January, 1980] *Bull. Chem. Soc. Jpn.*, ***53****, 19—21 (1980)*

Diffusion Coefficients of Bolaform Electrolytes. Part II.[†] Diffusion Coefficients of Magnesium 1,2-Ethanedisulfonate and Magnesium 1,4-Butanedisulfonate in Aqueous Solution

Hisashi UEDAIRA* and Hatsuho UEDAIRA

Research Institute for Polymers and Textiles, 1-1-4 Yatabe-Higashi, Tsukuba, Ibaraki 305

(Received May 11, 1979)

The diffusion coefficients of magnesium 1,2-ethanedisulfonate and magnesium 1,4-butanedisulfonate in aqueous solutions have been measured at 25 °C. The concentration dependence of the diffusion coefficients of these salts was larger than those of the corresponding sodium salts. It has been shown that the 2:2 bolaform electrolyte behaves approximately like an ordinary 2:2 electrolyte. From these and previous results, it has been concluded that the diffusion behavior of bolaform electrolytes distinctively depend on the valency of the counterion.

In a previous report,[1] it was reported that diffusion of the 2:1 bolaform electrolyte, *i. e.*, the salt composed of a bolion[2] and two monovalent counterions, showed a peculiar behavior: the diffusion coefficients were significantly larger than that calculated according to the theory of diffusion of ordinary 2:1 electrolytes. The results were interpreted by assuming that the bolaform electrolyte behaves like an ordinary 1:1 electrolyte in the concentration range where the ionic atmosphere around each charged group is independent.

The spin-lattice relaxation time of ^{23}Na in aqueous solutions of sodium sulfonates has been reported.[3] The relaxation rate of ^{23}Na in ethanedisulfonate solution was reported to be smaller than that in butandisulfonate solution. If the both terminal sulfonic groups contribute to the relaxation rate of the Na^+ ion, the ^{23}Na relaxation rate in ethanedisulfonate solution should be larger. This result indicates that the Na^+ ions crowd separately around each sulfonic group and the electrostatic interaction between each crowd and the sulfonic group at one end is independent from the other terminal group.

In the case of the 2:2 bolaform electrolyte, the situation appears to be different. It is expected that the concentration dependence of the diffusion coefficients of 2:2 salts are larger than that of 2:1 salts. The diffusion coefficients of magnesium 1,2-ethanedisulfonate (MgEDS) and magnesium 1,4-butanedisulfonate (MgBuDS) in aqueous solution at 25 °C are presented and the effect of the valency of the counterion is discussed.

Experimental

MgEDS and MgBuDS (G. R., Tokyo Kasei Co.,) were recrystallized from water four times.

The diffusion experiments were performed at 25±0.01 °C using a Spinco Model H diffusion apparatus as Rayleigh interferometer. Details of the measurements are described elesewhere.[4]

Water, which was distilled after deionization, was used as the solvent. All the solutions were prepared by weight with the appropriate vacuum correction. The molar concentrations of the solutions were calculated from the densities, which were measured with a densimeter DMA O2C (Anton Paar Co.,) at 25±0.001 °C.

Results and Discussion

The mean concentration in each diffusion experiment and the corresponding value of the diffusion coefficient are given in Table 1. The diffusion coefficient of each salt at infinite dilution was calculated from the

TABLE 1. DIFFUSION COEFFICIENTS OF BOLAFORM ELECTROLYTES IN WATER AT 25 °C

Electrolytes	$c\times10^2$ / mol l^{-1}	$D\times10^5$ / cm^2 s^{-1}
1,2-MgEDS	0	0.7713
	0.4658	0.6695
	2.2667	0.6368
	3.0158	0.6338
	8.7935	0.6205
	12.4196	0.6211
	16.4742	0.6218
1,4-MgBuDS	0	0.7058
	0.7526	0.6314
	2.2524	0.6088
	4.0967	0.5985
	6.3088	0.5960
	8.9845	0.5921
	15.8497	0.5872

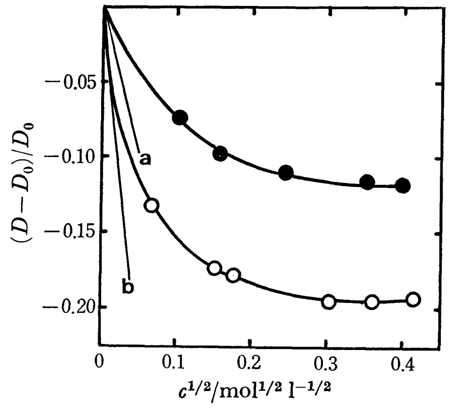

Fig. 1. Relative diffusion coefficients of MgEDS and Na_2EDS in aqueous solutions.
—●— Na_2EDS, —○— MgEDS.
a; The limiting slope for Na_2EDS, b; the limiting slope for MgEDS.

