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Ionic Partial Molar Volumes of Alkali Halides in Methanol as Evaluated from the Sedimentation Potentials

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Sedimentation potential (SP) measurements were carried out for solutions of alkali halides dissolved in methanol. With the SP data thus obtained, the partial molar volumes $\bar{V}_2^\infty$ of alkali halide MX, $\bar{V}_2^\infty$ (MX), were divided into cationic $\bar{V}_2^\infty$ (M^+) and anionic $\bar{V}_2^\infty$ (X^-) parts. The ionic partial molar volumes evaluated showed a reasonable agreement with each other. These values of $\bar{V}_2^\infty$ (M^+) and $\bar{V}_2^\infty$ (X^-) are numerically compatible with those reported earlier by Kawaizumi and Zana using the ultrasonic vibration potential method and those given more recently by French and Criss based on the apportionment of the estimated $\bar{V}_2^\infty$ value for the large complex [Ph_4PBPh_4] (*J. Solution Chem.*, **11**, 625 (1982).) The magnitude of the concentration dependence of SP was evaluated theoretically by expressing the apparent molar volume, the transport number, and the density of a solution as functions of the solute concentration.

The evaluation of the anionic and cationic contributions to the properties of an electrolyte which consists of these ions has been one of the most important tasks in the physical chemistry of electrolytes and the goal of many studies. A thorough comparison of the properties of various ions is possible only after individual ionic properties have been evaluated in a convincing manner. For aqueous solvent media, the numerical values of the thermodynamic properties of ions evaluated by many investigators based on different methods are in good, or at least fair, agreement.

Conway1) reviewed the earlier work related to the evaluation of ionic properties and discussed the reliability of the various methods and assumptions adopted up to that time for the assessment of the contribution of each ionic species to the physicochemical properties of the electrolyte as a whole. In his review, Conway judged that, in water, both the ultrasonic vibration potential (abbreviated hereafter as UVP) method2–4) and the extrapolation method5) can lead to excellent results for the division of the partial molar volume $\bar{V}_2^\infty$ of an electrolyte MX, $\bar{V}_2^\infty$ (MX), into cationic $\bar{V}_2^\infty$ (M^+) and anionic $\bar{V}_2^\infty$ (X^-) parts. Contrary to the other methods, the UVP method has been the only one that is completely free from any kind of extrathermodynamic assumption. However, because of the technical difficulty in the UVP method, no widespread use of this important method has yet been made.

For individual ionic properties in nonaqueous solvent systems, marked differences have often been observed among the reported values. These large differences may be attributed to the following three factors. First, the thermodynamic properties of an electrolyte are themselves determined less accurately in nonaqueous media than in aqueous media; hence, the ionic molar quantities derived from them necessarily contain much uncertainty. Second, in evaluating ionic contributions we are forced to rely upon assumptions and semiempirical relations that are physically questionable. Third, the paucity of various kinds of fundamental data prevents us from comparing the numerical values of individual ionic properties given by different authors. For these reasons, we are not certain which results are the more correct.

To date, the ionic division of the partial molar volume of an electrolyte in nonaqueous media using the UVP technique has been done by Zana and his co-workers for methanol,6) ethanol,7) DMF,7) and DMSO.8) An alternative to the UVP method is the sedimentation potential (abbreviated hereafter as SP) method. In the first paper9) of this series, the present authors described an apparatus for measuring the SP designed by one of them (H. H) and the results of the SP measurements of a number of inorganic salts dissolved in water. With this apparatus we have previously measured the SP of aqueous solutions of bolaform electrolytes10) and nitroamminecobalt(III) complexes,11) as well as solutions of LiCl, NaCl, and KCl in mixed water-methanol solvents.12)

In this paper, the results of the SP measurement of alkali halides in methanol will be presented. As has just been mentioned, the ionic partial molar volumes in methanol based on the UVP method6) are available. More recently, French and Criss13) compared the numerical values of the partial molar volume for the Br^- ion, $\bar{V}_2^\infty$ (Br^-), in water and in methanol; these values had been obtained by various methods. Based on the apportionment of the estimated $\bar{V}_2^\infty$ value for the large complex [Ph_4PBPh_4] between cationic and anionic parts in view of the charge effect, they suggested that $\bar{V}_2^\infty (Br^-) = 19.7 \pm 2$ cm^3 mol^{-1} in methanol; their conclusion was that the $\bar{V}_2^\infty$ (Br^-) in methanol is between 17 and 20 cm^3 mol^{-1}. The method of apportionment gives results compatible with those of the UVP method, not only in aqueous systems but also in methanol systems. However, the values of $\bar{V}_2^\infty$ (Br^-) considered in the paper of French and Criss13) are almost incredibly scattered, ranging from −30.5 to 21.7 cm^3 mol^{-1}. In view of this, it is of considerable interest to measure the SP of simple electrolyte alkali halides in methanol and to determine the individual partial molar volumes of alkali metal ions and halide ions from the SP data

Experimental

Specimens. The solvent methanol used was of an extra pure grade, and it was used without further purification. Commercial products of alkali halide (guaranteed or extra-pure-grade regent) were dissolved in this methanol to prepare a stock solution at the concentration of 0.1 mol dm^{-3}. Sample solutions at each concentration were prepared by the dilution of the stock solution.

