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Formulation of Stokes' Radii in DMF, DMSO and Propylene Carbonate with Solvent Structure Cavity Size as Parameter

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Conductance of univalent ions in DMSO (dimethyl sulfoxide), DMF (dimethylformamide) and PC (propylene carbonate) was determined by use of tetrabutylammonium-tetrabutylborate as standard electrolyte of equal cationic and anionic conductance. Empirical formulation of Stokes' radius was attempted on the assumption of a structure-cavity affecting the ionic transport in a medium of aprotic and polar solvent as well as water. By application of classical fluid dynamics Stokes' radius r_s is given in terms of $-(2/3)\ r_c+(1/\sigma_s)\ (r_c-r_o)^2$, where r_c is crystal ionic radius, r_o and σ_s are parameters characteristic of the cavity and molecular sizes, respectively, with respect the solvent.

According to hydrodynamic theory the force acting on the hard shere with a radius a moving with a steady velocity of v_∞ in an incompressible fluid with a viscosity coefficient η is given by Eq. (1).

$$F = 4\pi\eta\cdot a\cdot v_\infty + 2\pi\eta\cdot a\cdot v_\infty \tag{1}$$

Equation (1) implies two terms of the friction drag acting tangentially on the sphere and the normal drag. The deviation from Stokes' law is obvious in ionic transport, if the crystal ionic radius is employed for a hard sphere chosen as a model. If the ion were to take as shape greatly deformed from the sphere under the influence of solvent structure according to the size fittness between the structure cavity and ions, the normal drag of the second term in (1) would be greatly reduced. A modification of Stokes' theory is required even in the frame of hydrodynamic theory by consideration of the sticky and slipping boundary.[1] The slippy boundary between the moving sphere and the medium leads to a Stokes' force of $4\pi\eta\cdot a\cdot v_\infty$ with the second term in (1) dropped. The solvation of ions explains qualitatively the deviation from Stokes' law, but a concept of negative solvation,[2] or some other hypotheses is inevitable. For a quantitative aspect of ionic transport, a number of more elaborate and sophisticated theories of solvation have been proposed, such as the Zwanzing theory of dielectric drag,[3] Uedaira's micro-viscosity of a solvent molecule just around the ions,[4] and a chemical-bond theory of solvent structure with a microscopic dipole moment.[5]

In recent works,[6~8] the transfer free energy of ions in aprotic solvents, involving PC, EC, DMF, and DMSO, were determined. These and similar data of enthalpy reported by Krishnan and Friedman[9] enable us to estimate the entropy of transfer of ions from water to the aprotic solvents. A large negative value of solvation entropy suggests that a certain liquid structure of solvent plays an important role in decreasing solvation entropy by producing an ordered arrangement even in these aprotic solvents. Accordingly, a comparative study of the Walden product was attempted in this work in various aprotic solvents other than water.

Unusual behavior of ionic conductance has been observed in some ionic species whose solvated radius (apparent Stokes' radius) is smaller than the crystal ionic radius. Kiso has compiled a large number of ionic conductance data with a variety of charges and sizes, concluding that a maximum ionic conductance can be seen for an ionic diameter of about 2.8 Å in aqueous medium which corresponds to the cavity size of water structure.[10] On this basis, Kiso proposed a slipped transport with a minimum friction involving a tangential shear alone, if the ionic size fits the size of a cavity present in the fluid medium. This model is helpful for understanding the apparent Stokes' radius which shows occasionally a radius smaller than the actual crystal ionic radius.

Experimental

Conductance of Cell. A conductance cell of 500 ml capacity was constructed according to the Erlenmeyer flask design of Kraus *et al.*[11] An electrode chamber is attached to the flask in such a way that the chamber liquid is thoroughly mixed with the solution in the main body of the cell. The electrodes were two platinum of 12 mm diameter, their distance being 10 mm. The cell constant of 0.4070 $\mathrm{cm^{-1}}$ was determined by eight KCl aqueous solutions in the concentration range from 3×10^{-3} to 8.5×10^{-3} M as referred to the value of 146.98×10^{-6} mho for KCl solution at 1×10^{-3} M at 25 °C.[12]

Procedure. Precaution was taken for precise conductance measurement particularly against pollution by impurities of water vapor, CO_2 and O_2. For preventing temperature and composition changes of liquid in the conductance cell, the temperature was controlled by a double chambered thermostat at 25±0.01 °C. The cell temperature change was readily detected by the shift of resistance readings exceeding 0.01%. The starting pure solvent was subjected to constant stirring with a teflon coated rotor of a magnetic stirrer for one hour, additional half-hour stirring being sufficient for each addition of electrolyte salt of about 100 mg. Direct transfer of the solvent from the 500 ml measuring flask kept in the thermostat to the conductance cell was made within 15 s. Stepwise increase of the electrolyte concentration was made by quick operation of transfer from weighing bottle to the conductance cell. Calibration for drainage on the wall of the flask, amounting to 0.5 ml or less, does not affect the acuracy of electrolyte concentration more than 0.1%. Repeated determination of cell constant was made for a series of runs with a given solvent system. Resistance was measured on a Model Yokogawa-Hewlette-Packard Universal Bridge.

