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Freezing Points of Aqueous Solutions. VIII. Mixtures of Sodium Chloride with Glycine and Ethyl Alcohol¹

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The analytical expression of the thermodynamic functions of solutions containing ions is more complicated than that for solutions containing only non-electrolytes¹ largely on account of the deviations from random distribution because each ion is surrounded by a medium bearing an electrical charge equal in magnitude and opposite in sign to its own charge. From the extension of the Debye-Hückel theory to ions of different radii² we should expect a power series expansion in the concentrations of the various components and in the square root of the ionic concentration, $\Gamma = \sum_i c_i z_i^2$ where z_i is the valence, to represent the variation of these functions if the coefficients have the following form

$$\frac{F}{RT} = \sum_i^0 n_i [K_i + \ln (n_i / \sum_i^0 n_i + \alpha_i \sqrt{\Gamma})] + \frac{1}{V} \sum_{ij}^0 n_i n_j (\beta_{ij} + \gamma_{ij} \sqrt{\Gamma}) + \frac{1}{V^2} \sum_{ijk}^0 n_i n_j n_k (\delta_{ijk} + \epsilon_{ijk} \sqrt{\Gamma}) + \dots \quad (1)$$

where F is the free energy, V the volume, n_i the number of molecules of the i 'th species, and the coefficients K_i , α_i , β_{ij} , γ_{ij} , δ_{ijk} , ϵ_{ijk} are functions only of the temperature and pressure. For solutions of non-electrolytes, in which the ionic concentration is zero, this reduces to equation (1) of the previous paper. Because of the necessity of electrical neutrality, the quantities of the ions cannot be varied independently, and therefore coefficients cannot be determined for each ion species. If n_p be the total number of ions an electrolyte produces, or is capable of producing, the coefficients with subscript p will be average values for the coefficients of these ions, and z_p^2 should be replaced by $\sum_i n_i z_i^2 / n_p$, the sum being taken over the ions of this electrolyte only. It follows that μ_p is the average chemical potential of these ions and γ_p the mean activity coefficient as defined by Lewis and Randall. Such coefficients are sufficient to determine the measurable thermodynamic functions of the solution and are all that can be determined from these functions alone. In another paper we shall discuss the

constants to be attributed to the ions in certain specially simple cases.

According to the theory of Debye and Hückel α_i represents the limiting law of the interaction of the ion with its ion atmosphere. β_{ij} represents the interactions of pairs of molecules; it includes the non-electrical type of interaction discussed in the previous paper, the interaction between the ionic charge of one molecule and the non-charge part of the other which is calculated in the Born theory from the radius of the first molecule and the effect of the second molecule on the dielectric constant, and the limitation of the electrostatic interaction of the ions due to their mutual repulsion calculated in the Debye-Hückel theory from the distance of closest approach, a . γ_{ij} represents the interaction of the pair of molecules with their ion atmospheres. Similarly δ_{ijk} represents the interaction of three molecules, and ϵ_{ijk} the interaction of the group with their ion atmospheres. γ_{ij} and ϵ_{ijk} are zero if all the molecules involved are uncharged. If only one of the molecules is an ion, they may be calculated from the charge of the ion and the effect of the uncharged molecules on the dielectric constant by the use of the Debye-Hückel theory and the additional assumption that a non-electrolyte mixture may be treated as a medium of uniform dielectric constant.

The "higher term" extension of Gronwall and La Mer has not been developed for two or more sizes of ions. For solutions of ions all of the same size it requires additional terms of the form

$$\sqrt{\Gamma} \sum_{\sigma} S_{\sigma} (\sqrt{\Gamma} \ln \Gamma)^{\sigma} \quad (2)$$

in which σ is summed from two to infinity if z^2 is the same for all the ions present, and from one to infinity if it is not. These terms are characterized by sharp minima not represented well by a short power series in $\sqrt{\Gamma}$. For aqueous solutions of univalent ions the calculated values are so small that the deviations from power series in $\sqrt{\Gamma}$ are negligible. However, for the representation of our freezing point measurements with ammonium salts or for the accurate representation of those with lithium chloride, some similar

(1) No. VII in this series appeared in *THIS JOURNAL*, **56**, 1486 (1934).

