B^{10}_2 molecules must be very nearly the same for each type of molecule.

Table VII also contains the monoisotopic spectra of the deuterated diboranes calculated from B_2D_6 ($B^{11}_2D_x$ and $B^{11}_2D_xH$) and from $B^{10}_2D_6$ ($B^{10}_2D_x$ and $B^{10}_2D_xH$). These samples contained 97–98% D and as a result there were some molecules of B_2-D_5H originally present. There is no way to distinguish between ions from B_2D_6 and from B_2D_5H once the H atom has been removed and the contributions to B_2D_4, B_2D_3, B_2D_2, etc., are the sums of the fragments from the B_2D_6 and B_2D_5H molecules.

The agreement between the monoisotopic spectra of deuterated diborane calculated from B_2D_6 and $B^{10}_2D_6$ is quite good, especially in view of the fact that there were slightly different total percentages of deuterium in the two compounds.

A comparison of the values obtained for the monoisotopic spectra of the diboranes and the deuterated diboranes confirms the observation made previously on normal deuterated diboranes[17] that there is an isotope effect in the fragmentation of deuterated diborane. Due to the scarcity of parent ions $B_2X_6^+$ in the diborane mass spectra, no attempt has been made to calculate the weighing factors for the rupture of B–H or B–D bonds.

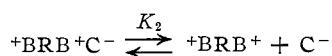BALTIMORE, MD.

Some Further Comments on the Properties of Bolaform Electrolytes

BY STUART A. RICE

The equilibrium and transport properties of bolaform electrolytes are considered with emphasis on the necessity for self-consistency of molecular parameters. It is shown that the application of the hydrodynamic theory of short chains leads to results in agreement with secondary dissociation constants and with the distribution of end to end distances. The diffusion coefficient of a bolaform electrolyte is calculated and the role of ion atmosphere asymmetry discussed, the result being: $\mathfrak{D} = \mathfrak{D}_0[1 + q_2q_1\kappa/2DkT + q_2q_1\kappa^2 h/4DkT]$.

I. Introduction

From the structural point of view bolaform electrolytes partially bridge the gap between ordinary electrolytes and polymeric electrolytes. It is therefore to be anticipated that the properties of solutions of bolaform electrolytes will likewise be intermediate between the properties of solutions of small electrolytes and of polyions. For example, the very precise conductance measurements of Fuoss, et al.,[1-4] have demonstrated the existence of ion pair formation between the bolaform ion (bolion) and its counterions even in solvents such as water. The magnitude of the dissociation con-

$$+BRB^+C^- \underset{\longleftarrow}{\overset{K_2}{\rightleftharpoons}} +BRB^+ + C^-$$

stant for the reaction varies with the dielectric constant in the expected manner,[1] and charge separations computed from the Bjerrum relation[5] for the ratio of the dissociation constants of a dibasic acid are consistent with the known structures of the bolions. It has been proposed that the phenomena of ion pair formation in bolaform electrolytes[6] is closely related to a similar phenomenon observed in solutions of polyelectrolytes.[7-9] A study of the equilibrium and transport properties of bolaform electrolytes therefore has relevance for the analogous but much more difficult problems arising in the consideration of these same properties of poly-

(1) R. M. Fuoss and D. Edelson, THIS JOURNAL, **73**, 269 (1951).

(2) R. M. Fuoss and V. H. Chu, ibid., **73**, 949 (1951).

(3) H. Eisenberg and R. M. Fuoss, ibid., **75**, 2914 (1953).

(4) O. V. Brody and R. M. Fuoss, J. Phys. Chem., **60**, 156 (1956).

(5) N. Bjerrum, Z. physik. Chem., **106**, 219 (1923).

(6) S. A. Rice, THIS JOURNAL, **78**, 5247 (1956).

(7) F. E. Harris and S. A. Rice, J. Phys. Chem., **58**, 725, 733 (1954).

(8) S. A. Rice and F. E. Harris, J. Chem. Phys., **24**, 326, 336 (1956).

(9) F. E. Harris and S. A. Rice, ibid., **25**, 955 (1956).

electrolytes. In this communication we shall extend our previous discussion[6] to an examination of the magnitude of the ion pair dissociation constant, of the limiting conductance and of the concentration dependence of the frictional coefficient in dilute solution. Throughout our emphasis will be on the necessity for internal consistency between molecular parameters deduced from equilibrium and non-equilibrium properties in a manner rather different from the classical analysis of Fuoss.[1,3]

II. The Secondary Dissociation Constant as a Function of Chain Length

We consider first the ion pair dissociation constants and the intercharge separations required to fit the experimental data. The dissociation equilibrium discussed in section I may be characterized by the mass action expression

$$K_2 = c_{C^-} \frac{K_s^0(2\alpha - 1) + \alpha c_{C^-}}{2K_s^0(1 - \alpha)} \tag{1}$$

where K_s^0 is the intrinsic dissociation constant for the group in question ($K_1 = 2K_s^0$), α is the degree of dissociation and c_{C^-} is the concentration of the counterions to the bolion. The relationship between the degree of dissociation α and the electrostatic energy of interaction, χ, readily can be shown to be[6]

$$\alpha = \frac{\lambda + \lambda^2 e^{-\chi/kT}}{1 + 2\lambda + \lambda^2 e^{-\chi/kT}} \tag{2}$$

where λ plays the role of an absolute activity. In general, the relation required for closure of the set of equations is

$$\ln a_{C^-} + \ln \lambda - \ln K_s^0 = 0 \tag{3}$$

where a_{C^-} is the activity of the counterions. Equations 2 and 3 suffice for the calculation of the counterion activity or, if this is known, of

the degree of dissociation presuming only that the intrinsic dissociation constant K_s^0 and the interaction energy χ are known. In sufficiently dilute solution the activity of the counterions may be approximated by the counterion concentration with the result that

$$\lambda = \frac{K_s^0}{c_{0^-}} \tag{4}$$

under the same conditions wherein Eq. 1 is accurate.[10]

