168. *Solutions in Sulphuric Acid. Part XXVIII.* Osmotic Coefficients of Some Electrolyte Solutions.*

By S. J. Bass, R. J. Gillespie, and J. V. Oubridge.

Osmotic coefficients of solutions of some metal hydrogen sulphates and of some organic bases have been calculated from the results of new freezing-point measurements on these solutions. The osmotic coefficients are shown to be consistent with an extended form of the Debye–Hückel equation involving an additional term which is linear in the ionic concentration. It is concluded that the non-ideal behaviour of electrolyte solutions in sulphuric acid can be attributed mainly to the effects of ion solvation and ion size. Electrostatic interionic forces have a small but not negligible effect which, because of the high dielectric constant of sulphuric acid and the high ionic strength of the pure solvent, is very nearly independent of the concentration of the electrolyte.

Values of the osmotic coefficients of some metal sulphate solutions have been calculated by Gillespie and Oubridge [1] from the results of their freezing-point measurements on these solutions. In the present paper we first discuss new values of the osmotic coefficients of solutions of the hydrogen sulphates of barium, sodium, lithium, potassium, ammonium, silver, and oxonium, and the conjugate acid of benzophenone, calculated from the new accurate freezing points obtained by the equilibrium method.[2] Then are given some less accurate values of the osmotic coefficients of the hydrogen sulphates of the conjugate acids of some ketones and amines, calculated from freezing-points obtained by the Beckmann method.

Osmotic Coefficients from Freezing Points.—Freezing-point depressions calculated from the freezing points given in Part XXVI [2] and the hypothetical freezing point of undissociated sulphuric acid,* $T_* = 10{\cdot}625°$, are given in Table 1. Osmotic coefficients ϕ were calculated by means of the equation (28) of Part XXVII, *viz.*:

$$\phi = \theta(1 + 0{\cdot}002\theta)/6{\cdot}12\Sigma m_{ij} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

with the values of $\sum m_{ij}$, the total concentration of solute species, given in Tables 2—4 of that paper; these osmotic coefficients are given in Table 2 and in Fig. 1. Ionic strengths I were calculated from molal concentrations, with the densities reported in the following paper. The interpretation of the curves in Fig. 1 is not straightforward as they refer, not to solutions of single electrolytes, but to mixtures of an electrolyte with the ions and molecules remaining from the solvent self-dissociation. The concentrations of the self-dissociation species are negligibly small at higher electrolyte concentrations but of increasing importance at lower concentrations until in an infinitely dilute solution of the electrolyte the solution contains only the self-dissociation species. An ionic strength less than that of 100% sulphuric acid cannot be obtained, and all the osmotic coefficient curves terminate at $I^{\frac{1}{2}} = 0{\cdot}189$ and $\phi = 0{\cdot}98$ which are the values for 100% H_2SO_4. For simplicity we shall treat these solutions as if they contained a single electrolyte only and bear in mind that the agreement between the experimental curves and theoretical curves may not be very good at the lower electrolyte concentrations. The variation of the osmotic coefficient with concentration may be accounted for by means of an equation of the form:

$$\phi = 1 + \phi^{el} + b\Sigma m_i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where ϕ^{el} is the contribution of electrostatic interionic forces to the osmotic coefficient, b is an arbitrary parameter, and $\sum m_i$ is the total concentration of ionic species in the solution.

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* Part XXVII, preceding paper.

[1] Gillespie and Oubridge, *J.*, 1956, 80.

[2] Gillespie and Bass, *J.*, 1960, 814.