(2) G. Scatchard, *Physik. Z.*, **33**, 22 (1932).

function with a sharp minimum would be necessary.

Just as $1/V$ was represented by $1/n_0$ times a power series in the concentrations of the solutes, $1/D$ may be represented by a similar power series. Therefore any of the half powers of either may be represented by similar series, and a change in variable similar to that in the previous paper leads to

$$\frac{F - F^*}{RT} = \sum_i n_i \left(\ln \frac{n_i}{w_0 n_0} - 1 + A_i \sqrt{I} \right) + \sum_{ij} \frac{n_i n_j}{w_0 n_0} (B_{ij} + C_{ij} \sqrt{I}) + \sum_{ijk} \frac{n_i n_j n_k}{w_0^2 n_0^2} (D_{ijk} + E_{ijk} \sqrt{I}) + \dots \quad (3)$$

where $I = \sum_i m_i z_i^2$ or twice the ionic strength, and w_0 is the molecular weight of the solvent divided by 1000.

$$\varphi_\mu = \frac{\mu_0^* - \mu_0}{w_0 RT M} = 1 + \frac{1}{2} \sqrt{I} \sum_i A_i x_i + M \sum_{ij} x_i x_j (B_{ij} + \frac{1}{2} C_{ij} \sqrt{I}) + M^2 \sum_{ijk} x_i x_j x_k (2D_{ijk} + \frac{3}{2} E_{ijk} \sqrt{I}) + \dots \quad (4)$$

$$\frac{\mu_p - \mu_0^*}{RT} - \ln m_p = \ln \gamma_p = \frac{1}{2} A_p \sqrt{I} + 2 \sum_{ij} B_{ij} m_i + (2 \sum_{ij} C_{ij} m_i + \frac{z_i^2}{2I} \sum_{ij} C_{ij} m_i m_j) \sqrt{I} + 3 \sum_{ij} D_{ijp} m_i m_j + (3 \sum_{ij} E_{ijp} m_i m_j + \frac{z_p^2}{2I} \sum_{ijk} E_{ijk} m_i m_j m_k) \sqrt{I} + \dots \quad (5)$$

$$m_i = n_i/w_0 n_0, \quad M = \sum_i m_i \quad \text{and} \quad x_i = m_i/M$$

Similarly

$$\frac{H - H^*}{RT} = \sqrt{I} \sum_i a_i n_i + \sum_{ij} \frac{n_i n_j}{w_0 n_0} (b_{ij} + c_{ij} \sqrt{I}) + \sum_{ijk} \frac{n_i n_j n_k}{w_0^2 n_0^2} (d_{ijk} + e_{ijk} \sqrt{I}) + \dots \quad (6)$$

From the Debye-Hückel limiting law

$$A_i = - \frac{(0.008 \pi)^{1/2} N^2 \epsilon^2 z_i^2}{3 \rho_0^{1/2} (D_0 RT)^{3/2}} \quad (7)$$

$$a_i = - \frac{(0.008 \pi)^{1/2} N^2 \epsilon^2 z_i^2}{2 \rho_0^{1/2} (D_0 RT)^{3/2}} \left(1 + \frac{d \ln D_0}{d \ln T} - \frac{1}{3} \frac{d \ln \rho_0}{d \ln T} \right) \quad (8)$$

ρ_0 is the density of the solvent, and D_0 is its dielectric constant.

Just as for non-electrolyte solutions, the osmotic coefficient for the chemical potential at the freezing point of the solution may be expressed as φ'_μ . Then the coefficient at the freezing point of the solvent is given by

$$\varphi_\mu = \varphi'_\mu - \frac{\lambda}{T_0} \left[\frac{a}{2} M^{3/2} + \left(b + \frac{aA}{4} \right) M^2 + \left(\frac{3c}{2} + \frac{bA}{2} + \frac{aB}{2} + \frac{a\lambda}{2T_0} \right) M^{5/2} + \dots \right] \quad (9)$$

φ_μ differs from φ'_μ only in terms in the three-halves and higher powers of the concentration. The coefficient of the three-halves power may be

calculated from the theory, but, if the higher terms are neglected, it is generally more accurate to omit this term also.