There are two matters which must be considered before the calculations can be made. These are the assignment of the dielectric constant for the interaction of the two charges on the same bolion and the magnitude of the intrinsic dissociation constant. The work of Hasted, Ritson and Collie[11] indicates that the dielectric constant in the immediate vicinity of a charge is very much lower than the bulk value. From studies of the dielectric properties of electrolytes in water these investigators found that the dielectric constant was as low as 5 at a distance of about 1 Å. and that it rose to the bulk value only when the distance from the ion had increased to about 4–5 Å. In the particular case of bolaform electrolytes most of the data in the literature[1–4] refer to solutions in alcohols and other organic solvents of moderate to low dielectric constant. The dissociation data for the compounds chosen for comparison in this note refer to methanol solutions. Alcohols in general have less "quasi-crystalline" structure than water and though one would expect a similar decrease in dielectric constant as the ion is approached, this effect should not persist to as great distances from the ion as is the case in water. We shall use the bulk dielectric constant for the interaction of all charged groups separated by more than 4 Å. in methanol. Effective dielectric constants computed from the theory of Kirkwood and Westheimer[12] are in agreement with this choice. The assignment of the intrinsic dissociation constant presents problems of a different nature. Of course, we are guided by the knowledge that for a strong electrolyte the intrinsic dissociation constant must be large. There is, however, no reliable method of estimation available inasmuch as the dissociation constant may depend upon other factors than the bulk dielectric properties of the medium.[13] Therefore, the experimental value of the dissociation constant for one compound together with an assumed charge separation has been used

to compute a value of K_s^0 and then this value of K_s^0 employed to calculate the dissociation constants for other homologous compounds. The values of K_s^0 and the assumed distance are not arbitrary since they must satisfy a self-consistency condition which will become apparent later.

Using 31.5 for the dielectric constant of methanol, and an assumed charge separation of 8.8 Å., the observed dissociation constant (4.4×10^{-3}) of $Br(Me_3N)CH_2)_2CO_2(CH_2)_2CO_2(CH_2)_2NMe_3)Br$ leads to a computed intrinsic dissociation constant of 6.6×10^{-2}. This is comparable with experimental data for similar type dissociations of other quaternary ammonium salts. In Table I are listed the charge separations and the corresponding calculated values of K_2 for two similar compounds.

TABLE I

Compound	K_2(expt.)[1–4]	K_2(calcd.)	Charge sepn., Å.
$BrMe_3N(CH_2)_3NMe_3Br$	1.04×10^{-3}	1.05×10^{-3}	5.1
$BrMe_3N(CH_2)_5NMe_3Br$	1.58×10^{-3}	1.52×10^{-3}	5.7

The implication of the computed distances will be discussed in the next section. Here we merely note that the increment of 0.3 Å./CH_2 group indicated is far less than that expected for a completely extended chain.

Before leaving this section it is pertinent to make some comments about the nature of the equilibrium constant K_2. Fuoss[4] has proposed that K_2 is not a true equilibrium constant determined by the usual criteria of thermodynamic equilibrium but rather depends upon some geometric factors which determine the kinetics of the association reaction at the charge site.

It is important to note that on general grounds the use of a steric factor cannot be correct since: (a) the use of the steric factor suggested by Fuoss would lead to a difference between primary and secondary dissociation constants in a molecule with non-interacting groups other than that due to the symmetry properties of the molecule and (b) the effective volume (kinetic) blocked by the molecule should be effectively independent of charge separation. Deduction (a) is in direct conflict with general and well established statistical principles and the comment (b) leads to conclusions at variance with experiment. Further, if it is to be claimed that the steric factor appears in both the primary and secondary dissociations, then it will cancel when their ratio is taken. Since the Bjerrum theory discusses only the ratio of dissociation constants, it cannot be used to deduce evidence for such a steric effect. For these reasons Fuoss' proposal must be rejected.

III. Configurational Properties of the Molecule

We now turn to an examination of the change in chain configuration with a change in charge state or ionic strength. As previously demonstrated[6] eq. 3 is valid only if there is no change in the dimensions of the molecule when charged. If such a change does occur, then the free energy arising from the interaction between charged groups on the same bolion consists of both the electrostatic self energy of the ion and the free energy change

(10) We prefer to write the secondary dissociation constant in the form (1) with the supplementary condition (2) because the end to end separation may change as a result of ionization. Equations; 1 through 4 are equivalent to the Bjerrum relation *only when there is no change in molecular dimensions on ionization.* See reference 6 for a discussion of the details.

Note that it is not necessary to include activity coefficients in eq. 1 since any convenient low value of c_{0^-} may be chosen for computation purposes, and K_2 is independent of c_{0^-}. To determine K_2 from *experimental* measurements of α, eq. 1 would have to be modified to correct for intermolecular interactions, but that is not the problem under consideration here.

(11) J. B. Hasted, D. M. Ritson and C. H. Collie, *J. Chem. Phys.,* **16**, 1 (1948).

(12) J. G. Kirkwood and F. H. Westheimer, *ibid.,* **6**, 506, 513 (1938).

(13) See for example: C. A. Kraus, *Ann. N. Y. Acad Sci.,* **51**, 789 (1949).

on expansion. Under these conditions eq. 3 is modified to read

$$\ln a_{0^-} + \ln \lambda - \ln K_s^0 + \left(\frac{\partial F_{\text{expansion}}}{\partial \alpha}\right) = 0 \quad (5)$$

Under many conditions the expansion free energy is small relative to the other contributions[7] so that the dominant forces at equilibrium are just those already discussed. If the molecules are sufficiently long the distribution of chain lengths will be gaussian. For a gaussian distribution of end to end separations it may be shown readily that

$$\frac{h_1}{h_0} = \left[1 + \frac{\nu^2 q^2 e^{-\kappa h_1}}{3DkTh_1}(1 + \kappa h_1)\right]^{1/2} \quad (6)$$

with ν the number of charges per chain end, h_1 the root mean square separation of the chain ends in the given charge state, and h_0 the unperturbed (uncharged molecule) root mean square separation of the chain ends. The difference between eq. 6 and the similar relation describing the configurational properties of polyelectrolytes[14] arises from a difference in the distribution of charges along the molecular skeleton.

