September, 1988] **NOTES** Bull. Chem. Soc. Jpn., 61, 3315—3316 (1988) 3315

Determination of Ionic Partial Molar Volumes of Bolaform Electrolytes by Means of Sedimentation Potential Measurements

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(Received March 31, 1988)

Synopsis. Sedimentation potentials (SP) and electrical conductivities have been measured in aqueous solutions of three kinds of bolaform electrolytes, $[R_3N\text{-}(CH_2)_n\text{-}NR_3]Br_2$ where R stands for ethyl group and n is equal to 4, 6, and 10. Using the SP and conductivity data the partial molar volumes of the bolaform salts were divided into cationic and anionic parts. Two ionic sites of the bolaform electrolytes behave independently.

Partial molar quantities of a dissolved electrolyte are known to give much information on various aspects of solute-solvent interactions. Among them, partial molar volumes V_2^0 is perhaps one of the most familiar and useful quantities, since its accurate values can be determined directly from density measurements. Inspection of the temperature dependence of partial molar volumes of electrolytes indicates that significant differences in ion-water interactions exist for cations and anions. For detailed discussion of V_2^0 data, ionic division of V_2^0 of electrolytes is indispensable. A number of workers have carried out the ionic division based on various theoretical and/or empirical criteria. The criteria or assumptions adopted and the results obtained are given in a review.[1]

Method of ionic division founded on a firm theoretical ground has long been restricted to the ultrasonic vibration potential (UVP) measurement. Unfortunately, special techniques are needed to use this valuable method. An alternative to the UVP method is the sedimentation potential (SP) measurement. Recently a sedimentation potential generating apparatus (SPGA) was designed by one of the present authors (H.H) and the sedimentation potentials were measured with sufficient accuracy for aqueous solutions of ordinary inorganic electrolytes.[2] In this note, we will report first the results of sedimentation potential measurement on bolaform electrolytes in aqueous solutions and then discuss the ionic partial molar volumes evaluated.

Bolaform electrolyte is a class of salts with general formula $[R_3N\text{-}(CH_2)_n\text{-}NR_3]Br_2$. Following the official nomenclature it is expressed as bis(tetraalkylammonio)alkaline dibromide. In this work three kinds of bolaform salts were used as samples for which R=ethyl, and n is equal to 4, 6, and 10. These samples will be abbreviated as J4, J6, and J10, respectively. Samples were prepared and purified as described elsewhere.[3]

The experimental procedures of SP measurements are the same as those in our previous paper.[2] For the ionic division of V_2^0 transference numbers are necessary. These values are not found in the literature. For this reason as part of this work, electric conductivities were measured using a Fuso 360 linear-bridge conductometer. The cell constant of the cell used in the present study was 0.1240 cm^{-1} and the concentration ranges were 10^{-4} to 10^{-3} mol dm^{-3}.

All measurements were done at 25 °C.

The concentration dependences of SP of bolaform electrolytes in aqueous solutions are shown in Fig. 1. Negative values of SP were observed for all samples investigated and the values decreased with increasing concentration. At lower concentrations, the SP values became independent of concentration of the salts. With increasing molecular weight, the absolute values of SP increased.

The limiting conductivities of bolaform electrolyte were evaluated from the least squares fitting of the following Debye-Hückel-Onsager equation;

$$\Lambda = \Lambda^\infty - (B_1\Lambda^\infty + B_2)c^{1/2} \qquad (1)$$

where c is the concentration in mol dm^{-3} and B_1 and B_2 are the parameters given by the theory. For the sample J4, down ward deviation from Eq. 1 was observed, suggesting that ion-pairing occurs for this salt. But no further discussion on the conductivity will be done, since the conductivity data at infinite dilution are needed at this stage for the evaluation of the transference number only. The limiting values Λ^∞ obtained are summarized in the third column of Table 1.

The SP generated in aqueous electrolyte solutions

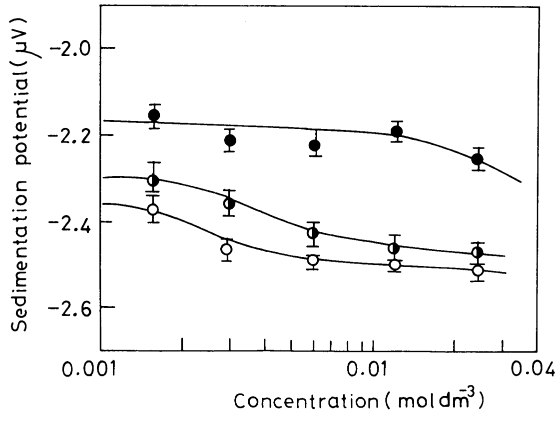

Fig. 1. Sedimentation potential for bolaform electrolytes as a function of concentration: ●J4; ◑J6; ○J10.

Table 1. Sedimentation Potential (SP) and Limiting Molar Conductivity of Bolaform Salts in Aqueous Solutions and Calculated Partial Molar Volumes for Cation and Anion

	SP	Λ^{∞}	$V_2{}^0$	$V_+{}^0$	$V_-{}^0$
	μV	S cm^2 mol^{-1}	cm^3 mol^{-1}	cm^3 mol^{-1}	cm^3 mol^{-1}
J4	−2.16	232.7	322.28[a]	267.0	27.5
J6	−2.30	237.6	356.50[a]	303.3	26.6
J10	−2.35	240.5	420.26[a]	365.3	27.5

a) Ref. 4.

using our apparatus is expressed as follows;[2)]

$$V = 1.015 \times 10^{-6}\left[\frac{t_+}{z_+}(m_+ - V_+{}^0\rho) - \frac{t_-}{z_-}(m_- - V_-{}^0\rho)\right]x_0 \quad (2)$$

where t is the transference number, z is the charge, m is the molecular weight of the ion, ρ is the density of solvent, x_0 is the velocity amplitude, and the other symbols have their usual meanings. Since $V_2{}^0 = \nu_+V_+{}^0 + \nu_-V_-{}^0$, by combining the partial molar volume and the SP of an electrolyte, one can evaluate the partial molar volumes of the constituent ions without relaying on any kind of extra-thermodyamic or semiempirical assumptions. The partial molar volumes of J4, J6, and J10 are found in the literature.[4)] The transference numbers t_+ and t_- were calculated from the limiting ionic conductivities given in Table 1 and the literature value[5)] of $\Lambda^{\infty}(\mathrm{Br}^-)=78.14$ S cm^2 mol^{-1}. The estimated transference numbers of bolaform ions are 0.4944, 0.5100, and 0.5187, for J4, J6, and J10, respectively. The individual ionic partial molar volumes obtained are included in Table 1. The values of $V_-{}^0(\mathrm{Br}^-)$ in Table 1 are all around 27.2 cm^{3}mol^{-1}. These values are a little smaller than those generally accepted; $V_-{}^0(\mathrm{Br}^-)=29.2$—30.9 cm^3 mol^{-1} according to the compilation of Millero.[1)] However, in view of the precision of SP measurements[4)] this difference has no significance. Rather, our work can serve as experimental evidence that ionic additivity of partial molar volume holds for these bolaform electrolytes. The ionic additivity corresponds to the independent behavior of the two separated ionic sites in the bolaform cations in aqueous solutions. The relationship for increment of partial molar volume and number of methylene groups in bolaform salts has been discussed elsewhere.[4)]

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