R$^-$, and causing complete reaction of these to produce two R's and a photon. The total moles of photons produced in any time increment are used to calculate ZLUM.

These calculations are continued for each time increment until the next reversal occurs.

The program allows calculation of concentration profiles and intensity–time and current–time curves. A complete listing of the FORTRAN program and an explanation of it is available.[8]

The accuracy of the simulation depends upon the number of iterations in each cycle. The results here were obtained with 200 interations per cycle (*i.e.*, 10,000 iterations for the complete 50-cycle output) and gave values for the current–time behavior and concentration profiles during the first potential step which agreed with the known analytical solutions for this case (*e.g.*, the Cotrell equation) to within 0.5%. ECL calculations in the absence of kinetic effects gave results in excellent agreement with those of Feldberg.[3]

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# Electrical Conductance of Bolaform Electrolytes in Viscous Solvents. Manganese(II) *m*-Benzenedisulfonate and Manganese(II) 4,4'-Biphenyldisulfonate in Water–Ethylene Glycol Mixtures at 25°[1]

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**Abstract:** The electrical conductances of the Mn(II) salts of *m*-benzenedisulfonate (BDS$^{2-}$) and of 4,4'-biphenyldisulfonate (BPDS$^{2-}$) have been measured in mixtures of water–ethylene glycol at 25° up to 0.56 and 0.40 mole fraction of glycol, respectively. The data are interpreted by means of the Fuoss–Onsager 1959 equation for conductance. MnBDS is partially associated in the mixtures, while MnBPDS is substantially unassociated. The $a_A$, $a_J$, and $a_K$ (for the associated electrolyte) show a fair consistency. It is shown that the BPDS$^{2-}$ ion frictional coefficient can be calculated theoretically using the hydrodynamic radius of the benzenesulfonate ion and the Perrin rigid elipsoid model.

Bolaform ions[3] are ions whose total charge is split into discrete charges separated by uncharged areas. This is also the structural feature of both synthetic and biological polyelectrolytes. In fact, the bolaform ion may resemble a segment of the chain of a polyion.

The study of the hydrodynamic and kinetic properties of these ions and their interactions and association with the counterions may link the properties of simple and polyelectrolytes. Indeed the behavior of some bolaform ions can still be interpreted by the theories of simple electrolytes.

The study of this class of electrolytes was initiated by Fuoss and his school at Yale University.[3] Rice[4] reexamined the conductance of some diquaternary ammonium salts[3] and demonstrated the validity of the present conductance theories[5] in the analysis of association and hydrodynamic parameters.

Among the bolaform ions the benzenedisulfonate anions and their derivatives are particularly important. Because of the rigidity of the inert frame interposed between the charges, their properties can be sucessfully interpreted in terms of simple geometrical models.

Atkinson and his associates[6] studied the conductance of these electrolytes rather extensively in water as well as in mixtures of water with organic liquids in order to lower the dielectric constant of the medium. In this laboratory it was decided to extend this research to media of higher viscosity, namely water-ethylene glycol mixtures. It was of interest to study the hydrodynamic and thermodynamic properties of these ions and compare them with the simpler ion $SO_4^{2-}$ in these solvents. In particular it was of interest to study the effect of the progressive separation of the charges (going from the $SO_4^{2-}$ to the BPDS$^{2-}$ ion) on the hydrodynamic and association properties of these ions. As counterion Mn(II) was chosen in view of a previous study of $MnSO_4$ in water–glycol at 25°.[7]

## Experimental Part

Mn(*m*)BDS was prepared as described in the literature.[6] It was crystallized twice from conductance water and dried at 105° to the form MnBDS·3.5$H_2O$ as checked by cation exchange and titration of the acid. MnBPDS was prepared by a similar preparation

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[1] This work is part of the thesis of Paul Hemmes in partial fulfillment of the requirements of the Ph.D. degree.

[2] National Science Foundation Kirk Fellow of the Polytechnic Institute of Brooklyn.

