The hitherto unaccountable similarity in the behavior of various oxidants of widely divergent potentials toward hydrazine is now explained on the ground that they are either *mono-delectronators*, yielding ammonia as the only by-product of the reaction, or *di-delectronators*, yielding both ammonia and hydronitric acid.

Further applications of this idea are projected, particularly for the case of other oxidation-reduction reactions in the fields of inorganic and organic chemistry in which intermediate products are formed.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

MICELLES AND THE ACTIVITY COEFFICIENT IN ALKALI SILICATE SOLUTIONS

BY MERLE RANDALL AND JESSIE Y. CANN

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The theory of colloidal electrolytes as used by McBain[1] postulates the replacement of a simple ion formed by the dissociation of an electrolyte, by a heavily hydrated polyvalent micelle or ion "which carries the equivalent sum-total of electrical charges" of the ions which it replaces. This theory was carefully considered by McBain and Salmon,[2] and by McBain, Laing and Titley,[3] who determined the dew point lowering and freezing point lowering of soap solutions. And from their data, Randall, McBain and White[4] calculated the activity coefficients.

McBain and Salmon[2] predicted that solutions of sodium silicate and certain other salts of the heavy metals, as well as the soaps, would be found to contain varying quantities of micelles. Recently, Harman[5] has postulated on the basis of his freezing point measurements, the existence of micelles in concentrated sodium silicate solutions containing a large excess of silica.

Before considering the constitution of the alkali silicate solutions as determined by their colligative properties, we will examine the significance of the activity coefficient of a solution in which micelles may be formed.

The Activity Coefficient in Solutions Containing Micelles

The activity of a solute is the ratio of the escaping tendency, or fugacity, of that constituent of a solution divided by the escaping tendency of the constituent in some standard state which is arbitrarily chosen.[6] The escaping tendency is, of course, independent of any assumed constitution

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[1] (a) McBain, *Trans. Faraday Soc.*, **9**, 99 (1913); (b) *Kolloid Z.*, **12**, 256 (1913).

[2] McBain and Salmon, THIS JOURNAL, **42**, 426 (1920).

[3] McBain, Laing and Titley, *J. Chem. Soc.*, **115**, 1289 (1919).

[4] Randall, McBain and White, THIS JOURNAL, **48**, 2517 (1926).

[5] Harman, *J. Phys. Chem.*, **31**, 355 (1927).

[6] See Randall, *Trans. Faraday Soc.*, **23**, 498 (1927).

of the solute. For convenience, when dealing with electrolytes, the chosen standard state is defined with reference to the infinitely dilute solution, and the activity is taken equal to the product of the activities of the ions into which the electrolyte is assumed to dissociate.[7] The activity coefficient of an ion is the number by which the stoichiometrical molality of the ion is multiplied to obtain the activity, and the activity coefficient of the solute is the geometrical mean of the activity coefficients of the ions.

We shall consider a solute in which the negative ions of a uni-univalent strong electrolyte are replaced by ionic micelles. Let us call m the molality of the solute AB, and n the number of univalent negative ions which unite to form an ionic micelle. The molality of the positive ion constituent is also m. If the negative ion constituent is present only in the form $(B_n)^{n-}$, then the molality of the solute and also the molality of the micelle ion is $m' = m/n$. Neglecting the hydration,[6] we may write

$$A_nB_n = nA^+ + (B_n)^{n-};\ a_2 = a_+{}^n \cdot a_- \qquad (1)$$

where a_2 is the activity of the solute, and a_+ and a_- are the activities of the positive ion and negative micelle, respectively. For the mean molality, we find

$$m_\pm = (m_\pm{}^n m')^{1/(n+1)} = m_+/n^{1/(n+1)} \qquad (2)$$

From Equation 2, we see that as n becomes a very large number, the mean molality of the ions becomes nearly equal to the molality of the positive ion constituent. Or, if n is infinite, we should say that the whole of the solute was a single particle, possessing the entire negative charge of the solution, surrounded by the univalent positive ions. If all the ions obeyed the law of the perfect solution, then the freezing point lowering of such a solute would be the same as that of a non-electrolyte having the same molality as that of the positive ion constituent. Consequently, in the limit, when n becomes very large, ν, the number of ions produced by the dissociation of each molecule of AB, approaches unity. Following the treatment by Bjerrum,[8] we should expect a micelle as formulated in Equation 1 to be a progressively weaker electrolyte as the value of n is increased. In the limit, when n becomes very large, perhaps the micelle would no longer behave as an electrolyte. We shall show in a later section that the micelles of sodium acid silicate behave as slightly weak electrolytes. The un-ionized micelles postulated by McBain and Salmon[2] can possibly be explained in this way.

