

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN]

## Ion Association in Polyvalent Symmetrical Electrolytes. III. The Conductance of Copper 4,4'-Biphenyldisulfonate and Related Salts in Water at 25°

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The conductances of the Na<sup>+</sup>, K<sup>+</sup> and Cu<sup>+2</sup> salts of 4,4'-biphenyldisulfonic acid (H<sub>2</sub>BPDS) and the Na<sup>+</sup> and K<sup>+</sup> salts of benzenesulfonic acid (HBS) have been measured in water at 25°. The equivalent conductances are analyzed by the Fuoss-Onsager equation to obtain  $\Lambda^0$  and  $a^0$  parameters. CuBPDS is an essentially unassociated 2-2 electrolyte while the Na<sup>+</sup> and K<sup>+</sup> salts are strong 2-1 salts. The mobilities of the BS<sup>-</sup> and BPDS<sup>-</sup> ions are compared and it is shown that BPDS<sup>-</sup> can be considered as a rigid ellipsoidal dimer of BS<sup>-</sup>.

In recent work<sup>1,2</sup> it was demonstrated that the Cu<sup>+2</sup> and Mn<sup>+2</sup> salts of *m*-benzenedisulfonic acid were much less associated in aqueous solution than the corresponding sulfates. The measured degree of association for MnBDS, for example, is 0.005 ± 0.005 at a concentration of 3 × 10<sup>-3</sup> mole/liter. This was calculated using the Fuoss-Onsager extended equation for slightly associated salts<sup>3</sup> and by extrapolation of association constants found in lower dielectric constant solvent mixtures. These interesting salts demonstrate quite conclusively the adequacy of the Fuoss-Onsager theory for 2-2 salts over the concentration range where the theory can be expected to be valid,<sup>4</sup>  $\kappa_a < 0.2$ . These results would be even more convincing if we understood the reason for this behavior of the BDS anion. The original idea behind the choice of this anion was the naive one that one could decrease short-range associative interactions by separating the -2 charge into two -1 charges separated by a semi-inert framework. In an attempt to probe this idea further we decided to investigate some of the salts of 4,4'-biphenyldisulfonic acid. Here the same charge carrying groups are separated by a much larger distance. The Cu<sup>+2</sup> salt was chosen to be analogous to the CuBDS, and the Na<sup>+</sup> and K<sup>+</sup> salts to help establish the  $\lambda_-^0$  of the biphenyl disulfonate anion (BPDS). Finally the Na<sup>+</sup> and K<sup>+</sup> salts of benzenesulfonic acid were to be investigated since they are formally one-half of the Na<sub>2</sub>BPDS and K<sub>2</sub>BPDS. Since Na<sub>2</sub>BPDS is a "polymer" of NaBS of degree of polymerization 2, it is of interest to compare their conductances with the theories of polymer conductance.<sup>5</sup>

### Experimental

Na<sub>2</sub>BPDS can be obtained in a reasonably pure form commercially<sup>6</sup> and was further purified in the following way. It was first converted to K<sub>2</sub>BPDS and recrystallized several times from water. Since K<sub>2</sub>BPDS is much less soluble in cold water than K<sub>2</sub>SO<sub>4</sub>,<sup>7</sup> this gave a good separation from the main impurity, sulfate. The K<sub>2</sub>BPDS was partially converted to acid using cation exchange techniques and the acid used to prepare the Cu<sup>+2</sup> and Na<sup>+</sup> salts by reaction with CuCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>. The K<sup>+</sup> and Na<sup>+</sup> salts of benzene sulfonic acid were prepared by neutralizing HBS<sup>8</sup> with

Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub>. All salts then were recrystallized from conductivity water twice, dried and analyzed. CuBPDS dries to a definite hexahydrate over CaCl<sub>2</sub> at room temperature. The other salts all were dried to the anhydrous form at 110°.