Sometimes the solution properties of nonaqueous solvent systems are significantly affected by the presence of a trace quantity of water. Fortunately, the SP measurements carried out in the mixed water-methanol solvents[12] indicate that it is unnecessary to use absolute methanol as solvent, so long as the water content in the solvent methanol is sufficiently low. In fact, in the UVP measurement,[6] the water in the methanolic electrolyte solution gave rise to no appreciable change in the potentials up to a water content of 1%.

Apparatus and Measurements. The experimental set-up and the procedures of the SP measurement are identical with those described before.[9] The SP measurements were carried out at 23 °C—25 °C.

Results and Discussion

SP Values Observed. Figure 1 shows the results of the SP measurements for alkali chlorides and bromides. The fluorides and iodides also showed a similar concentration dependence. The variation in SP with the salt concentration will be analyzed below. It will be seen there that the use of the logarithmic concentration scale in describing the concentration dependence of SP is acceptable.

The SP values at concentration ranges from 10^{-3} to 10^{-2} mol dm^{-3} were taken as the limiting SP values, and the partial molar volumes of the ions were calculated using these limiting values.

Partial Molar Volumes of Alkali Halides in Methanol. In the introduction, we mentioned that very large differences can be found in the literature values of the physical parameters of electrolytes in nonaqueous solvent systems. For the case of the partial molar volume, for example, the reported values of V_2^∞ for NaCl in methanol are scattered between -5.5[14] $cm^3 mol^{-1}$ and 2.0[15] $cm^3 mol^{-1}$. Such differences seem to arise from the facts that the density of a pure nonaqueous solvent varies during density measurements, because of the atmospheric humidity and that extrapolation to an infinite dilution is seldom carried out as is required by the Debye-Hückel theory.

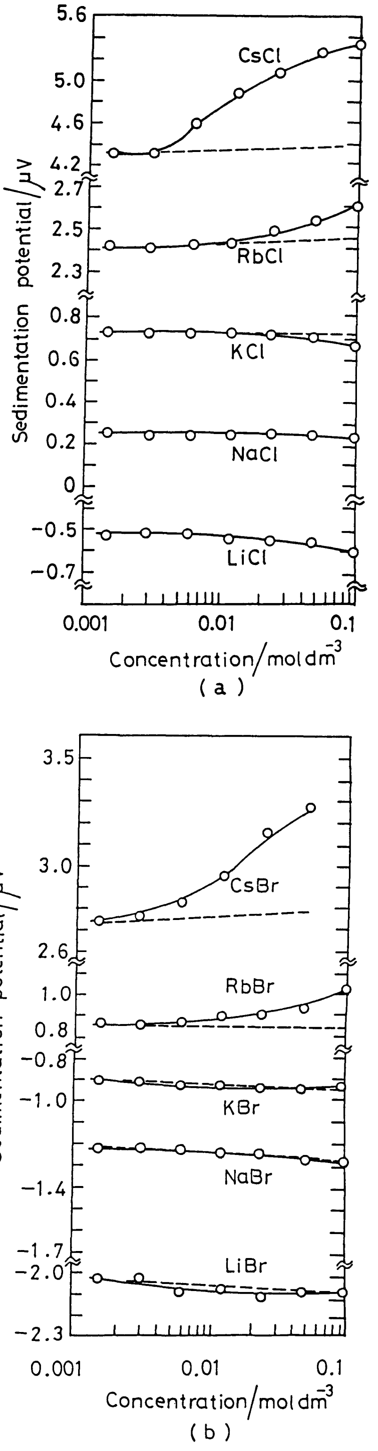

Fig. 1. Sedimentation potential in methanol for (a) chloride and (b) bromide as a function of concentration; —○— experimental; -------- calculated values obtained as explained in the text.

