Determination of Individual Partial Molar Volumes of Ions in Water from Measurements of Ultrasonic Vibration Potentials

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A new apparatus for measurements of ionic vibration potentials generated by the propagation of ultrasonic waves through electrolyte solutions was constructed, and used for the determination of partial molar volumes of ions in aqueous solutions of uni-univalent electrolytes. The apparatus, based on the method of ultrasonic vibration potentials (Zana and Yeager), was improved in two points through the introduction of the Doppler effect: a small measuring cell (about 50 cm^3) and very low noises (50 nV). Then, measurements of temperature variation of ultrasonic vibration potentials have become possible. Partial molar volumes of hydrogen, alkali metal, and halide ions in water were determined in the range of temperature, 15—45 °C.

The ionic partial molar volume has turned out to be a very useful tool in elucidating the nature of ion-solvent interactions in electrolyte solutions.[1,2] For the direct experimental determination of partial molar volumes of individual ions, the method of ultrasonic vibration potentials (UVP) has been found to be the still unique experimental means available to obtain those data. The theoretical basis of the method of UVP was given by Debye,[3] and others,[4,5] formerly, and Zana and Yeager[6] constructed the experimental apparatus for the measurements of UVP in 1967.

In the apparatus used by Zana et al.[6,7] the measuring unit was, however, too large in its size and therefore measurements have been confined near room temperature only. Then, we have undertaken to improve the experimental method of UVP given first by Zana and others, especially aiming at obtaining the data at various temperatures.

Theory and Experimental Procedures

Theory. In a sound field the difference in the dynamical responses between cations and anions within an electrolyte solution produces an alternating potential (ionic vibration potential/ultrasonic vibration potential).

The forces acting on an ion (the jth type) within the solution are expressed as follows,[3,6]

$$e_jE - \mu_j(u_j - u_0) + d_0v_j\frac{\partial u_0}{\partial t} = m_j\frac{\partial u_j}{\partial t}. \quad (1)$$

m_j, e_j, v_j, and u_j, is the mass, the charge, the volume, and the velocity of the ion, respectively. μ_j is the frictional coefficient acting on the ion, d_0 and u_0 the density and the velocity of the solvent molecule, E the strength of the field, and t time.

The Poisson equation is

$$\varepsilon\frac{\partial E}{\partial x} = \Sigma n_j e_j, \quad (2)$$

where ε is the permittivity of the medium, n_j the number density of the jth ions, and x the coordinate (the propagation distance of the sound wave), and the equation of continuity becomes

$$\frac{\partial n_j}{\partial t} + \frac{\partial(n_j u_j)}{\partial x} = 0. \quad (3)$$

The velocity of the ion and solvent in the sound field is expressed as

$$u_j = a_j e^{i(\omega t - kx)}, \quad (4a)$$

$$u_0 = a_0 e^{i(\omega t - kx)}, \quad (4b)$$

where ω and k is the angular frequency and the propagation constant of the sound wave, and $k=\omega/c$ (c; sound velocity). Here, we define α_j as

$$\alpha_j = \frac{a_j m_j - a_0 d_0 v_j}{m_j - d_0 v_j} = \frac{a_j m_j - a_0 d_0 v_j}{w_j}, \quad (5)$$

and the UVP becomes

$$\Phi = -\int E dx = \Phi_0 e^{i(\omega t - kx)}. \quad (6)$$

In the following we treat the case of solutions of uni-univalent electrolyte, where suffixes 1 and 2 denote cations and anions, respectively. Then we can derive the equation of UVP from Eqs. 1—6[6]

$$\Phi_0 F = c(\alpha_1 W_1 t_1 - \alpha_2 W_2 t_2) f(\omega), \quad (7)$$

and

$$f(\omega) = (\sigma/\varepsilon\omega)/[1 + (\sigma/\varepsilon\omega)^2]^{1/2},$$

where F is the Faraday constant, σ the electrolytic conductivity, and t_i (i=1,2) the transport number at the concentration. When the concentration is not so extremly dilute and the sound frequency is not so high, $f(\omega)$ is safely regarded as $f(\omega)=1$[3] and the factor in Eq. 7 can be eliminated. In Eq. 7 W_i (i=1,2) originally defined in Eq. 5 is expressed as molar quantities.

