results of work on weak acids in which he reported accurate relative values of the classical dissociation constants. In this report he notes that the deviation from linearity occurs at about this same concentration. As he states, these experiments were performed principally with the view of substantiating the theoretical slope, which they do, but no great absolute accuracy was attempted. The value deduced for the thermodynamic constant is higher than ours.

Rørdam[16] extrapolated the data of Schaller[17] and reports a value of 6.61×10^{-5} at 25°. Larsson[18] records a value of 5.83×10^{-5} at 18°.

Due acknowledgment is made of a grant from the Faculty Research Committee of the University which defrayed part of the cost of the apparatus and made available the services of a mechanic.

Summary

The equivalent conductivities of solutions of potassium benzoate and of benzoic acid have been determined.

The thermodynamic dissociation constant for benzoic acid has been calculated and is 6.312×10^{-5}.

The results confirm the limiting law of Debye and Hückel.

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[16] Rørdam, Inaugural Dissertation, Copenhagen, 1925.

[17] Schaller, *Z. physik. Chem.*, **25**, 497 (1898).

[18] Larsson, *ibid.*, **A148**, 148 (1930).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 332]

Freezing Points of Aqueous Solutions. VII. Ethyl Alcohol, Glycine and their Mixtures[1]

BY GEORGE SCATCHARD AND S. S. PRENTISS

Thermodynamic Calculations in Solutions more Complex than Binary.—The application of chemical potentials, or activities, most interesting to chemists is the study of chemical equilibria, most of which involve mixtures of several components. Yet relatively few such systems have been studied systematically. One reason for this hiatus is the lack of a satisfactory method of interpolation. For a binary system the variation with composition at constant temperature and pressure of any property may be represented by a line, and graphic interpolation is satisfactory. A ternary system requires a surface for the same representation, and more complicated systems go beyond the limits of ordinary geometry. Some analytical expression of the results is necessary, and it is highly desirable to have one which reduces as far as possible the number of experimental points necessary for accurate interpolation.

According to the physical theory of mixtures the free energy of a quantity of fluid may be expressed as

$$\frac{F}{RT} = \sum\nolimits_i^0 n_i\left(K_i + \ln\frac{n_i}{\sum_j^0 n_j}\right) + \frac{1}{V}\sum\nolimits_{ij}^0 \beta_{ij}n_in_j + \frac{1}{V^2}\sum\nolimits_{ijk}^0 \delta_{ijk}n_in_jn_k + \ldots \qquad (1)$$

where n_i is the number of moles of the i'th component, V the volume of the system and K_i, β_{ij} and δ_{ijk} functions only of the temperature and pressure. $\sum_{ijk}^0$ represents the triple sum $\sum_i\sum_j\sum_k$, etc., where each sum is carried over all the components. We shall later use $\sum_{ijk}$ for the same sum in which the solvent is omitted in the summation. Coefficients with the same subscripts but in different orders cannot be measured separately, so we shall represent their sum by a single one of the coefficients with the proper numerical factor. These factors are the same as the coefficients of the corresponding terms in the multinomial expansion of $(\sum_i n_i)^\nu$, where ν is 2 for the β's, 3 for the δ's, etc.[2]

The first term on the right of Equation (1) is the perfect gas term and represents the effects of the individual molecules. The second arises from the interaction of the molecules in pairs, and is just as complicated as the possible types of pairs. The third term includes the interactions in groups of three, and is as complicated as the possible types of groups of three, etc.

The volume of the system is fixed, at constant temperature and pressure, by the quantities of

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[1] Paper VI in this series appeared in THIS JOURNAL, **56**, 807 (1934).