TABLE 1. *Freezing-point depressions (equilibrium method).*

m^s	$Ph_2C(OH)\cdot HSO_4$	$NaHSO_4$	$LiHSO_4$	$KHSO_4$	NH_4HSO_4	$AgHSO_4$	H_3O,HSO_4	$Ba(HSO_4)_2$
0·000	0·254	0·254	0·254	0·254	0·254	0·254	0·254	0·254
0·005	—	0·286	0·286	0·286	0·286	—	0·261	—
0·010	—	0·325	0·324	0·324	0·323	—	0·279	0·350
0·015	—	0·366	0·365	0·365	0·364	—	0·308	—
0·020	—	0·412	0·411	0·411	0·410	—	0·345	0·489
0·025	—	0·461	0·460	0·460	0·459	—	0·389	—
0·030	0·520	0·512	0·510	0·510	0·508	0·507	0·433	0·660
0·035	0·575	0·564	0·563	0·563	0·558	0·558	0·479	—
0·040	0·631	0·619	0·616	0·616	0·610	0·607	0·531	0·850
0·05	0·747	0·730	0·723	0·723	0·720	0·710	0·632	1·044
0·06	0·863	0·846	0·840	0·840	0·832	0·819	0·741	1·239
0·07	0·987	0·961	0·955	0·955	0·946	0·926	0·842	1·434
0·08	1·008	1·079	1·070	1·070	1·059	1·035	0·951	1·631
0·09	1·239	1·198	1·190	1·190	1·178	1·145	1·061	1·830
0·10	1·365	1·321	1·309	1·309	1·293	1·255	1·172	2·037
0·12	1·630	1·569	1·551	1·546	1·525	1·474	1·384	—
0·14	1·902	1·827	1·794	1·789	1·759	1·695	1·601	—
0·16	2·178	2·082	2·043	2·035	1·993	1·913	1·818	—
0·18	2·461	2·342	2·289	2·280	2·225	2·131	2·034	—
0·20	2·748	2·603	2·533	2·524	2·459	2·345	2·250	—
0·22	3·035	2·869	2·787	2·777	2·693	2·559	2·457	—
0·24	3·345	3·140	3·048	3·025	2·930	2·770	2·669	—
0·26	—	3·413	3·307	—	—	2·983	2·880	—
0·28	—	3·677	—	—	—	3·193	3·088	—
0·32	—	—	—	—	—	—	3·495	—
0·36	—	—	—	—	—	—	3·900	—
0·40	—	—	—	—	—	—	4·301	—

TABLE 2. *Osmotic coefficients of some electrolyte solutions.*

m^s	$Ph_2C(OH)\cdot HSO_4$	$NaHSO_4$	$LiHSO_4$	$KHSO_4$	NH_4HSO_4	$AgHSO_4$	$AgHSO_4$*	H_3O,HSO_4	H_2O,HSO_4*	$Ba(HSO_4)_2$
0·000	0·980	0·980	0·980	0·980	0·980	0·980	0·980	0·980	0·980	0·980
0·005	—	0·979	0·979	0·979	0·979	—	—	0·984	0·981	—
0·010	—	0·980	0·980	0·980	0·978	—	—	0·976	0·976	0·979
0·015	—	0·982	0·979	0·979	0·977	—	—	0·975	0·976	—
0·020	—	0·982	0·979	0·979	0·973	—	—	0·975	0·978	0·971
0·025	—	0·983	0·981	0·981	0·979	—	—	0·978	0·979	—
0·030	1·001	0·985	0·981	0·981	0·978	0·976	0·988	0·970	0·976	0·986
0·035	1·008	0·987	0·984	0·984	0·977	0·976	0·989	—	—	—
0·040	1·008	0·989	0·983	0·983	0·974	0·969	0·985	0·967	0·979	1·011
0·05	1·011	0·989	0·981	0·980	0·975	0·962	0·983	—	—	1·025
0·06	1·012	0·992	0·985	0·985	0·976	0·960	0·983	0·953	0·979	1·035
0·07	1·020	0·994	0·988	0·988	0·978	0·958	0·983	—	—	1·042
0·08	1·022	0·996	0·988	0·988	0·978	0·954	0·983	0·942	0·977	1·047
0·09	1·029	0·996	0·989	0·989	0·979	0·952	0·981	—	—	1·055
0·10	1·032	0·998	0·989	0·989	0·977	0·948	0·986	0·937	0·979	1·062
0·12	1·042	1·003	0·993	0·991	0·977	0·944	0·989	0·933	0·978	—
0·14	1·056	1·013	0·996	0·993	0·976	0·940	0·992	0·927	0·982	—
0·16	1·067	1·020	1·001	0·997	0·977	0·937	0·995	0·924	0·987	—
0·18	1·078	1·031	1·004	1·000	0·976	0·935	0·997	0·921	0·988	—
0·20	1·089	1·032	1·005	1·001	0·975	0·930	1·000	0·920	0·992	—
0·22	1·098	1·038	1·007	1·003	0·974	0·921	1·002	0·914	0·992	—
0·24	1·112	1·044	1·015	1·006	0·975	0·915	1·003	0·911	0·992	—
0·26	—	1·051	1·018	—	—	0·913	1·006	0·908	0·993	—
0·28	—	1·054	—	—	—	0·910	1·006	0·906	0·997	—
0·32	—	—	—	—	—	—	—	0·898	0·998	—
0·36	—	—	—	—	—	—	—	0·893	1·000	—
0·40	—	—	—	—	—	—	—	0·888	1·005	—

* $K_b = 1$.