The applicability of eq. 6 to the compounds under discussion is questionable since it is well known that chains containing small numbers of links do not have a gaussian distribution of end to end distances. In connection with a different problem, machine computations have been made by other investigators of the probability of a given end to end distance for chains of 5, 6, 7 and 8 links, with a fixed bond angle of 110° and where one link in each case is 2.0 Å. long and all the others are 1.5 Å. in length.[15] Some of the results are plotted in Figs. 1 and 2. In Fig. 1 there also appears the probability of a given end to end distance as computed from random statistics with an average bond length dictated by the chain composition mentioned above. As expected, in all cases the machine calculations indicate that the chain is more extended than the equivalent random chain. Of greater importance is the manner in which the distribution of chain lengths changes with distance. From Fig. 1 it is seen that the probability of a given end to end distance tends to zero extremely rapidly once the most probable end to end distance has been exceeded. This decay is much faster than the similar decline for the equivalent randomly coiled chain. Thus, it will require a much greater force to extend the real chain (machine calculations) than the randomly coiled chain. The expansion of the equivalent random chain may be estimated from eq. 6. When $\kappa h_1 \approx 0$ so that the electrostatic interactions are at maximum strength, a random chain of seven links without fixed bond angles expands from 4.18 to 5.89 Å., a factor of 1.41, whereas a random chain of seven links with fixed bond angles of 110° but free rotation about each bond would expand from 5.90 to 7.7 Å., a factor of 1.31. Both of these computations greatly overestimate the expansion due to the fact that a gaussian distribution of end to end separations is only valid when $h_1/L < 0.3$. Since the contour length of the molecule, L, is only 9.06 Å. this con-

(14) F. E. Harris and S. A. Rice, *J. Polymer Sci.*, **15**, 151 (1955).

(15) F. A. Cotton and F. E. Harris, *J. Phys. Chem.*, **60**, 1451 (1956). We wish to thank Prof. F. E. Harris for permission to use his data.
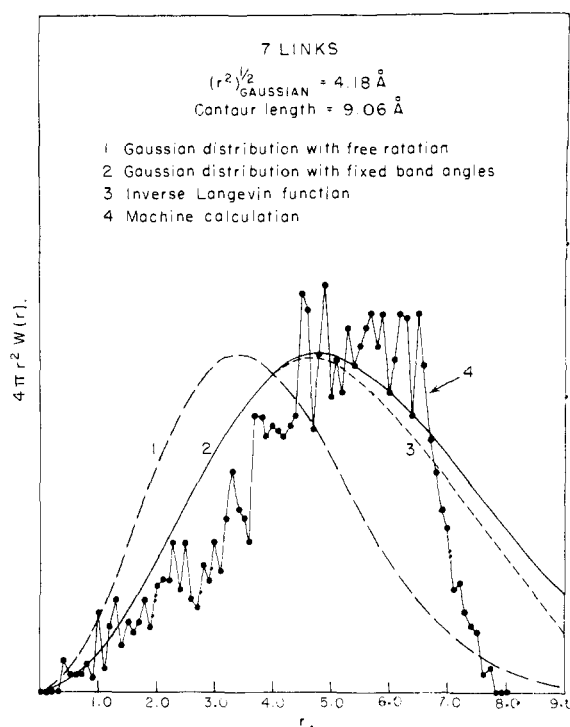

Fig. 1.—Probability of an end to end separation h as a function of h for a chain of 7 links. Note that the contour length is listed as 9.06 Å. This is the contour length with a valence angle of 110°. If the chain had universal joints, the contour length would be 11.06 Å. This latter value was used in the computations with the inverse Langevin function (curve 3).
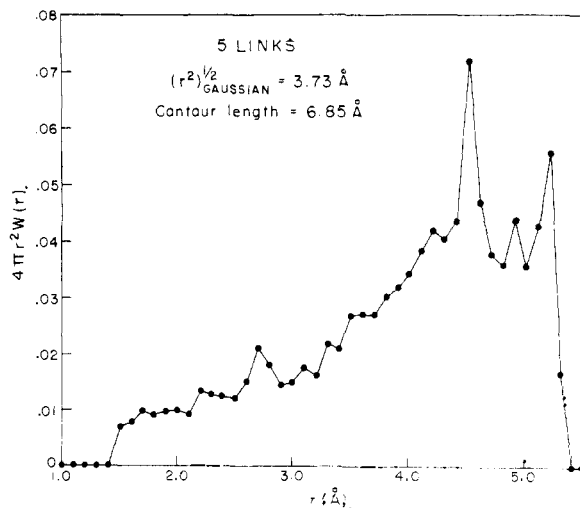

Fig. 2.—Probability of an end to end separation h as a function of h for a chain of 5 links.

dition is clearly violated. The physical reason for the overexpansions is that the gaussian distribution overweights configurations in which the chain ends are far apart by failing to take cognizance of the finite contour length of the molecule. An estimate of the error incurred is obtained easily. The gaussian distribution of end to end separations is only an approximation to the correct distribution function defined by

$$W(h_1)\mathrm{d}h_1 = \text{const.} \times$$

$$\exp\left[-\frac{L}{Zb^2}\int_0^{h_1} L^{-1}(x)\mathrm{d}x\right] 4\pi h_1^2 \mathrm{d}h_1 \quad (7)$$

where b is the length of the monomer and Z the degree of polymerization. With the approximation[16]

$$L^{-1}(x) = 3x\left[1 + \frac{0.6x^2}{1-x^2}\right] \quad (8)$$

where $L^{-1}(x)$ is the inverse Langevin function, the free energy change on stretching the molecule from h_0 to h_1 becomes

$$F_{\text{expansion}} = \frac{3kT}{2}\left[0.4\left(\frac{h_1}{h_0}\right)^2 - 1 - 0.6\left(\frac{L}{h_0}\right)^2 \ln\left(1 - \left(\frac{h_1}{L}\right)^2\right)\right] \quad (9)$$

which leads to the relation

$$\frac{h_1}{h_0} = \left[\frac{1 + \nu^2 q^2 e^{-\kappa h_1}\left(\frac{1 + \kappa h_1}{3DkTh_1}\right)}{0.4 + \frac{0.6}{1-(h_1/L)^2}}\right]^{1/2} \quad (10)$$

Using a charge separation of 5.90 Å. for the unperturbed state, eq. (10) predicts that the chain will only expand, by a factor of 1.13 to 6.63 Å. Moreover, when κh_1 is not small, these expansions will be markedly reduced. The physical basis for the trend in expansions indicated above is qualitatively clear from an examination of Fig. 1. The probability of large end .to end separations is smaller for the distribution function (7) than for a gaussian distribution function. For a real chain (machine calculations) the probability of large chain extensions is still smaller than for the chain described by the distribution function 7. It is clear that when the weighting of large chain extensions is decreased, the root mean square separation of the chain ends must also decrease. The obvious conclusion to be drawn is that to a first approximation the equilibrium end to end separation of short chains remains effectively constant. Care must be exercised in the use of this deduction which may be an adequate approximation for equilibrium properties but which also must certainly be more inaccurate for the description of transport phenomena.