In order for the evaluated ionic partial molar volumes to be reliable and comparable with other reported values on a common basis, we must rely upon the most reliable and "normalized" values of the partial molar volumes, V_2^∞, for which the additivity rule $V_2^\infty = V_+^\infty + V_-^\infty$ should hold (hereafter the subscripts + and − refer to the cation and the anion respectively). For this reason we adopted principally the V_2^∞ of the electrolyte obtained by adding the V_+^∞ and V_-^∞ values listed in the latest publication of French and Criss.[13] These V_2^∞ values generally agree with those given by different authors, within a precision of

2 cm^3 mol^{-1} or better. Only for CsCl does the difference in V_2^∞ value amount to 3.1 cm^3 mol^{-1} (14.7 cm^3 mol^{-1} by the additivity rule, while the value of 17.8 cm^3 mol^{-1} is found in the literature[6]). Even for this case, we have used the value based on the results of French and Criss[13] in order to maintain the internal consistency of this work. However, they gave no value for the V_2^∞ of the Rb^+ ion, V_2^∞ (Rb^+), so this value was estimated by subtracting V_2^∞ (Cl^-), (Br^-), and V_2^∞ (I^-) from the respective values for rubidium salts found in the literature[6] and by then averaging the three resultant V_2^∞ (Rb^+) values.

Ionic Partial Molar Volumes in Methanol. As was done in our previous papers,[9–12] by solving simultaneously the additivity relation $V_2^\infty=V_+^\infty+V_-^\infty$ and Eq. 1; we can obtain numerical values of V_+^∞ and V_-^∞ which are free from any extrathermodynamic assumptions:

$$E=(ad/F)\cdot[(t_+/z_+)\cdot(m_+-V_+^\infty\rho)-(t_-/z_-)\cdot(m_--V_-^\infty\rho)] \quad (1)$$

Here, E is the SP; a, the acceleration; d, the distance between the two electrodes; F the Faraday constant; t, the transport number; z, the charge number; m, the molar mass of the ion, and ρ, the density. In our SP measurements the acceleration a is given as $\omega^2 x$, where ω is the angular frequency, and x, the amplitude of the oscillation generated in the SP apparatus. The partial molar volumes of the cation $V_+^\infty=V_2^\infty$ (M^+) and of the anion $V_-^\infty=V_2^\infty$ (X^-) evaluated for each alkali halide MX are summarized in Table 1, along with the values of t_+, t_-, and V_2^∞ used in the calculation.

Apparently the numerical values of V_2^∞ (M^+) and V_2^∞ (X^-) shown in Table 1 agree within the precision of SP measurements. The ionic partial molar volumes V_2^∞ (M^+) and V_2^∞ (X^-) given in Table 1 were averaged to give, respectively, the values for the M^+ and X^- ions in methanol. The results are shown in Table 2. In methanol, the transport numbers are known less accurately than in water. Differences of 5 units in the third decimal place of t_+ or t_- appear in different sources; this uncertsinty in the transport number alone will effect the ionic partial molar volumes by a little less than 1 cm^3 mol^{-1}. Therefore, Table 2 shows that the ionic partial molar volumes in methanol, as evaluated by three completely different methods agree well. Especially for V_2^∞ (Br^-), which was taken by French and Criss as a reference for ionic division, the agreement is better than we expected.

Analysis of the Concentration Dependence of SP. The experimental concentration dependences of the SP of the salts may be classified into three groups:

(1) salts with small concentration dependences; LiCl, NaCl, KCl, LiBr, NaBr, KRr, KI, RbI, and CsI.

(2) salts with moderate concentration dependences; NaF, KF, RbF, RbCl, RbBr, LiI, and NaI.

(3) salts with large concentration dependences; CsF, CsCl, and CsBr.

Table 1. Sedimentation Potential, E, Alkali Halides, and Calculated Ionic Partial Molar Volumes for Cations and Anions in Methanol at 23 °C—25 °C

Sample	E / μV	t_+[a)]	t_-[a)]	V_2^∞[b)] / cm^{3}mol^{-1}	V_+^∞ / cm^{3}mol^{-1}	V_-^∞ / cm^{3}mol^{-1}
NaF	0.72	0.520	0.480	−16.3	−16.24	−0.06
KF	1.15	0.557	0.443	−6.8	−5.23	−1.57
RbF	2.88	0.573	0.427	−1.5[c)]	3.16	−4.66
CsF	5.10	0.593	0.407	2.0	6.10	−4.10
LiCl	−0.53	0.431	0.569	−4.9	−14.79	10.89
NaCl	0.25	0.463	0.537	−3.6	−16.75	13.15
KCl	0.73	0.500	0.500	5.9	−6.88	12.78
RbCl	2.40	0.516	0.484	11.2[c)]	−0.30	11.60
CsCl	4.30	0.538	0.462	14.7	5.01	9.69
LiBr	−2.03	0.412	0.588	2.3	−20.80	23.10
NaBr	−1.23	0.445	0.555	3.6	−20.79	24.39
KBr	−0.90	0.482	0.518	13.1	−6.89	19.99
RbBr	0.86	0.498	0.502	18.4[c)]	−2.09	20.49
CsBr	2.73	0.519	0.481	21.9	3.71	18.20
LiI	−3.76	0.387	0.613	11.5	−25.64	37.14
NaI	−3.14	0.419	0.581	12.8	−21.65	34.45
KI	−2.84	0.455	0.545	22.3	−5.67	27.97
RbI	−1.03	0.471	0.529	27.6[c)]	−2.33	29.93
CsI	0.83	0.493	0.507	31.1	3.27	27.83

a)Calculated from the molar conductivities given in''Physical Chemistry of Origanic Solvents Systems,'' ed by A. K. Covington and T. Dickson, Plenum Press, New York (1973), p. 673. b) Ref. 13. c) See text.

