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Sedimentation Potential Measurements and Partial Molar Volumes of Univalent Ions in Water–Acetone Mixtures

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Synopsis. Sedimentation potentials and electrical conductivities were measured for NaCl, NaBr, sodium tetraphenylborate Na[BPh$_4$], and tetraphenylphosphonium chloride [Ph$_4$P]Cl in water–acetone systems (up to 50 wt% of acetone). Using the data obtained and the reported values of partial molar volumes V_2^∞, the ionic division of V_2^∞ was carried out. The values of V_2^∞ (Na$^+$) evaluated for NaCl, NaBr, and Na[BPh$_4$] were self-consistent and they work as references for ionic division of V_2^∞ (MX).

As a continuation of our series of work on the division of the partial molar volume of an electrolyte V_2^∞ (MX) to the cationic and anionic parts,[1–4] we have measured the sedimentation potentials for NaCl, NaBr, Na[BPh$_4$], [Ph$_4$P]Cl, and [Ph$_4$P]Br dissolved in water–acetone mixtures up to 50 wt% of acetone.

We reported earlier[5] that in water–acetone system, the V_2^∞'s of NaCl, KCl, CsCl, NaBr, KBr, and [Ph$_4$P]Cl vary only slightly with solvent composition, while for the salt Na[BPh$_4$], rather abrupt increase in V_2^∞ appears in solvents containing 10 to 30 wt% of acetone. Main purpose of this work is to see whether this increase of V_2^∞ (Na[BPh$_4$]) is attributable to the ion Na$^+$ or the ion [BPh$_4$]$^-$.

For the ionic division of V_2^∞ of an electrolyte MX, data of transport number of the electrolyte MX are needed. Thus, conductivities of the sample salts have also been measured.

Experimental

Samples. Commercially available highest grade Na[BPh$_4$] (Dojin Co., Ltd. or Fluka) was used without further purification. The [Ph$_4$P]Cl and [Ph$_4$P]Br used were the products of Fluka or Merck. The solvent acetone was purified for conductivity measurements by refluxing the guaranteed grade sample with molecular sieves but no purification was done for acetone for sedimentation potential measurements.

Sedimentation Potentials. The sedimentation potentials were measured at Kagoshima University. The experimental set-up was principally the same as before,[1] but in the course of this work some modifications were given on the sample cell and the measuring procedures. First, we prepared a new sample cell which is wholly made of teflon, while so far[1–4] part of the cell was made of acrylic resin. The platinum electrodes in the sample cell were directly connected to the outer electric circuit through a coaxial connector. Second, in our previous work[1–4] the electrodynamic vibrator was vibrated at frequency 100 Hz but in this work the frequency was 150 Hz for NaCl, NaBr, and [Ph$_4$P]Cl, and 1000 Hz for Na[BPh$_4$] and [Ph$_4$P]Br. By adopting higher frequencies, we can reduce the effects of the so-call $1/f$ noise and the interference by the commercial AC of 60 Hz. The theory[6] predicts that even at frequency 1000 Hz no relaxation due to the electrophoretic effect of the ionic cloud appears in solutions with solute concentration less than 10^{-3} mol dm^{-3}.

In our sedimentation potential measurements, the amount of acceleration applied externally by the electrodynamic vibrator is expressed as $\omega^2 x$, where ω is the angular frequency and x is the amplitude of oscillation produced in solution. Thus far we have evaluated the magnitude of acceleration by measuring the amplitude x with stroboscope and microscope. We confirmed that change of the frequency from 100 to 150 Hz accompanies the corresponding decrease of the amplitude, the acceleration remaining constant. At frequency 1000 Hz, we monitored the degree of acceleration by an accelerometer, for the amplitude of vibration is too small to observe by microscope. The accelerometer (IMV Co., Ltd.) consists of a piezoelectric acceleration pick-up (IH-02) and a digital charge vibrometer (VM-1970). The acceleration applied to the cell was 7.0 G. Combined use of higher vibration frequencies and aceceleration meter permitted us to reduce the number of run needed to have the reliable sedimentation potential values in solutions.