The internal consistency of the proposed bolion model requires that the mean end to end separation of the chain ends be the same as computed either from the secondary dissociation constant K_2 or from the distribution functions plotted in Figs. 1 and 2. From Fig. 1 it is noted that the equilibrium separation of the chain ends of the uncharged chain of seven links is between 5.5 and 6.5 Å. This corresponds very well to the computed charge separation of 5.7 Å. Figure 2 is a plot of the probability of a given end to end distance for a chain of five links. It is seen readily that the probability that the chain be maximally extended is very large. Therefore, for the compound $BrMe_3N(CH_2)_3NMe_3Br$, consisting of four links, it may reasonably be assumed that the chain is maximally extended. This would correspond to a charge separation of 4.93 Å. in good agreement with the computed value of 5.1 Å. This is the first of our internal checks. The use of a different value of K_s^0 would not result in such good agree-

(16) W. Kuhn and F. Grun, *Kolloid Z.*, 101, 248 (1942).

ment so that both the arbitrary choice of charge separation and K_s^0 is severely restricted.

IV. Transport Properties at Infinite Dilution

In this section we shall briefly discuss the conductance of solutions of bolaform electrolytes with a view to ultimate application of similar ideas to polyelectrolyte solutions. Our attention will be focused on testing the relation between conductance and frictional coefficient for consistency with the charge separations already computed. We reserve for the following section our comments about the effects to be expected at finite concentrations.

To determine the frictional forces exerted by the solvent upon a molecule dragged through it the following assumptions are made: (a) The hydrodynamic situation can be described by the usual equations of viscous fluid motion with all effects due to the molecular nature of the flow process absorbed into a frictional coefficient for the chain subunit. (b) The molecule may be adequately approximated by a model in which a series of beads are connected by massless rods. There is a bead at the junction of every two rods, and the rods make a fixed angle $\pi\text{-}\vartheta$ with one another. Due to the perturbation of the flow field about the j'th bead by the presence of the other parts of the molecule, the velocity of the j'th bead contains components arising from all other parts of the molecule. For this model it can be shown that the frictional coefficient for the entire molecule is[17]

$$\zeta = \frac{Z\zeta_0}{1 + \frac{a_0}{Z}\sum_p \frac{Z-p}{r_p}} \quad (11)$$

where ζ_0 is the frictional coefficient for a single bead, Z is the number of beads (degree of polymerization) and a_0 is defined by the Stokes relation

$$\zeta_0 = 6\pi a_0 \eta_0 \quad (12)$$

Peterlin has calculated values of $Z\zeta_0/\zeta$ for $Z = 1$ to $Z = 100$ for various values of the "valence angle" $\pi\text{-}\vartheta$ and for several ratios of the bead diameter to the interbead separation. For very large Z the molecule becomes randomly coiled and the frictional coefficient becomes

$$\zeta = \frac{Z\zeta_0}{1 + \frac{8}{3}\sqrt{\frac{6}{\pi}\frac{Za_0}{h_1}}} \quad (13)$$

whereas if the molecules were rod-like the frictional coefficient would be[18]

$$\zeta = \frac{6\pi\eta_0 b_0 Z}{\ln Z - \left(1 - \frac{6\pi\eta_0 b_0}{2\zeta_0}\right)} \quad (14)$$

where b_0 is the interbead separation. Note the difference between this model and the more familiar rigid ellipsoid for which[19]

$$\zeta = \frac{6\pi\eta_0(b'^2 - a'^2)^{1/2}}{\ln\left(\frac{b'}{a'} + \sqrt{\left(\frac{b'}{a'}\right)^2 - 1}\right)} \xrightarrow[b' \gg a']{} \frac{6\pi\eta_0 b'}{\ln\left(\frac{2b'}{a'}\right)} \quad (15)$$

(17) A. Peterlin, *J. Chim. Phys.*, 47, 7–8, 669 (1950); 48, 1–2, 13 (1951); *J. Polymer Sci.*, 8, 173 (1952).
(18) J. Riseman and J. G. Kirkwood, *J. Chem. Phys.*, 18, 512 (1950).
(19) F. Perrin, *J. Phys. Rad.*, 7, 1 (1936).

where b' and a' are the semi-major and semi-minor axes of the ellipsoid and η_0 is the viscosity of the solvent.

It usually has been assumed tacitly that molecules as small as those under consideration can be adequately approximated as rigid ellipsoids. Accordingly, if the parameter a' or ζ_0 is fixed by one experimental point, then the lengths or the conductances of a homologous series can be calculated from eq. 14 or eq. 15. For the conductance of the polymethylene salts in methanol, fixing a' in eq. 15 with the experimental conductance of $BrMe_3N$-$(CH_2)_5NMe_3Br$ and the length 9.8 Å. (5.7 Å. for the charge separation plus twice the covalent radius of a methyl group), an excellent correlation is found between the computed lengths and the number of atoms in the chain.[20] The conductance data require that there be an increase of 0.89 Å. per CH_2 group added. The increment to be expected if the chain were fully extended is 1.32 Å. This is inconsistent with the increment of 0.3 Å. per CH_2 obtained from the charge separations required to fit the secondary dissociation constant. The discrepancy may be attributed to the fact that even molecules as small as these are far from rigid ellipsoids.