Table 2. Ionic Partial Molar Volumes/(cm^3 mol^{-1}) in Methanol at 25 °C

Ion	K-Z[a)]	F-C[b)]	This work
Li^+	−17.9	−17.5	−20.7±4.0
Na^+	−17.1	−16.2	−19.9±2.4
K^+	−7.3	−6.7	−6.2±0.7
Rb^+	−1.7	—	−0.4±2.2
Cs^+	4.8	2.1	4.5±1.1
F^-	−1.3	−0.1	−2.6±1.9
Cl^-	13.0	12.6	11.6±1.3
Br^-	18.3	19.8	21.2±2.2
I^-	28.2	29.0	31.5±3.7

a) Ref. 6. b) Ref. 13.

In our previous papers,[9–12] no attempt has been made to analyze the concentration dependence of SP. This has been done first in this work as follows: Equation 1 should describe the variation in SP with the concentration of the salts provided that the terms t_+, t_-, V_+, V_-, and d involved in Eq. 1 are given as functions of the solute concentration. As is well-known, these terms are satisfactorily expressed by the following relations:

$$t_\pm=\frac{\lambda_\pm^\infty-\frac{1}{2}B_2\sqrt{c}/(1+\kappa a_0)}{\Lambda^\infty-B_2\sqrt{c}/(1+\kappa a_0)} \quad (2)$$

$$V_\pm=V_\pm^\infty+\frac{3}{4}S_v\cdot c^{1/2} \quad (3)$$

and

$$\rho = \rho^0 + \frac{M - \rho^0 V_2^\infty}{1000} c + \frac{S_v \rho^0}{1000} c^{3/2} \qquad (4)$$

In the above equations, the subscript ± is used instead of using separately the + or − sign to refer to a cation or an anion. The parameters have the following meanings; $\Lambda_\pm^\infty$ and $\lambda_\pm^\infty$ are, respectively, the limiting molar electric conductivities of an electrolyte and that of ions constituting the electrolyte; B_2 is a constant depending on the viscosity, the dielectric constant and the temperature of the solvent; κ is the reciprocal length of the ionic atmosphere; a_0 is the distsnce of the closest approach of two ions; S_v is the coefficient derived from the Debye-Hückel theory; c is the molar concentration ($\mathrm{mol\,dm^{-3}}$) of the electrolyte; M is the molar mass, and the superscript 0 refers to a pure solvent. The a_0's in Eq. 2 were set equal to the sum of the hydrodynamic Stokes radius of cation and that of anion, which can be calculated from the ionic molar conductivities found in the literature.[16] For S_v, we adopted the value of 14.19[14] $\mathrm{cm^3\,mol^{-3/2}\,dm^{3/2}}$. By inserting Eqs. 2—4 into Eq. 1 and using the V_+^∞ and V_-^∞ values listed in Table 1, we can see theoretically how the SP varies with the concentration. The results of this evaluation are represented in Fig. 1 by the dotted lines. As the $V_\pm^\infty$'s are calculated with the SP values at low concentrations, the dotted lines in Fig. 1 agree with the experimental observations in the lower concentration regions. For the salts with small cations (i.e., lithium, sodium, and potassium salts), the evaluated and observed SP variations agree well, while for rubidium salts the experimental SP values deviate upwards from the theoretical curve, and this deviation becomes much larger still for the largest cationic salts, CsCl and CsBr. Any further attempts at the analysis of the behavior of CsCl and CsBr seem to be speculative at present. The significance of the present analysis is that an increase or decrease in the SP with the salt concentration can be predicted in a qualitative manner from a combination of Eqs. 1 through 4. At any rate, the magnitude of the variation in the SP with the salt concentration is small; hence, the problem of selecting a concentration scale (an ordinary concentration scale or logarithmic concentration one) for representing the concentration dependence of SP is reduced to a matter of convenience.

Conclusion

The division of the partial molar volumes into cationic and anionic parts based on the results of SP measurements carried out for 1-1 type inorganic electrolytes dissolved in methanol leads to results which are completely in agreement with those of the UVP method used by Kawaizumi and Zana[6] and the apportionment between ionic parts of a complex salt with a large volume proposed by French and Criss.[13]

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