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Published on: 01 Jan 1974 - Journal of Solution Chemistry (Kluwer Academic Publishers-Plenum Publishers)

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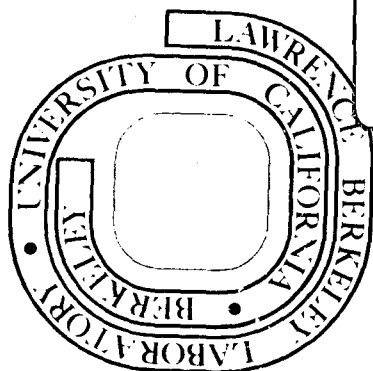
Kenneth S. Pitzer and Guillermo Mayorga

October 1973

Prepared for the U. S. Atomic Energy Commission
under Contract W-7405-ENG-48

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THERMODYNAMICS OF ELECTROLYTES. III. ACTIVITY
AND OSMOTIC COEFFICIENTS FOR 2-2 ELECTROLYTES.

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(Abstract)

The peculiar behavior of 2-2 and higher valence type electrolytes is discussed in terms of various theories some of which assume and others do not assume an equilibrium between separated ions and ion pairs as distinct chemical species. It is recognized that in some cases a distinct species of inner-shell ion pairs is indicated by spectroscopic or ultrasonic data. Nevertheless, there are many advantages in representing, if possible, the properties of these electrolytes by appropriate virial coefficients and without chemical association equilibria. It is shown that this is possible and is conveniently accomplished by the addition of one term to the equations of parts I and II of this series. The coefficients of these equations are given for nine solutes. It is also noted that these equations have been successfully applied to mixed electrolytes involving one component of the 2-2-type.

(end of abstract)

The consideration of 2-2 and higher valence types of aqueous electrolytes was omitted from parts I¹ and II² of the present series (cited hereafter as I and II) because of certain well-known peculiarities of such solutes.

Soon after the publication of the Debye-Hückel theory, Bjerrum³ showed that an ion association effect could be expected on the basis of purely electrostatic forces for 2-2 electrolytes in water or for lower valence types in solvents of lower dielectric constant. Various authors have dealt with the experimental data for the bivalent metal sulfates and other 2-2 solutes on this basis; recent papers are by Gardner and Glueckauf⁴ and by Pitzer.⁵ Although these ion-association treatments fitted the data well, there are serious disadvantages which lead one to seek a better method.

It has also been shown by Grenwall, LaMer and Sandved⁶ and later with steadily improving rigor and accuracy by Guggenheim,⁷ by Gardner and Glueckauf,⁸ and by Rasaiah⁹ that these 2-2 electrolytes could be treated by statistical theory without the assumption of an association equilibrium provided one avoids the Debye-Hückel approximation of linearization of the exponential in the Boltzmann distribution. The equations now become so complex, however, that one has only a few numerical results for particular ionic models.

Thus we seek equations which are simpler than those now available but which still reflect adequately the complexities of actual thermodynamic properties of these solutions.

Discussion - Association or Non-Association

While we have noted that the thermodynamic properties of 2-2 electrolytes do not require the assumption of a discrete chemical species of ion pairs, we recognize that spectroscopic^{10,11} and ultrasonic^{12,13} measurements do indicate a discrete species of inner-shell ion-pairs in some cases. Thus for some purposes it is clear that ion association must be recognized. In many cases, however, the proportion of inner-shell ion-pairs is never large, and it may be a satisfactory approximation for thermodynamic purposes to ignore the distinction between inner-shell and solvent-separated ion pairs. In that case one has returned to the broader question whether ion pairing need be explicitly recognized as the formation of a distinct species or merely as the inner portion of a continuous radial distribution.