Interionic Forces.—The contribution of electrostatic interionic forces to the osmotic coefficient may be obtained from the Debye–Hückel theory. The exact expression for the contribution of interionic electrostatic forces to the free energy of the solution G^{el} has been given by Fowler and Guggenheim[3] (equation 918·1) and from this it may be shown that ϕ^{el} is given by the expression:

$$\phi^{el} = -0{\cdot}223 I^{\frac{1}{2}} |z_+ z_-| \sigma(0{\cdot}273 \mathring{a} I^{\frac{1}{2}}) \, . \, c/m\rho \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

where σ is of the form $\sigma(x) = 3/x^3[(1 + x) - 2 \ln (1 + x) - 1/(1 + x)]$; c is the molar concentration of electrolyte, m its molal concentration, I is the ionic strength $[\frac{1}{2}c(\nu_+ z_+^2 + \nu_- z_-^2)]$, ν_+ and ν_- are the numbers of moles of cation and anions respectively produced by one mole of electrolyte, z_+ and z_- are the valencies of the cations and anions respectively, $\mathring{a}$ is the distance of closest approach of cation and anion, and ρ is the density of the solution. As explained in Part XXVII the numerical constants in this equation have been calculated by using a value of 120 at 10° for the dielectric constant of sulphuric acid.

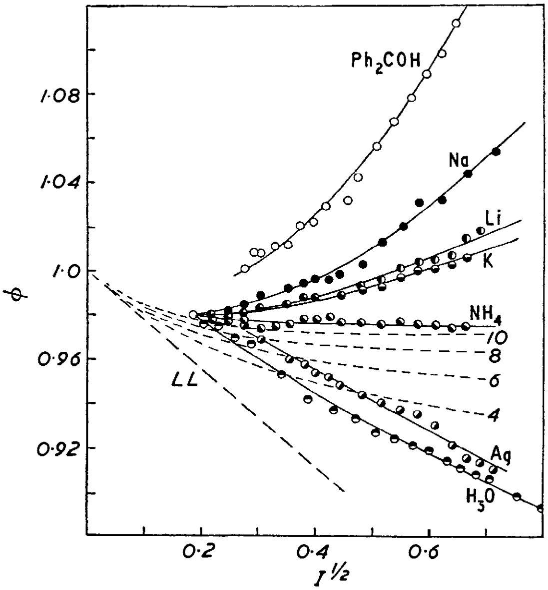

FIG. 1. *Osmotic coefficients.*
---- *Calculated curves* $(1 + \phi^{el})$ (*equation* 3. *with the values of* $\mathring{a}$ *indicated*). *LL* = *Debye-Hückel limiting law.*

The term $(1 + \phi^{el})$ is plotted against $I^{\frac{1}{2}}$ for different values of the parameter $\mathring{a}$ in Fig. 1. For $\mathring{a} \geqslant 10$ the value of $1 + \phi^{el}$ is almost independent of concentration over the range accessible in sulphuric acid.

It may be seen that the electrostatic term alone is not sufficient to account for the osmotic coefficients of most of the electrolytes studied. Ionic solvation and other factors not considered in the Debye-Hückel theory are allowed for in an empirical manner by the linear term $b\sum m_i$ where b is an arbitrary constant.

Determination of $\mathring{a}$ *and* b *Values.*—A plot of $(\phi - \phi^{el})$ against $\sum m_i$ should be a straight line of slope b intersecting the vertical axis at $\phi - \phi^{el} = 1{\cdot}0$. A set of such plots for $KHSO_4$ for different values of $\mathring{a}$ is shown in Fig. 2. Only $\mathring{a} = 10$ gives a straight line that extrapolates satisfactorily to $\phi - \phi^{el} = 1{\cdot}0$, and this is chosen to be the best value for this electrolyte. Although the plots for other values of $\mathring{a}$ are not straight lines over the whole of the concentration range their linear portions all have very nearly the same slope, so that the value of b can be determined almost independently of $\mathring{a}$. For $KHSO_4$ the value of b was found to be 0·07. Values for $\mathring{a}$ of 10 ± 2 were obtained in the same way for all the electrolytes, except silver and hydroxonium hydrogen sulphates which gave much smaller values, of the order of 2. The results for the last two electrolytes could be fitted almost as well with $\mathring{a} = 10$ and a negative value for b of $-0{\cdot}1$. Plots of $(\phi - \phi^{el})$ for all the

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[3] Fowler and Guggenheim, "Statistical Thermodynamics," Cambridge Univ. Press, 1949.