These equations are here applied to the results of the freezing point measurements with mixtures of sodium chloride, glycine and ethyl alcohol. The measurements on the single solute systems and on the mixtures of glycine and alcohol have already been reported. The other solutes studied are: two-thirds sodium chloride (as ions) with one-third glycine, and with one-third alcohol; one-third sodium chloride with two-thirds glycine, with two-thirds alcohol, and with one-third glycine and one-third alcohol.

Experimental

The materials used and the methods of measurement were the same as in the study of the single solute systems, where the difficulties with solutions containing alcohol are also discussed, except that the concentrations were determined by conductance as with the salt solutions. As before the concentrations were determined from a deviation plot of I/L against \sqrt{L} . For other purposes, however, it is more interesting to express L/I as a function of I . We have used expressions of the type

$$L/I = (L/I)_0 + \alpha I^{1/2} + \beta I + \gamma I^{3/2} + \delta I^2 + \epsilon I^{5/2} \quad (10)$$

Since I is the total ion concentration and since the density of water is practically unity at 10° $(L/I)_0$ is half the ordinary equivalent conductance at zero concentration. The coefficients of equation 9 were determined by the method of least squares. $(L/I)_0$ and α were determined together by means of the Onsager equation

$$-\alpha = 28.7 + 0.1572 (L/I)_0 \quad (11)$$

Since these two constants must be the same for all the mixtures of the type we have studied, they were determined from the measurements on sodium chloride alone. The variation in β with added non-electrolyte includes the effects of dilution and of change of viscosity on the limiting conductance. The constants are given in Table I, and the deviations of the individual measurements of $(L/I)/(L/I)_0$ from the values calculated from these constants are shown in Fig. 1.

Table II gives the constants necessary for the expression of the thermodynamic functions of the three solute system, and Fig. 2 shows the deviation of the individual measurements of φ'_μ from the values computed from the equations with these

TABLE I
COEFFICIENTS OF EQUATION 10 FOR CONDUCTANCE AT 10°
(L/M)₀ = 44.566. α = 21.360

		β	γ	δ	ϵ
A	NaCl	+17.832	-9.916	+2.164	-0.047
B	NaCl(2)-Glycine(1)	+15.143	-8.131	+0.580	-.472
C	NaCl(2)-Alcohol(1)	+11.965	-5.793	-.250	+.643
D	NaCl(1)-Glycine(2)	+7.098	-2.567	-5.670	+3.510
E	NaCl(1)-G(1)-A(1)	+1.789	+1.157	-5.357	+3.061
F	NaCl(1)-Alcohol(2)	-0.986	-4.777	+6.111	-1.577

TABLE II
COEFFICIENTS FOR THERMODYNAMIC FUNCTIONS

A_1'	0.0		D_{111}'	+0.01216	E_{111}'	0.0	
A_2'	.0		D_{222}'	+.00552	E_{222}'	.0	
A_3'	-.52864		D_{333}'	+.09600	E_{333}'	-.01603	
			D_{112}'	-.00509	E_{112}'	.0	
B_{11}'	-.11411	C_{11}'	0.0	D_{122}'	-.00219	E_{122}'	.0
B_{22}'	-.02920	C_{22}'	.0	D_{118}'	+.02482	E_{118}'	-.01656
B_{33}'	+.38628	C_{33}'	-.24194	D_{138}'	-.04773	E_{138}'	+.01438
B_{12}'	+.12340	C_{12}'	.0	D_{223}'	-.00539	E_{223}'	+.00388
B_{13}'	-.16317	C_{13}'	+.13173	D_{238}'	+.07312	E_{238}'	-.02284
B_{23}'	+.14050	C_{23}'	-.12989	D_{128}'	-.00131	E_{128}'	-.00183

constants. The B' coefficients are determined to fit the two mixtures of the same pair of solutes,