The recent theoretical paper of Rasaiah⁹ presents not only his calculations by the HNC method for 2-2 electrolytes but also comparisons with other methods. Especially interesting are his radial charge density curves which are reproduced in figure 1. These are for the "primitive" model with a hard core diameter $a = 4.2 \text{ \AA}$, the macroscopic dielectric constant of water, and a temperature of 25°C . The curves are presented in terms of a relative radius r/a and a reduced radial charge density defined as

$$s^* = 4\pi r^2 ac (g_{+-} - g_{++}) \quad (1)$$

where c is the concentration (shown as m on the figure) and g_{+-} and g_{++} are the radial distribution functions for unlike and like pairs of ions, respectively. The figure shows the curves calculated by the HNC method for 1-1 as well as 2-2 electrolytes at equal ionic strength and for the Debye-Hückel theory. The latter theory yields the simple equation

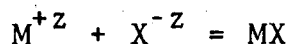
$$s_{DH}^* = \frac{\kappa^2 ar}{1+\kappa a} e^{-\kappa(r-a)} \quad (2)$$

where κ is the usual Debye-Hückel inverse distance.

The striking aspect of the results shown on figure 1 is that the HNC charge distributions for 1-1 and 2-2 electrolytes differ most at a very low, but finite, concentration and then become more nearly alike at higher concentration. All three curves are, of course, exactly alike in the limit of zero concentration. At $\kappa a = 0.44$ the ion association effect for 2-2 solutes is clearly shown by the sudden increase in charge density at r/a just above unity which is absent in the 1-1 case. But as the concentration increases further, this region of anomalously large charge density expands while the "normal" diffuse charge cloud is contracting. Thus at $\kappa a = 1.75$ the 1-1 and 2-2 curves are similar in placing almost all the charge in the range 1 to 2 in r/a with only a small oscillating density beyond.

The osmotic coefficient for CuSO_4 shown in figure 2 displays this same peculiarity in another way. The solid curve fitting the data at low as well as higher concentrations approaches the theoretical Debye-Hückel slope from the lower side at very low concentration. The dashed curve fits the data above 0.1 M equally well but has a simpler form typical of 1-1 or 2-1 electrolytes and approaches the theoretical slope from the upper side. Thus the difference or anomaly is confined to an intermediate concentration range approximately 0.0001 to 0.1 M. Various authors¹⁴ have had no difficulty fitting the data for 2-2 electrolytes above 0.1 M to the normal equations used for other types of strong electrolytes.

Further insight into this situation may be obtained from a simple calculation assuming ion association. The equations are familiar and are written for a symmetrical z-z electrolyte



$$K_{eq} = \left[\frac{\alpha}{(1-\alpha)^2} \right] \left[\frac{\gamma_{MX}}{m \gamma_M \gamma_X} \right]. \quad (3)$$

Here m is the molality, αm is the molality of the ion pair, and the activity coefficients have their usual meaning. For 1-1 electrolytes the second bracketed factor unambiguously decreases with increase in m since changes in the γ 's are relatively small. Thus the association steadily increases with molality (even though it may be very small

at all molalities of interest). For 2-2 electrolytes it becomes important to specify the distance of closest approach used in an expression for activity coefficients. If this is several times the hard core diameter, as suggested by Bjerrum and adopted by others, then a similar steady increase in association with concentration is observed:

But it seems also possible to regard the MX species as only the excess of closely paired ions over a "normal" distribution and to use a typical hard core diameter of 3 or 4 Å in the activity coefficient expression. Then it is found for 2-2 and higher types (in water at room temperature) that the activity coefficients γ_M and γ_X decrease so rapidly that the entire second bracketed factor in equation (3) actually passes through a minimum at some low concentration and then increases with further increase in m . Consequently one would have a maximum degree of association at this intermediate concentration.

Davies¹⁵ has discussed this type of calculation in detail, both on the basis given above and on the basis of conductance data, and shows that maxima of association are found for typical 2-2 electrolytes in the range 0.03 to 0.1 M and for 3-2, 4-2, or 3-3 electrolytes at even lower concentrations.

It is certainly possible to deal with these electrolytes on the basis of association equilibria, but there are at least two objections. From the view point of theoretical

elegance, the need to assume an arbitrary maximum distance of separation for ion pairs is distasteful. Association equilibrium constants are meaningless unless this distance is specified as well as the formulas for the individual ion activity coefficients. Probably more serious is the ambiguity in the ionic strength, which also depends on these rather arbitrary assumptions, yet is a quantity one wishes to use in various parts of the calculation. In mixed electrolytes this becomes particularly troublesome since the ionic strength will affect the properties of other components as well. In addition there is the practical disadvantage of an ionic strength which depends on an association equilibrium; this introduces the complexity of iterative solution of simultaneous equations of complicated types.