TABLE 3. *Values of å, b and s from equilibrium freezing points.*

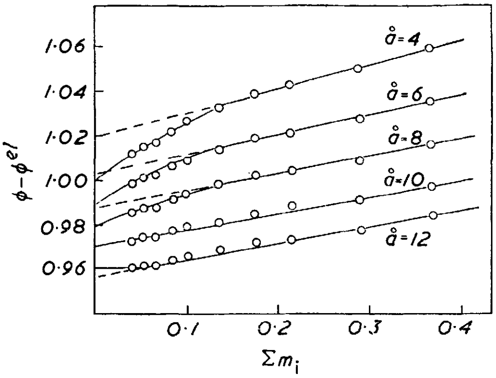
Cation	å (exp.)	å (calc.)	b	s (eq. 7)	s (eq. 12)	h *
Ba^{++}	10	10·1	0·32	11·5	6·5	3·0
Ph_2COH^+	10	—	0·28	6·6	1·3	—
Na^+	10	9·7	0·14	3·8	3·0	2·0
Li^+	10	9·3	0·08	2·6	2·3	3·4
K^+	10	10·0	0·07	2·4	2·1	0·6
NH_4^+	10	10·2	0·015	1·2	1·2	0·2
Ag^+	2	10·0	0	—	—	—
H_3O^+	2	10·2	0	—	—	4·0
Ag^+ ($K_b = 1$)	10	10·0	0·07	2·4	2·1	—
H_3O^+ ($K_b = 1$)	10	10·2	0·06	2·1	1·8	4·0

* Hydration numbers in aqueous solution (ref. 7).

electrolytes, and for å = 10 in each case, are shown in Fig. 3 and the corresponding values of b are given in Table 3.

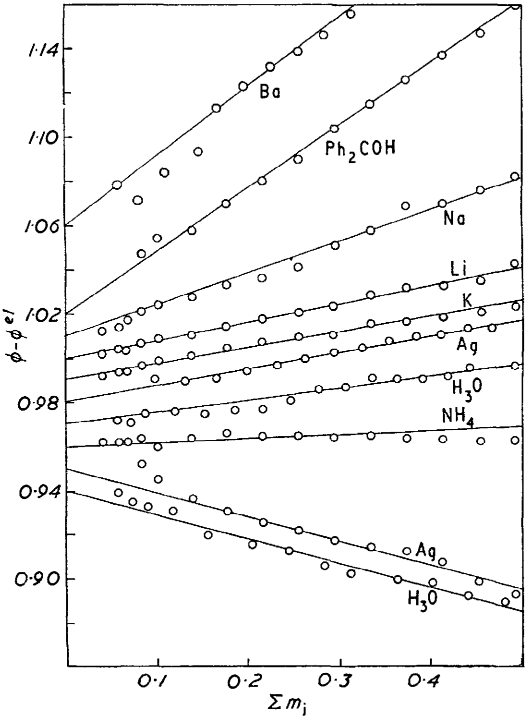
In view of the limited accuracy with which they can be determined no significance can be attached to small differences between the å values for different electrolytes. The value of å = 10 is larger than is generally found for electrolytes in aqueous solution. Gillespie and Oubridge [1] pointed out that such a value could be accounted for if it was assumed that there is a solvation sheath at least one solvent molecule thick between oppositely charged ions when they collide. Wicke and Eigen [4] have previously made this assumption for

FIG. 2. *Determination of the value of å for potassium hydrogen sulphate.*



The plots are vertical with respect to the upper one by −0·01 *on the vertical axis.*

FIG. 3. *Plots of* (ϕ − ϕ^{el}) *for determining b values.*



The curves are shifted vertically with respect to that for $LiHSO_4$ *by the following amounts*: Na +0·01, Ph_2COH +0·02, Ba +0·6, K −0·01, Ag −0·02, H_3O −0·03, NH_4 −0·04.

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[4] Wicke and Eigen, *Z. Elektrochem.*, 1953, **57**, 319.

strong electrolytes in aqueous solutions. Collision diameters calculated on this basis from the ionic crystal radii of the cations (r^+) and estimated values[1] of the radii of the hydrogen sulphate ion ($r^- = 2{\cdot}90$ Å) and the diameter of a sulphuric acid molecule ($d = 5{\cdot}80$ Å), *i.e.*, $\mathring{a} = r^+ + r^- + d$, are given in Table 3. They agree well with the observed values.