A better model to use for these compounds is a short stiff chain as described previously. Arbitrarily choosing $a_0/b_0 = 0.5$ (other choices have little effect) and using the same compound as above to fix the frictional coefficient per bead, ζ_0, the conductances for all the members of the series that have been measured are shown in Table II. Two different choices of the "valence angle" have been made, $\cos \vartheta = 0.5$ corresponding to a moderate barrier to rotation when the true valence angle is $110°$, and $\cos \vartheta = 0.3$ corresponding to no barrier to rotation for the same valence angle.

TABLE II

n	λ^+ (expt.)	λ^+ (rigid ellipsoid)[a] (eq. 15)	λ^+ (short chain) (eq. 2) $\cos \vartheta = 0.5$	$\cos \vartheta = 0.3$	$2b'$ (Å., rigid ellipsoid)[b]
3	(85)	80.7	90.7	89.7	(8.1)
4	81.1	80.0	85.5	85.0	9.0
6	75.4	78.2	75.3	76.3	11.0
10	66.8	74.5	65.0	66.3	14.3

[a] Computed using 0.3 Å. CH_2 group obtained from the charge separations for $n = 3,5$.   [b] Length required to obtain exact agreement between eq. 15 and expt.

The rigid ellipsoid model predicts a rate of change of the limiting conductance with concentration which is much too small to fit the data. On the other hand, despite the discrepancies between the observed and calculated conductances for the shortest chains, the chain model is in much better over-all agreement with experiment. What is of even greater moment is that the use of the chain model is internally consistent with the charge separations computed from the secondary dissociation constant whereas a glance at the last column of Table II will demonstrate strikingly the extent of the inconsistency between the rigid ellipsoid model and the considerations previously cited. For in-

(20) It is necessary to either neglect the point for the compound $BrMe_3N(CH_2)_3NMe_3Br$ or to reassign it a conductance of about 85. That the conductance of this compound was low was also pointed out by Fuoss.[4]

stance, for $n = 3$ using the charge separation from Table I plus twice the covalent radius of a methyl group leads to a prediction of $2b' = 9.2$ Å., whereas experiment requires $2b' = 8.1$ Å. on a rod model.

V. The Diffusion Coefficient in Dilute Solution

At any finite concentration the speed with which a bolion moves under the influence of an applied force depends upon the well known ion atmosphere relaxation and electrophoretic effects. Only at extreme dilution where $1/\kappa \gg h_1$ is it a valid approximation to assume that the bolion is a divalent ion and that the ion atmosphere is spherically symmetric. When $1/\kappa \leqslant h_1/2$ it is a more reasonable approximation to assume that the atmospheres about each of the charges are almost independent. If it be further assumed that these atmospheres are nearly spherically symmetric, then the relaxation and electrophoretic effects for a bolion are just twice those for an ordinary ion. In the intermediate range the ion atmosphere is not spherically symmetric. Whereas the limiting behavior at infinite dilution is the same for bolions and ordinary divalent ions, this similarity will not persist at higher concentrations. To the effects already mentioned must be added the change in frictional coefficient due to changes in the intercharge separation. Since the intercharge separation is concentration dependent (even though only slightly so for short chains), there will be a continuously increasing difference between a bolion and a divalent ion as the concentration is increased from that corresponding to infinite dilution. These same considerations arise in the discussion of the conductance of polyelectrolytes. Thus, if the number of charges is small and $1/\kappa < R/2$, where R is the charge separation, the atmospheres may be thought of as independent. However, when $1/\kappa \sim R$ the ion atmospheres overlap and form a sort of sausage casing around the polyion. Concerning the other limiting case, it is doubtful if solutions can be obtained which are sufficiently dilute that the total atmosphere of a polyion is spherically symmetric. Moreover, the effects of changing polyion dimension with changing concentration are very large and probably dominate the other two terms in the frictional force.

Consider a completely dissociated bolion. The effect of association will be discussed later. To calculate the frictional coefficient or the diffusion coefficient of a bolion, it is necessary to consider the mutal perturbation of the flow fields about each ion due to the presence of other ions. This perturbation is of the same origin as the perturbation to the flow field about one bead arising from another bead on the same molecule. Let the fluid be moving with a uniform velocity $\mathbf{C}$ in the x-direction. If a force $\mathbf{F}$ with components F_x, F_y, F_z acts at the origin, then the increment in the velocity of the fluid at the point r is, in component form

$$\delta u = \frac{1}{8\pi\eta}\left[F_x\nabla^2\phi - F_x\frac{\partial^2\phi}{\partial x^2} - F_y\frac{\partial^2\phi}{\partial x\partial y} - F_z\frac{\partial^2\phi}{\partial x\partial z}\right]$$

$$\delta v = \frac{1}{8\pi\eta}\left[F_y\nabla^2\phi - F_x\frac{\partial^2\phi}{\partial x\partial y} - F_y\frac{\partial^2\phi}{\partial y^2} - F_z\frac{\partial^2\phi}{\partial y\partial z}\right]$$

$$\delta w = \frac{1}{8\pi\eta}\left[F_z\nabla^2\phi - F_x\frac{\partial^2\phi}{\partial x\partial z} - F_y\frac{\partial^2\phi}{\partial y\partial z} - F_z\frac{\partial^2\phi}{\partial z^2}\right]$$

$$(16)$$

where, in general, ϕ is a function of r, the fluid density ρ, the fluid velocity C and the viscosity η given by

$$\phi = \frac{2\eta}{\rho C} \int_0^{\frac{\rho C(r-x)}{2\eta}} \frac{1-e^{-t}}{t} dt \qquad (17)$$

When $\rho(C(r-x)/2\eta)$ is small, ϕ may be expanded in a Taylor's series and only the first two terms retained. The result of this expansion when substituted into the eq. 16 is the well known equation of motion[21]

$$\delta u = \frac{1}{8\pi\eta}\left[\frac{F_x}{r} + \frac{F\cdot r}{r^3} x\right]$$

$$\delta v = \frac{1}{8\pi\eta}\left[\frac{F_y}{r} + \frac{F\cdot r}{r^3} y\right]$$

$$\delta w = \frac{1}{8\pi\eta}\left[\frac{F_z}{r} + \frac{F\cdot r}{r^3} z\right]$$

$$(18)$$

Consider now some one bolion surrounded by its counterions. Let the origin be located at the center of mass of the bolion. The total velocity imparted at the origin by the forces acting on the surrounding counterions is simply the integral of eq. 18 over all space, i.e.