[†] For Part I in this series see Ref. 1.

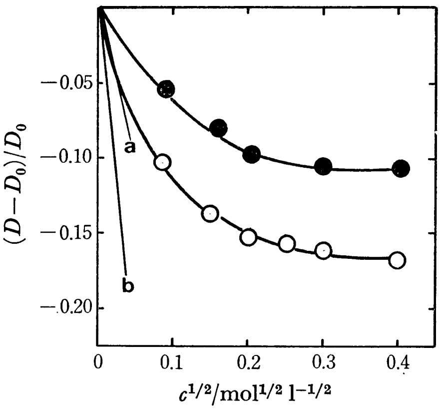

Fig. 2. Relative diffusion coefficients of MgBuDS and Na_2BuDS in aqueous solutions.
—●— Na_2BuDS, —○— MgBuDS.
a; The limiting slope for Na_2BuDS, b; the limiting slope for MgBuDS.

limiting mobilities of the relevant ions by the Nernst equation. The limiting mobilities of EDS^{2-}, $BuDS^{2-}$, and Mg^{2+} ions are 63.9[1] 63.1,[1] and 50.03[5] cm^2 Ω^{-1} equiv^{-1}, respectively.

Figures 1 and 2 show plot of $(D-D_0)/D_0$ against $c^{1/2}$ for ethanedisulfonates and butanedisulfonates, respectively. The concentration dependence of the diffusion coefficients of the magnesium salts is larger than that of the sodium salts as expected. For the magnesium salts as well as the sodium salts, the dependence is smaller for butanedisulfonate than for ethanedisulfonate.

The diffusion coefficient of an electrolyte in aqueous solution may be given by

$$D = (D_0+\Delta_1)\left(1+c\frac{\mathrm{d}\ln y}{\mathrm{d}c}\right) \tag{1}$$

where D_0 is the Nernst limiting value of the diffusion coefficient, c the molarity and y the activity coefficient in molarity scale. Δ_1 is the first-order electrophoretic term.

The limiting equation for the diffusion coefficient may be obtained from the limiting mobilities of the cation and bolaform anion;[6]

$$D = D_0 - 3.63\times10^{-5}\sqrt{c} \tag{2}$$

for MgEDS, and

$$D = D_0 - 3.32\times10^{-5}\sqrt{c} \tag{3}$$

for MgBuDS.

In Figs. 1 and 2, the limiting slopes for 2:1 and 2:2 bolaform electrolyte are shown. The curves drawn through the experimental values approach asymptotically to the limiting slope only for the 2:2 bolaform electrolyte.

For 2:2 electrolytes, Δ_1 and the rational activity coefficient $f_\pm$ at 25 °C may be expressed by following relations, respectively.[5]

$$\Delta_1 = -8.07\times10^{-6}\frac{(\lambda_0^+-\lambda_0^-)^2}{\lambda_0^2}\cdot\frac{\sqrt{c}}{1+\kappa a} \tag{4}$$

$$\ln f_\pm = -\frac{9.42\sqrt{c}}{1+0.658a\sqrt{c}} + bc \tag{5}$$

where λ_0^+ and λ_0^- are the limiting mobilities of the cation and bolion, respectively. $\lambda_0=\lambda_0^++\lambda_0^-$. a and b are the constants adjustable to fit the experimental curve of the activity coefficient. κ has the usual meaning. The experimental data for the activity coefficients for MgEDS and MgBuDS are, however, not available at present. Consequently the values of a and b in Eq. 5 were estimated as follows.

In a previous report,[1] a was reported as 0.396 nm for Na_2EDS. Since a is related to the closest distance between the cation and the charged group of bolion, a is given as 0.553 nm for MgEDS by employing the Stokes radius for the cations.[5] The empirical relation given by Davis[5] $b=0.1\ |z_+z_-|$, was then employed, where z_+ and z_- are the valencies of the cation and anion, respectively.

The calculated diffusion coefficient for MgEDS is compared with the experimental value in Fig. 3. The decrease of the diffusion coefficient comes from that of the activity coefficient, since the Δ_1 value is of the order 10^{-8}—10^{-9} cm^2 s^{-1} and negligible compared with D_0. Similarly, the second-order electrophoretic term Δ_2 is of the order 10^{-9} cm^2 s^{-1} and of negligible contribution.

The density term of the activity coefficient ln y is small and contributes *ca.* 2% to the diffusion coefficient at 0.16 mol l^{-1}, becoming negligible below 0.07 mol l^{-1}.