[2] For a derivation in the simple case for which nothing beyond the β term is necessary, see: G. Scatchard, *Chem. Rev.*, **8**, 321 (1931); J. H. Hildebrand and S. E. Wood, *J. Chem. Phys.*, **1**, 817 (1933).

the various components. We are particularly interested in liquid mixtures in which the quantity of one component, the solvent, is much greater than the quantity of all the others. We may then express the volume as

$$\frac{1}{V} = \frac{1}{n_0 V_0^*}\left(1 - \sum_j \frac{n_j V_j^*}{n_0 V_0^*} + \ldots\right) \qquad (2)$$

where the V^*'s are the partial molal volumes at infinite dilution. We may make the substitution of (2) in (1) and group all terms with the same summation index. It is convenient to include the volumes in the β coefficients, etc., to deduct unity from the α coefficients and to express the logarithmic term in the following way

$$\begin{aligned}\ln \frac{n_i}{\sum_j^0 n_j} &= \ln \frac{n_i}{n_0} + \ln \frac{n_0}{\sum_j^0 n_j} \\ &= \ln \frac{n_i}{n_0} - \frac{\sum_j n_j}{n_0} + \frac{1}{2}\left(\frac{\sum_j n_j}{n_0}\right)^2 - \ldots \qquad (3)\end{aligned}$$

where the sum is now taken over the solutes only. Making the appropriate substitutions in (1) gives

$$\frac{F}{RT} = \sum_i^0 n_i\left(K_i + \ln \frac{n_i}{n_0} - 1\right) + \frac{1}{n_0}\sum_{ij}^0 \beta_{ij} n_i n_j + \frac{1}{n_0^2}\sum_{ijk}^0 \delta_{ijk} n_i n_j n_k + \ldots \qquad (4)$$

It is obvious that every term with no index other than zero may be included in K_0', every term with only one index different from zero included in the appropriate K_i', every one with only two indices different from zero included in the appropriate β_{ij}', etc. Therefore, by adding $n_0 K_0''$ equation (4) may be taken with all the sums extending over the solutes only. It is important to note that the terms with one or more indices zero disappear for purely mathematical reasons and not because any action of the solvent is overlooked.

If F^*/RT be defined as $F/RT - \sum_i n_i \ln n_i/n_0$ for an infinitely dilute solution minus F/RT of the water necessary for dilution we may write

$$\frac{F - F^*}{RT} = \sum_i n_i\left(\ln \frac{n_i}{n_0} - 1\right) + \frac{1}{n_0}\sum_{ij} \beta_{ij}'' n_i n_j + \frac{1}{n_0^2}\sum_{ijk} \delta_{ijk} n_i n_j n_k + \ldots \qquad (5)$$

The standard state is here so defined that the activity of each component is equal to its mole fraction at infinite dilution. We may equally well let it be equal to the molality $n_i/W_0 n_0$, where W_0 is the molecular weight of the solvent divided by one thousand, giving

$$\begin{aligned}\frac{F - F^*}{RT} &= \sum_i n_i\left(\ln \frac{n_i}{W_0 n_0} - 1\right) + \frac{1}{W_0^2 n_0}\sum_{ij} B_{ij} n_i n_j + \frac{1}{W_0^3 n_0^2}\sum_{ijk} D_{ijk} n_i n_j n_k + \ldots \\ &= W_0 n_0 \sum_i m_i (\ln m_i - 1) + n_0 \sum_{ij} B_{ij} m_i m_j + n_0 \sum_{ijk} D_{ijk} m_i m_j m_k + \ldots \\ &= W_0 n_0 M \sum_i x_i (\ln m_i - 1) + n_0 M^2 \sum_{ij} B_{ij} x_i x_j + n_0 M^3 \sum_{ijk} D_{ijk} x_i x_j x_k + \ldots \qquad (6)\end{aligned}$$

where

$$M = \sum_i m_i \qquad (7)$$

and

$$x_i = m_i/M \qquad (8)$$

If there were chemical reactions with no other causes for deviation from ideality, the series in equation (1) would contain powers of $1/\sum_i^0 n_i$ instead of $1/V$. Some approximate theories of physical interaction lead to the same series. Langmuir's theory demands the replacement of $1/V$ by $1/\sum_i^0 n_i S_i$, where S_i is the molal surface. It is clear that either of these may be reduced to equations (4), (5) and (6). It would also be possible to write a similar expansion in terms of the volume concentrations or of the mole fractions. The method chosen has the disadvantage that the sum does not reduce to the first term alone for ideal solutions. This is more than outweighed, however, in the case of solutions with more than one solute by the fact that the variation of the quantity of a solute does not change the "concentration" of any other solute.