Here, according to Zana et al.,[6] we use following notations with respect to the molar mass of solvated ions,

$$M_i = M_{i0} + M_{iw}, \quad i = 1, 2, \quad (8)$$

where M_{i0} is the molar mass of bare ions and M_{iw} that of solvents solvated to ions. Then, apparent molar volumes of ions φ_i are

$$\varphi_i = V_i - M_{iw}/d_0, \quad i = 1, 2, \tag{9}$$

and the apparent molar volume of the salts φ is

$$\varphi = \varphi_1 + \varphi_2.$$

From Eqs. 7, 8, and 9,

$$\varphi_1 = \frac{1}{d_0(\alpha_1 t_1 + \alpha_2 t_2)} \times [\alpha_1 t_1 M_{10} - \alpha_2 t_2 M_{20} + d_0 \alpha_2 t_2 \varphi - \frac{\Phi_0 F}{c}], \tag{10a}$$

$$\varphi_2 = \frac{1}{d_0(\alpha_1 t_1 + \alpha_2 t_2)} \times [\alpha_2 t_2 M_{20} - \alpha_1 t_1 M_{10} + d_0 \alpha_1 t_1 \varphi + \frac{\Phi_0 F}{c}]. \tag{10b}$$

At this step, if we take for

$$\alpha_1 = \alpha_2 = a_0 \quad \text{(this means } a_1 = a_2 = a_0\text{)}, \tag{11}$$

Eqs. 10 become

$$\varphi_1 = \frac{1}{d_0}(t_1 M_{10} - t_2 M_{20}) + t_2 \varphi - \frac{\Phi_0 F}{a_0 d_0 c}, \tag{12a}$$

$$\varphi_2 = \frac{1}{d_0}(t_2 M_{20} - t_1 M_{10}) + t_1 \varphi + \frac{\Phi_0 F}{a_0 d_0 c}. \tag{12b}$$

Eqs. 12a and 12b are quite identical with those given and used by Zana et al.[6,7] The introduction of the assumption, Eq. 11, means an approximation that, in the derivation of Eqs. 12, the factor $\partial u_j/\partial t$ in the right hand side of Eq. 1 is replaced by $\partial u_0/\partial t$ at this step. Then we adopt here another approximation instead of Eq. 11 as follows,

$$\alpha_1 = \alpha_2 = \alpha \quad (\neq a_0). \tag{13}$$

Using Eq. 13, Eqs. 10a and 10b become respectively

$$\varphi_1 = \frac{1}{d_0}(t_1 M_{10} - t_2 M_{20}) + t_2 \varphi - \frac{\Phi_0 F}{\alpha d_0 c}, \tag{14a}$$

$$\varphi_2 = \frac{1}{d_0}(t_2 M_{20} - t_1 M_{10}) + t_1 \varphi + \frac{\Phi_0 F}{\alpha d_0 c}. \tag{14b}$$

We use Eqs. 14a and 14b here instead of Eqs. 12a and 12b. That is, we measure Φ_0 for two electrolyte solutions containing common ions, for example, NaCl and LiCl, at the same concentration and from the two values of Φ_0, using Eqs. 14a and 14b, we can determine the magnitudes of φ_{Na^+}, φ_{Li^+}, φ_{Cl^-}, and α.

Apparatus and Experimental Procedures. The block diagram of the apparatus constructed is shown in Fig. 1. A 1 MHz ultrasonic wave is propagated in the cell through a transducer by excitation from the 1 MHz oscillator, and the UVP is produced within the