[3] R. M. Fuoss and D. Edelson, *J. Am. Chem. Soc.*, 73, 269 (1951).

[4] S. A. Rice and M. Nagasawa, "Polyelectrolyte Solutions," Academic Press, New York, N. Y., 1961.

[5] R. M. Fuoss and F. Accascina "Electrolytic Conductance," Interscience Publishers, New York, N. Y., 1959.

[6] (a) G. Atkinson, M. Yokoi, and C. J. Hallada, *J. Am. Chem. Soc.*, **83**, 1570 (1961); (b) C. J. Hallada and G. Atkinson, *ibid.*, **83**, 3759 (1961); (c) G. Atkinson and C. J. Hallada, *ibid.*, **84**, 721 (1962); (d) G. Atkinson and S. Petrucci, *J. Phys. Chem.*, **67**, 337 (1963); (e) *ibid.*, **67**, 1880 (1963); (f) G. Atkinson and S. Petrucci, *J. Am. Chem. Soc.*, **86**, 7 (1964); (g) B. R. Staples and G. Atkinson, *J. Phys. Chem.*, **71**, 667 (1967).

[7] S. Petrucci, P. Hemmes, and M. Battistini, *J. Am. Chem. Soc.*, **89**, 5552 (1967).

as reported for CuBPDS;[8] namely, $K_2BPDS$ prepurified from $K_2SO_4$ impurities was converted to the acid by cation-exchange technique. The acid was then allowed to react with $MnCO_3$ to prepare the MnBPDS salt. MnBPDS was crystallized from hot water and dried to anhydrous form at 105°. Ethylene glycol (Fisher reagent) was distilled under vacuum as described before.[7] Equipment and procedure were the same as for the case of $MnSO_4$ in water–glycol.[7]

## Results

The results for the concentrations $C$ (moles/liter) and corresponding equivalent conductances $\Lambda$ (ohm$^{-1}$ cm$^2$ equiv$^{-1}$) for water and the various mixtures investigated are reported in Table I. At least one decimal figure in excess is given (on $C$ and $\Lambda$) than is significant in terms of the precision so that others may reanalyze the data and avoid rounding-off errors.

**Table I.** Conductance Results for MnBDS and MnBPDS in Water–Glycol Mixtures at 25°

| | | MnBDS | | | |
|---|---|---|---|---|---|
| $C \times 10^4$ | $\Lambda$ | $C \times 10^4$ | $\Lambda$ | $C \times 10^4$ | $\Lambda$ |
| $X_{\text{glycol}} = 0.00$ | | $X_{\text{glycol}} = 0.20$ | | $X_{\text{glycol}} = 0.30$ | |
| 3.5822 | 103.498 | 1.5153 | 33.812 | 4.0255 | 21.049 |
| 5.7819 | 101.170 | 3.5156 | 32.549 | 7.3358 | 19.930 |
| 8.3193 | 99.071 | 11.319 | 29.659 | 11.245 | 19.063 |
| 11.907 | 96.754 | 16.687 | 28.570 | 16.309 | 18.294 |
| 15.593 | 94.969 | 21.532 | 27.829 | 25.015 | 17.380 |
| 17.273 | 94.225 | 27.782 | 27.100 | | |
| 23.565 | 91.881 | | | | |
| 26.013 | 91.186 | | | | |
| $X_{\text{glycol}} = 0.50$ | | $X_{\text{glycol}} = 0.555$ | | | |
| 2.4870 | 11.842 | 1.5817 | 10.515 | | |
| 6.9045 | 10.594 | 2.8513 | 10.098 | | |
| 9.8821 | 10.124 | 5.1496 | 9.491 | | |
| 14.075 | 9.647 | 9.4059 | 8.751 | | |
| 21.332 | 9.084 | 15.224 | 8.169 | | |
| 29.237 | 8.662 | | | | |
| | | MnBPDS | | | |
| $C \times 10^4$ | $\Lambda$ | $C \times 10^4$ | $\Lambda$ | | |
| $X_{\text{glycol}} = 0.00$ | | $X_{\text{glycol}} = 0.20$ | | | |
| 1.1100 | 97.596 | 3.3147 | 29.609 | | |
| 5.6684 | 92.079 | 5.8892 | 28.540 | | |
| 8.1681 | 90.382 | 8.7613 | 27.730 | | |
| 11.247 | 88.843 | 12.140 | 26.995 | | |
| 14.067 | 87.719 | 17.036 | 26.208 | | |
| 16.755 | 86.722 | 20.415 | 25.750 | | |
| 23.399 | 84.967 | | | | |
| $X_{\text{glycol}} = 0.30$ | | $X_{\text{glycol}} = 0.40$ | | | |
| 2.8212 | 19.696 | 4.1004 | 14.173 | | |
| 4.8226 | 18.984 | 5.9003 | 13.674 | | |
| 6.8252 | 18.468 | 10.115 | 12.898 | | |
| 12.350 | 17.489 | 14.596 | 12.446 | | |
| 17.237 | 16.865 | 20.950 | 11.941 | | |
| 21.410 | 16.493 | 27.425 | 11.572 | | |