The chemical potentials are most easily obtained by differentiating the first form of equation (6).

$$\ln \gamma_p = \frac{\mu_p - \mu_p^*}{RT} - \ln m_p = 2\sum_i B_{ip} m_i + 3\sum_{ij} D_{ijp} m_i m_j + \ldots \qquad (9)$$

$$\varphi_\mu = \frac{\mu_0^* - \mu_0}{W_0 RTM} = 1 + M\sum_{ij} B_{ij} x_i x_j + 2M^2 \sum_{ijk} D_{ijk} x_i x_j x_k + \ldots \qquad (10)$$

where γ_p is the molality activity coefficient of the p'th component (a solute) and φ_μ is the osmotic coefficient for the chemical potential. μ_p is the chemical potential per mole. It is worth noting that, except for the expression of concentrations in terms of moles per kilogram solvent instead of volume concentrations, equations (6) and (9) have the form of the equations for a gaseous mixture of the solutes with the pressure a variable. In the case of a gas the osmotic coefficient is $pV/RT\sum_i n_i$.

To insure against misunderstanding of our summations, we shall expand them for a ternary solute.

This expansion includes the single and binary solutes if one or more concentrations are taken as zero, and the extension to more complicated solutions is obvious.

$$\ln \gamma_1 = 2B_{11}m_1 + 2B_{12}m_2 + 2B_{13}m_3 + 3D_{111}m_1^2 + 6D_{112}m_1m_2 + 6D_{113}m_1m_3 + 3D_{122}m_2^2 + 3D_{133}m_3^2 + 6D_{123}m_2m_3 + \ldots \tag{11}$$

$$\varphi_\mu = 1 + M(B_{11}x_1^2 + B_{22}x_2^2 + B_{33}x_3^2 + 2B_{12}x_1x_2 + 2B_{13}x_1x_3 + 2B_{23}x_2x_3) + 2M^2(D_{111}x_1^3 + D_{222}x_2^3 + D_{333}x_3^3 + 3D_{112}x_1^2x_2 + 3D_{113}x_1^2x_3 + 3D_{122}x_1x_2^2 + 3D_{223}x_2^2x_3 + 3D_{133}x_1x_3^2 + 3D_{233}x_2x_3^2 + 6D_{123}x_1x_2x_3) + \ldots \tag{12}$$

Expansions similar to equations (6), (9) and (10) have frequently been used in connection with more specific theories, such as the van der Waals gas theory, the Debye theory of salting out and the Brönsted theory of the "specific interaction of ions." As far as we know they have never been used alone. Such a treatment is, however, general providing that the forces between molecules fall off with increasing distance between them more rapidly than $1/r^3$ (extension to ionic solutions, for which this condition is not fulfilled, will be given in a later paper), and there is every reason to expect that it is simple enough to be important. It is certainly powerful enough to be very useful. For example, the *B* terms in the chemical potential of any component in any solution with two solutes may be determined from the osmotic coefficients of the two single solute systems and of one mixture; and for any more complicated system from its single solute systems and one mixture for each possible pair of solutes. The *D* terms require a study of one more mixture for each pair of solutes, and one (only) of each possible group of three, etc. We find it unnecessary to include terms higher than *D* up to a concentration of two molal, which is the limit of our freezing-point measurements.