In the ordinary manner, we have the ionic strength of the solution

$$\mu = (m_+ + m'n^2)/2 = m_+(n + 1)/2 \qquad (3)$$

As n increases, the ionic strength rapidly increases and becomes infinity in the limit when n becomes infinite.

[7] See Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, Chap. XXVI.

[8] Bjerrum, *Kgl. Danske Videnskab. Selskab Math.-fys. Medd.*, **7**, No. 9 (1926).

The activity coefficient of a solute is proportional to the square root of the ionic strength. If the solution is completely dissociated, the activity coefficient for a given ionic strength will be less, the greater[9] the value of n. The "association" in the Bjerrum[8] sense would still further reduce the expected activity coefficient of the micelles.

In the discussion of the activity coefficient of soaps by Randall, McBain and White,[4] the activity of the solute was set equal to the square of the product of the stoichiometrical molality and the activity coefficient, and we shall adopt the same convention in discussing the sodium acid silicates. Although, if for purposes of formulating a mechanism which will explain the divergence of the activity coefficients of these substances from those of typical uni-univalent electrolytes, we assume the existence of micelles, this device is in no way essential to the thermodynamic treatment. We selected as the solutes[6] the sodium ion and hydrosilicate ion, or sodium ion and univalent soap ion, because they were simple, and because in the dilute solution the behavior of the electrolytes was the same as that of typical electrolytes. The actual molality of the various ionic micelles, or of the various hydrates, or of the neutral micelles, or of undissociated substances is unknown; but their fugacity is the same as that of the solutes arbitrarily chosen, for they are in equilibrium with these substances. As long as no solute molecule is present whose composition cannot be expressed in terms of the ions chosen as solutes, and as long as these substances are in equilibrium, it is immaterial which of the species is chosen as the solute. Accordingly, the species with the simplest formula is used.

In the case of the hydrolysis of one of the ions, as that of SiO_3^{--}, the case is different, for the composition of the products of hydrolysis cannot be expressed in terms of the ions formed from the chosen solute. But, by drawing the curve as we shall do in Fig. 1, we assume that the curve as drawn is the curve which would be given by a substance of this nature if no hydrolysis occurred. Therefore, in taking the area under the curve, we obtain, with no great error, the activity coefficient of the normal silicate, without hydrolysis.

We shall now consider the various experimental determinations of the freezing point lowering,[10] vapor pressure lowering,[10a] dew point lowering[11] and boiling point raising[12] of the various sodium silicate solutions.

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[9] See Brönsted, *Trans. Faraday Soc.*, **23**, 416 (1927), who reviews the earlier literature.

[10] (a) Harman, *J. Phys. Chem.*, **31**, 355 (1927); (b) Kahlenberg and Lincoln, *ibid.*, **2**, 77 (1898), also Li, K, Rb and Cs silicates; (c) Loomis, *Phys. Rev.*, [1] **4**, 273 (1897); *Ann. Physik. Chem.*, [3] **60**, 523 (1897); (d) Thompson, Manuscript Thesis, Worcester Polytechnic Institute, Worcester, Mass., 1923.

[11] Bennett, *J. Phys. Chem.*, **31**, 890 (1927).

[12] (a) Cann and Cheek, *Ind. Eng. Chem.*, **17**, 512 (1925); (b) Cann and Gilmore, *J. Phys. Chem.*, **32**, No. 1 (1928).

Activity Coefficient of Sodium Silicate Solutions

Harman,[10a] Bennett[11] and Cann and Gilmore,[12b] took the molality of their silicate solutions equal to twice the molality of the sodium ion constituent. Numerous investigators[13] have shown that hydrolysis of the solutions is increased with dilution and with increase of temperature. For this reason, Harman,[10a] Bennett[11] and Cann and Gilmore,[12b] took the value of ν in the freezing point equation of Lewis and Randall[7] equal to 4, for solutions of all ratios of Na_2O to SiO_2. They then calculated the activity coefficients of the various solutions by the methods of Lewis and Randall.[7] Their calculations tacitly assume for the reaction

$$Na_2SiO_3\ (aq) + H_2O\ (l) = 2Na^+ + OH^- + HSiO_3^- \qquad (4)$$

$K = 1$, in accordance with the conventions adopted by Lewis and Randall in developing the basic equations used. In other words the activity of the sodium silicate is made equal to the geometric product of the activities of the ions on the right of Equation 4.