### ANALYTICAL RESULTS

Salt	Method <sup>a</sup>	% Anion	
		Obsd.	Calcd.
CuBPDS·6H <sub>2</sub> O	Electrodeposition	64.44	64.53
	Total cation	64.49	64.53
Na <sub>2</sub> BPDS	Total cation	87.13	87.16
K <sub>2</sub> BPDS	Total cation	79.89	79.97
NaBS	Total cation	87.11	87.16
KBS	Total cation	79.94	79.97

<sup>a</sup> Total cation results were obtained by cation exchange.

The organic component purity can be checked by conversion of the potassium salts to the respective sulfonyl chlorides and checking the melting point.

The experimental techniques used for the conductance measurements and the hydrolysis correction for the Cu<sup>+2</sup> ion are exactly as described previously.<sup>1</sup>

### Calculation of Results

The equivalent conductances of the five salts are given in Table I. All data were treated using the Fuoss-Onsager equation for unassociated electrolytes<sup>9</sup>

$$\Lambda = \Lambda^0 - SC^{1/2} + EC \log C + JC$$

In the actual calculations the following technique was used.

$$\Lambda' \equiv \Lambda + SC^{1/2} - E_C \log C \equiv \Lambda^0 + JC$$

An approximate  $\Lambda^0$  is estimated from the  $(\Lambda, C^{1/2})$  plot and used to calculate  $S$  and  $E$ .  $\Lambda'$  is then calculated and treated by least squares techniques to obtain a new  $\Lambda^0$  and  $J$ . If the new  $\Lambda^0$  is sufficiently different from the original, the cycle is repeated until further cycling gives no significant change in  $\Lambda^0$ . The process is somewhat more complicated for the unsymmetricals where both  $\lambda_+^0$  and  $\lambda_-^0$  must be used.

To cut down arithmetical mistakes and avoid too frequent personal judgments, the above calculations were programmed for the IBM 704 computer. The program does the cycling automatically and yields the "best"  $\Lambda^0$  and  $J$  as well as the calculated  $\Lambda$  for each point. It also calculates  $a^0$  from  $J$  using normal computer techniques. In the least squares treatment of  $\Lambda'$  no weighting factor is used to represent error since we do not feel that the weighting factor previously used<sup>10</sup> adequately represents the error trend. The computer output also includes a standard deviation from the "best"

(9) Ref. 2, Chapt. XV (for application to 2-1 and 2-2 salts see ref. 1).

(10) R. L. Kay, *J. Am. Chem. Soc.*, **82**, 2099 (1960).

(1) G. Atkinson, M. Yokoi and C. J. Hallada, *J. Am. Chem. Soc.*, **83**, 1570 (1961).

(2) C. J. Hallada and G. Atkinson, *ibid.*, **83**, 3759 (1961).

(3) R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience Publishers, Inc., New York, N. Y., 1959.

(4) Ref. 3, Chapt. XI.

(5) E.g., S. A. Rice, *J. Am. Chem. Soc.*, **80**, 3207 (1958).

(6) Eastman Organic Chemicals, Rochester, N. Y., Item P4590.

(7) R. Fittig, *Ann.*, **132**, 201 (1866).

(8) Eastman Organic Chemicals, Rochester, N. Y., Item P2313.