Application to Freezing Point Depressions.—The osmotic coefficient for freezing points, φ_f, is given by

$$\begin{aligned}\varphi_f &= \Theta/\lambda M \\ &= \Theta/1.858\, M \text{ for aqueous solutions}\end{aligned} \tag{13}$$

where Θ is the freezing point depression and λ the molal freezing point depression. It differs slightly from the osmotic coefficient for chemical potentials because the heat of fusion varies slightly with the temperature. In their treatment of solutions with a single solute, Lewis and Randall[3] take this into account only when they integrate to obtain $\ln \gamma'$. In our treatment it is much more convenient to make the correction before integration. Using their equation XXIII-21

$$\ln a_0 = -0.009696\Theta - 0.0000051\Theta^2$$

we obtain

$$\varphi'_\mu = \varphi_f\,(1 + 0.001\,\varphi_f\,M) \tag{14}$$

φ'_μ contains the chemical potential of the solvent at the freezing point of the solution. This symbol is used to indicate the slight variation from isothermal conditions and the value of $\ln \gamma$ obtained from it is the $\ln \gamma'$ of Lewis and Randall. We shall express our results in terms of φ'_μ. Since the difference between φ'_μ and φ_f never exceeds 0.3%, the latter and the Lewis and Randall *j* function ($j = 1 - \varphi_f$) may be calculated with sufficient accuracy from the relation

$$\varphi_f = \varphi'_\mu\,(1 - 0.001\,\varphi'_\mu\,M) \tag{15}$$

If equation (6) is to hold over a range of temperatures it follows immediately that

$$\frac{H - H^*}{RT} = \mathrm{d}\left(\frac{F - F^*}{RT}\right) \Big/ \mathrm{d}\left(\frac{1}{T}\right) = n_0M^2\,\Sigma_{ij}b_{ij}x_ix_j + n_0M^3\Sigma_{ijk}d_{ijk}x_ix_jx_k + \ldots \tag{16}$$

where *H* is the heat content of the system and

$$b_{ij} = \mathrm{d}B_{ij}/\mathrm{d}(1/T), \text{ etc.}$$

Calculating *T* from equations (13) and (15) and then φ_μ at the freezing point of the solvent by standard methods we obtain

$$\varphi_\mu = \varphi'_\mu + \frac{\lambda}{T_0}\,[M^2\,\Sigma_{ij}b_{ij}x_ix_j + \ldots] \tag{17}$$

The *B* terms are unchanged and the *b*'s go with the *D*'s, etc. Moreover, the coefficients of the heat content are generally of about the same magnitude as those of the free energy, so the factor λ/T_0 reduces the correction (for aqueous solutions) to less than 1%. We need merely state that any deviations from additivity of the heat capacities affect no term below M^3 in φ_μ at the freezing point, and that the calculation of φ_μ at any other temperature includes terms for the heat of dilution and the deviation of the heat capacities from additivity with the same power of the concentration as they appear in the original functions. The calculation of $\ln \gamma$ at any temperature from φ_μ at that temperature follows simply by the calculation of new constants for φ_μ at that temperature.

Experimental

The freezing point measurements with the single solute systems were conducted just as those with salt solutions in our earlier work. With the mixtures the bubbling of nitrogen was omitted, for any evaporation of alcohol would

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[3] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923.

change the ratio of the solutes. The solutions were analyzed in a 4-cm. cell (8-cm. light path) of a Zeiss portable interferometer. This instrument was kept in a room of the Spectroscopic Laboratory whose temperature seldom varied more than half a degree, and never more than a degree, from 23°C. One scale division corresponds to about 4×10^{-5} *M* glycine and about 2×10^{-4} *M* alcohol. Since the measurements were limited to the first 1200 scale divisions, all but the most dilute solutions required dilution before analysis. Therefore the calibration was made in weight per cent. of solute, *p*, *vs.* scale divisions, *d*. Since the absolute error is practically independent of the concentration the deviations from an empirical equation

$$p = \text{const. } d$$

were plotted against *d*. For solutions containing glycine the color of the bands shifted with changing concentration as has often been noted for salt solutions. In the range measured the black band shifted five band widths for glycine itself. Therefore the positions of three or four bands were determined for each calibration measurement, and the position of at least two bands for each analysis, and the color of the bands was carefully noted. An error in the position of the central band would introduce an error of at least 1.5% in the concentration and could not fail of detection. No such error was made in the course of our determinations. Although the makers state that it is not worth while to read the interferometer more closely than one scale division (about one-fifteenth of a band width), we found an average deviation of 0.2–0.3 divisions from our curves. This was checked by the consistency of the freezing point measurements, by the agreement in the determinations of concentrations from different bands, and by the fact, discovered after these measurements were completed, that they could be represented to an average deviation of 0.2–0.3 scale divisions by quadratic equations. For the single solutes these equations are