## Calculations

The analysis of the data has been made by the 1959 Fuoss–Onsager relations[5] expressing the isothermal dependence of the equivalent conductance with concentration of electrolyte

$$\Lambda = \Lambda_0 - S\sqrt{c} + Ec \log c + Jc \qquad (1)$$

$$\Lambda = \Lambda_0 - S\sqrt{c\gamma} + Ec\gamma \log c\gamma + Jc\gamma - K_A c\gamma f^2 \Lambda \qquad (2)$$

Equation 1 holds for unassociated electrolytes, while eq 2 is valid for partially associated electrolytes. Both equations should be valid up to $xa = 0.20$.[5] Symbols in the above have been extensively illustrated for 2:2 electrolytes previously.[5,7]

The analysis was performed by a computer program. MnBDS shows a small but definite association while MnBPDS is substantially unassociated in all the range of glycol composition investigated. Table II reports the results of this analysis in terms of the parameters $\Lambda_0$, $J$, $a_J$, $K_A$ together with the dielectric constant $D$, and viscosities $\eta$ of the corresponding solvent mixtures. The fitting of the computer can be judged from Figures 1 and 2 when the $(\Lambda_{\text{calcd}} - \Lambda_{\text{Onsager}})$'s are plotted *vs. c*. $\Lambda_{\text{Onsager}}$ is the quantity $\Lambda_0 - S\sqrt{c}$ or $\Lambda_0 - S\sqrt{c\gamma}$, respectively. $\Lambda_{\text{calcd}}$ is the calculated value of $\Lambda$ by eq 1 or 2 and the parameters of Table II. The experimental points indicated on Figures 1 and 2 are obtained as $(\Lambda_{\text{exptl}} - \Lambda_{\text{Onsager}})$. The quantities $\overline{|\Lambda_{\text{calcd}} - \Lambda_{\text{exptl}}|}$ in Tables I and II are the average deviations between the calculated and experimental conductances.

## Discussion

For the MnBDS in view of the presence of association the Fuoss equation[8]

$$K_A = K_0 e^b \qquad (3)$$

has been considered in order to correlate the association constant of the various mixtures. In the above $K_0$ is the geometrical term[8]

$$K_0 = 4\pi N a^3/3000 \qquad (4)$$

and $b$ is the Bjerrum parameter[9]

$$b = |Z_+ Z_-| e^2/aDkT \qquad (5)$$

where $e$ is the electronic charge and $Z_+$ and $Z_-$ are the ionic valencies; other symbols have their usual meaning.[5,7]

In Figure 3 a plot of log $K_A$ *vs.* $1/D$ gives a straight line passing within experimental errors through both the closed and open points. These latter in turn correspond to the association data for MnBDS in water–dioxane.[8] From the slope of the graph assuming eq 3, one can evaluate a minimum approach parameter $a_K = 4.7 \times 10^{-8}$ cm in fair accord with the average $a_J = 5.5\ 10^{-8}$ cm from Table II.