In a later paper, Harman[14] calculated the two dissociation constants of metasilicic acid from electrometric titration curves. His curves show definitely two "breaks" such as are found when sodium carbonate is titrated with hydrochloric acid.

We have recalculated the values of the activity functions[15] $h/m^{1/2}$ and $j/m^{1/2}$ for all the above measurements. We have used $\nu = 3$ for ratios of 1:1 of Na_2O to SiO_2 and $\nu = 2$ for ratios of 1:2 to 1:5. In the latter case, the molality was taken equal to the number of gram atoms of sodium ion constituent. These assumptions correspond to $K = 1$ for the reactions

$$Na_2SiO_3\ (aq) = 2Na^+ + SiO_3^{--} \qquad (5)$$

$$NaHSiO_3\ (aq) = Na^+ + HSiO_3^- \qquad (6)$$

It has been impossible to eliminate the effect of hydrolysis, but in the concentrated solutions this effect cannot be large,[13] and the method of extrapolation here used eliminates to a great extent the effect in the more dilute solutions.

Sodium Metasilicate.—The values of $j/m^{1/2}$ and $h/m^{1/2}$ for the various silicates containing $1Na_2O{:}1SiO_2$ are shown plotted against the square root of the molality in Fig. 1. The average values of $j/m^{1/2}$ for barium

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[13] (a) Kohlrausch, *Z. physik. Chem.*, **12**, 773 (1893); see also (b) Bogue, This Journal, **42**, 2575 (1920); (c) Cann and Cheek, ref. 12 a; (d) Harman, *J. Phys. Chem.*, **29**, 1155 (1925); (e) *ibid.*, **30**, 359 (1926); (f) *ibid.*, **30**, 917 (1926); (g) *ibid.*, **30**, 1100 (1926); (h) *ibid.*, **31**, 355 (1927); (i) Kahlenberg and Lincoln, ref. 10 b; (j) Loomis, ref. 10 c; (k) Thompson, ref. 10 d.

[14] Harman, *J. Phys. Chem.*, **31**, 616 (1927).

[15] (a) Randall, This Journal, **48**, 2512 (1926); (b) Randall and White, *ibid.*, **48**, 2514 (1926); (c) Randall, *Trans. Faraday Soc.*, **23**, 502 (1927); $j = 1 - (\theta/\nu\lambda m)$, where θ is the freezing-point lowering, ν the number of ions formed from one molecule, $\lambda = 1.858$, the freezing-point constant and m the molality; $h = 1 + (55.51 \ln a_1)/\nu m$, where a_1 is the activity of the solvent.

nitrate[16] are shown as the dotted curve. Fig. 1 also shows for comparison the values of $j/m^{1/2}$ for the ratio $Na_2O{:}1.4SiO_2$, if we assume the molality equal to the moles of Na_2O and $\nu = 3$.

The effect of hydrolysis is seen in the negative values of $j/m^{1/2}$ and $h/m^{1/2}$ which, for a hydrolyzed substance will approach $-\infty$ at infinite dilution. In molal solution the hydrolysis is not large and we gain an idea of the activity coefficient of sodium silicate, when defined in accordance with Equation 5, by drawing the solid curve, to follow the general direction of the curve for barium nitrate. The activity coefficient of the normal sodium silicate as calculated by the equation

