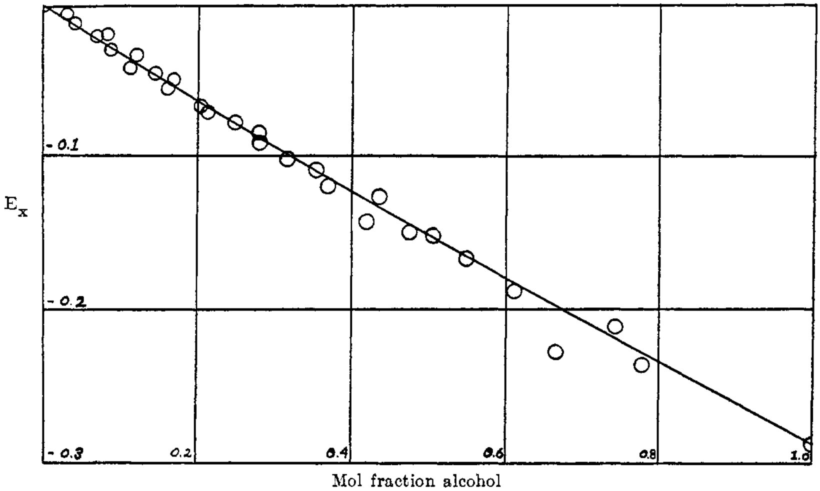

Fig. 1. Sodium Chloride in Water-Ethyl Alcohol Mixtures

To illustrate the method of the inverse problem we will compute the solubility of sodium chloride in 50 mol per cent (71.9 weight per cent) alcohol, for which $D = 37.1$ and $B = 0.161$. From equations 6 and 13, $E_x = -0.1521$. So $E - E_x = 0.2671$, and $a_\pm = 0.00552$. Since $f_\pm$ is a complicated function of $x_\pm$, the simplest method of calculating the latter is by trial and error. The solution is $x_\pm = 0.0198$, $\Gamma = 0.674$, $f_\pm = 0.279$.[15]

The determination of the electromotive force of a cell containing a solution of any concentration introduces nothing new since it requires merely the computation of E_x by the method of the last paragraph, and of $E_x - E$ by the method of the two preceding paragraphs.

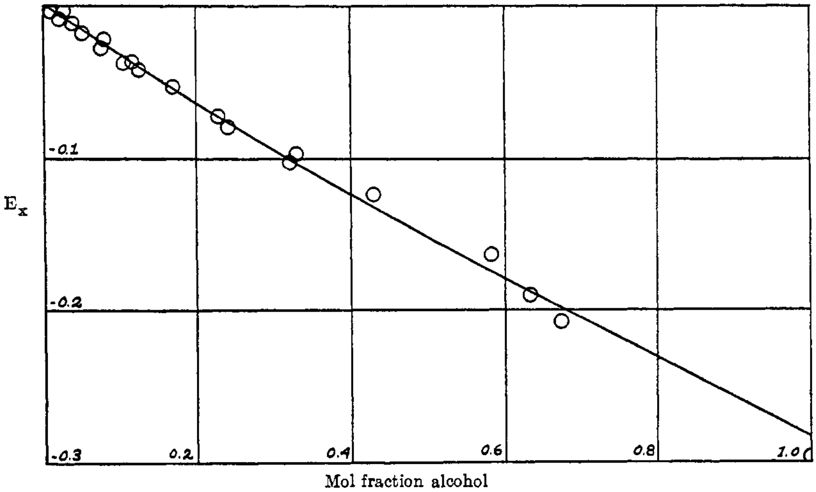

FIG. 2. POTASSIUM CHLORIDE IN WATER-ETHYL ALCOHOL MIXTURES

Figure 2 shows similar results for potassium chloride. It is less conclusive for there are no very accurate measurements in pure alcohol, so the curve has to be drawn from the intermediate points. The computed radius, b, is 1.35×10^{-8}, only slightly larger than that of sodium chloride.

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[15] The volume is computed by adding to the volume of the solvent 0.020 liter for each mol of salt, an approximation which is sufficiently accurate for the computation of $f_\pm$.