It is definitely not possible to account for the observed osmotic coefficients with a collision diameter as small as the sum of the ionic radii, which is 3·5—4·5 Å, when a radius of 2·9 Å is assumed for the hydrogen sulphate ion.[1] Gurney[5] pointed out for the case of aqueous solutions that, because of the high dielectric constant of the solvent and the consequent reduction in the electrostatic forces between the ions, approximately 1 Å should be added to the sum of the crystal radii in order to obtain the distance of closest approach of oppositely charged ions in solution. A similar calculation, with allowance for the higher dielectric constant of sulphuric acid, shows that not more than 2 Å should be added, leading to expected values of the distance of closest approach of the order of 5·5—6·5 Å. The higher observed value seems to provide evidence of the existence of a solvation sheath around at least one of the ions which is not penetrated on collision with an ion of opposite charge.

This rather large value of $\mathring{a}$ and the high ionic strength of the pure solvent mean that although interionic forces are not negligible in sulphuric acid their effect is practically constant over all the accessible range of ionic strengths (Fig. 1).

Ion Solvation.—The linear term $b\Sigma m_i$ in equation 1 was interpreted by Gillespie and Oubridge[1] in terms of ion–solvent interaction. If we similarly assume that, apart from the effects of electrostatic forces between solvated ions, the only contribution to the non-ideality of the solutions considered comes from the removal of solvent molecules by ion solvation, then we can write for the free energy of the solution:

$$G = n_1\mu_1^\circ + n_2\mu_2^\circ + G^{\text{el}} + \boldsymbol{R}T\left[n_1\nu_+ \ln\frac{n_1\nu_+}{\nu n_1 + n_2} + n_1\nu_- \ln\frac{n_1\nu_-}{\nu n_1 + n_2} + n_2 \ln\frac{n_2}{\nu n_1 + n_2}\right] \quad (4)$$

where n_1 is the number of moles of " free " solvent, n_2 is the number of moles of solute, ν_+ is the number of moles of positive ions, ν_- the number of moles of negative ions, and $\nu = \nu_+ + \nu_-$ is the total number of ions produced by one mole of the solute, G^{el} is the electrical contribution to the free energy, and μ_1° and μ_2° are the standard-state chemical potentials of the solvent and solute respectively.

If n_s is the total number of moles of solvent, *i.e.*, $n_s = n_1 - n_2 s$, where s is the solvation number of the solute, then differentiating with respect to n_s at constant n_2 gives:

$$\mu_s = \mu_s^\circ + \boldsymbol{R}T \ln\frac{n_s - n_2 s}{n_2(\nu - s) + n_s} + \mu^{\text{el}} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Now since $n_2/n_s = m/M$, where m is the molality of the solute and M is the number of moles of solute per kg. of solvent, and the osmotic coefficient is defined by:

$$\mu_s = \mu_s^\circ - \boldsymbol{R}T\nu m\phi/M$$

we have

$$\phi = 1 + \phi^{\text{el}} + (2s - \nu)m/2M \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

For sulphuric acid solutions we replace m by $\Sigma m_{ij}/2$ and since $M = 10{\cdot}2$ we see by comparison with equation 1 that

$$b = (2s - \nu)/40{\cdot}8, \text{ i.e., } s = 20{\cdot}4 + \nu/2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Values of s calculated from equation 7 are given in Table 3.

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[5] Gurney, " Ionic Processes in Solution," McGraw-Hill, New York, 1953.

Entropy of Mixing.—Glueckauf[6] has pointed out that this type of treatment ignores the entropy of mixing of the solvent molecules and the solvated ions which will in general differ in size. He pointed out that this can be conveniently allowed for by using volume-fraction rather than mole-fraction statistics. Thus the expression for the free energy is written in the form:

$$G = n_1\mu_1^\circ + n_2\mu_2^\circ + G^{\text{el}} + \boldsymbol{R}T\left[n_2\nu_+ \ln \nu_+ \frac{n_2\bar{v}_2{}^+}{V} + n_2\nu_- \ln \nu_- \frac{n_2\bar{v}_2{}^-}{V} + n_1 \ln \frac{n_1\bar{v}_s}{V}\right] \quad (8)$$

where $\bar{v}_2{}^+$ and $\bar{v}_2{}^-$ are the partial molar volumes of the hydrated ions, $\bar{v}_s$ is the partial molar volume of the solvent, and V is the volume of the solution

$$V = n_2\,(\nu_+\bar{v}_2{}^+ + \nu - \bar{v}_2{}^-) + n_2\bar{v}_s = n_2\phi_v + n_s v_s{}^\circ \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where ϕ_v is the apparent molar volume of the electrolyte (unsolvated), and $v_s{}^\circ$ is the molar volume of the pure solvent.