Sedimentation potentials should be proportional to the externally applied acceleration. As is shown in Fig. 1, excellent linear relations passing through the origin hold for solutions of NaBr dissolved in water and in the solvent containing 30 wt% of acetone. In our apparatus, the vibration at frequency 100 Hz and amplitude 0.062 cm produces the acceleration 17.7 G. Extrapolation of the linear relations of Fig. 1 to the state of 17.7 G gives the identical values obtained at 100 Hz and amplitude 0.062 cm. The sedimentation potentials in aqueous solutions of Na[BPh$_4$] and [Ph$_4$P]Br at 7.0 G also

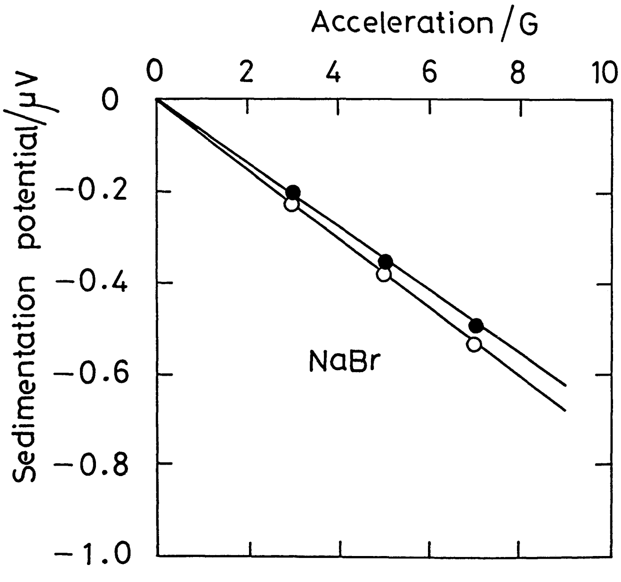

Fig. 1. Relation between the applied acceleration and the sedimentation potentials produced in solutions of NaBr dissolved in water (—○—) and 30 wt% of acetone (—●—).

correspond excellently to the values obtained at 100 Hz and amplitude 0.062 cm.

Electric Conductivities. The conductivities were measured at Shinshu University. The specific conductivities of the conductivity water and acetone were 1.3×10^{-7} and 0.9×10^{-8} S cm^2, respectively. A linear-type bridge and platinum black electrodes (cell constant 0.12305 cm^2) were used for the measurement. The sample solutions were in the ranges 10^{-4}—10^{-3} mol dm^{-3}, and the concentrations were changed in the cell by measuring the weight.

Results and Discussion

Electric Conductivities and Transport Numbers. We used the Fuoss–Onsager equation[7] to analyze the conductivity data:

$$\Lambda = \Lambda^{\infty} - S\,c^{1/2} + Ec\log c + Jc \qquad (1)$$

where c is the solute concentration in mol dm^{-3} and the coefficients S, E, and J are the parameters given by the

Table 1. Limiting Molar Conductivities of the Salts NaCl, NaBr, $[Ph_4P]Cl$, $[Ph_4P]Br$, and $Na[BPh_4]$ in Water–Acetone at 25 °C

[Acetone]	Λ^{∞} / S cm^2 mol^{-1}				
wt%	NaCl	NaBr	$[Ph_4P]Cl$	$[Ph_4P]Br$	$Na[BPh_4]$
0	126.6 126.45[a]	128.1 128.24[a]	96.63 96.76[b]	98.2	69.9 69.94[c]
10	102.5	104.0	76.2	77.7	59.2
20	86.1	87.5	65.0	66.5	52.1
30	76.1	77.5	58.5	60.1	48.0
40	71.4	72.8	55.0	56.4	46.3
50	68.9	70.3	54.0	56.0	46.5

a) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed, Butterworths. London (1970). p. 463. b) Ref. 9. c) J. K. Skinner and R. M. Fuoss, *J. Phys. Chem.*, **68**, 1882 (1964).