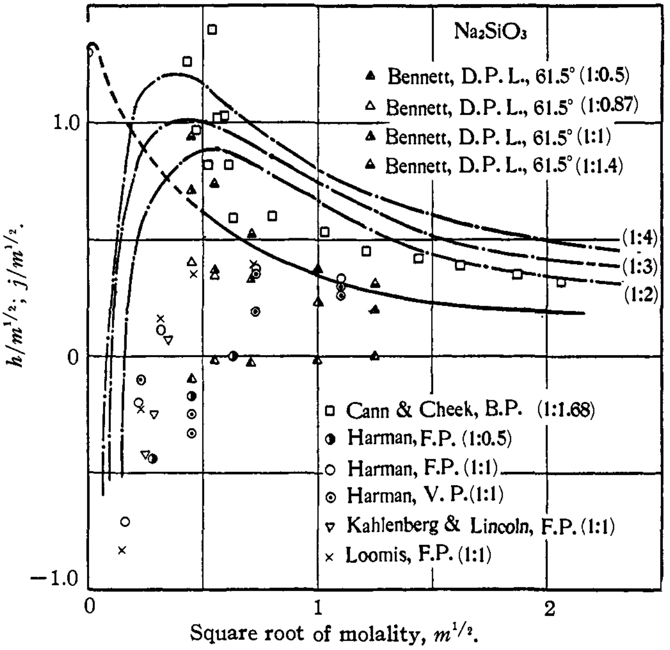

Fig. 1.—Activity function of sodium metasilicate.

$$\log \gamma = -j/2.303 - (2/2.303) \int_0^m (j/m^{1/2}) dm^{1/2} \qquad (7)$$

for round molalities is shown in the second row of Table I. The temperature coefficient of the activity coefficient has been neglected and the values are approximate for any temperature between 0 and 100°.

Table I

Activity Coefficients of Sodium Metasilicate Solutions, Na_2SiO_3

m	0.05	0.10	0.20	0.50	1.00	2.00
γ	.501	.408	.318	.232	.182	.141

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[16] Randall and Scott, This Journal, 49, 647 (1927).

The neutral sodium silicate is about as weak, that is, has the same activity coefficient, as barium nitrate, which was shown by Randall and Scott[16] to be weaker than typical strong electrolytes of the same valence type. We should, therefore, expect a slight "association" in the Bjerrum[8] sense, but such an effect is not apparent in the values of $j/m^{1/2}$, because of the large hydrolysis.

Our activity coefficient represents approximately the mean activity coefficient of the Na^+ and unhydrolyzed SiO_3^{--} ions present in any solution of an ionic strength three times the molality given in Row 1, when we assume the principle of the ionic strength.

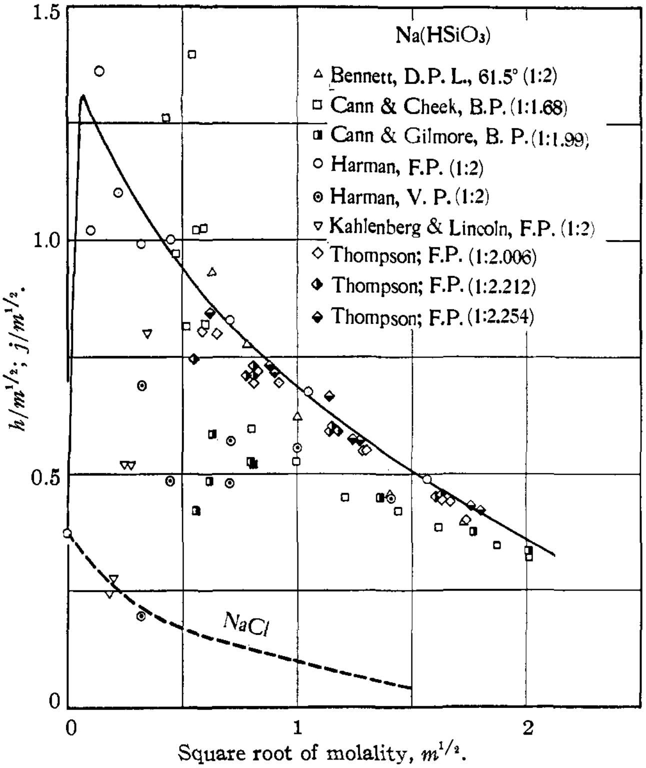

Fig. 2.—Activity function of sodium acid silicate.