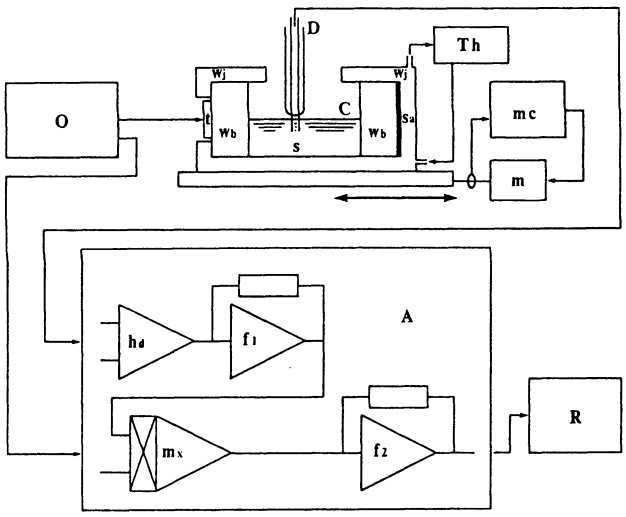

Fig. 1. Block diagram of the apparatus. O: oscillator, C: cell; t transducer (20 mmϕ, ceramics), s sample, w_b buffer (water), s_a sound absorber (butyl rubber), w_j water jacket, m motor, mc motor controller, D: detector, A: amplifier; h_d high input impedance differential amplifier, m_x mixer, f_1 bandpass filter (1 MHz), f_2 bandpass filter (1 Hz), R: recorder, T_h: thermostat.

sample solution. The detector consists of two iridium needles (0.127 mm ϕ) held parallel. In order to detect the UVP, it is rotated in the sample and fixed at an angle where the distance between two needles along the sound wave becomes $\lambda/2$ (λ: the wavelength of the sound wave), and then, as the result of the Doppler effect of the ultrasonic wave by moving the cell back and forth with a constant velocity of $10^{-6}c$, the UVP of $2\Phi_0$ (frequency 1 M$\pm$1 Hz) is produced in the sample and detected between two needles.

In the detecting device circuit, the UVP, via a high input impedance amplifier, is mixed with a direct output from the oscillator, and then, is converted to a 1 Hz wave and 2 M$\pm$1 Hz wave, where the leakage from power sources is converted to a non-alternating current drift and 2 MHz wave. These all waves are lead to a bandpass filter with a central frequency of 1 Hz, and we can easily take out the 1 Hz component only from the UVP. This 1 Hz component is recorded by a recorder of ordinary type, where the total gain of 5000 is required in the amplification device on the whole.

In the device described above, a part of the differential amplifier with high input impedance is shown in Fig. 2.

A typical pattern of UVP recorded for a solution of NaI is shown in Fig. 3. The wave shows the UVP after frequency conversion to 1 Hz. The straight broken line in the figure shows the position of the cell in its movement: the point (a) denotes the starting point and the point (b) the end point. If the cell comes to the end of the path, the cell is stopped and the UVP vanishes. The UVP pattern at the right half in Fig. 3, shows that

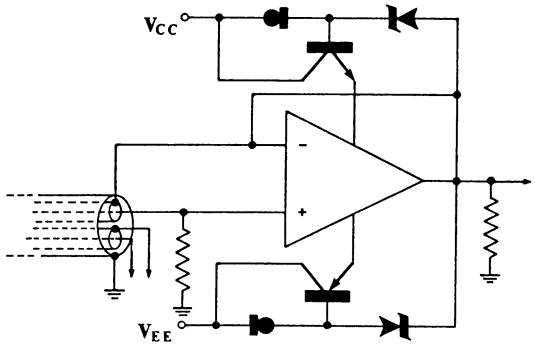

Fig. 2. A part of high input impedance differential amplifier. The amplifier made by a combination of bootstrap and driven shield circuit.

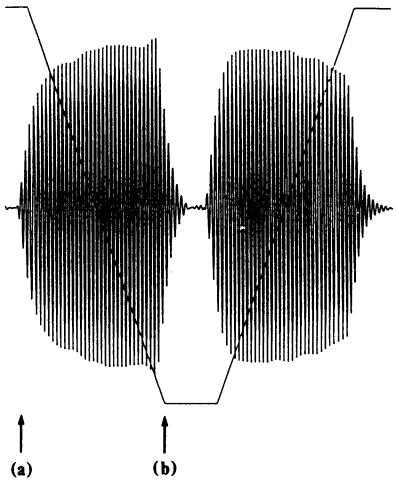

Fig. 3. Typical pattern of UVP recorded (NaI, 0.01 mol dm^{-3}).

on the backward shift of the cell.