$$\text{Glycine} \quad p = k + 2.8617 \times 10^{-4}\, d - 1.088 \times 10^{-8} d^2$$
$$\text{Alcohol} \quad p = k + 8.884 \times 10^{-4}\, d - 4.44 \times 10^{-8} d^2$$

The constant *k* depends upon the position of the band measured relative to the central band for water. It is zero for this central band. This accuracy corresponds to about two-hundred thousandths of a degree for glycine solutions, or about the accuracy of the freezing point measurements, and to about five times this quantity of the alcohol solutions.

The glycine used was very kindly furnished by Drs. Cohn and McMeekin of the Harvard Medical School. It was a C. P. product further purified by repeated precipitation from water solution with alcohol, and found by them to contain 0.06% volatile at 105° and about 0.001% ash. We determined the conductance at 10° and found

M	Sp. cond. × 10^6	Molal cond. × 10^3
0.0000	0.28	..
.0099	.53	25
.0718	1.22	13
.793	7.40	9.0

The molal conductance is $1\text{–}3 \times 10^{-4}$ times that of a uni-univalent salt solution, which corresponds closely to that calculated for the $C_2H_7O_2N^+$ and $C_2H_5O_2N^-$ ions from the dissociation constants, plus a contribution in dilute solutions for the hydrogen ion arising from the difference of the isoelectric point from neutrality. The concentration of foreign electrolyte must have been extremely small.

The alcohol was commercial absolute ethyl alcohol purified by the method of Harris[4] and in the same apparatus. It was purified in the summer and with no special precautions to protect from water. Its density (d_4^{25}) was determined by Dr. A. A. Ashdown as 0.78613, which corresponds to 0.35% water. The calibration curve was checked, and some of the freezing points were determined, with alcohol prepared by the same method by Mr. R. H. Armstrong, the density of which corresponded to 0.12% water. The agreement was better than 0.1%, correcting for the water content.

Difficulties with Solutions Containing Alcohol.—The constants for equation (10) for φ'_μ were determined by the method of least squares, the measurements on dilute solutions being weighted according to their *a priori* precision. It was found, however, that the results for no solution containing alcohol would extrapolate to unit osmotic coefficient at zero concentration without missing completely the results in dilute solutions, but all gave a smaller osmotic coefficient. It was necessary to use an equation of the type

$$\varphi' = 1 - k + B'M + 2D'M^2 \qquad (18)$$

and to determine *k* also from the measurements. This was also true of mixtures containing sodium chloride, using a more complicated equation to be

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[4] L. Harris, THIS JOURNAL, 55, 1940 (1933).

discussed later, for which the concentrations were determined by conductance. The values of k computed for the different solutions are

Composition	
Alcohol	0.0040
Alcohol (2)–Glycine (1)	.0040
Alcohol (1)–Glycine (2)	.0029
Alcohol (4)–NaCl (1)	.0048
Alcohol (1)–NaCl (1)	.0046
Alcohol (2)–Glycine (2)–NaCl (1)	.0026

Similar results were found by Raoult and by Loomis by the Beckmann method.[5] Their measurements give a k equal to 0.015. Loomis attributes this to evaporation of the volatile alcohol. Since ethyl alcohol affects the refractive index much less than glycine and the conductance not at all in dilute solutions, this explanation might apply to our mixtures, and may indeed explain the fact that k decreases less rapidly than the fraction of alcohol. For alcohol itself, however, evaporation of alcohol would give a positive k only if it occurred in the preparation of the solutions for calibration. This possibility was definitely excluded by weighing alcohol in a sealed bulb which was broken under the surface of the water in a tightly stoppered flask.