It is noteworthy that the association of $MnSO_4 >$ MnBDS > MnBPDS, therefore decreasing with the size of the anion. Simple electrostatic considerations would suggest that indeed this has to be the case. However, it has been pointed out[7] that eq 3 shows a minimum by increasing $a$ because of the competition of the $K_0$ and exp ($b$) factors with increasing the parameter $a$.

The physical origin of the above lies in the nature of the geometrical factor $K_0$ that expresses the excluded volume from the solution by the ions or in other words the increase of probability of association by increase of the diameter of the ions. Exp($b$) on the contrary decreases with $a$ because the potential energy $|Z_+Z_-| e^2/aD$ (in the $b$ parameter) decreases with $a$.

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(8) M. Yokoi and G. Atkinson, *J. Am. Chem. Soc.*, **83**, 4367 (1961).

(9) N. Bjerrum, *Kgl. Danske Videnskab. Selskab*, **7**, No. 9 (1926).

**Table II.** Results of Conductance Analysis for MnBDS and MnBPDS in Water–Glycol at 25°

| $X_{\text{glycol}}$ | $10^2\eta$, poise | $D$ | $\Lambda_0$, ohm$^{-1}$ cm$^2$ equiv$^{-1}$ | $J$ | $10^8 a_J$, cm | $K_A$, $M^{-1}$ | $\Lambda_0\eta$ | $\lvert\Lambda_{\text{calcd}} - \Lambda_{\text{exptl}}\rvert$ |
|---|---|---|---|---|---|---|---|---|
| | | | | MnBDS | | | | |
| 0.00 | 0.895 | 78.54 | 112.80 | 8700 | 5.5 | (5)[a] | 1.009 | 0.079 |
| 0.20 | 2.80 | 65.6 | 36.33 | 4960 | 5.7 | 16 | 1.017 | 0.038 |
| 0.30 | 4.15 | 60.7 | 24.25 | 4100 | 5.7 | 26 | 1.006 | 0.044 |
| 0.50 | 7.25 | 53.1 | 13.57 | 3453 | 5.5 | 77 | 0.984 | 0.040 |
| 0.555 | 8.25 | 51.1 | 11.80$_6$ | 3390 | 5.1 | 110 | 0.974 | 0.022 |
| | | | | MnBPDS | | | | |
| 0.00 | 0.895 | 78.54 | 102.40 | 8920 | 6.7 | | 0.916 | 0.087 |
| 0.20 | 2.80 | 65.6 | 32.99 | 4440 | 5.8 | | 0.924 | 0.024 |
| 0.30 | 4.15 | 60.7 | 22.04 | 3650 | 5.5 | | 0.915 | 0.018 |
| 0.40 | 5.56 | 57.0 | 16.47 | 3250 | 5.4 | | 0.916 | 0.045 |

[a] The value of $K_A$ in water has been estimated from extrapolation of the log $K_A$–$(1/D)$ plot (Figure 3).

The minimum of $K_A$ is easily found by setting the derivative of (3) with respect to $a$ equal to zero; the root is

$$a_{\min} = |Z_1Z_2|e^2/3DkT \tag{6}$$

In water for a 2:2 electrolyte $a_{\min} = 9.51$ Å. By lowering the dielectric constant $a_{\min}$ increases. Therefore the $a_J$'s for $MnSO_4$, MnBDS, and also MnBPDS are inferior to $a_{\min}$ and in the region where the electrostatic term still predominates over the entropic one, $K_0$, in accord with eq 3.