Table 2. Observed Sedimentation Potentials E, Cation Transport Numbers t_+, Partial Molar Volumes V_2^{∞}, and Ionic Partial Molar Volumes V_+^{∞} and V_-^{∞} for NaCl, NaBr, $[Ph_4P]Cl$, $[Ph_4P]Br$, and $Na[BPh_4]$ in Water–Acetone at 25 °C

[Acetone]	ρ	E[a]	t_+[b]	V_2^{∞}[c]	V_+^{∞}	V_-^{∞}
wt%	g cm^{-3}	μV		cm^3 mol^{-1}	cm^3 mol^{-1}	cm^3 mol^{-1}
			NaCl			
0	0.9970	+0.08	0.396	16.7	−3.56	20.26
10	0.9833	+0.10	0.417	16.7	−3.19	19.89
20	0.9694	+0.13	0.425	16.8	−3.47	20.27
30	0.9638	+0.12	0.430	16.6	−3.40	20.00
40	0.9360	+0.16	0.438	16.3	−4.15	20.45
50	0.9160	+0.18	0.444	16.7	−4.28	20.98
			NaBr			
0	0.9970	−1.32	0.391	23.4	−4.03	27.43
10	0.9833	−1.27	0.411	23.1	−3.67	26.77
20	0.9694	−1.22	0.418	23.8	−3.76	27.56
30	0.9638	−1.20	0.421	23.7	−4.20	27.90
40	0.9360	−1.17	0.430	23.5	−4.40	27.90
50	0.9160	−1.19	0.444	23.8	−3.82	27.62
			$[Ph_4P]Cl$			
0	0.9970	−0.58	0.211	312.2	299.37	12.83
10	0.9832	−0.56	0.217	314.3	301.84	12.46
20	0.9694	−0.52	0.238	314.7	303.81	10.89
30	0.9639	−0.51	0.261	311.2	303.90	7.30
40	0.9360	−0.48	0.273	310.0	305.00	5.00
50	0.9160	−0.42	0.294	309.2	307.21	1.99
			$[Ph_4P]Br$			
0	0.9970	−0.71	0.207	318.9	288.51	30.39
10	0.9833	−0.72	0.212	320.7	291.37	29.33
20	0.9694	−0.70	0.233	321.7	294.21	27.50
30	0.9639	−0.73	0.255	318.3	296.31	21.99
40	0.9360	−0.72	0.266	317.2	297.62	19.58
50	0.9160	−0.72	0.284	316.3	300.92	15.38
			$Na[BPh_4]$			
0	0.9970	+0.21	0.716	277.2	−4.19	281.39
10	0.9833	+0.20	0.721	279.3	−4.00	283.30
20	0.9694	+0.24	0.702	294.6	−3.68	298.28
30	0.9638	+0.21	0.681	300.1	−3.50	303.60
40	0.9360	+0.21	0.676	299.9	−5.78	305.68
50	0.9160	+0.08	0.658	300.1	−3.56	303.66

a) For NaCl, NaBr, and $[Ph_4P]Cl$, values at 17.7 G. For $[Ph_4P]Br$ and $Na[BPh_4]$, values at 7.0 G. b) Calculated from the electrical conductivities given in Table 1. c) For $[Ph_4P]Br$, see the text.

theory.[7] Data anaylsis showed that in any case investigated ion association is negligible. The limiting molar conductivities determined are summarized in Table 1. We then estimated the ionic molar conductivities based on the assumption that Λ^∞ ($[\mathrm{Ph_4P}]^+$)=Λ^∞ ($[\mathrm{BPh_4}]^-$). We have two ways of estimation:

$$\begin{aligned}\Lambda^\infty([\mathrm{Ph_4P}]^+) &= \Lambda^\infty([\mathrm{BPh_4}]^-)\\ &= (1/2)\{\Lambda^\infty(\mathrm{Na[BPh_4]}) + \Lambda^\infty([\mathrm{Ph_4P}]\mathrm{Cl}) - \Lambda^\infty(\mathrm{NaCl})\}\\ &= (1/2)\{\Lambda^\infty(\mathrm{Na[BPh_4]}) + \Lambda^\infty([\mathrm{Ph_4P}]\mathrm{Br}) - \Lambda^\infty(\mathrm{NaBr})\}.\end{aligned}$$

Both estimations lead to practically identical ionic molar conductivities. The worst is the system with 50 wt% of acetone for which the differences amount to three in the first decimal place. Transport numbers for each electrolyte were calculated using the ionic molar conductivities thus estimated. Our transport number for the ion $\mathrm{Na^+}$ 0.418 for NaBr in 20 wt% of acetone is in fair agreement with the literature value 0.425.[8]

Sedimentation Potentials. The limiting sedimentation potentials[1] are given in Table 2 along with the numerical values of the solvent density used in the calculation.