Sodium Acid Silicates.—The values of $j/m^{1/2}$ and $h/m^{1/2}$ for the various silicates with ratios $1Na_2O:1.68SiO_2$ to $1Na_2O:2SiO_2$ are shown in Fig. 2; those for ratios $1Na_2O:2.55SiO_2$ to $1Na_2O:3SiO_2$ are shown in Fig. 3; those for ratios $1Na_2O:3.154SiO_2$ to $1Na_2O:5SiO_2$ are given in Fig. 4. The molality is that of sodium ion constituent and the acid silicates have been assumed to dissociate in accordance with Equation 6. The silica in excess of 2 moles of SiO_2 per Na_2O has been assumed to be combined in the univalent negative ion. Fig. 2 also shows as a dotted curve the average values of $j/m^{1/2}$ for sodium chloride.

The curves of Figs. 2 to 4 are similar to those obtained for moderately strong acids, such as dichloro-acetic. No typical uni-univalent salts, such as the uni-bivalent cadmium chloride or mercuric chloride, with low activity coefficients, have been noted, although one of us has plotted the values of $j/m^{1/2}$ and $h/m^{1/2}$ for all published measurements.

Randall, McBain and White[4] plotted the values of $j/m^{1/2}$ and $h/m^{1/2}$ for the various sodium and potassium soap solutions. In the dilute solutions the values appear to be about the same as those for potassium chloride. At a concentration of about 0.05 M for a soap with a large number of carbon atoms to about 0.2 M for a soap with a small number, the values of $j/m^{1/2}$ begin to increase (log γ to decrease), the increase becoming larger, the greater the molecular weight of the soap. This rise is at the concentration in which micelles were assumed to begin to form as determined by conductance, viscosity and other data. The curves of Figs. 2 to 4 resemble the portions of the plots[4] of the data for the soaps in the higher concentrations. If the data are to be considered reliable, there is no evidence of behavior like that of sodium chloride in dilute solutions, and if the silicates give a rapid rise in the $j/m^{1/2}$ curve, as in the soap solutions, then this rise occurs in much more dilute solutions.

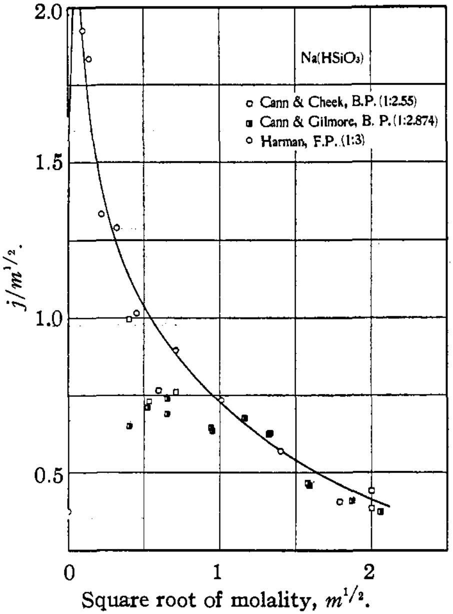

Fig. 3.—Activity function of sodium acid silicate.

Micelles can be assumed to form according to the equation

$$n(HSiO_3 \cdot ySiO_2 \cdot zH_2O^-) = [rHSiO_3 \cdot sSiO_2 \cdot wH_2O]^{n-} + xH_2O \qquad (8)$$

in which molecules of monovalent hydrosilicate ion with an indefinite amount of added water and silica unite to form the micelle with n negative charges and a new indefinite amount of water and silica of solvation. All of the silica will presumably remain in the micelle. The value of n may be a fairly large constant number, or it may vary with the concentration. We can confidently expect that in the infinitely dilute solution, the micelles will be completely dissociated or hydrolyzed, in which case $j/m^{1/2}$ will approach the same limit as typical uni-univalent electrolytes, just as

Bjerrum[8] has assumed for the behavior of partly associated substances. If the micelles persist to a sufficiently low concentration, then there will appear no such minimum in the $j/m^{1/2}$ curves as was found in the case of the soaps, and we may draw our average curve, somewhat as shown in Figs. 2 to 4. The approximate activity coefficients as calculated from these curves for the various ratios are shown in Table II.