D_{128}' and E_{128}' are left to be determined from measurements on this mixture. In Fig. 3 are shown the osmotic coefficients of mixtures con-

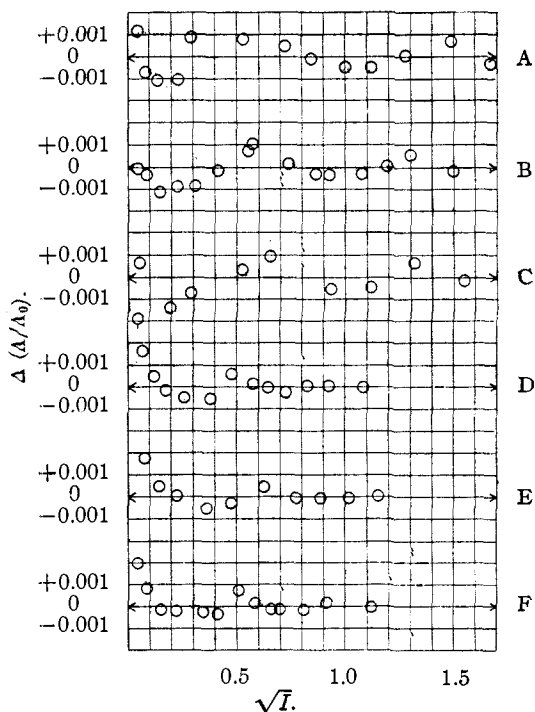


Fig. 1.—Deviations of conductance ratios: for compositions see Table I.

as in the previous paper. Then the C' coefficients are adjusted in the same way, and the D' and E' coefficients determined together. For the ternary solute the B' and C' coefficients are all fixed by the determinations with binary solutes, and only

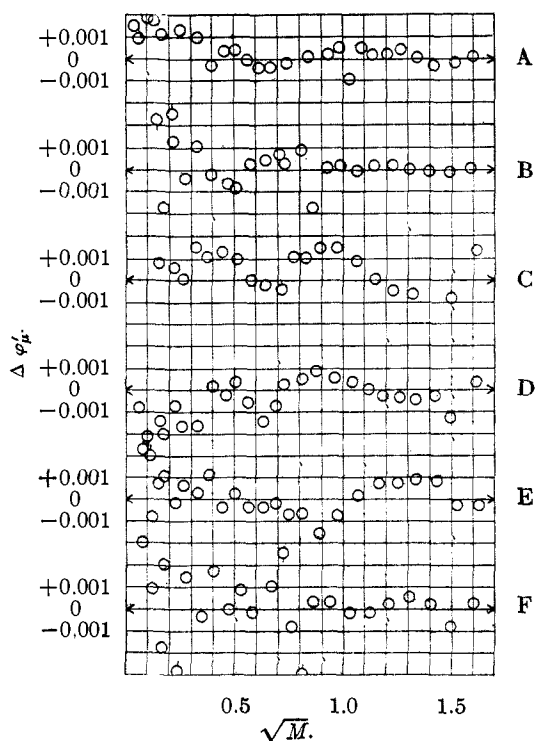


Fig. 2.—Deviations of osmotic coefficients: for compositions see Table I. A few large deviations in very dilute solutions are not shown.

taining two-thirds salt, and the coefficients of pure sodium chloride are shown as a broken line.

Figure 4 gives the osmotic coefficients of mixtures containing one-third salt.

The coefficients of sodium chloride, which is typical of the uni-univalent electrolytes we have studied, are much larger than those of the non-electrolytes. They decrease rapidly, however, with increasing powers of M . Even at the limit of our measurements, at M about 2.0, the contribution of the D term is much smaller than that of the B or C term, and that of the E term is much smaller still. This is also true of the mixtures containing sodium chloride.