Differentiating with respect to n_s at constant n_2 and substituting $r = \phi/v_s{}^\circ$ we obtain:

$$\phi = \phi^{\text{el}} + \frac{m}{M\nu}\left[\frac{(r+s)^2}{2} - r\nu\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

For sulphuric acid solutions we replace m by $\Sigma m_{ij}/2$ and hence

$$b = \left[\frac{(r+s)^2}{2} - r\nu\right]\Big/2M \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

or

$$b = \frac{(r+s)^2}{40{\cdot}8} - \frac{r}{20{\cdot}4},\ \textit{i.e.},\ s = [2\nu(20{\cdot}4b + r)]^{\frac{1}{2}} - r \quad . \quad . \quad . \quad (12)$$

The apparent molar volumes, ϕ_v, are given in the following paper. Values of s calculated from equation (12) are given in Table 3.

Since all the electrolytes studied have the hydrogen sulphate ion as a common cation, the solvation numbers reflect the relative extents of solvation of the cations. In view of the large size of the hydrogen sulphate ion and its general similarity to the solvent molecules, it is, perhaps, not unreasonable to assume that the hydrogen sulphate ion is not solvated, in which case, the observed values may be regarded as the solvation numbers of the cations.

It is interesting that equation (12) gives a smaller and more reasonable solvation number for the highly solvated, and therefore large, barium ion, and also for the large Ph_2CO,H^+ ion than does equation (7). The solvation numbers given by the Glueckauf treatment are of reasonable magnitude for primary solvation numbers and generally show the expected variation with ion size and charge. Lithium appears to be anomalous in that its solvation number is less than that of sodium. This can probably be attributed to the fact that the maximum co-ordination number of the lithium ion for sulphuric acid molecules is only three while that of the sodium ion is four.[1] Solvation numbers in sulphuric acid generally appear to be rather larger than in aqueous solution (Table 3), and this is consistent with the probably greater polarity of the sulphuric acid molecule. An exception is provided by the hydroxonium ion which has a solvation number of 1·8 in sulphuric acid but a hydration number of 4·0 in water; the high hydration number of the oxonium ion can be attributed to its special relation to the structure of water.[7]

Silver and Hydroxonium Hydrogen Sulphates.—The interpretation of the low osmotic coefficients of the solutions of $AgHSO_4$ and H_3O,HSO_4 is not quite certain. In view of the incomplete dissociation shown by some silver salts in aqueous solution, and the incomplete dissociation of liquid sulphuric acid monohydrate,[8] it does not seem unreasonable to

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[6] Glueckauf, *Trans. Faraday Soc.*, 1955, **51**, 1235.

[7] Bascombe and Bell, *Discuss. Faraday Soc.*, 1957, **24**, 158; Ackermann, *ibid.*, p. 180.

[8] Young and Blatz, *Chem. Rev.*, 1949, **44**, 93; Young, in "The Structure of Electrolyic Solutions," ed. Hamer, Wiley, New York, 1959.

assume that $AgHSO_4$ and H_3O,HSO_4 might be incompletely dissociated in dilute solution in sulphuric acid. In the former case there could be some covalent contribution to the bonding between the silver and the hydrogen sulphate, and in the latter there could be strong hydrogen-bonding between an H_3O^+ ion and an HSO_4^- ion or between a water molecule and a sulphuric acid molecule, *i.e.* $H_2OH^+ \cdots OSO_3H$ or $H_2O \cdots HOSO_3H$. In fact, if a dissociation constant of the order of unity is assumed for both these electrolytes then their osmotic coefficient curves closely resemble those of the other electrolytes studied (Fig. 4). Ionic concentrations for solutions of water ($K_b = 1$) have been given in the preceding paper. The ionic concentrations for silver hydrogen sulphate ($K_b = 1$) were calculated in the same manner. However, it is rather difficult to reconcile this explanation of the osmotic coefficients of the solutions with their electrical conductivities (to be discussed in a following paper) and a possible alternative explanation would be that H_3O^+ and Ag^+ are " structure-breaking " ions although it is not easy to see why they should differ from ions such as K^+ and NH_4^+ in this respect.