In the next case we have at least one effect in addition to the electrical forces. Figure 3 shows E_x for hydrogen chloride in the same solutions, computed by the method given above from direct measurements of electromotive force.[5] The broken line corresponds to the curves which describe the behavior of the alkali chlorides. It does not agree at all with the experimental points. There is evidence from other sources that in water the hydrogen ion does not exist as H^+ but combines with one molecule of water to form H_3O^+. The simplest assumption to handle mathematically is that this reaction is practically complete even in solutions consisting mostly of alcohol, although it might be nearer the truth to assume that there is some alcoholated hydrogen ion in the latter solutions. Electromotive force measurements give the activity of the simple ion, which may be calculated from that of the hydrated ion and the vapor pressure of water from the solution. The full curve is the theoretical one for a pair of ions of size 5×10^{-8} cm., the size determined from the measurements in water and in 50 mol per cent alcohol. It is carried only to 95 per cent alcohol, for in pure alcohol our assump-

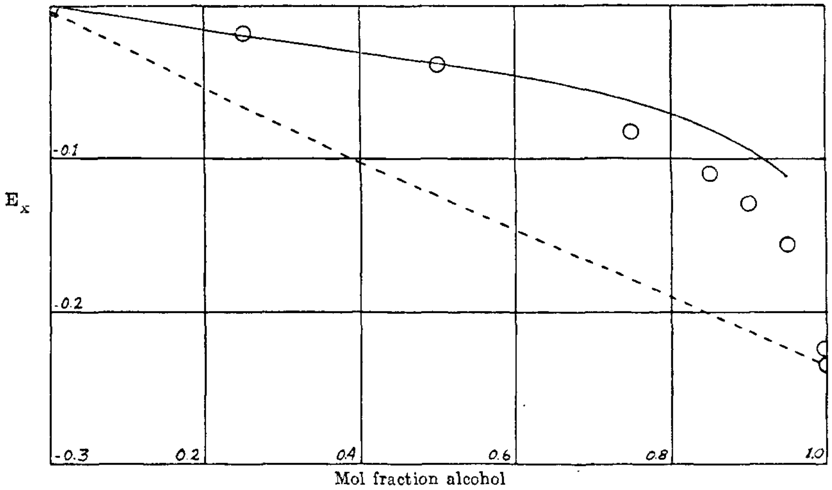

FIG. 3. HYDROCHLORIC ACID IN WATER-ETHYL ALCOHOL MIXTURES

- - - - Hydrogen ion not hydrated

——— Hydrogen ion hydrated

tion becomes absurd. The agreement is only fair, which indicates that our assumption is too simple. In spite of the failure to agree exactly it seems to me that this is the best evidence so far that the hydrogen ion combines with one molecule of water. The evidence is equally good that it does not combine with more than one molecule and that the alkali and chloride ions combine with none at all.

Figure 4 illustrates the effect of another factor. It shows the change in electromotive force, E, of a cell containing 0.1 N HCl and varying amounts of sucrose.[16] Seven hundred grams of sucrose per liter is only about 6 mol per cent, so that this whole diagram corresponds to a thin slice from the left side of the last one. The circles give the experimental measurements, the broken line corresponds to the one which fits for alcohol solutions. Some years ago I showed that the vapor pressure of water from