The noise level in our device is below 50 nV. This noise level is of the order of 1/100, or so, of that observed in the apparatus used by Zana and Yeager.[6,7]

Results and Discussion

We have chosen a pair of salts, LiCl and NaCl, as a standard pair of samples to be measured in the present experiment according to the theoretical procedure using Eqs. 14a and 14b. In applying the procedure, the effectiveness of the approximation, Eq. 13, must be taken into consideration. Too large values of Φ_0 are supposed to violate the approximation. Then, the magnitude of Φ_0 should be not too large. The pair of LiCl and NaCl fits the condition in addition to the merit that the Φ_0 for the pair is determined with high accuracy.

We measured the magnitudes of UVP, Φ_0, for the NaCl solution as well as for the LiCl solution at the same concentrations, and determined the values of φ_{Na^+}, φ_{Li^+}, φ_{Cl^-}, and Φ_0/α. The observed values of Φ_0 at 15—45 °C are given in Table 1. The accuracy of those at $C>0.1$ mol dm^{-3}, is found to be smaller than ±5%. The magnitudes of Φ_0 and Φ_0/α at 25 °C are shown in Fig. 4. The increasing trend of UVP with decrease of concentration at low concentrations, $C\leqq 0.1$ mol dm^{-3}, is clearly seen in the figure, which was pointed out by Hunter et al.[8,9] previously. Then for the analysis below, we used the data at $C>0.1$ mol dm^{-3}, where, with respect to the transport number of ions and the apparent molar volume of salts, literature values were used.[10–15] The literature values of transport numbers and apparent molar volumes are shown in Table 2.

The values of φ_{Li^+}, φ_{Na^+}, φ_{Cl^-}, and α obtained at 25 °C are given in Table 3. The magnitudes of φ_{Na^+}, at

Table 1. Observed UVP

Solute	θ/°C	$\lvert 2\Phi_0\rvert$/μV								
		C/mol dm^{-3}								
		0.01	0.05	0.10	0.125	0.15	0.175	0.20	0.225	0.25
LiCl	15	4.1$_8$	3.1$_0$	2.5$_0$	2.4$_5$	2.4$_5$	2.4$_8$	2.5$_0$	2.5$_3$	2.5$_5$
	25	4.3$_9$	4.3$_2$	2.6$_6$	2.6$_6$	2.6$_7$	2.6$_9$	2.6$_9$	2.7$_1$	2.7$_4$
	35	4.9$_0$	3.6$_7$	2.9$_5$	2.7$_4$	2.7$_6$	2.8$_2$	2.8$_5$	2.8$_7$	2.9$_3$
	45	4.8$_2$	3.6$_7$	3.0$_2$	3.0$_5$	3.1$_0$	3.1$_5$	3.1$_7$	3.2$_0$	3.2$_5$
NaCl	15	2.5$_9$	1.9$_4$	1.8$_0$	1.8$_0$	1.7$_8$	1.7$_7$	1.7$_6$	1.7$_5$	1.7$_4$
	25	2.6$_6$	2.2$_3$	2.0$_3$	2.0$_2$	1.9$_8$	1.9$_6$	1.9$_4$	1.9$_3$	1.9$_2$
	35	2.6$_6$	2.3$_0$	2.0$_9$	2.0$_8$	2.0$_8$	2.0$_7$	2.0$_6$	2.0$_5$	2.0$_6$
	45	3.1$_0$	2.5$_2$	2.3$_4$	2.3$_4$	2.3$_3$	2.3$_2$	2.3$_2$	2.3$_0$	2.3$_1$

Table 2. Values of Transport Numbers and Apparent Molar Volumes at 25 °C

	C/mol dm^{-3}	0.125	0.15	0.175	0.20	0.225	0.25	Ref.
LiCl	t^+	0.305	0.302	0.300	0.298	0.296	0.294	10, 15
NaCl	t^+	0.379	0.377	0.376	0.374	0.373	0.372	10
LiCl	φ_{LiCl}/cm^3 mol^{-1}	17.53	17.58	17.63	17.67	17.72	17.76	13
NaCl	φ_{NaCl}/cm^3 mol^{-1}	17.29	17.36	17.42	17.47	17.52	17.57	13, 14