FIG. 4. *Effect of allowing for the possible incomplete dissociation of silver and hydroxonium hydrogen sulphates on the osmotic coefficients of their solutions.*

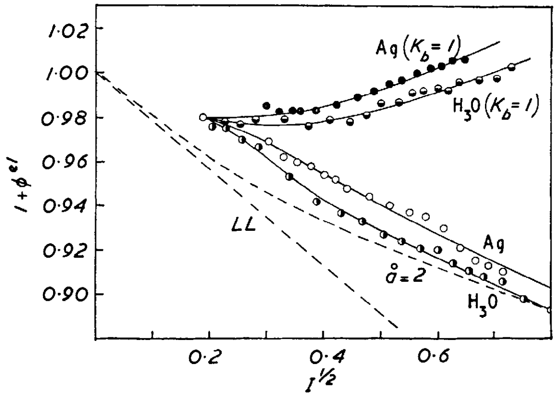
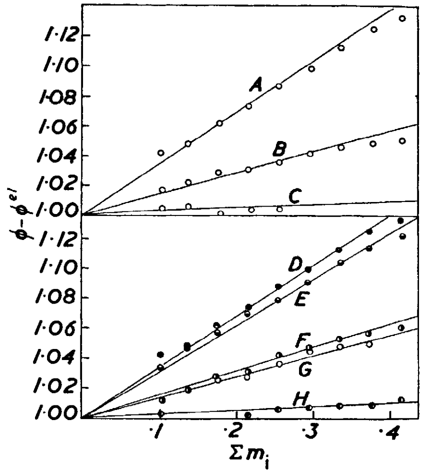


FIG. 5. *Plots of* ($\phi - \phi^{el}$) *for organic bases.*



A, NPh_3. *B*, $NHPh_2$. *C*, NH_2Ph. *D*, (p-Me·$C_6H_4)_2CO$. *E*, $COPh_2$. *F*, COPhMe. *G*, (p-Cl·$C_6H_4)_2CO$. *H*, $COMe_2$.

Organic Bases.—The deviations from ideal behaviour caused by the large size of the conjugate acid of benzophenone are large enough to have shown themselves in the early measurements of Treffers and Hammett.[9] They found the apparent ν values (or *i*-factors) for this substance to increase from 1·94 to 2·31 with increasing concentration. Similar results were later obtained by Leisten [10] who pointed out that it was unlikely that they could be attributed to solvation since this would require unreasonably large solvation numbers. In order to investigate more fully the non-ideality of solutions of electrolytes with large cations, freezing points of solutions of a number of organic ketones and amines were measured by the Beckmann method. Freezing-point depressions calculated from the hypothetical freezing point of undissociated sulphuric acid (10·625°) are given in Table 4. They are not as accurate as the equilibrium measurements discussed above, but they are somewhat better than the measurements of Gillespie and Oubridge [1] because of the use of an improved supercooling correction (see Experimental section). It may be seen in the case of benzophenone that the freezing-point depressions obtained by the

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[9] Treffers and Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 1708.
[10] Leisten, Thesis, London, 1952.

Beckmann and the equilibrium method agree within 1% (Tables 1 and 4). The differences between the freezing-point depressions of the various bases are generally considerably larger than this, so the osmotic coefficients at least have a relative significance. The freezing-point depressions show that all these organic bases, including the very weakly basic triphenylamine, are fully ionised according to the equation: $B + H_2SO_4 = BH^+ + HSO_4^-$, and this has been confirmed by conductivity measurements. Osmotic coefficients calculated by means of equation 1, with the values of Σm_{ij} given in Table 2 of Part XXVII, are given here in Table 5. In many cases large deviations from ideal behaviour are shown and for a given type of base these deviations increase with increasing size of the cation.

Values of the parameter b were again obtained from plots of $(\phi - \phi^{el})$ against Σm_{ij}. These were found to be straight lines, except at the highest concentrations, with intercepts on the vertical axis close to the expected value of 1·0 if $\mathring{a}$ was given a value of 10 as before (Fig. 5). By use of the Robinson–Stokes theory (equation 7) solvation numbers were calculated from the b values and are given in Table 6: here the larger organic bases have large apparent solvation numbers. By allowing for the effect of the size of the electrolytes according to the Glueckauf theory (equation 12), the smaller and more reasonable solvation numbers also given in Table 6 were obtained. It is thus clearly demonstrated that the large deviations from ideal behaviour shown by these organic bases are mainly due to their size.

TABLE 4. *Freezing-point depressions (Beckmann method).*

m^s	$COMe_2$	COPhMe	$COPh_2$	$(p\text{-}Me\cdot C_6H_4)_2CO$	$(p\text{-}Cl\cdot C_6H_4)_2CO$	NH_2Ph	$NHPh_2$	NPh_3
0·04	0·612°	0·629°	0·632°	0·637°	0·618°	0·613°	0·620°	0·648°
0·06	0·841	0·864	0·869	0·870	0·846	0·834	0·849	0·895
0·08	1·069	1·096	1·115	1·122	1·090	1·054	1·086	1·150
0·10	1·288	1·338	1·377	1·384	1·334	1·289	1·328	1·403
0·12	1·527	1·584	1·644	1·653	1·584	1·521	1·575	1·669
0·14	1·764	1·834	1·914	1·929	1·836	—	1·827	1·952
0·16	2·002	2·084	2·196	2·216	2·093	—	2·079	2·234
0·18	2·247	2·336	2·479	2·503	2·351	—	2·332	2·511
0·20	2·488	—	2·761	2·787	2·607	—	2·582	—