It seemed possible that alcohol and water form solid solutions. To explain the results with the Beckmann method, the concentration of alcohol in the solid phase must be about 1.5% of that in the liquid. The fact that we found a much smaller deviation might be attributed to failure to reach equilibrium in large pieces of originally pure ice which are slowly melting during the course of the measurement. To test this hypothesis about a kilo of ice was frozen in the form of small crystals from four kilos of a solution one molal in alcohol and half molal in sodium chloride. The salt certainly does not form solid solutions. The crystals were poured into a large funnel, washed three times with 300 cc. of ice water with suction, and then allowed to melt. In one experiment the suction was continued during the melting, in the other it was not. The resulting liquid was collected in fractions and analyzed by conductance and in the interferometer. In the later fractions the salt concentration was reduced to less than 10^{-4} molal, and the alcohol concentration corresponded to that of the salt within one division of the interferometer scale, being as often too small as too large. If there is any solid solution the equilibrium between the solid and liquid phases must be established as rapidly as the solid melts. This seems highly improbable.

The agreement between different observers[6] for the density of anhydrous ethyl alcohol makes it also seem highly improbable that this alcohol should contain 0.4% water. It is barely possible that, in the high humidity of the summer, an electrical leak should make our electromotive force measurements too small by about 0.4%. For all these explanations the change of the osmotic coefficient should be independent of the concentration, and it is extremely improbable that the osmotic coefficient for the chemical potential should not approach unity at zero concentration. We therefore believe it preferable to add k to the observed values of φ_f.[6a]

The Results

Measurements were made on solutions of glycine, of alcohol and of mixtures of one mole of glycine to two of alcohol and of two moles of glycine to one of alcohol, to concentrations of about two molal. The most concentrated glycine solution is more concentrated than the saturated solution calculated from the equation of Dalton and Schmidt[7] for its solubility, but it is certainly more dilute than the real eutectic solution. In calculating the constants by the method of least squares, each series was first treated independently. Then the B' constants for the mixtures were so adjusted that B'_{12} is the same for both. The constants so determined are

B'_{11} − 0.11411
B'_{22} − 0.02920
B'_{12} + 0.12340

D'_{111} + 0.01216
D'_{222} + 0.00552
D'_{112} − 0.00509
D'_{122} − 0.00219

They are primed to indicate that they correspond to φ'_μ and $\ln \gamma'$. In Fig. 1 are given the osmotic

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[5] F. M. Raoult, *Z. physik. Chem.*, **27**, 617 (1898); E. H. Loomis, *ibid.*, **32**, 592 (1900).

[6] See Brunel, Crenshaw and Tobin, THIS JOURNAL, **43**, 561 (1921).

[6a] We are unable to gain any further insight into this difficulty from the very recent measurements of T. J. Webb and C. H. Lindsley [THIS JOURNAL, **56**, 874 (1934)]. The deviations of their measurements on ethyl alcohol from the equation fitting our measurements may be expressed as $\delta\varphi = -0.002 + 10^{-4}/m$. The same equation fits the deviations of their measurements on mannitol from $\varphi = 1$; the figures in their article indicate that this behavior is common to all their measurements. A term proportional to $1/m$ shows a constant error in temperature or concentration, the most probable source of which is a difference in the degree of saturation with air of the water and the solution. One cannot state that their measurements are subject to such an error, but, depending upon the amount of faith placed in the measurements on dilute solutions and upon the interpretation of them, one may extrapolate to any value of φ at zero concentration between 0.994 and infinity.

[7] J. B. Dalton and C. L. A. Schmidt, *J. Biol. Chem.*, **103**, 549 (1933).

coefficients of these four solutions, and the deviations of the individual measurements are given in Fig. 2 on a much larger scale. In Fig. 2 the abscissas are $\sqrt{M}$, not because there should be any term in φ'_{μ} proportional to $\sqrt{M}$, but only because this gives a convenient method of spreading the points in dilute solutions. Figure 3 gives the variation of the constants with the composition of the solute. Figures 1 and 3 show clearly the great deviations from additivity and the necessity for some generalization to avoid an undue number of measurements.