We conclude that it is desirable to represent the properties of these 2-2 and higher valence types of solutes without a dissociation equilibrium if possible. The test of success with a particular form of equation will be the accuracy of representation of observed properties of mixed as well as pure electrolytes.

Equations for Pure 2-2 Electrolytes

Since the peculiarities under discussion relate to interactions between pairs of ions, we must seek to account for them by the second virial coefficient. Let us consider an equation of the form adopted in I and II but with one

additional term

$$B\phi = \beta^{(0)} + \beta^{(1)} e^{-\alpha_1 I^{1/2}} + \beta^{(2)} e^{-\alpha_2 I^{1/2}} \quad (4)$$

If $\beta^{(0)}$ and $\beta^{(1)}$ represent the same effects of short range forces for 2-2 electrolytes as for other types of solutes, we can seek values for $\beta^{(2)}$ and α_2 which reproduce the anomalous behavior of 2-2 electrolytes in the range below 0.1 M. It is found that this is accomplished with a large negative value of $\beta^{(2)}$ and a large positive α_2 . Also one can show theoretically by an appropriate expansion that in the limit of very dilute solutions the ion-pair association constant, K , is $-2\beta^{(2)}$ and α_2 is $32A_\phi$ where A_ϕ is the Debye-Hückel coefficient for the osmotic coefficient. For water at room temperature $32A_\phi = 12.5$. Our purpose, however, is to fit the osmotic coefficient over the entire concentration range; hence we regard the results of the expansion for very dilute solutions merely as a confirmation of the plausibility of the mathematical form of equation (4).

The available data for 2-2 electrolytes were discussed in some detail in a recent publication⁵ where the correction of osmotic coefficients from 0 to 25°C was also considered. The only addition we now make is a recent series of isopiestic measurements¹⁶ on $MgSO_4$. In the present calculations we used osmotic coefficients directly from Robinson and Stokes¹⁷ or those corrected to 25° from the values of Brown and Prue.¹⁸ In the case of $CdSO_4$ one

must depend on electrochemical cell measurements, and we worked with the osmotic coefficients previously reported⁵ to be consistent with the cell potentials.

The complete equation, including the Debye-Hückel term and a simple third virial coefficient, is for a 2-2 electrolyte as follows:

$$\phi - 1 = 4f^\phi + mB_{MX}^\phi + m^2 C_{MX}^\phi \quad (5)$$

$$f^\phi = -A_\phi [I^{1/2} / (1 + bI^{1/2})] \quad (6)$$

$$B_{MX}^\phi = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} e^{-\alpha_1 I^{1/2}} + \beta_{MX}^{(2)} e^{-\alpha_2 I^{1/2}} \quad (7)$$

For the activity coefficient the corresponding equation is

$$\ln \gamma = 4f^\gamma + mB_{MX}^\gamma + m^2 C_{MX}^\gamma \quad (8)$$

$$f^\gamma = -A_\phi [I^{1/2} / (1 + bI^{1/2}) + (2/b) \ln (1 + bI^{1/2})] \quad (9)$$

$$B_{MX}^\gamma = 2\beta_{MX}^{(0)} + (2\beta_{MX}^{(1)} / \alpha_1^2 I) [1 - (1 + \alpha_1 I^{1/2} - \frac{1}{2}\alpha_1^2 I) e^{-\alpha_1 I^{1/2}}] \\ + (2\beta_{MX}^{(2)} / \alpha_2^2 I) [1 - (1 + \alpha_2 I^{1/2} - \frac{1}{2}\alpha_2^2 I) e^{-\alpha_2 I^{1/2}}] \quad (10)$$

$$C_{MX}^\gamma = (3/2) C_{MX}^\phi \quad (11)$$

Here the terminology is the same as in I and II, and the value $b = 1.20$ is retained. The differences are the addition of the last term in second virial coefficient and

the substitution of numerical values for a 2-2 electrolyte. Note that the superscripts ϕ , γ , and (0), etc. are labels rather than exponents. All parameters that are adjusted for each substance are given the subscript MX.