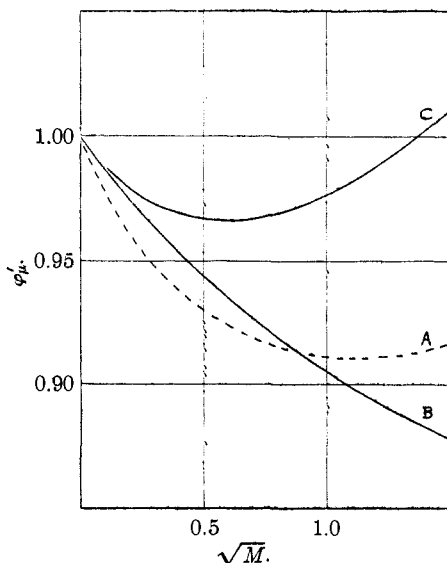


Fig. 3.—Osmotic coefficients: for compositions see Table I.

Discussion

This particular system was chosen for our first study of solutions with more than one solute because of its bearing on the study of the properties of amino acid solutions being made by Professor E. J. Cohn and his collaborators at the Harvard Medical School, a study in which we have been much interested. Much of the discussion will be left for the publication of their more comprehensive results.

Lewis³ has measured freezing points of sodium chloride-glycine mixtures, but we are unable to determine the freezing point depressions from the data he presents.

The discussion of the excellent agreement with Joseph's measurements of the effect of glycine on the electromotive force of sodium chloride concentration cells⁴ will be left for the detailed description of his results.

(3) W. C. McC. Lewis, *Chem. Rev.*, **8**, 151 (1931).

(4) N. R. Joseph, *Proc. Am. Soc. Biol. Chem.*, **28**, 43 (1934).

The comparison with other measurements requires certain assumptions. Since $\gamma_1 m_1$ is the

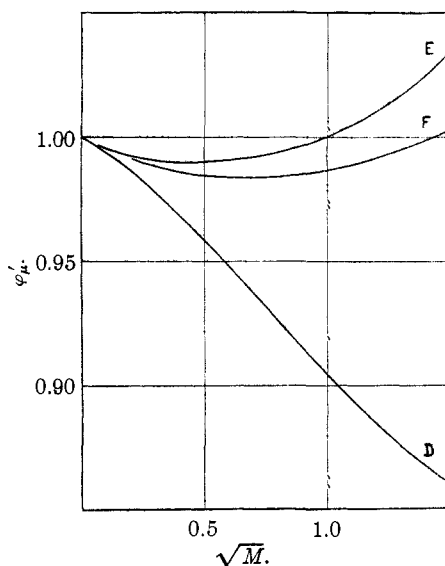


Fig. 4.—Osmotic coefficients: for compositions see Table I. D, $\frac{2}{3}$ glycine; E, $\frac{2}{3}$ alcohol; F, $\frac{1}{3}$ glycine + $\frac{1}{3}$ alcohol.

same for all solutions saturated with glycine (at constant temperature), it is possible to calculate the effect of alcohol or of salt on the solubility of glycine at 0° , solving the appropriate equation by successive approximations. This requires an extrapolation beyond the range of our measurements by about the concentration of the added substance. Such solubility changes have been measured, however, only at higher temperatures, and comparison with them requires a much greater extrapolation because of the increased solubility of the glycine. It also requires an assumption about the change of the coefficients with temperature. We shall assume that they do not change. In spite of these difficulties the limiting slopes are given quite accurately. For the solubility of glycine in sodium chloride solutions at 20° ,⁵ the agreement soon becomes very poor, as might be expected of an *extrapolation* by an equation with eight empirically determined parameters. Alcohol-glycine solutions give a much simpler equation, and the agreement with the measurements of the solubility of glycine in alcohol solutions at 25° is much better.^{6,7} Even in 4 M alcohol, almost three times the total concentration of

(5) P. Pfeiffer and J. Würzler, *Hoppe-Seyler's Z.*, **133**, 180 (1924).

(6) E. J. Cohn, T. L. McMeekin, J. H. Edsall and T. H. Weare, *THIS JOURNAL*, **56**, 2270 (1934).

(7) Preliminary results are given by E. J. Cohn, *Naturwissenschaften*, **36**, 663 (1932).

any of our measurements, the logarithm of the ratio of the solubility to that in water is given to about 20% by our equations.