The experimental and calculated values show greater agreement for MgEDS than for Na_2EDS, *i. e.*, at $c=0.16$ mol l^{-1}, the ratio of these values is 1.5 for Na_2EDS, but only 1.04 for MgEDS. The experimental determination of the activity coefficient of MgEDS will bring the calculated coefficient closer to the experimental one, since the correct value of b for MgEDS is probably larger than 0.4 as judged from 0.335 for Na_2EDS.[1]

A 2:1 bolaform electrolyte behaves approximately as a 1:1 electrolyte,[1] when the ionic atmosphere around each charged group is independent under the condition $\kappa R>1$, where R is the charge distance of the bolion. That is to say, a bolion behaves like two monovalent ions

If the 2:2 boalform electrolyte behaved like the 2:1 bolaform electrolyte under the conditions $\kappa R>1$, it would behave like an ordinary 1:2 electrolyte.

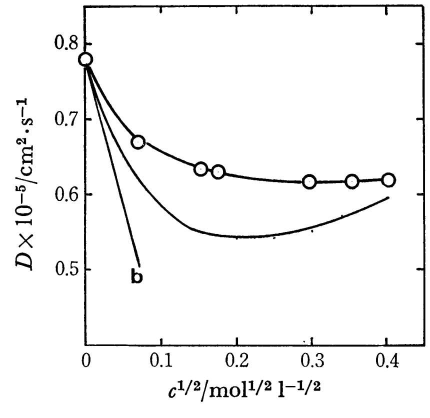

Fig. 3. Diffusion coefficients of MgEDS in aqueous solution.
—○— Experimental values, ——— calculated values, b; limiting slope.

From Figs. 1, 2, and 3, it is evident that the behavior of 2:2 bolaform electrolytes are quite different from that of the ordinary 1:2 electrolytes but resemble the ordinary 2:2 electrolytes. This is reasonable since the divalent counterion must contribute to the formation of the ionic atmospheres around the two charged groups of a bolion or bolions.

The motion of a charged group in a bolion is restricted by the other one connected to the skelton. In the diffusion process, the cation and anion move with the same velocity; hence a divalent counterion and two charged groups of two bolions or a counterion and a bolion move with the same velocity, *i.e.*, a counterion and a bolion move with the same veloctiy. That is, the 2:2 bolaform electrolyte behaves approximately like an ordinary 2:2 electrolyte.

There is a difference between the concentration dependence of the diffusion coefficient of the 2:2 bolaform electrolyte and that of the ordinary 2:2 electrolyte. The diffusion coefficient of the latter shows a minimum but that of the former shows a monotonical tendency to approach a constant value. Rice[7] pointed out that the assymmetry of the ion atmosphere leads to an additional retarding effect which will compensate for the increase in the diffusion coefficient by the thermodynamic term.

The concentration dependence of the diffusion coefficients of magnesium salts is larger than that of sodium salts. The explanation for this is that the concentration dependence of the activity coefficient of magnesium salts is larger than that of the sodium salts (compare Eq. 5 with Eq. 5 Ref. 1). And this is due to the ionic distribution which depends strongly on the valency of the counterion.

In the case of 2:1 bolaform electrolytes, Thomson *et al.*[8] found that the diffusion coefficients of potassium *p*-benzenedisulfonate and potassium 4,4′-biphenyldisulfonate in aqueous solution show no concentration dependence. The authors have shown that the sodium salts of several alkyl and aromatic disulfonic acids behave like 1:1 electrolytes rather than 2:1 electrolytes. The origin of this difference in diffusion has not yet been clarified. Such peculiar diffusion behavior probably only occurs in the case of 2:1 bolaform electrolytes with monoatomic counterions.

The authors would like to thank Dr. J. Komiyama (Tokyo Institute of Technology) for his interesting and helpful discussions.

References

1) H. Uedaira, *Bull. Chem. Soc. Jpn.*, **46**, 401 (1973).
2) R. M. Fuoss, *J. Am. Chem. Soc.*, **77**, 198 (1955).
3) H. Uedaira and H. Uedaira, 38th National Meeting of the Chemical Society of Japan, Nagoya, October 1978, Abstr. No. 2T11.
4) H. Uedaira and H. Uedaira, *Bull. Chem. Soc. Jpn.*, **42**, 2140 (1969).
5) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed Butterworths, London (1959).
6) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolyte Solutions," 3rd ed Reinhold, New York (1958).
7) S. A. Rice, *J. Am. Chem. Soc.*, **80**, 3207 (1958).
8) G. Thomson, S. A. Rice, and M. Nagasawa, *J. Am. Chem. Soc.*, **85**, 2537 (1963).