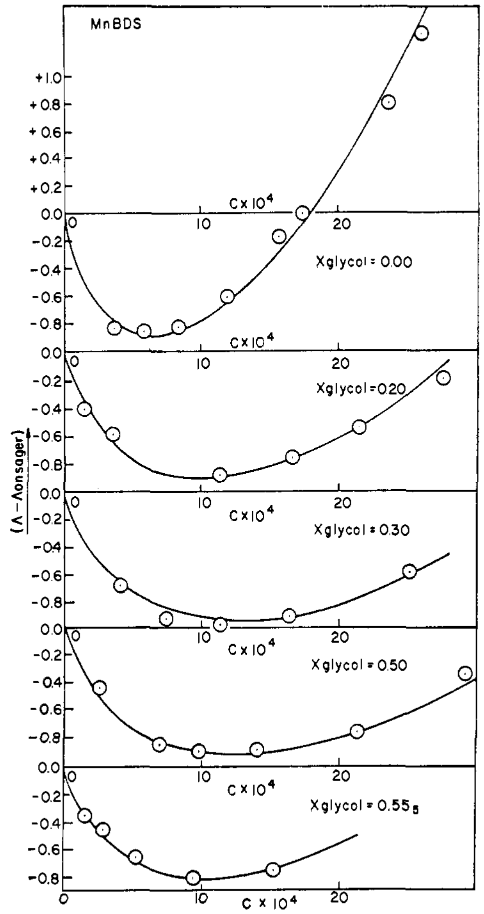

Figure 1. Plot of $(\Lambda_{\text{calcd}} - \Lambda_{\text{Onsager}})$ for MnBDS in water-glycol mixtures at 25°.

In Table III the Stokes hydrodynamic radius of $Mn^{2+}$ and $SO_4^{2-}$ and $BDS^{2-}$ are reported in $H_2O$–glycol at 25°. These values were calculated from the formula

$$R_{\pm} = FZ_{\pm}e/6\pi\lambda^0{}_{\pm}\eta \tag{7}$$

where $F$ is the Faraday constant; $Z_+$ (and $Z_-$) are the ionic valencies; $\lambda_+{}^0$ (and $\lambda_-{}^0$) are the limiting conductivities. Notice that the $R_+$'s are in excellent numerical accord when calculated from $MnSO_4$, MnBDS, and MnBPDS as one could predict from the almost perfect

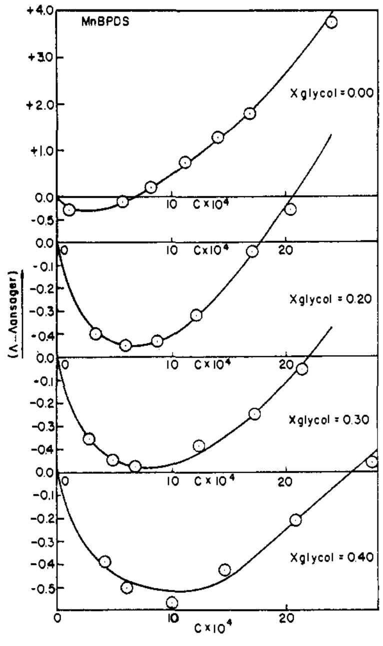

Figure 2. Plot of $(\Lambda_{\text{calcd}} - \Lambda_{\text{Onsager}})$ for MnBPDS in water-glycol mixtures at 25°.

**Table III.** Calculated Stokes Hydrodynamic Parameters for $Mn^{2+}$, $SO_4^{2-}$, $BDS^{2-}$, and $BPDS^{2-}$ in Water-Glycol Mixtures at Infinite Dilution[a]