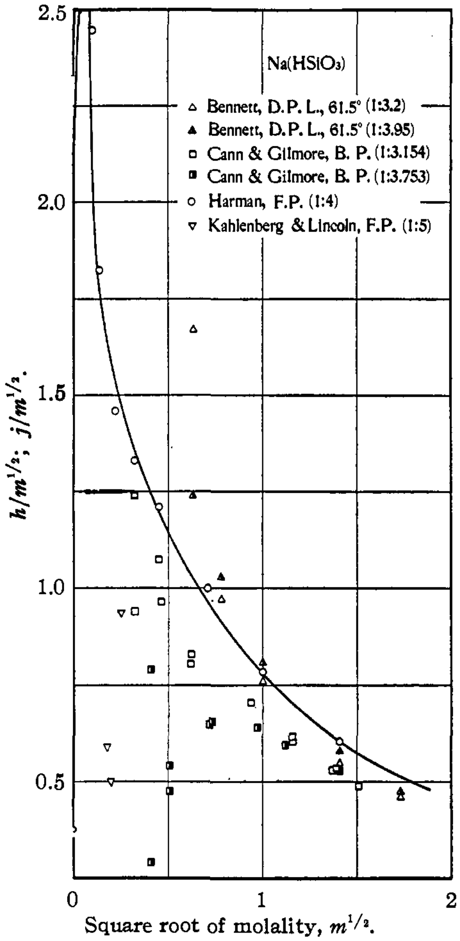

Fig. 4.—Activity function of sodium acid silicate.

The existence[17] of crystalline salts of the type $Na_2Si_2O_5$ is cited as an argument for the existence of $Si_2O_5^{--}$ in solution. The acid salt, $KHSi_2O_5$,[17b] has been prepared. However, the existence or non-existence of a crystalline salt does not necessarily indicate the presence of a considerable amount of the corresponding ions in solution, for they may react with the water, or may be in rapid equilibrium with an ion such as $HSiO_3^-$. Silicate solutions are known to change their thermodynamic properties with time, and some of these reactions may be slow. In the case of the measurements used in Figs. 1 to 4, a sufficient time to reach a stable state elapsed.

The broken curves of Fig. 1 show the average curves which correspond to the final mean curves taken from Figs. 2 to 4, when the molality of the acid silicates is taken as equal to one-half that of the sodium ion constituent and the divalent hydrated $Si_2O_5^{--}$ is assumed to be the principal negative constituent of the solutions. The excess silica is assumed to be combined in this negative ion in a way similar to that used in the former consideration of univalent $HSiO_3^-$. The values of $j/m^{1/2}$ for the acid sili-

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[17] (a) Niggli, THIS JOURNAL, **35**, 1693 (1913); (b) Morey, *ibid.*, **36**, 215 (1914); (c) Morey and Bowen, *J. Phys. Chem.*, **28**, 1169 (1924); (d) Thompson, ref. 10 d; (e) Harman, *J. Phys. Chem.*, **31**, 511 (1927); see also (f) Jordis, *Z. anorg. Chem.*, **56**, 305 (1907); (g) Westerberg, *Z. anorg. Chem.*, **88**, 341 (1915).

Table II

Activity Coefficients of Sodium Acid Silicate Solutions, $Na(HSiO_3)$

m	(1:2)	(1:3)	(1:4)
0.05	0.464	0.341	0.268
.10	.347	.247	.187
.20	.246	.169	.121
.50	.131	.088	.060
1.00	.076	.049	.033
2.00	.043	.027	.017
4.00	.027	.015	.008

cates, calculated on the basis of $\nu = 3$, $(Na_2Si_2O_5)$, show a larger number of negative values in the dilute solutions than those calculated on the basis of $\nu = 2$, and this may be taken as an argument for the use of our convention.

Since the curves of Figs. 2 to 4 can be explained by assuming the existence of micelles, we will study the solutions of the highest silica-sodium oxide ratios on the basis of the limiting case, that the number of charges upon the micelles is very large. But before proceeding, we will digress to consider the freezing point function in a mixture of electrolytes.

The Freezing Point Function in Mixtures

If, for any particular type of electrolyte, the values of $j/m^{1/2}$, or $h/m^{1/2}$, are divided by the value of the limit[15a] (at the temperature considered) at zero molality $(j^\circ/m^{\circ 1/2})$, and these numbers are plotted against the square root of the molality, as in Fig. 5, the curves for all strong electrolytes of the various valence types will coincide if the effect of the size of the ions, hydration, etc., is the same.[18]

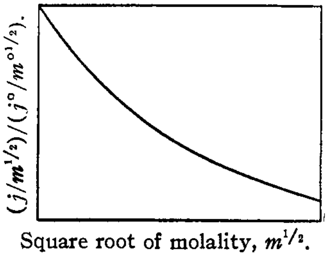

Fig. 5.