The full array of data for the sulfates of Mg, Ni, Cu, Zn, and Cd were fitted by least-squares adjustment of the four parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^ϕ for each substance. A series of values of α_1 and α_2 were used. While the optimum values of α_1 and α_2 varied a little from case to case, the values $\alpha_1 = 1.4$ and $\alpha_2 = 12.0$ fitted all cases very well and were adopted for all 2-2 electrolytes. This value of α_1 is somewhat smaller than the value 2.0 used previously in I and II. The value 12 for α_2 is close to that suggested by the theory mentioned above. The resulting values, the concentration range of data used, and the accuracy of fit are given in Table I. It is apparent that agreement is obtained substantially within experimental error.

Table I. Parameters for Thermodynamic Functions
for 2-2 Electrolytes in Water at 25°.

($b = 1.2$, $\alpha_1 = 1.4$, $\alpha_2 = 12.0$ throughout)

Electrolyte	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C\phi$	range	σ
MgSO ₄	0.2210	3.343	-37.23	0.0250	0.006-3.0	0.004
NiSO ₄	.1702	2.907	-40.06	.0366	.005-2.5	.005
CuSO ₄	.2358	2.485	-47.35	-.0012	.005-1.4	.003
ZnSO ₄	.1949	2.883	-32.81	.0290	.005-3.5	.004
CdSO ₄	.2053	2.617	-48.07	.0114	.005-3.5	.002
CoSO ₄	.20	2.70	-30.7	-	.006-.10	.003
CaSO ₄	.20	2.65	-55.7	-	.004-.011	.003
BeSO ₄	.317	2.914	(-100)	.0062	.1-4.0	.004
MnSO ₄	.201	2.980	(-40)	.0182	.1-4.0	.003

For the first five solutes in Table I the data extend over a wide concentration range and the resulting parameters should be reliable. Since data for CoSO_4 and CaSO_4 are limited to dilute solutions, because of solubility in the case of the calcium salt, the third virial coefficient was omitted and $\beta^{(0)}$ was set at 0.20 on the basis of the results for other solutes. The data sufficed to evaluate the two remaining parameters.¹⁹

There are no data below 0.1M for the last two solutes, BeSO_4 and MnSO_4 , hence only rough estimates can be made for the $\beta^{(2)}$ values.

For the osmotic coefficient the large value of α_2 makes the term in $\beta^{(2)}$ negligible above 0.1M. We see from equation (10), however, that the corresponding term in the activity coefficient equation approaches the constant value $\beta^{(2)}/288$ at high concentration. Since this term is constant, it does not affect the relative values of the activity coefficient (or other functions) at various concentrations above 0.1M, but it does affect the relationship to the solute standard state and the absolute values of the activity coefficients. This indicates the category of calculations which are valid even though $\beta^{(2)}$ is not known and the different category where $\beta^{(2)}$ is required.

This last point becomes especially important for still higher charged electrolytes, e.g., 2-3, 2-4, and 3-3 types, where the $\beta^{(2)}$ term will be important at lower concentrations than for 2-2 solutes. There are, to our knowledge, no cases

where this effect can now be adequately evaluated for these higher charge types; hence their omission from this paper.

Mixed electrolytes are currently being investigated with these equations. Solutions involving MgSO_4 as one component have been successfully fitted on the basis of these parameters and an ionic strength calculated without assuming any association. These results, which will be reported in detail in part IV of this series, offer further support to this method of representation of the properties of 2-2 electrolytes.

ACKNOWLEDGEMENT

This research was sponsored by the U. S. Atomic Energy Commission.

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19. The freezing point data for CoSO_4 appear to depart slightly from the family of curves for other bivalent sulfates. The parameters in Table I suppress this anomaly and yield the best fit within the normal pattern. If all three β parameters are adjusted freely a set such as 0.70, 1.60, and -25.0 yields better agreement, $\sigma = 0.002$, but these parameters are so inconsistent with the general pattern that we hesitate to recommend their use.

FIGURE CAPTIONS

Figure 1. Radial charge distributions for 1-1 and 2-2 electrolytes at three different ionic strengths.