| Solvent compn | $MnSO_4$ | | MnBDS | | MnBPDS | |
|---|---|---|---|---|---|---|
| $X_{\text{glycol}}$ | $R_+$ | $R_-$ | $R_+$ | $R_-$ | $R_+$ | $R_-$ |
| 0.00 | 3.42 | 2.29 | 3.41 | 3.09 | 3.41 | 3.76 |
| 0.10 | 3.38 | 2.26 | ... | ... | ... | ... |
| 0.20 | ... | ... | 3.38 | 3.07 | 3.38 | 3.73 |
| 0.30 | 3.51 | 2.35 | 3.42 | 3.11 | 3.42 | 3.79 |
| 0.40 | ... | ... | ... | ... | 3.41 | 3.76 |
| 0.50 | 3.32 | 2.22 | 3.50 | 3.17 | ... | ... |
| $0.55_5$ | ... | ... | 3.53 | 3.21 | ... | ... |

[a] The values of $R_{\pm}$ are in ångströms.

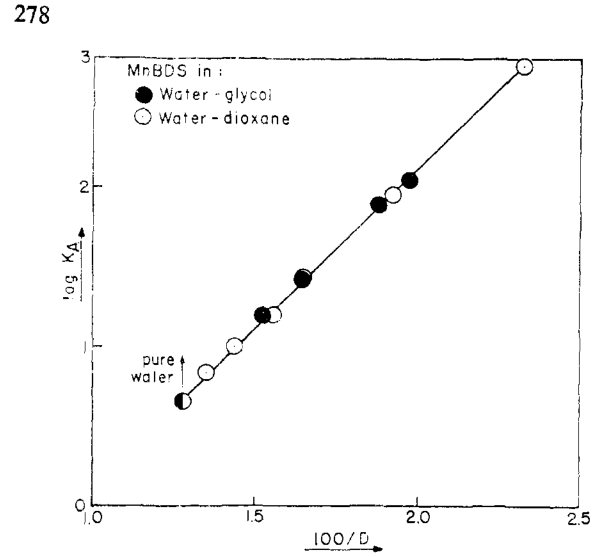

Figure 3. Plot of log $K_A$ *vs.* $1/D$ for MnBDS in water-glycol mixtures at 25°.

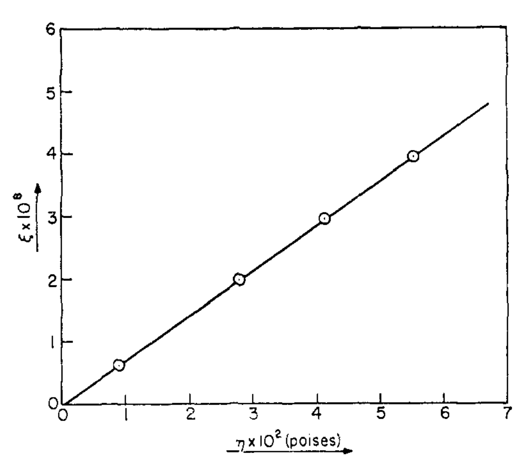

Figure 4. Plot of the frictional coefficient $\xi$ *vs.* the viscosity $\eta$ for $BPDS^{2-}$ in water-glycol mixtures at 25°.

validity of the Walden rule (Table II) with solvent composition.

The numerical value of $R_+$ may also suggest the speculation that a hexaquo $Mn(H_2O)_6^{2+}$ is the kinetic entity even in $H_2O$-glycol mixtures. This speculation of specific preferential solvation by water is corroborated by ultrasonic results of $MnSO_4$ in $H_2O$-glycol mixtures.[10] Notice also that $R_-$ increases from an average $2.28 \times 10^{-8}$ cm for $SO_4^{2-}$ to $3.13 \times 10^{-8}$ cm for $BDS^{2-}$ and to $3.76 \times 10^{-8}$ cm for $BPDS^{2-}$ as one would have intuitively predicted. (In the above calculations the transport number of $Mn^{2+}$ at infinite dilution has been assumed constant with glycol compositions and equal to $n_+^0 = 0.401$ for $MnSO_4$, 0.476 for MnBDS, and 0.525 for MnBPDS.)