Division of Partial Molar Volume into V_2^∞ into V_+^∞ and V_-^∞. The relation between the sedimentation potential E and the ionic partial molar volumes V_+^∞ and V_-^∞ is expressed as follows:[4]

$$E=(ad/F)\cdot[(t_+/z_+)\cdot(m_+-V_+^\infty\rho) - (t_-/z_-)\cdot(m_--V_-^\infty\rho)], \qquad (2)$$

where the symbols are the same as in our previous work.[4] We have divided the partial molar volumes V_2^∞ (MX) of a salt MX into two ionic parts V_+^∞ ($\mathrm{M^+}$) and V_-^∞ ($\mathrm{X^-}$) by combining Eq. 2 and the additivity rule that V_2^∞ (MX)=V_+^∞($\mathrm{M^+}$) + V_-^∞($\mathrm{X^-}$). The V_2^∞ (MX) values are available,[5] except for V_2^∞ ($[\mathrm{Ph_4P}]$Br), which were estimated from V_2^∞ ($[\mathrm{Ph_4P}]$Cl), V_2^∞ (NaCl), and V_2^∞ (NaBr).

Ionic partial molar volumes obtained are included in Table 2. The values of V_+^∞ ($\mathrm{Na^+}$) calculated from V_2^∞'s of NaCl, NaBr, and Na$[\mathrm{BPh_4}]$ agree each other within experimental errors over the whole solvent composition investigated. On the contrary, the V_-^∞ ($\mathrm{Br^-}$) values calculated from V_2^∞ (NaBr) and V_2^∞ ($[\mathrm{Ph_4P}]$Br) differ considerably in solvents containing more than 30 wt% of acetone. As for the ion $[\mathrm{Ph_4P}]^+$, the values from ($[\mathrm{Ph_4P}]$Cl) are always larger than those from the V_2^∞ ($[\mathrm{Ph_4P}]$Br) by 6—11 $\mathrm{cm^3\,mol^{-1}}$. For the ion $\mathrm{Cl^-}$, differences in the values of V_-^∞ ($\mathrm{Cl^-}$) from V_2^∞ (NaCl) and V_2^∞ ($[\mathrm{Ph_4P}]$Cl) become progressively larger with the amount of acetone in the solvent. The reason for these inconsistent results for the salt $[\mathrm{Ph_4P}]$X (X=Cl or Br) is unclear for us at present. According to Perie, Perie, and Chemla,[9] the ion $[\mathrm{Ph_4P}]^+$ decomposes at the cathode, although they mentioned nothing about the degree of decomposition. Taking into account all factors we have taken the values of V_+^∞ ($\mathrm{Na^+}$) averaged over those calculated from V_2^∞ (NaCl), V_2^∞ (NaBr), and V_2^∞ (Na$[\mathrm{BPh_4}]$) as references for ionic division of V_2^∞ (MX). The values of V_+^∞ ($\mathrm{Na^+}$) are: −3.9, −3.6, −3.6, −3.7, −4.3 (averaged over NaCl and NaBr), and −3.9 $\mathrm{cm^3\,mol^{-1}}$ at 0, 10, 20, 30, 40, and 50 wt % of acetone, respectively.

Dielectric constant of water–acetone mixture decreases with wt% of acetone. In spite of the decrease in the dielectric constant, the ionic partial molar volumes of the simple univalent ions $\mathrm{Na^+}$, $\mathrm{Cl^-}$, and $\mathrm{Br^-}$, hence, the V_2^∞ (NaCl) and V_2^∞ (NaBr) remain practically constant. Also the ion $[\mathrm{Ph_4P}]^+$ shows the behavior independent of the solvent composition. Through ionic division of V_2^∞, it has become clear that the abrupt increase of V_2^∞ (Na$[\mathrm{BPh_4}]$) in the solvent composition ranges 20—30 wt % of acetone as reported earlier[5] is due to the ion $[\mathrm{BPh_4}]^-$ and not to the ion $\mathrm{Na^+}$.

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