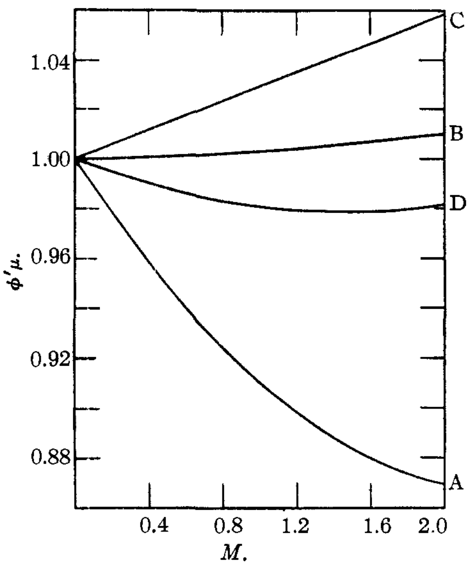

Fig. 1.—Osmotic coefficients: A, glycine; B, $^2/_3$ glycine–$^1/_3$ alcohol; C, $^1/_3$ glycine–$^2/_3$ alcohol, D, ethyl alcohol.

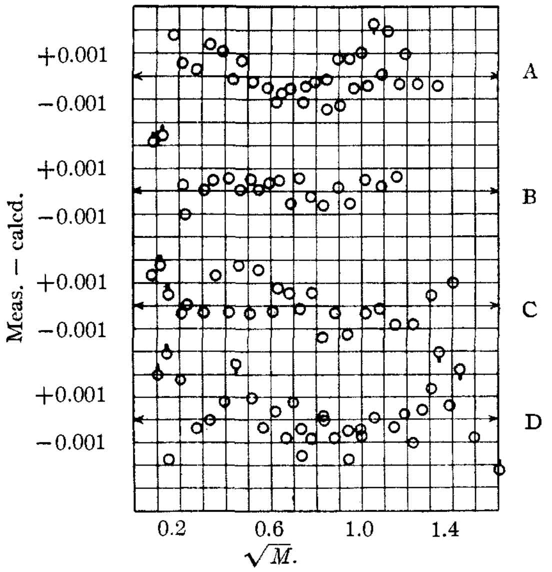

Fig. 2.—Deviations of osmotic coefficients from Equation 10: all circles deviating more than 0.002 have stems pointing toward line of zero deviation. To facilitate accurate reading the outer diameters of the circles are made just one-half the square sides.

Several points in Fig. 2 are worthy of attention. First of all it shows how accurately a quadratic equation can fit the results of our measurements. The best smooth curve through the measurements would differ very little from the horizontal line of zero deviation. The fact that the agreement for the mixtures is as good as for the single solutes confirms the quadratic expression for *B*. Our measurements give no test of the expression of *D'* as a cubic, but its variation is so small that it would be very hard to test this expression with any number of measurements. This figure also shows the necessity of extrapolation to some value other than unity at zero concentration. A limit of unity would demand a curve with a horizontal asymptote 0.002 to 0.004 (the exact value is *k* of the table) above the line of zero deviation. Finally the figure shows that for glycine there can be no term proportional to $\sqrt{M}$ of a magnitude comparable to that for salts (0.3738 *M* for a 1–1 salt).

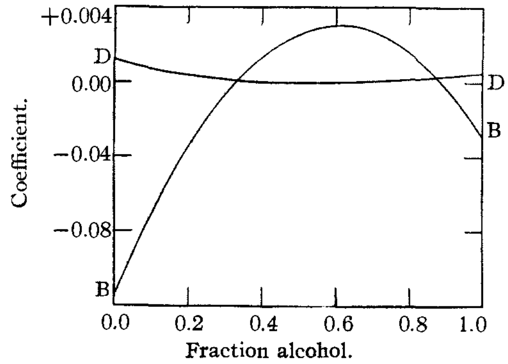

Fig. 3.—Variation of coefficients with solute composition.