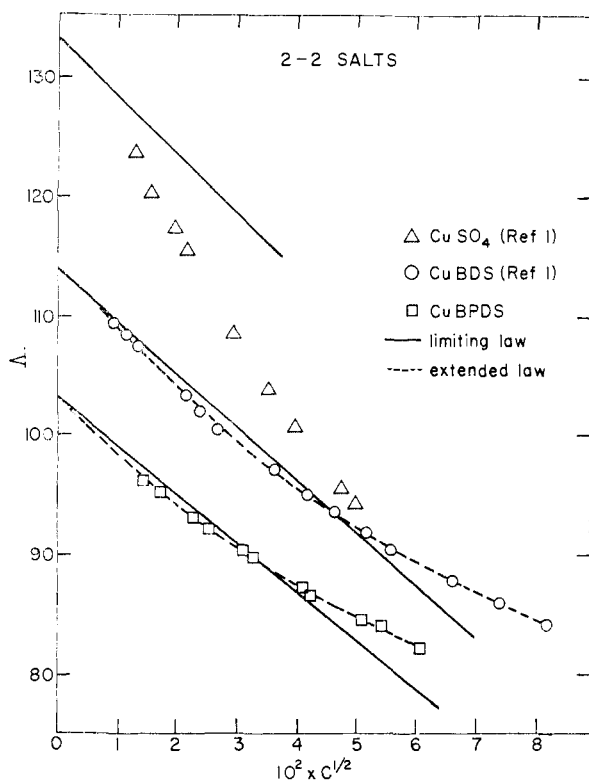


Fig. 1.

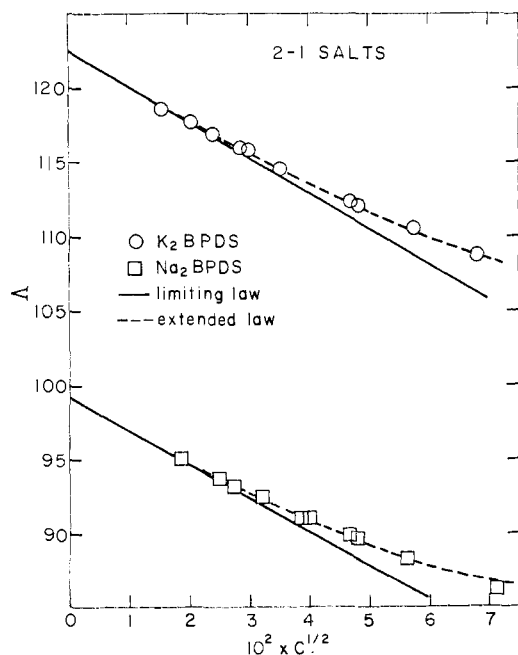


Fig. 2.

$\Lambda'$  line as well as individual deviations for each point.

Table II gives the results obtained from the calculations.

Figure 1 compares the  $(\Lambda, C^{1/2})$  plots of CuBPDS, CuBDS and  $\text{CuSO}_4$ , a typical associated electrolyte of this charge type. The CuBPDS exhibits the same crossover behavior shown by

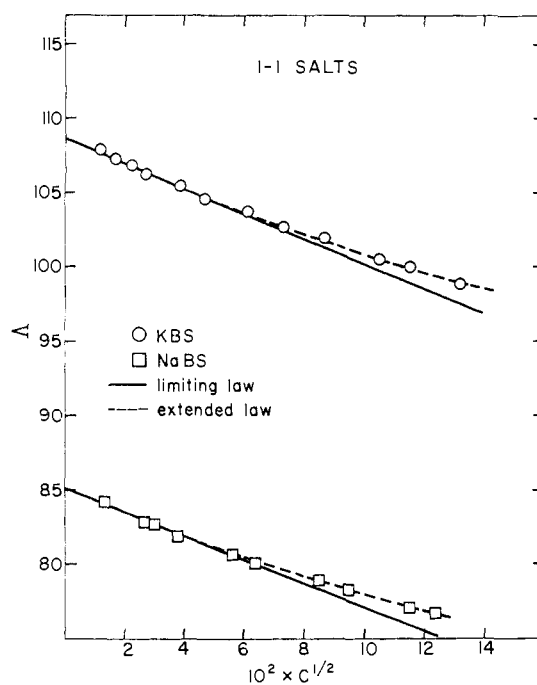


Fig. 3.