It is possible to compare the glycine-salt effect with that in alcohol rich solutions, using only very general theoretical assumptions. If the salt effect is entirely electrostatic and small enough so that the Boltzmann expression may be represented by the first two terms of its series expansion, as in the Debye-Hückel approximation of interionic attraction, $(TD/T_0D_0) \ln f$ should be the same function of $(T_0D_0/TD)\Gamma$ for any solvent at any temperature, if f is the activity coefficient in terms of mole fractions referred to the salt-free solution in the same solvent. Cohn⁷ has shown that this relation (at constant temperature) holds accurately from 60 to 90% alcohol, where the glycine solubility is so low that its influence on the medium may be neglected, but that for saturated solutions in water⁸ the function is less than half its value in alcohol rich solutions. The full line in Fig. 5 is calculated for zero concentration of

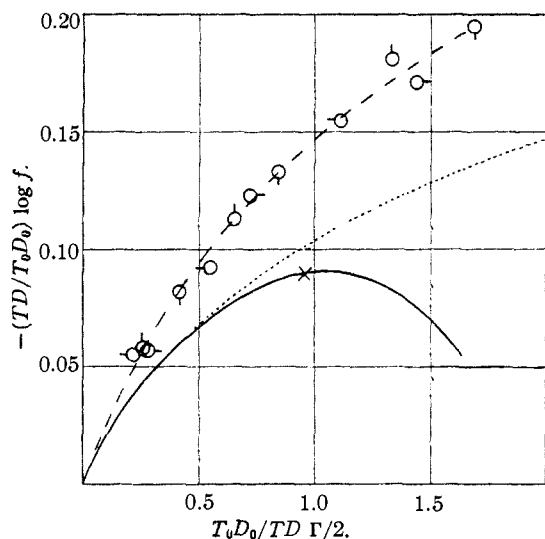


Fig. 5.—Salt effect on glycine at various alcohol concentrations.

glycine and of alcohol from our freezing point measurements, and the cross marks the upper limit of our measurements. The circles represent the measurements of the effect of lithium chloride, which is essentially the same as that of sodium chloride, in alcohol rich solutions.^{7,8} The volume percentages of alcohol are, in order: 80, 90, 95, 60 (repeat). The broken line represents the equation

$$y = 0.3080x - 0.2032x^{3/2} + 0.0419x^2$$

(8) Cohn, Edsall, McMeekin and Weare, not yet published.

where y is the ordinate and x the abscissa of the figure, determined from these measurements by least squares. The initial slopes of the two curves differ by only 3%, which is less than the error of determining either. The curvatures are, however, widely different, showing that the regularities of the alcohol rich solutions disappear for water even in the limit of zero glycine concentration.

For comparison with theoretical calculations it is desirable to have the deviations from the laws of ideal solutions, expressed in mole fractions. For an ideal solution

$$\varphi = \frac{\ln(1 + w_0M)}{w_0M} = 1 - w_0M/2 + (w_0M)^2/3 + \dots$$

Therefore, if we designate by B^I , etc., the coefficients giving the deviations from the laws of ideal solutions, $A^I = A$; $B^I = B + w_0/2$; $C^I = C$; $D^I = D - w_0^2/6$; $E^I = E$. For aqueous solutions $w_0/2 = 0.00901$ and $w_0^2/6 = 0.000054$. In considering such comparisons it is well to remember that, although the experimental accuracy can be reproduced only if some of the coefficients are carried to five places, no one of these coefficients is determined with any such accuracy. We shall, therefore, make the comparisons which follow only to two places.

The Born-Debye theory gives the B coefficient for electrolyte-non-electrolyte interaction in terms of the effect of the non-electrolyte on the dielectric constant and the radii of the ions.⁹ The Debye-Hückel limiting law, applied to mixed solvents, gives the C coefficients from the effect on the dielectric constant alone. Kirkwood's extension of these theories to zwitterions¹⁰ does not use the effect of the zwitterion on the dielectric constant, but requires the radius of the zwitterion and the length of its dipole. We shall use as radii of the sodium and chloride ions 0.87 and 1.59 Å, determined by Pauling¹¹ from crystal data, and as radius of glycine 2.82 Å, determined by Cohn and collaborators¹² from the volume in solution. The dielectric constant of dilute solutions¹³ may be expressed by the equations

$$D_0/D = 1 - 0.270 m_1 \text{ for glycine}$$

$$D_0/D = 1 + 0.028 m_2 \text{ for alcohol}$$

(9) G. Scatchard, *Chem. Rev.*, **3**, 333 (1927).