The only measurements on ethyl alcohol in the literature have already been cited. There have been several recent measurements on glycine solutions, all by the Beckmann method.[8] Our own curve corresponds very closely to the average of these results except for very dilute solutions, for which the older measurements scatter widely. Large values of the osmotic coefficient have been attributed to ionization of the glycine, and a dissociation constant has been calculated from

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(8) W. A. Roth, *Z. physik. Chem.*, **43**, 539 (1903); M. Frankel, *Biochem. Z.*, **217**, 378 (1930); W. C. M. Lewis, *Chem. Rev.*, **8**, 151 (1931); G. A. Anslow, M. L. Foster, and C. Klinger, *J. Biol. Chem.*, **103**, 81 (1933).

them.[9] Our results show that they must be attributed to experimental error. The conductance measurements show definitely that the ionization is not greater than 0.1% even in 0.01 *M* solution.

The behavior of mixtures of glycine and alcohol indicates an explanation of the fact that the higher α-amino acids, which may be looked upon as a mixture within a single molecule of glycine and something resembling ethyl alcohol, have osmotic coefficients more nearly unity than that of glycine. The further discussion of these results will be deferred to a later paper.

We take this opportunity to express our thanks to our various colleagues for the materials, use of apparatus and facilities and assistance acknowledged above.

Summary

A method is developed for the analytical expression of the thermodynamic functions of dilute solutions of several non-electrolyte components which reduces to a minimum the number of measurements necessary to determine the chemical potential (or activity) of any component in a solution of any composition.

The freezing point depressions of aqueous solutions of glycine, of ethyl alcohol and of two mixtures of them have been determined, and the above method applied to them.

CAMBRIDGE, MASS. RECEIVED MARCH 27, 1934

(9) J. Y. Cann, *J. Phys. Chem.*, **36,** 2813 (1932).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Kinetics of the Saponification of Acetylated Hydroxy Acids*

BY VICTOR K. LA MER AND JOSEPH GREENSPAN

Introduction

Recent developments in the theory of ionic reactions, particularly in relating structure to reaction rate,[1a,2a,3,4] indicated the need for an ionic reaction which would be sufficiently general to permit more extensive studies of such relationships in a series of structurally different ions. The essential requisites of such a reaction, besides general applicability, are a rate suitable for measurement, freedom from side reactions, adherence to a simple kinetic equation over the major part of the reaction, available analytical methods for precise measurement and a constant ionic strength during reaction. Simplicity of experimental procedure and ease in preparation of compounds are desirable, although not essential.

Precise studies of only five more or less general ionic reactions are available at the present time.

$$\mathrm{RCH(X)COO^- + S_2O_3^{=} \longrightarrow RCH(S_2O_3)COO^{=} + X^-}$$

I[2,5,6,7,8b]

$$\mathrm{RCH(X)COO^- + SCN^- \longrightarrow RCH(SCN)COO^- + X^-}$$

II[8b,9,10]

$$\mathrm{RCH(X)COO^- + SO_3^{=} \longrightarrow RCH(SO_3)COO^{=} + X^-}$$

III[8]

$$\mathrm{RCH(X)COO^- + OH^- \longrightarrow RCH(OH)COO^- + X^-}$$

$$\mathrm{\longrightarrow R{=}CHCOO^- + X^-}$$

IV[11,13]

$$\mathrm{R'OOCRCOO^- + OH^- \longrightarrow {}^-OOCRCOO^- + R'OH}$$

V[3,12]

(X represents a halogen atom.)

Reaction I possesses the advantage of high precision in the analytical determination of thiosulfate ion but has a slow rate for long chain compounds (k at 25° is 10^{-3} for α-bromopropionate ion[2b] and still less for γ-bromobutyrate ion[2e]). This reaction is not applicable to benzene ring compounds of the type: $\mathrm{^-OOCC_6H_4Br + S_2O_3^{=}}$. Furthermore, the chemistry of the resultant organic thiosulfate compounds has not been extensively investigated.

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