$\text{CuBDS}^1$  Figure 2 shows the phoreograms of the 2-1 salts and Fig. 3 those of the 1-1 salts. It is quite apparent that these are all unassociated salts to a very good approximation. The crossover on the CuBPDS appears quite different from that of CuBDS. This is because the crossover parameters are very sensitive to the values of  $E$  and  $J$ , depending on them in a logarithmic fashion. The  $a^0$  parameters for the  $\text{Na}^+$  and  $\text{K}^+$  salts are fairly self-consistent. If we compare the results found here with those of Kay for the chlorides, we find the  $\Delta a^0$ 's ( $\text{NaX-KX}$ ) are 0.12 ( $\text{Cl}^-$ ), 0.18 ( $\text{BS}^-$ ) and 0.14 ( $\text{BPDS}^-$ ). At the present time we do not care to make any further attempt to correlate  $a^0$ 's with simple crystalline structural parameters. When the  $\lambda_-^0$  (av.) for  $\text{BPDS}^-$  from the  $\text{Na}^+$  and  $\text{K}^+$  salts is used to calculate  $\lambda_+^0$  for  $\text{Cu}^{++}$  using the Kohlrausch rule, a value is obtained somewhat lower than that found from the previous  $\text{BDS}^-$  work. The significance of this is not clear.

#### Discussion

A further examination of the  $\text{BS}^-$  and  $\text{BPDS}^-$  anions gives some interesting results. By definition

$$\omega_i = \text{ionic mobility of the } i\text{th ion} = \frac{300 \lambda_i}{96500 |Z_i| \epsilon}$$

where

$$\begin{aligned} \lambda_i &= \text{equivalent conductance of } i\text{th ion} \\ |Z_i| &= \text{absolute charge on } i\text{th ion} \\ \epsilon &= \text{electronic charge} \end{aligned}$$

Then, Stokes law can be written

$$\frac{1}{\omega_i} = \xi_i = 6\pi\eta_0 a_i$$

where

$$\begin{aligned} \xi_i &= \text{frictional coefficient} \\ \eta_0 &= \text{solvent viscosity} \\ a_i &= \text{hydrodynamic radius} \end{aligned}$$

TABLE I  
 CONDUCTANCE DATA<sup>a, b</sup>

NaBS				CuBPDS		Na <sub>2</sub> BPDS		K <sub>2</sub> BPDS	
10°C	Λ	10°C	Λ	10°C	Λ	10°C	Λ	10°C	Λ
1.9177	84.190	1.4381	107.982	2.3051	96.351	3.4720	95.04	4.3012	117.68
7.4035	82.910	2.7077	107.287	2.8066	95.610	6.2670	93.78	5.9150	116.92
8.7756	82.842	5.0285	106.898	5.3696	93.322	7.5950	93.15	8.4950	115.97
14.565	82.025	7.5088	106.184	6.5955	92.309	10.318	92.52	8.9330	115.79
31.896	80.780	15.375	105.462	9.7567	90.375	14.949	91.12	12.690	114.50
40.987	80.339	22.551	104.626	10.802	89.912	16.047	91.12	22.241	112.30
71.869	78.984	37.258	103.761	16.922	87.336	21.542	89.82	23.175	112.11
89.870	78.392	53.917	102.733	17.355	87.080	23.222	89.74	33.220	110.46
132.87	77.198	75.504	101.950	26.368	84.422	31.699	88.33	46.315	108.69
152.10	76.811	110.50	100.647	29.605	84.227	50.900	86.19	67.410	106.51
		133.76	100.081	36.253	82.217				
		175.00	98.921						

<sup>a</sup> Concentration units are mole/l., conductance units are equivalent conductances (ohm<sup>-1</sup> cm.<sup>2</sup> eq.<sup>-1</sup>). <sup>b</sup> The number of figures reported for Λ and C are greater than the probable errors would deem significant. This is so that other workers may recalculate the results without experiencing rounding-off errors.

 TABLE II  
 CONDUCTANCE PARAMETERS

Salt	Λ <sup>0</sup>	λ <sub>+</sub> <sup>00</sup>	λ <sub>-</sub> <sup>0</sup>	a <sub>j</sub> (Å.)
NaBS	85.09	(50.18)	34.91	3.36
KBS	108.51	(73.55)	34.96	3.18
Na <sub>2</sub> BPDS	99.22	(50.18)	49.02	4.64
K <sub>2</sub> BPDS	122.51	(73.55)	48.96	4.50
CuBPDS	103.37	54.38	(48.99)	6.26

<sup>a</sup> The λ<sub>+</sub><sup>0</sup> for Na<sup>+</sup> and K<sup>+</sup> are standard values. <sup>b</sup> The λ<sub>-</sub><sup>0</sup> used to calculate λ<sub>Cu</sub><sup>0</sup> from the Kohlrausch rule is the average of the values obtained from Na<sub>2</sub>BPDS and K<sub>2</sub>BPDS.