$$u = \frac{1}{8\pi\eta} \int \left[\frac{F_x}{r} + \frac{F\cdot r}{r^3} x\right] d\tau$$

$$v = \frac{1}{8\pi\eta} \int \left[\frac{F_y}{r} + \frac{F\cdot r}{r^3} y\right] d\tau$$

$$w = \frac{1}{8\pi\eta} \int \left[\frac{F_z}{r} + \frac{F\cdot r}{r^3} z\right] d\tau$$

$$(19)$$

In the case of diffusion the bulk velocity of the fluid is zero and the driving force is just the gradient of the chemical potential. We thus have

$$F d\tau = \sum_{i=1}^{r} [n_i \nabla \mu_i + n_i q_i \nabla \psi] d\tau \qquad (20)$$

where the conventional but arbitrary separation of the chemical potential into "chemical" and "electrical" parts has been made, n_i is the concentration of species i (moles per unit volume of solvent), q_i the charge on the ion and ψ the mean electrostatic potential.

To determine the force acting the electrostatic potential must be known. It can be shown readily that to terms of order κ, the potential at a point P, a distance r_1 and r_2 from the two charges of the bolion is given by[9,22]

$$\psi = \frac{q_1 e^{-\kappa r_1}}{D r_1} + \frac{q_1 e^{-\kappa r_2}}{D r_2}$$

$$\kappa^2 = \frac{4\pi}{DkT} \sum_{i=1}^{r} n_i^0 q_i^2$$

$$(21)$$

where n_i^0 is the bulk concentration of species i and D is the dielectric constant of the system. Throughout we are treating the charge sites as point ions. To the same approximation that eq. 21 represents the potential, the chemical potential of the bolion is[22]

(21) See for example, J. J. Hermans, J. Polymer Sci., 18, 527 (1956), for a treatment similar to the one presented herein. The method used is also discussed by Hermans in Rec. trav. chim. Pays Bas, 56, 635 (1939).

(22) G. Scatchard and J. G. Kirkwood, Physik. Z., 33, 297 (1932).

$$\mu_1 = \mu_1^0(T,p) + kT \ln n_1 - \frac{q_1^2}{D}\left[\kappa - \frac{1}{h_1}(e^{-\kappa h_1} - 1)\right] \qquad (22)$$

where, as before, h_1 is the separation of the charges of a bolion. Equation 21 may be used in conjunction with the Boltzmann relation in the usual manner to determine the mean concentration of species i about the bolion. Thus

$$n_i = n_i^0 e^{-q_i\psi/kT} = n_i^0\left[1 - \frac{q_1 q_i e^{-\kappa r_1}}{D r_1 kT} - \frac{q_1 q_i e^{-\kappa r_2}}{D r_2 kT}\right] + \cdots \qquad (23)$$

and substitution of eq. 23 into eq. 20 gives

$$F = \sum_{i=1}^{r}\left\{n_i^0\left[\frac{q_1 q_i e^{-\kappa r_1}}{D r_1 kT} + \frac{q_1 q_i e^{-\kappa r_2}}{D r_2 kT}\right]\nabla\mu_i + \left[\frac{q_1 q_i e^{-\kappa r_1}}{D r_1 kT} + \frac{q_1 q_i e^{-\kappa r_2}}{D r_2 kT}\right]n_i^0 q_i \nabla\psi_i\right\} \qquad (24)$$

where the Gibbs–Duhem relation and the condition of electroneutrality have been employed. After carrying out the indicated differentiations and using eq. 22 some algebraic manipulation leads to the result

$$F = \frac{q_1}{DkT}\left[\frac{e^{-\kappa r_1}}{r_1} + \frac{e^{-\kappa r_2}}{r_2}\right]\left[(q_1^2 n_1^0 + q_2^2 n_2^0)\nabla\psi\right] \qquad (25)$$

where a term in $\nabla\kappa$ has been neglected as being very much smaller than the term retained.

It is convenient at this point to make an approximation in the hydrodynamic treatment and replace the potential used in eq. 21 by an average potential at a distance r from the center of mass of the bolion. If the electrostatic potential of eq. 21 is averaged over the surface of a sphere of radius r, the result is

$$<\psi> = \frac{2q_1}{D h_1 r\kappa} e^{-\kappa r}\left[e^{\kappa h_1/2} - e^{-\kappa h_1/2}\right] \qquad (26)$$

Note that eq. 26 reduces correctly to

$$<\psi>_{h_1=0} = \frac{2q_1}{Dr} e^{-\kappa r} \qquad (27)$$

in the limit as h_1 tends to zero and the bolion becomes a divalent ion. The force F may now be written in the form

$$F = \frac{4q_1}{DkT} \frac{e^{-\kappa r}}{h_1\kappa r} \sinh\frac{\kappa h_1}{2} (q_1^2 n_1^0 + q_2^2 n_2^0)\nabla\psi \qquad (28)$$

Let the x-axis be along $\nabla\psi$. From eq. 19 it is readily found that

$$u = \frac{1}{2\pi\eta} \frac{q_1 \sinh\frac{\kappa h_1}{2}}{DkT h_1\kappa} (q_1^2 n_1^0 + q_2^2 n_2^0)\nabla\psi \int \frac{e^{-\kappa r}}{r} \times \left(\frac{1}{r} + \frac{x^2}{r^3}\right) d\tau \qquad (29)$$

and this integral is evaluated easily in polar coordinates with the result that

$$u = \frac{2q_1 \sinh\frac{\kappa h_1}{2}}{3\pi\eta h_1} \nabla\psi \qquad (30)$$