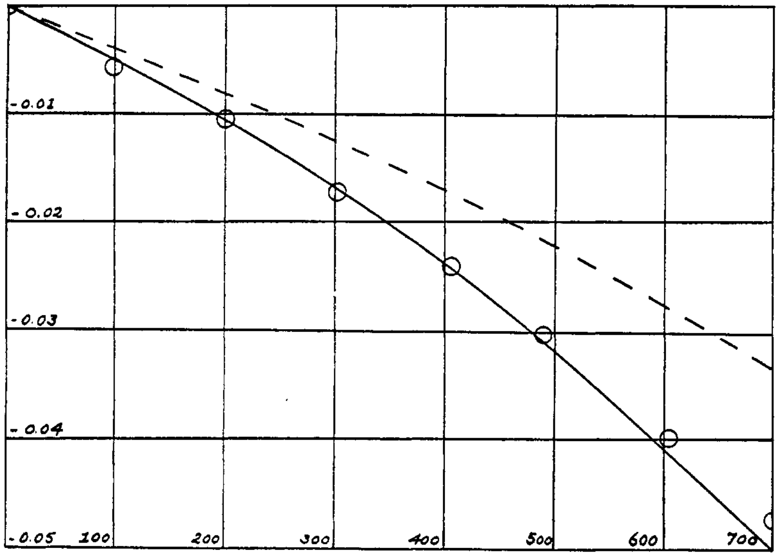

FIG. 4. HYDROCHLORIC ACID (0.1N) IN WATER-SUCROSE MIXTURES
- - - - Sucrose not hydrated
——— Sucrose hydrated

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[16] Scatchard, *J. Amer. Chem. Soc.*, **48**, 2026 (1926).

sucrose solutions could be accounted for by assuming that all the deviation from the laws of ideal solutions is caused by the formation of a hydrate of sucrose. Taking into account this hydration in computing the mol fraction of the ions gives the full curve which agrees very well with the experiments. The discrepancy of about three millivolts in the most concentrated solution may be due to experimental error for electromotive force measurements in these solutions are very difficult.

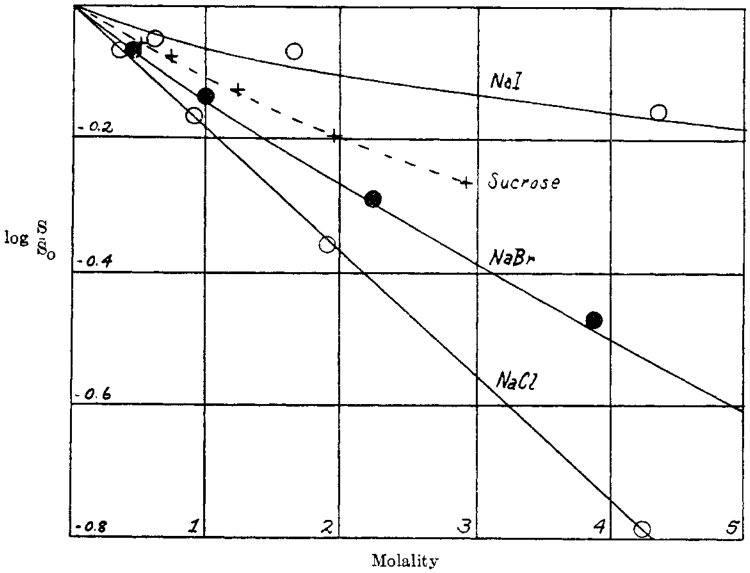

FIG. 5. SOLUBILITY OF ETHYL ACETATE AT 25°

We have seen that the electrostatic forces will account completely for the properties of sodium and potassium chlorides in alcohol-water mixtures. For hydrochloric acid in the same solutions there is the additional effect of the hydration of the hydrogen ion. In sucrose solutions the hydration of the sucrose also shows an influence.

ACTIVITY OF THE NON-ELECTROLYTES

In considering the effect of salts on the activities of non-electrolytes it is not possible to isolate the separate disturbing factors. Our theory says that the logarithm of the solubility, expressed as mol fraction, of a non-electrolyte is a linear function of the ionic strength in very dilute solutions. Practically this relation holds approximately, and sometimes very accurately, up to very high salt concentrations, but the agreement is probably due to the compensation of several disturbing factors. Figure 5 shows the results for ethyl acetate in water.[17] The curve for sodium chloride is a straight line up to 5 molal. Those for sodium bromide and sodium iodide curve but it is possible to determine the value of *b* from the limiting slope at zero concentration. The dotted line shows the solubility in sucrose solutions and indicates how large the non-electrical effects may become. Probably it represents an extreme case.