TABLE 5. *Osmotic coefficients of some organic bases.*

m^s	$COMe_2$	COPhMe	$COPh_2$	$(p\text{-}Me\cdot C_6H_4)_2CO$	$(p\text{-}Cl\cdot C_6H_4)_2CO$	NH_2Ph	$NHPh_2$	NPh_3
0·04	0·976	1·002	1·008	1·016	0·986	0·978	0·989	1·023
0·06	0·987	1·012	1·019	1·021	0·992	0·978	0·995	1·034
0·08	0·986	1·010	1·029	1·034	1·000	0·972	1·001	1·060
0·10	0·974	1·011	1·042	1·046	1·002	0·975	1·003	1·066
0·12	0·978	1·014	1·051	1·059	1·014	0·975	1·008	1·085
0·14	0·979	1·017	1·063	1·071	1·019	—	1·014	1·091
0·16	0·981	1·020	1·076	1·085	1·025	—	1·018	1·105
0·18	0·981	1·022	1·086	1·097	1·029	—	1·021	1·117
0·20	0·985	—	1·094	1·105	1·033	—	1·023	1·124

TABLE 6. *Values of b and s for organic bases.*

	b	s (eq. 7)	s (eq. 12)		b	s (eq. 7)	s (eq. 12)
$COMe_2$	0·025	1·5	1·0	$(p\text{-}Cl\cdot C_6H_4)_2CO$	0·15	4·0	0·5
COPhMe	0·14	3·8	1·4	NH_2Ph	0·025	1·5	0·8
$COPh_2$	0·31	7·2	1·3	$NHPh_2$	0·14	3·8	0·6
$(p\text{-}Me\cdot C_6H_4)_2CO$	0·34	7·8	1·1	NPh_3	0·31	7·2	0·6

It seems that in many cases the plots of $(\phi - \phi^{el})$ are not quite linear at high concentrations, but their slope decreases, corresponding to the apparent decrease in the solvation number, with increasing concentration. This might be due to experimental error in the freezing points but it seems to be more noticeable with the larger cations and may well be a real effect. Because of their large size these organic cations will be surrounded in the solution by a large number of (probably ten or more) sulphuric acid molecules. Since the measured solvation numbers are much smaller than this, one must suppose that these solvent molecules are held only rather loosely by the cation, the measured solvation number representing the equivalent number of more strongly held solvent molecules. It then seems plausible that in relatively concentrated solutions competition for solvent molecules between neighbouring cations will become noticeable, leading to a decrease in the solvation number. In a 0·2m-solution there are 50 solvent molecules for each cation–anion pair. If the cation has ten or more solvent molecules in its first solvation shell, there will be competition for molecules in the second solvation layer. A similar effect was noticed by Stokes and Robinson [11] who found an apparent decrease in solvation numbers in aqueous solution when 20—25% of all the water molecules are bound to ions as water of hydration.

Conclusion.—The non-ideal behaviour of electrolyte solutions in sulphuric acid can be attributed mainly to the effects of ion solvation and ion size. Electrostatic interionic forces are not negligible but because of the high dielectric constant of sulphuric acid and the high ionic strength of the pure solvent the effect of these forces is almost independent of the concentration of any electrolyte. This largely accounts for the fact that the effects of interionic forces were not noticed by earlier workers [9,12] who incorrectly concluded that interionic forces in sulphuric acid were negligible.

Experimental.—The experimental determination of the equilibrium freezing points has been described in a preceding paper.[2] The experimental procedure for the Beckmann method of measuring freezing points has been previously described.[12] A modified supercooling correction, $\delta T = 0{\cdot}03S\theta_{obs}$ where S in the amount of supercooling and θ_{obs} the observed freezing-point depression, was used. The factor 0·03 replaces the factor 0·012 used previously and makes an approximate allowance for the heat capacity of the cryoscope. This was obtained by direct measurement and also by comparison of the freezing points of metal sulphate solutions determined by both the equilibrium and the Beckmann method.

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[11] Stokes and Robinson, *J. Amer. Chem. Soc.*, 1948, **70**, 1870.
[12] Gillespie, Hughes, and Ingold, *J.*, 1950, 2473.