This velocity represents the amount by which the motion of the central ion is decreased due to the fact that the flow field about it is perturbed by its atmosphere. The equations of motion for the bolion and a small ion now assume the form

$$\zeta_1 \left[C' - \frac{2q_1 \sinh \frac{\kappa h_1}{2}}{3\pi\eta n_1} \nabla\psi \right] = -\nabla\mu_1 - 2q_1\nabla\psi \quad (31)$$

$$\zeta_2 \left[C' - \frac{q_2\kappa}{6\pi\eta} \nabla\psi \right] = -\nabla\mu_2 - q_2\nabla\psi$$

with ζ_1 and ζ_2 the frictional coefficients of the bolion and counterion, respectively, and C' the mean velocity (the same for bolion and counterions) with which the ions move in the absence of any perturbation. Equations 31 may be solved for nC' where

$$nq^2 = n_1{}^0 q_1{}^2 + n_2{}^0 q_2{}^2 \quad (32)$$

After some tedious algebra it is finally found that

$$nC' = -kT\nabla n \frac{q_2 - 2q_1}{\zeta_1 q_2 - 2\zeta_2 q_1} \left[1 + \frac{2q_2 q_1\kappa}{4DkT} + \frac{2q_2 q_1\kappa^2 h_1}{8DkT} \right] \quad (33)$$

where a term in κ has been neglected as being negligible relative to the terms retained. In the limit as the separation of the charges tends to zero, eq. 33 reduces to the well known result for small electrolytes. The last term on the right-hand side contains a factor κ^2 but since h_1 is of order κ^{-1} especially for the larger bolions, the total magnitude of this term is of order κ. The diffusion coefficient finally becomes

$$\mathfrak{D} = \mathfrak{D}_0 \left[1 + \frac{q_2 q_1\kappa}{2DkT} + \frac{q_2 q_1\kappa^2 h_1}{4DkT} \right] \quad (34)$$

where $\mathfrak{D}_0$ the diffusion coefficient of the ideal solution, is itself concentration dependent through the dependence of the frictional coefficient ζ_1 on the intercharge separation. The asymmetry of the ion atmosphere is seen to lead to an additional retarding force on the bolion which ultimately reduces the flux of matter by about $\mathfrak{D}_0 |\kappa^2 h_1 q_2 q_1/4DkT|$. This term is of the same order of magnitude as the term in κ arising for ordinary electrolytes. The ratio of the third term to the second term is, in fact, $\kappa h_1/2$, which has the value 0.2 for a $10^{-3}N$ solution of the $n = 10$ compound (see Table II) in methanol at 25°. It should further be noted that since the frictional coefficient of the bolion increases as the charge separation increases, the diffusion coefficient of a bolaform electrolyte will always be smaller than the diffusion coefficient of a corresponding ordinary 2:1 electrolyte.

When ion association is taken into account, it is necessary to note that much of the transport of solute occurs *via* singly charged and uncharged species. The electrophoretic effect is reduced to that at the appropriate ionic concentration, but a similar hydrodynamic interaction, due to the correlation in the relative motion of any two bodies, also exists for the uncharged species. The concentration dependence of $\mathfrak{D}$ becomes still more complicated by the inclusion of this effect. If only the singly and doubly charged ions are present in the solution, then the electrophoretic effect may be calculated for each as in the preceding. The total diffusion coefficient may then be approximated as

$$\mathfrak{D} = \alpha\mathfrak{D}_B{}^{++} + \frac{3}{2}(1 - \alpha)\mathfrak{D}_{BC}{}^+ \quad (35)$$

and each term contains both the electrophoretic correction and the appropriate interaction correc-

tion, both tending to retard the motion of the diffusing entity.

VI. Discussion

The purpose of this note has been to interpret the properties of solutions of bolaform electrolytes in terms of an internally consistent model with emphasis on the special role played by the intercharge separation and its variation with concentration. The extent to which self-consistency is attainable with reference to an available model is best judged by the reader in terms of the numerical examples cited.

A most important feature of solutions of bolaform electrolytes is the presence of ion pairs whose dissociation is described by the constant K_2. The problem of the molecular nature of the ion paired state is an old and still unsettled one. Nevertheless, recent considerations by Gilkerson[23] suggest that the most appropriate model describing an ion pair is one in which the ions are much more intimately associated than in the simple spatial classification scheme proposed by Bjerrum.[24] Whether or not this association involves the contact of solvated ions is immaterial. The important feature of the free volume model is that the ion pairs are much closer together than ion atmosphere dimensions and exclude a negligible portion of the configurations usually considered in the Debye–Hückel theory. Gilkerson's detailed molecular considerations supplement thermodynamic arguments previously presented for an intimate association of the ions in pair formation.[6]

There is, of course, considerable interplay between the intercharge separation and the extent of ion-pairing. Because the molecules under consideration are not rigid, the total free energy change on ionization must include contributions arising from the change in entropy when the molecular configuration is changed. Energy changes, which have not been considered in this note, may or may not accompany configurational changes dependent upon whether or not there is considerable overlap of hydrogen atoms or other groups or whether internal hydrogen bonding exists, and so forth. Since the total free energy must be minimized simultaneously with respect to h_1 and α, it is not strictly correct to use the simple Bjerrum relation which assumes that there is no change in molecular configuration on ionization. The error involved may not be large for small molecules, but it certainly becomes larger as the limiting case of the polyion is approached.

In this note the theory of transport in solutions of bolaform electrolytes has been approached with emphasis on the asymmetric nature of the ion atmosphere. It has been shown that there exists a retarding force due to the hydrodynamic interaction of the charge cloud on one end of the bolion with the charge on the other end. This retarding force is in addition to the retarding forces that would exist for a spherically symmetric divalent ion. Moreover, both the charge-charge separation and the mean charge on a bolion are concentration dependent (the latter due to incomplete dissocia-

(23) W. R. Gilkerson, *J. Chem. Phys.*, **26**, 1199 (1957).
(24) N. Bjerrum, *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.*, **7**, No. 9 (1926).

tion.) Since the steady state established in diffusion or conductance is the result of a complicated interplay between competing forces, the resultant concentration dependence of these properties can be very different from the pattern typical of small strong electrolytes. To treat the conductance it would be necessary to compute the retarding force due to ion atmosphere lag and relaxation, an effect which does not alter the diffusion coefficient because all ions move with the same mean velocity. It is anticipated that the asymmetry of the ion atmosphere plays a relatively larger role in relaxation phenomena, which themselves result from atmosphere asymmetry, than in electrophoretic phenomena which result from the bulk motion of the entire atmosphere. The corresponding problems for polyelectrolytes are still more complex.