From the above it can be concluded that MnBDS still behaves according to a model assuming ions as spheres which can be described in their hydrodynamic and thermodynamic properties through the Fuoss–Onsager theories.[5]

MnBPDS can also be described as two spheres according to the Fuoss–Onsager theories.[5] There are two points of interest, however. First one should notice the surprising resemblance of the $a_J$ values going from MnBDS to MnBPDS (Table II) and of the $a_K$ values of MnBDS compared to $MnSO_4$.[7] If this has any physical significance one would be tempted to speculate that Mn(II) interacts mainly with one of the two $SO_3^-$ groups instead of occupying an equilibrium position in between the charges. However, it has been pointed out that the converse ought to be true on the basis of electrostatic calculations.[6g] The second point of interest is that the value of $R_- = 3.76 \times 10^{-8}$ cm does not correspond to any likely molecular model for the $BPDS^{2-}$. Because of the structure of this ion, a model different from a sphere may seem a logical alternate choice. A treatment of the hydrodynamic properties of the $BPDS^{2-}$ ion at infinite dilution in water-glycol mixtures has been tried by assuming the Perrin rigid ellipsoid model[11] for the ion with the two charges occupying the foci of the ellipsoid.

The frictional coefficient $\xi_{\text{Perrin}}$ is then

$$\xi_{\text{Perrin}} \cong 6\pi\eta b'/\ln{(2b'/a')} \tag{8}$$

where $b'$ and $a'$ are the semiaxes of the ellipse. $\xi$ can also be calculated independently from the conductance data

$$\xi_{\text{exptl}} = \frac{1}{w_i} = \frac{F|z_i|e}{300\lambda_i^0} \tag{9}$$

where $w_i$ is the mobility of the ion $i$ of equivalent conductance $\lambda_i^0$ at infinite dilution and charge $z_i$.

A plot of $\xi_{\text{exptl}}$ *vs.* $\eta$ should be linear according to the Perrin theory[11] with slope approximately equal to $6\pi b'/\ln{(2b'/a')}$.

In Figure 4 this plot is shown. The points reported are calculated from eq 9. The solid line has been calculated in the following way.[8] From the limiting conductance in water of KBS and NaBS where $BS^-$ is the benezenesulfonate ion, $\lambda_0^- = 34.93$. Assuming the Stokes law for this ion

$$\frac{1}{w_{\text{BS}}} = \xi_{\text{BS}} = \frac{96{,}500|Z_{\text{BS}}|e}{300\lambda_{\text{BS}}} = 6\pi\eta a_{\text{BS}} \tag{10}$$

resulting in $a_{\text{BS}} = 2.61 \times 10^{-8}$ cm as the hydrodynamic radius. Then taking for $BPDS^{2-}$ $a_{\text{BS}} = a'$ and $b' = 2a'$, the slope of eq 8 can be calculated as $7.099 \times 10^{-7}$, and the solid line is constructed as reported in Figure 4. $b' = 5.22$ Å is in fair accord with half of the $BPDS^{2-}$ ion length calculated from molecular models. The results of this calculation are reported in Table IV. The accord between theoretical and experimental values is surprisingly good considering the naivety of the model and the numerical approximations introduced.

Table IV. Calculated and Experimental Frictional Coefficients for $BPDS^{2-}$ in Water–Glycol at 25°

| $X_{\text{glycol}}$ | $\eta \times 10^2$, poises | $\xi_{\text{Perrin}} \times 10^8$ | $\xi_{\text{exptl}} \times 10^8$ |
|---|---|---|---|
| 0.00 | 0.895 | 0.635 | 0.637 |
| 0.20 | 2.80 | 1.988 | 1.969 |
| 0.30 | 4.15 | 2.946 | 2.960 |
| 0.40 | 5.56 | 3.947 | 3.943 |

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(10) P. Hemmes, F. Fittipaldi, and S. Petrucci, submitted for publication.

(11) F. Perrin, *J. Phys. Radium*, 7, 1 (1936).