Rice has summarized the common equations for the frictional coefficient of a polymer molecule of the type of BPDS<sup>-</sup> as

$$\xi = \frac{6\pi\eta_0 b_0 Z}{\ln Z - \left(1 - \frac{6\pi\eta_0 b_0}{2\xi_0}\right)} \quad (\text{Short stiff chain}^{11})$$

and

$$\xi \approx \frac{6\pi\eta_0 b'}{\ln \left(\frac{2b'}{a'}\right)} \quad (\text{Rigid ellipsoid}^{12})$$

where

- Z = degree of polymerization
- b<sub>0</sub> = interbead separation
- ξ = frictional coefficient of monomer unit
- b' = semi-major axis of ellipsoid
- a' = semi-minor axis of ellipsoid

The calculation of the hydrodynamic properties of the BPDS<sup>-</sup> ion from the properties of the BS<sup>-</sup> ion is summarized below. The rigid ellipsoid seems

$$\text{BS}^- \text{ ion } \xi_M = 4.40 \times 10^{-9} \text{ sec.-cm.}^{-1}$$

$$\text{Stokes radius} = a_M = 2.61 \text{ \AA.}$$

$$\text{BPDS}^- \text{ (ellipsoid) } Z = 2, a' = a_M = 2.61 \text{ \AA.}$$

$$b' = 2a_M = 5.22 \text{ \AA.}$$

$$\rightarrow \xi_D = 6.35 \times 10^{-9} \text{ sec.-cm.}^{-1}$$

(11) J. Riseman and J. G. Kirkwood, *J. Chem. Phys.*, **18**, 512 (1950).

(12) F. Perrin, *J. Phys. Rad.*, **7**, 1 (1936).

$$\xi_D \text{ (exp.)} = 6.24 \times 10^{-9} \text{ sec.-cm.}^{-1}$$

$$\text{BPDS}^- \text{ (chain) } Z = 2, b_0 = 2a_M = 5.22 \text{ \AA.}$$

$$\rightarrow \xi_D = 2.54 \times 10^{-8} \text{ sec.-cm.}^{-1}$$

$$Z = 2, b_0 = a_M = 2.61 \text{ \AA.}$$

$$\rightarrow \xi_D = 4.56 \times 10^{-8} \text{ sec.-cm.}^{-1}$$

to provide a much better hydrodynamic description of the BPDS<sup>-</sup> ion than the short stiff chain. This is in contrast to Rice's findings<sup>5</sup> on the series (Me)<sub>3</sub>N<sup>+</sup>(CH<sub>2</sub>)<sub>n</sub>N<sup>+</sup>(Me)<sub>3</sub> (n = 3,4,6,10) where the chain model gave a very nice description. These divergent explanations can, of course, be rationalized by the fact that the BPDS<sup>-</sup> ion is rigid while the diquatery salts have flexibility. The data are too scant, however, to pursue this further at this time.

Since it does not seem possible to obtain a dissociation constant for the M<sub>2</sub>BPDS salts in water, Rice's treatment of this aspect of bolion behavior must be ignored at present. It would be extremely worthwhile to extend these experiments to solvent-mixtures of lower dielectric constant so that ion-pairing could be examined. It is also of interest to examine bolions where the sulfonate charges are farther apart than in BPDS<sup>-</sup>. These areas are being pursued in this Laboratory.

In conclusion we can say that we have shown CuBPDS to be another essentially unassociated 2-2 electrolyte and have found that the hydrodynamic behavior of the BPDS<sup>-</sup> anion can be correlated very well with its monomer unit, the BS<sup>-</sup> ion. It then becomes apparent that such bolaform disulfonates can furnish an extremely valuable tool for the examination of the theories of polyelectrolyte behavior.

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