It would be of great interest to construct well defined models of polyions by synthesizing electrolytes with small numbers of charges distributed in some known manner on the molecular skeleton. Triply charged molecules with dimensions of the order of magnitude of those of the bolaform electrolytes considered herein would be a further step in bridging the gap between small electrolytes and polyelectrolytes. The study of such model compounds would undoubtedly contribute to the construction of a more definitive theory of polyelectrolyte solutions.

CHICAGO 37, ILLINOIS

Preparation and Structure of the Strontium and Barium Tantalates Sr₃TaO₅.₅ and Ba₃TaO₅.₅

BY LOTHAR H. BRIXNER

$Sr_3TaO_{5.5}$ and $Ba_3TaO_{5.5}$ have been prepared by the reaction of Ta_2O_5 with equivalent amounts of the corresponding carbonates at 1100° in oxygen. The compounds crystallize in the face centered cubic structure of $(NH_4)_3FeF_6$ with the space group, O_h^5. Four molecules constitute the unit cell with a lattice constant of 8.34 Å. for $Sr_3TaO_{5.5}$ and 8.69 Å. for $Ba_3TaO_{5.5}$. The pycnometric densities of 5.93₅ g. cc.$^{-1}$ and 6.79₈ g. cc.$^{-1}$ are in good agreement with the X-ray densities of 6.088 g. cc.$^{-1}$ and 6.906 g. cc.$^{-1}$, respectively. The dielectric constant of $Sr_3TaO_{5.5}$ is 14.3, and that of $Ba_3TaO_{5.5}$ is 13.18.
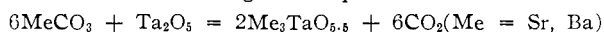
Introduction

Pauling[1] was the first to determine the structure of $(NH_4)_3FeF_6$, which is common to a series of compounds of the A_3BX_6-type. Between the straight complex fluorides, such as $(NH_4)_3FeF_6$, and the ternary oxides such as A_3BO_6, $(NH_4)_3MoO_3F_3$ constitutes an intermediate link, which also was investigated by Pauling earlier.[1] In 1951, Steward and Rooksby[2] found a series of tungstates, such as di-barium mono-calcium hexa-oxo-tungstate, which also belong to this class; and Ruedorff[3] characterized Ba_3UO_6 as another member of this series.

A fully-coördinated tantalate of the same type can only be expected when one of the cationic alkaline earth ions is replaced by a trivalent rare earth ion, such as trivalent lanthanum. Therefore, the compounds Sr_2LaTaO_6 with an $a_0 = 8.57$ Å. and Ba_2LaTaO_6 with an $a_0 = 8.62$ Å. were first prepared. However, when Ta_2O_5 was treated with $BaCO_3$ or $SrCO_3$ alone in a mole ratio 1:3, the X-ray pattern of the resulting compound could also be completely indexed according to the $(NH_4)_3FeF_6$ structure. This behavior can only be interpreted if one assumes an anion deficient structure for $Sr_3TaO_{5.5}$ and $Ba_3TaO_{5.5}$, similar to $SrTiO_{2.5}$, which Ward[4] recently found to crystallize in the perovskite structure of $SrTiO_3$.

Experimental

The new anion deficient strontium and barium tantalates are obtained readily by treating strontium or barium carbon-

(1) L. Pauling, THIS JOURNAL, 46, 2738 (1924).
(2) Rooksby and Steward, Acta Cryst., 4, 503 (1951).
(3) W. Ruedorff, Z. Naturforsch., 9b, Heft 8, 568 (1954).
(4) M. Kestigian, J. G. Dickinson and R. Ward, THIS JOURNAL, 79, 5598 (1957).

ate with Ta_2O_5 according to the equation

$$6MeCO_3 + Ta_2O_5 = 2Me_3TaO_{5.5} + 6CO_2 (Me = Sr, Ba)$$

This mixture is presintered at 800° for one hour in air and then ball-milled in a mechanical agate ball mill to ensure a homogeneous reaction mixture. The second firing takes place at 1100° in oxygen, using a platinum boat as a container. If amounts of 10–20 g. are processed, the evolution of CO_2 usually is complete after two hours, as is evident from the results in Table I.

TABLE I

CO₂ EVOLUTION DURING A 2-HR. FIRING PERIOD AT 1100° IN O₂

Compound	CO₂ calcd., g.	CO₂ given off, g.
$Sr_3TaO_{5.5}$	3.582	3.590
$Ba_3TaO_{5.5}$	2.985	2.979

The CO_2-free compounds were again ball milled, pressed into pellets under 40,000 p.s.i. and finally fired at 1200° for 1–2 hours. The strontium compound is white, while the barium compound is slightly yellow to pink.

Chemical Analysis.—The separation of strontium and tantalum was first attempted by dissolving the compound in molten $K_2S_2O_7$, precipitating $SrSO_4$ by diluting the melt in water, while tantalum was kept in solution with ammonium oxalate. The results are erratic because varying quantities of tantalum were precipitated with the strontium. Successful separation was effected by chlorinating the compounds with phosgene at 600° and leaching out the tantalum chloride with absolute alcohol. The alkaline earths were determined as sulfates; the tantalum, by precipitating in freshly filtered ammoniacal solution and igniting in air to the pentoxide.

The analytical results were as follows: $Sr_3TaO_{5.5}$, found, 34.97% Ta, 48.49% Sr, Sr:Ta = 1:2.97; calcd., 34.01% Ta, 49.44% Sr, Sr:Ta = 1:3.00. For $Ba_3TaO_{5.5}$, found, 26.49% Ta, 60.63% Ba, Ba:Ta = 1:3.01; calcd., 26.56% Ta, 60.51% Ba, Ba:Ta = 1:3.00.

Dielectric Constant.—For the measurement of the dielectric constant a pellet, 1.25 cm. in diameter, 2 mm. thick, was pressed at 40,000 p.s.i. and silver-coated on both sides. The measurement was carried out at 200 kilocycles. The dielectric constant of $Sr_3TaO_{5.5}$ was found to be 14.3, and that of $Ba_3TaO_{5.5}$, 13.18.