The function j is a property of the solvent. We may imagine the lowering of the freezing point to be the sum of the partial lowerings caused by each of the several constituents of a mixed electrolyte, such that $j = j_2 + j_3 + \ldots$. The value of $j_2/m_2^{1/2}$ or of $j_3/m_3^{1/2}$ will approach the same limit at infinite dilution as that approached by $j/m^{1/2}$ for a pure substance of the same valence type, but will depend upon the value of the ionic strength of the solution, rather than upon the molality of the particular constituent. If there is a common ion we must consider the function $j_2/m_{2\pm}^{1/2}$; but it is obvious from the definition[15] of j that if $m_\pm$ is substituted for m, then the sum of the various partial values of j will be greater than the total j. If the principle of the ionic strength is obeyed, then we should expect the curve of $(j_2/m_{2\pm}^{1/2})/(j_2^\circ/m_{2\pm}^{\circ 1/2})$ to be identical with the curve of Fig. 5.

The assumptions of the previous paragraph do not enable us to determine

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[18] Unpublished summary of colligative properties.

the activity coefficient of the several constituents of a mixture, nor the individual activity coefficients of the ions, for the division of the effect of the ions can only be made if we know the individual activities of the solutes. The idea, however, with the assumption of the principle of the ionic strength, enables us to examine qualitatively such curves as those of Fig. 6.

Micelles and Activity Coefficient of Sodium Ion

If a considerable portion of the hydrosilicate is in the form of large micelles, then in fact only one ion is formed per molecule of $NaHSiO_3$ dissociated, namely, a sodium ion; and the value of ν in the freezing point equation is one. We show the values of $j/m^{1/2}$ and $h/m^{1/2}$ calculated on this basis in Fig. 6. The limit at zero molality of $j/m^{1/2}$ for the freezing point measurements will be the same as that for uni-univalent substances, namely, 0.375, and if the usual assumptions[7] in estimating an individual ion activity are made, then the values should vary with the square root of the molality in about the same way as those for sodium chloride.

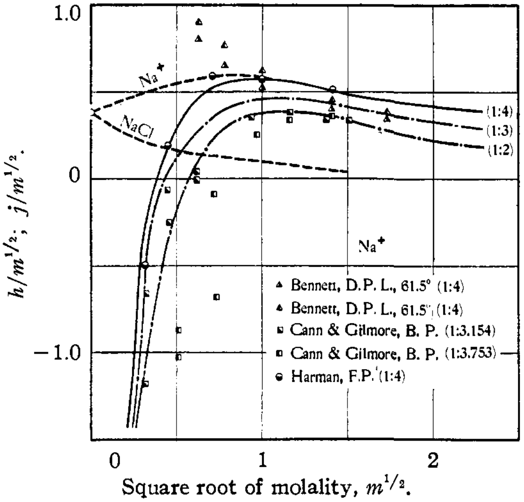

Fig. 6.—Activity function of sodium acid silicate.

Because of the very large charge upon the micelles, and the contribution to the ionic strength of a solution of these large ions, the scale of abscissas should be stretched to the right, and the values of $j_+/m_+^{1/2}$ should appear to decrease much less rapidly than those of sodium chloride. On the other hand, the presence of the large negative ions will cause an association in the Bjerrum[8] sense, because of the much larger distance of minimum approach of the centers of the charges, for complete dissociation, the effect of which would be shown in large values of $j/m^{1/2}$.

Below about 0.3 *M* the values of $j/m^{1/2}$ on the basis of $\nu = 1$ are in most cases negative, which is to be expected if the micelles dissociate to such an extent that the average number of ions formed per molecule is much greater than one.

We also show in Fig. 6 the values of $j/m^{1/2}$ calculated from the values of the freezing point lowering corresponding to the smoothed curves of Figs. 2 to 4. The values from the curves become negative at higher concentrations, the lower the silica-sodium oxide ratio in the silicates. This may be interpreted as indicating, as is also evident from the curves of Figs. 2 to 4, that the size and number of the micelles is less in the solutions of lower ratios.