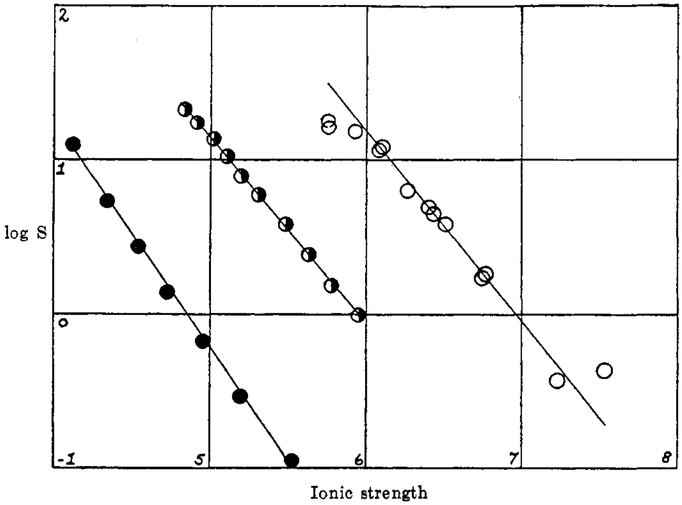

FIG. 6. SOLUBILITY OF PROTEINS IN AMMONIUM SULFATE SOLUTIONS

○ Egg albumin (C + M)
◑ Egg albumin (S + H)
● Pseudo globulin (S)

Figure 6 shows the effect of ammonium sulfate on the solubility of two proteins.[18] Please note that the change in solubility

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[17] Measurements of Glasstone and Pound, *J. Chem. Soc.*, **127**, 2660 (1925).

[18] Cohn, *Physiol. Rev.*, **5**, 410 (1925). Measurements of Chick and Martin, of Sørensen and Høyrup, and of Sørenson.

is much larger. For the same ionic strength the slope is about ten times as great for pseudoglobulin as for ethyl acetate. A factor of ten in a logarithmic expression is very important. While the solubility of ethyl acetate is reduced one-half, that of pseudoglobulin is reduced to one thousandth.

I have no data on osmotic pressures and the freezing points of electrolyte-non-electrolyte mixtures do not lend themselves to diagrammatic representation in two dimensions. However, the calculated size *b* remains constant within the limit of error of the most accurate measurements so far available up to salt concentrations of half molal and non-electrolyte concentrations of one molal, the highest concentrations tested. Table 1 gives some results for sodium chloride-ethyl alcohol mixtures in water which show the relative magnitude of the electrostatic effect and also the agreement between different experiments.

TABLE 1

Freezing points of aqueous sodium chloride-ethyl alcohol mixtures[19]

$m_3 = \mu$	m_2	θ_{n+s}	θ_n	θ_s	$\theta_{n+s}-\theta_n-\theta_s$	b
0.1274	0.5286	1.422	0.961	0.421	0.040	0.96
0.2430	0.5286	1.841	0.961	0.801	0.079	0.93
0.5038	0.5286	2.776	0.961	1.654	0.151	0.89
0.1851	1.1203	2.662	1.915	0.612	0.135	0.96
0.3082	1.1203	3.146	1.915	1.015	0.216	0.94
0.4969	1.1203	3.891	1.915	1.636	0.340	0.98

THE IONIC RADII

I want next to show you the test of the theory by comparing the sizes of some ions determined by different methods and in different systems. Instead of tabulating the size of the ions directly I have given their reciprocals because the salt effect is directly proportional to this quantity, it shows better the possible experimental error, which is of the order of 0.1 in the figures shown, and because it is this quantity which should be additive for the different ion pairs. Of course the value 1 in this table corresponds to a radius of 1×10^{-8} cm., 0.5 to twice that radius, 0.25 to four times, etc.

The first seven rows of table 2 give a direct test of the theory, and they represent the only systems for which the dielectric constants have been directly measured. The last two are taken as illustrative of a fairly large number of systems for which there are no measurements of the dielectric constant. Hydrogen and oxygen were chosen because it seems most improbable that they should show any specific effect. In these cases the value of β may be determined by using the value of b determined for some salt in another system. I have used sodium chloride as the reference salt because it has been included in every series, and because the size is particularly well determined from salt solubility measurements.