Figure 2. The osmotic coefficient of CuSO_4 . The solid line follows all experimental data; the straight dotted line is the Debye-Hückel limiting slope; the dashed line is an approximate curve typical of lower valence electrolytes which fits in this case only above 0.2 M and in the limit at infinite dilution.

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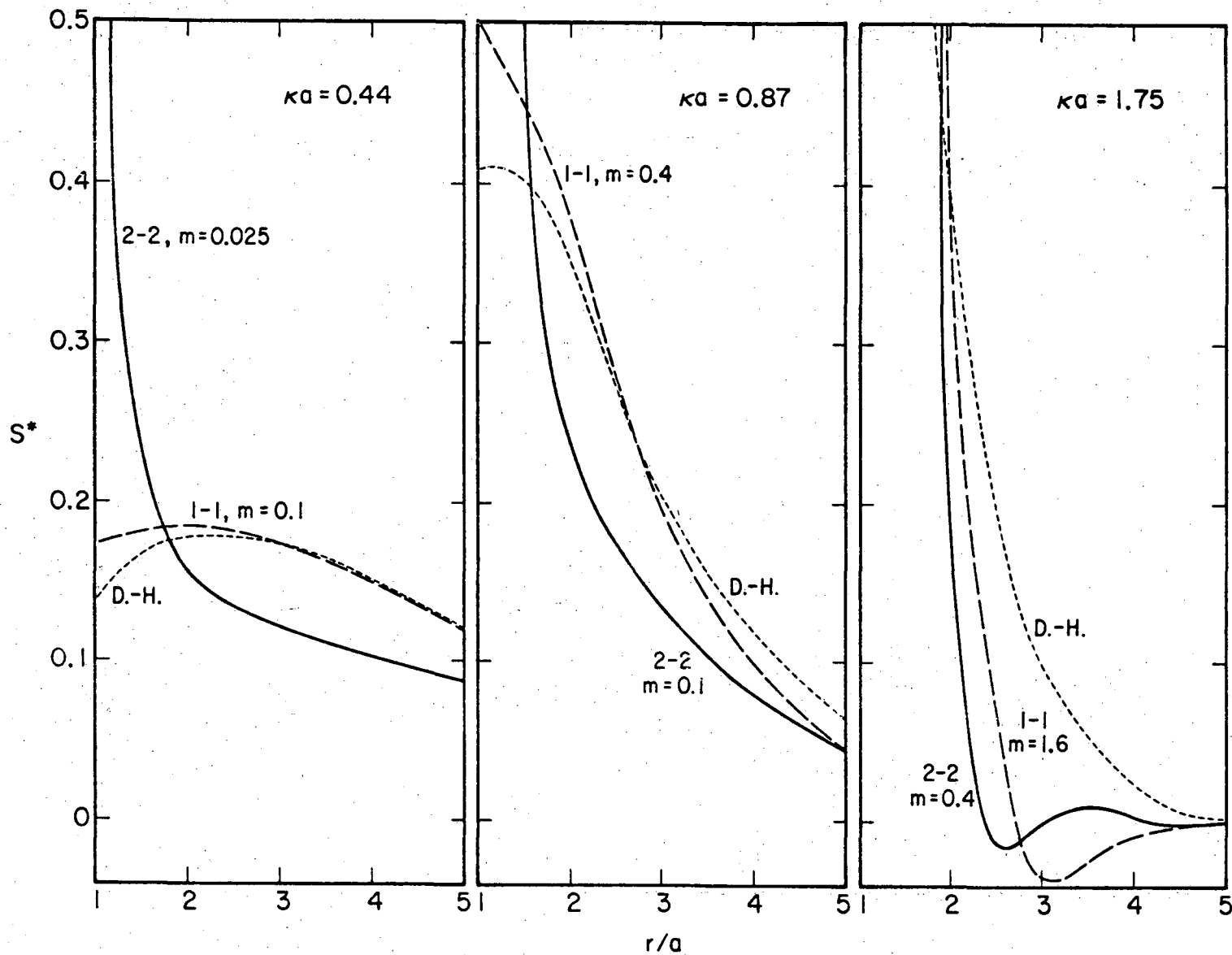
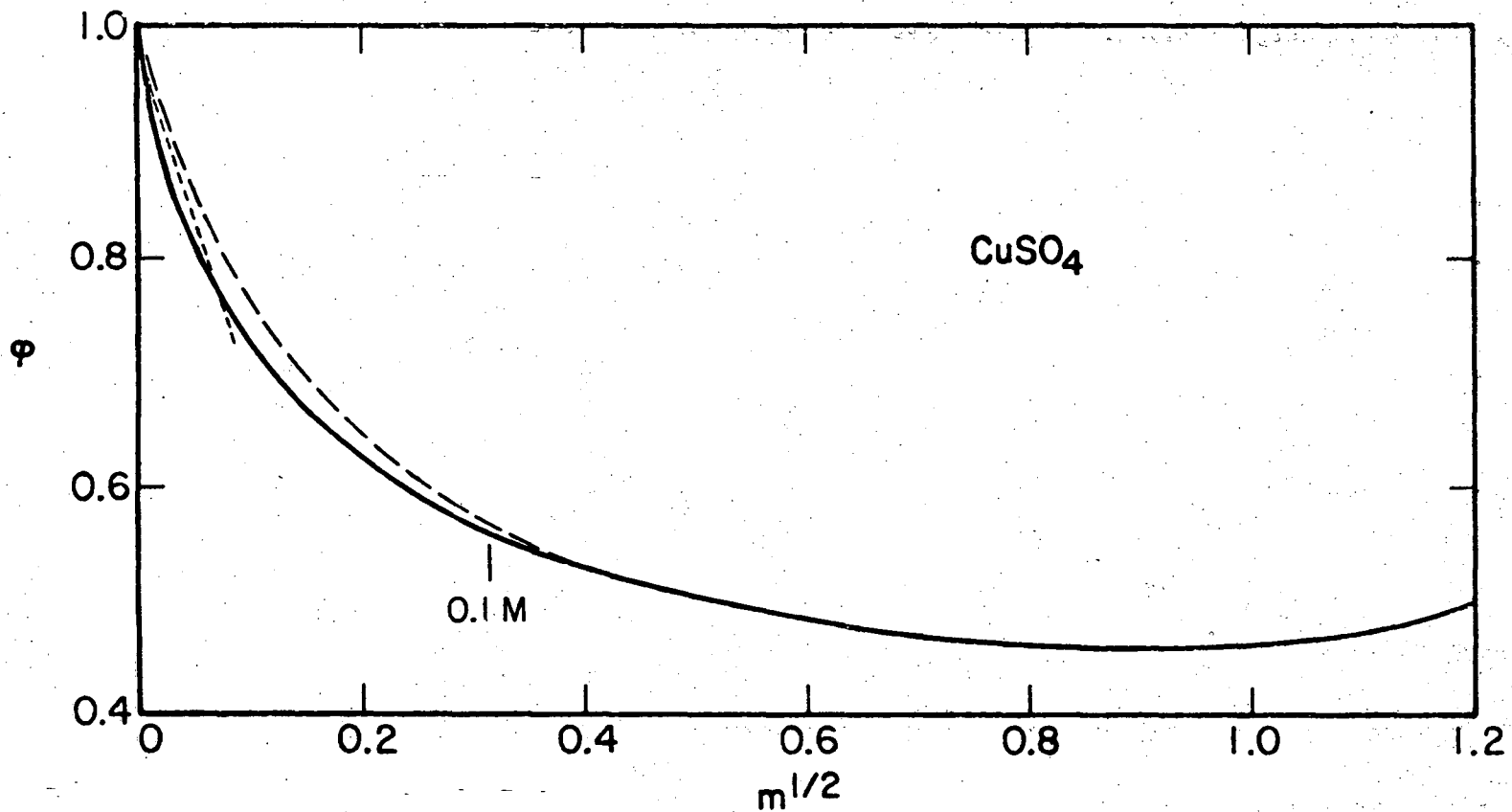


Figure 1. Radial charge distributions for 1-1 and 2-2 electrolytes at three different ionic strengths.

(18)



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Figure 2. The osmotic coefficient of CuSO_4 . The solid line follows all experimental data; the straight dotted line is the Debye-Hückel limiting slope; the dashed line is an approximate curve typical of lower valence electrolytes which fits in this case only above 0.2 M and in the limit at infinite dilution.

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