The charge of the micelle, if we are to explain the effects in this way, is greater, the greater the silica content of the negative constituent. The activity coefficient of the sodium ion, basis $\nu = 1$, is smaller ($j/m^{1/2}$ is larger) in accordance with the idea that the Bjerrum "minimum approach" is larger and "association" therefore greater. Further, we should expect the size of the micelle containing a given number of charges to be greater the greater the relative silica content; therefore the micelle which would have a certain charge density upon its surface (surface/charge) would have a greater number of charges.

In a very real sense the assumption that the ions existing in acid silica solutions are $Si_2O_5^{--}$ or some hydrated multiple thereof may be considered as the first stage in the formation of a micelle, for undoubtedly the negative constituent consists of many different sorts of micelles all in equilibrium (more or less rapid) with each other. But, as we do not have a method of picking out the concentrations of the individual species of micelles, we may as well take $HSiO_3^-$ just as we do in the case of water when we choose H_2O as the species to represent this substance.

Unfortunately, we are unable to fully interpret Harman's[13f] measurements with the sodium amalgam electrode, as the original data are not given and the correction for liquid potential used by him is uncertain. The values in the dilute solutions are the least valuable but the data in concentrated solutions indicate qualitatively that the activity of the sodium ion is smaller, at a given concentration, the higher the silica-sodium oxide ratio. This is in accord with the observations given in a previous paragraph.

All the micelles referred to have been considered to be ionic micelles. McBain and Salmon[2] postulate both ionic and neutral micelles. It is possible that the distinction between the two forms is the same as that between the "associated" (Bjerrum) barium nitrate[16] and the dissociated barium nitrate. There has been no suggestion of the separate existence of neutral (McBain and Salmon) micelles in the silicate solutions.

The results of conductivity measurements and other data do not contradict our explanations.[19]

Summary

1. The theoretical consequences of the choice of the standard state for solutes is considered in relation to the activity coefficient and ionic strength of solutions containing micelles.

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[19] The Editor has kindly called our attention to an article by Linderstrøm-Lang, *Compt. rend. trav. lab. Carlsberg*, 16, No. 6 (1926), in which is given a different explanation of the low activity coefficient of such solutions as are here considered.

2. The activity coefficient has been calculated for sodium silicate solutions with various ratios of sodium oxide to silica.

3. Sodium metasilicate solutions behave as typical uni-bivalent electrolytes. The value of ν in the freezing point equation is taken equal to 3 instead of 4 as taken by previous authors. Although sodium metasilicate solutions are largely hydrolyzed, the choice of $\nu = 4$ is not consistent with our conventions regarding the definition of activity coefficients.

4. Sodium acid silicates are not largely hydrolyzed. The formula is taken as $NaHSiO_3$ rather than $Na_2Si_2O_5$, and $\nu = 2$ rather than $\nu = 4$. The acid silicates show extremely low activity coefficients.

5. The low activity coefficients of the acid silicates are explained by the assumption of the existence of ionic micelles which are not entirely dissociated into simple ions except in very dilute solutions.

6. The percentage of substance existing as micelles in the silicates increases with the ratio of silica to sodium oxide.

7. The number of aggregated acid silicate ions forming a micelle increases as the percentage of silica increases.

8. The effect of the ionic micelle upon the individual ion activity of sodium ion is discussed.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE PHYSICO-CHEMICAL LABORATORY OF THE POLYTECHNIC INSTITUTE OF COPENHAGEN]

PRIMARY SALT EFFECT IN A ZERO TYPE REACTION

BY MARTIN KILPATRICK, JR.[1]

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The present work is a further attempt to distinguish experimentally between the "activity rate theory" and the Brönsted formula for reaction rate in dilute solution.

According to the activity rate theory, the velocity of a reaction between A and B can be expressed by the equation

$$v = ka_Aa_B$$

where a_A and a_B are the activities of A and B, respectively.

Brönsted's[2] general formula may be written

$$v = kc_Ac_B{\cdot}f_Af_B/f_X$$

where k depends on the temperature and the solvent and f_A, f_B and f_x are the activity coefficients of A, B and the "critical complex," respectively. For a solution so dilute that the activity coefficients of molecules and ions depend only on the charge, the general formula is

$$v = kc_Ac_B{\cdot}f_{z_A}f_{z_B}/f_{z_A} + z_B$$

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[2] Brönsted, *Z. physik. Chem.*, 102, 169 (1922).