Table 3. Apparent Molar Volumes of Ions at 25°C

C/mol dm^{-3}	0	0.125	0.15	0.175	0.20	0.225	0.25
φ_{Cl^-}/cm^3 mol^{-1}	22.9±0.3	23.4±0.2	23.4±0.2	23.5±0.2	23.5±0.2	23.6±0.2	23.6±0.2
φ_{Li^+}/cm^3 mol^{-1}	−6.0±0.3	−5.8±0.2	−5.8±0.2	−5.8±0.2	−5.8±0.2	−5.8±0.2	−5.8±0.2
φ_{Na^+}/cm^3 mol^{-1}	−6.3±0.3	−6.1±0.2	−6.1±0.2	−6.0±0.2	−6.0±0.2	−6.0±0.2	−6.0±0.2
α/cm s^{-1}		1.88	1.87	1.87	1.87	1.88	1.89

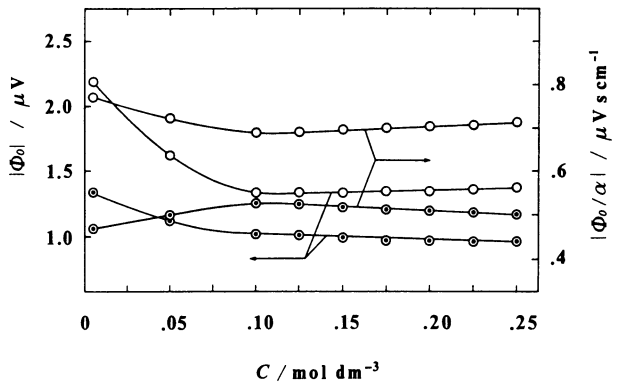

Fig. 4. Concentration dependence of $|\Phi_0|$ and $|\Phi_0/\alpha|$ at 25°C. ⊙: NaCl, O: LiCl.

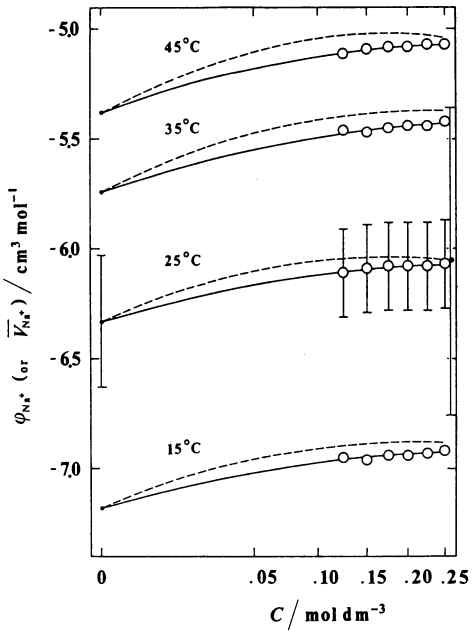

Fig. 5. Concentration dependence of φ_{Na^+} at various temperatures. O: observed, ——: best fitted by the formula (15), ------: $\overline{V}_{Na^+}$ calculated by the formula in Ref. 2; $\overline{V}_{Na^+}=\varphi^0_{Na^+}+(3/2)A\sqrt{C}+BC$.

various temperatures are given as circles in Fig. 5, where the thin solid lines and dashed lines represent the values determined according to the best-fit procedure with the following formula[2] and those of the partial molar volumes obtained.

$$\varphi_{Na^+} = \varphi^0_{Na^+} + \frac{A}{2}\sqrt{C} + BC, \qquad (15a)$$

Table 4. Comparison of Values for Partial Molar Volumes at Infinite Dilution at 25°C

Ions	$\overline{V}^0_{ion}$/cm^3 mol^{-1}		
	This work	Zana-Yeager	Hirakawa
H^+	−5.0±0.3	−5.4±0.2	(−6.26—−0.32)
Li^+	−6.0±0.3	−11.2±1.2	(−13.02—−1.29)
Na^+	−6.3±0.3	−7.4±1.9	(−9.46—−1.45)
K^+	3.9±0.3	3.4±0.6	(3.56— 9.23)
Rb^+	9.0±0.3	9.0±0.7	(7.50— 17.0)
Cs^+	16.2±0.3	15.5±0.3	(10.25— 24.90)
F^-	3.9±0.3	3.3±1.0	(−4.47— 4.05)
Cl^-	22.9±0.3	23.7±1.2	(14.0 — 23.21)
Br^-	29.8±0.3	30.2±0.2	(17.68— 30.13)
I^-	41.1±0.5	41.4±0.9	(33.47— 40.95)

$$A = F^2 e \frac{10^2}{2\pi}\left(\frac{1}{20\varepsilon RT}\right)^{1/2}\left(\frac{\partial \ln\varepsilon}{\partial p} - \frac{\beta}{3}\right), \qquad (15b)$$

where A is the Debye-Hückel constant, B the material constant, β the isothermal compressibility.