(10) J. G. Kirkwood, *J. Chem. Physics*, **2**, 351 (1934).

(11) L. Pauling, *THIS JOURNAL*, **50**, 1036 (1928).

(12) E. J. Cohn, T. L. McMeekin, J. T. Edsall and M. H. Blanchard, *ibid.*, **56**, 784 (1934).

(13) J. Wyman, *ibid.*, **53**, 3292 (1931); J. Wyman and T. L. McMeekin, *ibid.*, **55**, 908 (1933).

We see immediately that any theory which explains the interaction of electrolytes and non-electrolytes solely by the effect of the latter on the dielectric constant would give a ratio of -10 for the coefficients of glycine and of alcohol; we find a ratio of -1 .

For alcohol-salt solutions the Born and Debye theories give $B_{23}^I = +0.04$ and $C_{23}^I = -0.01$, and our measurements give $+0.15$ and -0.13 . For the application of Kirkwood's theory to glycine-alcohol solutions, we shall take the dipole length as 3.10 \AA ., determined from the glycine-salt effect later in the discussion. This gives $B_{12}^I = 0.03$ instead 0.12 determined from our measurements. The change of solubility of glycine from 40 to 80% alcohol,⁶ where the effect of glycine on the medium is small, corresponds to $B_{12}^I = 0.04$, so there is a great difference between this effect in water and in alcohol rich solutions. Our measurements give effects about four times those calculated theoretically for both the alcohol-salt and the glycine-alcohol effects. It would be surprising if the difficulties of extrapolating to zero concentration our measurements with solutions containing alcohol should affect both coefficients to the same extent, or that the influence should be nearly this large for the glycine-alcohol solutions, where practically the whole effect is given by the B 's. Our results suggest either that the first addition of alcohol to water decreases the dielectric constant much more rapidly than is indicated by Wyman's measurements on more concentrated solutions, or that there is an electrostatic effect not calculable for small alcohol concentrations from the macroscopic dielectric constant.

For glycine-salt solutions the Born and Debye theories give $B_{13}^I = -0.41$ and $C_{13}^I = +0.11$; our measurements give -0.15 and $+0.13$. The agreement of the C 's is excellent. The measured

B corresponds to a size more nearly equal to the mean diameter of the glycine molecule and an ion than to the ionic radii. Such a discrepancy is to be expected for a large molecule which owes its effect on the dielectric constant to a central dipole.

The radii given above yield 4.02 \AA . for the mean distance of closest approach of the ions to a glycine molecule. With this value and the initial slope of our results in Fig. 5, Kirkwood's theory¹⁰ gives 3.10 for the length of the glycine dipole. The curve calculated from Kirkwood's theory is represented by the dotted line in Fig. 5. It follows the curve for aqueous solutions closely in the dilute range but shows much less curvature in the concentrated range. This difference may be due to inaccuracies in our calculation of the higher coefficients.

The values for the distance of closest approach and the dipole length may be compared with the values 3.3 \AA . and 3.17 \AA . obtained by Kirkwood from the solubility measurements shown in Fig. 5. The somewhat larger dipole, and particularly the smaller mean diameter, give a limiting slope about 25% larger than ours and much less curvature. The two determinations of the dipole length differ by only 2% , and agree excellently with that to be predicted from the molecular structure.

Summary

The analytical expression of the thermodynamic functions of dilute solutions is extended to solutions containing ions.

The freezing point depressions of mixed aqueous solutions of sodium chloride with glycine and ethyl alcohol are measured and treated by this method.

The results are compared with the measurements of other properties of these solutions and with theoretical calculations.

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