TABLE 2

Reciprocal radii of ions—$10^{-8}/b$

METHOD	HCl	LiCl	NaCl	KCl
E.m.f. and salt solubility[5]	0.20	0.25[19a]	0.76	0.74
Freezing point, ethyl alcohol[19]			1.06	1.06
Freezing point, ethyl acetate[20]		0.75	0.97	0.98
Freezing point, sucrose[20]		1.25	0.93	0.75
Solubility of ethyl acetate, 25°[21]			0.71	0.61
Solubility of ethyl acetate, 25°[17]		0.63	0.70	0.69
Solubility of ethyl acetate, 50°[17]		0.64	0.80	0.85
Solubility of hydrogen, 15°[22]		0.72	(0.76)	0.80
Solubility of oxygen, 15°[23]	0.17		(0.76)	
Solubility of oxygen, 25° [23,24]	0.23	0.50	(0.76)	0.72

[19] Sachs, *Thesis*, Mass. Inst. Techn., 1925.

[19a] Based on the measurements of Pearce and Hart, Jour. Amer. Chem. Soc., **44**, 2411 (1922). Measurements on the same cell by Drucker and Schingnitz, Z. physikal. Chem., **122**, 149 (1926) lead to the value 0.74.

[20] Measurements of Rivett, *Medd. K. Vetenskapsakad. Nobelinst.*, **2**, No. 9, (1913).

[21] Measurements of Lunden, *ibid.*, No. 15 (1913).

[22] Measurements of Steiner, *Wied. Ann.*, **52**, 275 (1894).

[23] Measurements of Geffcken, *Z. physik. Chem.*, **49**, 257 (1904).

[24] Measurements of McArthur, *J. Physical Chem.*, **20**, 495 (1916).

The fact that reasonable sizes for the ions are obtained seems to me to give very good confirmation of the theory. The agreement between the values in the different series gives a still stronger confirmation. The values from the freezing points of ethyl alcohol and of ethyl acetate are relatively large. In these cases the value of β was measured at 18°, and it appears that it increases somewhat as the temperature is lowered to 0°. The other variations may be due to specific effects, but it is entirely possible that they are due merely to experimental error.

Table 3 shows the effect of various potassium salts with constants computed to give the relative salt effect at the same equivalent concentration, decreasing down the column. The three series place the different salts in the same order except for the nitrate and iodide, for which the difference is well within the experimental error. The difference in the magnitude of the change from salt to salt in the different series may be due to small specific effects, but it may also be due entirely to experimental error. It will be noted that table 2 gives a Hofmeister series for the anions with solutes which cannot be colloidal, which are not appreciably affected by the hydrogen-ion concentration, and for which the probability of specific chemical action is a minimum.

TABLE 3

Salt effects of potassium salts at equivalent concentrations

Valence factor × $10^{-8}/b$

ANION	VALENCE FACTOR	FREEZING POINT		GAS SOLUBILITY
		EtOH[19]	EtAc[20]	O_2 or H_2[22,23,24]
$HPO_4^{=}$	1.5	1.32		
$SO_4^{=}$	1.5	1.17	1.00	1.21
Cit.$^{=}$	2	1.14		
$CO_3^{=}$	1.5			1.10
OH^-	1			0.96
HCO_3^-	1	1.07		
Cl^-	1	1.06	0.98	0.76
Br^-	1	1.02	0.71	0.65
NO_3^-	1	0.82	0.58	0.51
I^-	1	0.89	0.48	0.43

THE CONSTANT β

In table 4 I have collected the values of β for various nonelectrolytes. β, you will remember, gives the relative depression of the dielectric constant, the relative effect on salt or water activity, and the relative susceptibility to salt effect. In the third column are values relative to that of hydrogen, which increase to 14 for pseudoglobulin, while urea has a negative value,—the dielectric constants of urea solutions are greater than that of water. The main factor in the change in dielectric constant is the displacement of water by another substance (generally) of lower dielectric constant. The magnitude of the effect depends upon the volume of water displaced and upon the dielectric constant of the displacing medium. To test the reasonableness of the values obtained indirectly the comparison should be made for equal volumes. Such a comparison is given approximately, except for hydrogen and possibly oxygen, in the last two columns which give the change per gram. On this basis hydrogen gives the largest effect and the two proteins lie betwen sucrose and urea, which appears reasonable. Although the data now available are too limited to permit of very certain conclusions, it seems probable that the proteins may be treated by the same simple theory as ordinary solutes, from which they differ only in those properties which may be attributed to the large size of the molecule.