The accuracy of each quantity is ±0.2, ±0.3, ±0.7** cm^3 mol^{-1} for φ_{ion}, φ^0_{ion} ($\equiv\overline{V}^0_{ion}$), and $\overline{V}_{ion}$ respectively.

The magnitudes of $\overline{V}^0_{Li^+}$, $\overline{V}^0_{Na^+}$, and $\overline{V}^0_{Cl^-}$ thus determined as well as those for other ions obtained from the values and $\overline{V}^0$ (partial molar volume of salts at infinite dilution) are given in Table 4, together with those of Zana-Yeager and Hirakawa[16] for comparison. Hirakawa constructed an apparatus for the measurement of the sedimentation potential in ionic solutions and obtained individual ionic partial molar volumes. The method of the sedimentation potential is essentially identical with the method of ultrasonic vibration potentials in principle, though vibration frequency is 100 Hz.[16]

As seen in Table 4, the values of the present work are found to be coincided with those of Zana and Yeager within the deviation of 1 cm^3 mol^{-1}, except for the case of Li^+. In the case of $\overline{V}^0_{Li^+}$, the absolute magnitudes of the values are found to deviate each other. Zana-Yeager's value of $|\overline{V}^0_{Li^+}|$ is clearly too large, being taken into consideration of the fact that in the case of the values of $\overline{V}^0_{Cl^-}$ as a counter ion, those of ours and Zana-Yeager's coincide within experimental errors. In Table 5, the present data are compared with the values calculated by the empirical formula of Mukerjee[17] and

** The accuracy of $\overline{V}_{ion}$ depends on the concentration. This value is that at C=0.25 mol dm^{-3}.

Table 5. Comparison of Values for Partial Molar Volumes with those from Empirical Formula

Ions	$\bar{V}^0_{ion}$/cm³ mol⁻¹		
	This work	Mukerjee	Conway et al.
H^+	−5.0	−4.5	−6.0
Li^+	−6.0	−5.2	−6.9
Na^+	−6.3	−5.7	−7.3
K^+	3.9	4.5	2.9
Rb^+	9.0	9.5	8.1
Cs^+	16.2	16.9	15.2
F^-	3.9	2.1	4.8
Cl^-	22.9	22.3	23.9
Br^-	29.8	29.2	30.9
I^-	41.1	40.8	42.2

Table 6. Partial Molar Volumes of Ions at Infinite Dilution at Various Temperature

Ions	$\bar{V}^0_{ion}$/cm³ mol⁻¹			
	15°C	25°C	35°C	45°C
H^+	−5.3	−5.0	−4.7	−4.6
Li^+	−6.1	−6.0	−6.1	−6.1
Na^+	−7.2	−6.3	−5.7	−5.4
K^+	3.2	3.9	4.3	4.5
Rb^+	8.2	9.0	9.4	9.8
Cs^+	15.2	16.2	16.8	17.3
Cl^-	22.8	22.9	23.0	23.0
Br^-	29.7	29.8	30.3	30.4
I^-	40.7	41.1	42.0	42.4

that of Conway et al.[18] The coincidence is fairly good on the whole.

Concerning the temperature dependence of partial molar volumes of ions at infinite dilution, the values for univalent ions at various temperatures are given in Table 6, where the accuracy of those is ±0.3 cm³ mol⁻¹ throughout all the temperature range observed. As seen in the table, the values for alkali metal ions except for Li^+ are clearly observed to increase with increasing temperature as well as those for H^+, while those for Li^+ and Cl^- are held to be nearly constant in this temperature range. For other halide ions, Br^- and I^-, the values increase very slowly with increase of temperature.

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