TABLE 4

Dielectric constants of aqueous solutions

SOLUTE	METHOD	β	REL.	β/M.W.	REL.
Hydrogen....	Solubility	0.05	1	0.025	1
Oxygen................	Solubility	0.06	1.2	0.0019	0.076
Ethyl alcohol[25].........	Direct	0.045	0.9	0.0010	0.040
Ethyl acetate[16].........	Direct	0.09	1.8	0.0010	0.040
Sucrose[26,27]............	Direct	0.08	1.6	0.00023	0.0092
Egg albumen...........	Solubility	0.6	12	0.00002	0.0008
Pseudoglobulin.........	Solubility	0.7	14	0.00001	0.0004
Urea..................	Direct	−0.04	−0.8	−0.00075	−0.030

[25] Nernst, *Z. physik. Chem.*, **14**, 622 (1894).

[26] Debye and Sack, private communication.

[27] Harrington, *Physical Rev.*. **8**, 581 (1916).

SUMMARY

I think that this much has been established. For the interactions of electrolytes with non-electrolytes, as for the interaction between ions, electrostatic forces must be taken into account. These forces give rise to an effect on the free energies which is proportional to the ion concentration, rather than to its square root, and which depends not only on the valence of the ion but also on a specific property—the equivalent radius. The effect also depends upon a specific property of the non-electrolyte—the molal depression of the dielectric constant. In some cases the simple electrostatic effect accounts completely for the free energy change. In some others the additional factors can be determined and accurately calculated. At present I do not pretend to be able to tell you with precision what the relative effects of different salts are when there are no additional factors, or to be able to predict when the additional factors will be operative. I think that such predictions could be made after the study of a number of systems. The freezing point method seems well adapted to the extension to a large variety of systems and to the development of a higher degree of precision than that attained in the measurements I have used for my calculations.

I trust that I have made it very clear that I am not here as an emissary of the physicists and physical chemists to present you with a new tool which they have perfected, together with complete directions when and how to use it, but that this is a sketch of a field as yet scarcely touched.

SYMBOLS

a = activity (with subscript)
a = diameter of ionic collision sphere (without subscript)
B = constant in equation 20
b = radius of electrification sphere
β = constant defined by equation 14
c = molal concentration = mols per liter
Γ = ionic strength (molal concentrations)
D = dielectric constant
d = density
Δ = function defined in note 9
E = electromotive force
E_x = electromotive force at equal, very small mol fractions
e = electric charge
ϵ = charge of hydrogen ion
F = free energy
f = activity coefficient, defined by Equation 3
κ = function defined by Equation 21
ln = natural logarithm
log = common logarithm
m = molality = mols per 1000 grams solvent
μ = ionic strength (molalities)
N = Avogadro's number
n = number of mols of a component in system
ν = number of ions from one molecule of electrolyte
P = osmotic pressure
π = ratio of circumference of circle to diameter
Φ = electrostatic potential at surface of ion
Q = molal heat of fusion
q = quantity of electricity (see Equation 6)
R = molal gas constant
s = solubility
T = absolute temperature, freezing point
Θ = freezing point depression
V = volume of system
v = molal volume
w = molecular weight divided by 1000
W_e = electrical work for system
w_e = electrical work per ion
x = mol fraction

SUPERSCRIPTS

$'$ = first system
$''$ = second system

SUBSCRIPTS

$_e$ = electrical
$_I$ = corresponding ideal solution
$_i$ = any component
$_{n+s}$ = system containing $n_1 + n_2 + n_3$
$_n$ = corresponding system with ration n_2/n_1 but with $n_3 = 0$
$_s$ = corresponding system with same ratio n_3/n_1 but with $n_2 = 0$
$_o$ = solvent (to indicate properties of pure solvent)
$_1$ = solvent
$_2$ = non-electrolyte solute
$_3$ = electrolyte
$_+$ = positive ions
$_-$ = negative ions
$_\pm$ = mean for positive and negative ions