Materials. The method of purification of solvent and electrolyte was as described.[6] The standard electrolyte of *n*-tetrabutylammonium *n*-tetrabutylborate, $(n\text{-Bu})_4\mathrm{N\cdot B}(n\text{-Bu})_4$,[13] was synthesized from borontrifluoride etherate and *n*-butylmagnesium bromide as starting materials, purification by recrystallization being repeated thrice for the crude preparation with a melting point of 110.6 °C to a final product with a melting point of 111.5 °C. All other chemicals were obtained from the Wako-Pure Chemicals Ltd.

Results and Discussion

The conductance of individual univalent ions at infinite dilution was studied in order to see how the ionic size regulates the ionic transport in non-aqueous solvent. The conductance at infinite dilution Λ° was determined by extrapolation of the observed Λ values from Λ-$\sqrt{c}$ plots for ten concentration points from 0.5×10^{-4} to 5×10^{-3} M. For dividing λ_∞ into each component of $\lambda_\infty^\pm$ an assumption was made of an equal conductance value for $(n\text{-Bu})_4\,N^+$ and $(n\text{-Bu})_4\,B^-$. The results on $\lambda_\infty^\pm$ are listed in Table 1 together with the calculated "apparent" Stokes' radius, r_s, according to the relation: $r_s = e\cdot E/6\pi\eta\lambda_\infty$. An empirical formulation of apparent Stokes' radius was attempted as a function of crystal ionic radius, r_c,[14] by introducting a solvent-dependent parameter, r_0. Starting with the assumption that hydrodynamic theory is valid even for ionic transport, we divided the force, for the sake of the formulation of r_s, into the tangential drag and the normal drag, corresponding to the first and the second terms, respectively, in Eq. (1). Hydrodynamic theory predicts that an air bubble of radius a passing through a liquid medium with velocity v_∞ has a drag force of $4\pi\eta a v_\infty$. If the moving ions make use of a vacant space of the solvent-structure cavity, the deviation of Stokes' law in ionic transport could be concentrated in the second ferm of the normal drag in Eq. (1) under the influence of the discrepancy between the ion-size and the cavity space. On this account, a correction was made by introducing a cavity-size parameter, r_o, for the second term of Eq. (1) in the form of Eq. (6) in consideration of the solvent-structure effect.

Table 1. Ionic conductance of individual univalent ions, λ_∞, at 25 °C

Identical values have been reported in the reference marked with a number just behind the asterisk.

Solvent Viscosity η (Poise)	DMSO 0.096 λ_∞	 r_s	DMF 0.00796 λ_∞	 r_s	PC 0.0253 $\lambda_\infty^{d)}$	 r_s
Li^+	13.15	3.18	25.0	4.11	9.61	3.37
Na^+	13.8$^{a)}$	3.03	29.9$^{b)}$	3.44	10.45	3.10
K^+	14.4$^{a)}$	2.91	30.8$^{b)}$	3.34	11.79	2.75
Rb^+	16.1_3	2.59	32.4$^{b)}$	3.18	14.0_5	2.31
Cs^+	17.0_2	2.46	34.6	2.98	14.7_4	2.20
Me_4N^+	18.6_8	2.25	38.9$^{c)}$	2.65	14.8_5	2.18
Et_4N^+	16.8_2	2.49	35.6	2.89	13.8_2	2.34
Pr_4N^+	13.4	3.12	29.2$^{c)}$	3.53	11.0_0	2.95
Bu_4N^+	11.2_9	3.74	26.9	3.83	9.32_5	3.47
NH_4^+			38.7$^{b)}$	2.66	14.45	2.24
Cl^-	24.4_0	1.71	55.1$^{b)}$	1.87	15.9_4	2.03
Br^-	24.2$^{a)}$	1.73	53.6$^{b)}$	1.92	18.7_5	1.73
I^-	23.8$^{a)}$	1.76	53.3$^{b)}$	1.97	19.0_9	1.70
ClO_4^-	$24.6_4$$^{a)}$	1.70	52.9$^{b)}$	1.96	18.2_8	1.77
NO_3^-	27.0$^{a)}$	1.55	38.7$^{b)}$	2.66	22.1_2	1.47

Data referred to a) P.G. Shears, G. R. Lester, and L. R. Dawson, *J. Phys. Chem.*, **60**, 1433 (1956). b) R. C. Paul, I. R. Suigla, and S. P. Narmal, *J. Phys. Chem.*, **741** (1961). c) J. E. Prue and P. T. Sherrington, *Trans. Faraday Soc.*, **57**, 1795 (1961). d) Similar data were reported recently by M. L. Jansen and H. L. Yeager, *J. Phys. Chem.*, **77**, 3089 (1973).

$$6\pi\eta\lambda_\infty r_s = 4\pi\eta\lambda_\infty r_c + f(r_c - r_o)$$

For finding the form of the function, $f(r_c - r_o)$, the value of $(r_s - (2/3)r_c)$ was plotted against r_c from the data shown in Table 1.

The results are shown in Figs. 1 and 2, in which $f(r_c - r_o)$ is approximated to a hyperbolic function in the form of $k(r_c - r_o)^2$.

It can be seen from the curves that a very small constant value, r_s°, is needed in some arbitary way for minimizing the deviation from $k(r_c - r_o)^2$ in Eq. (6).

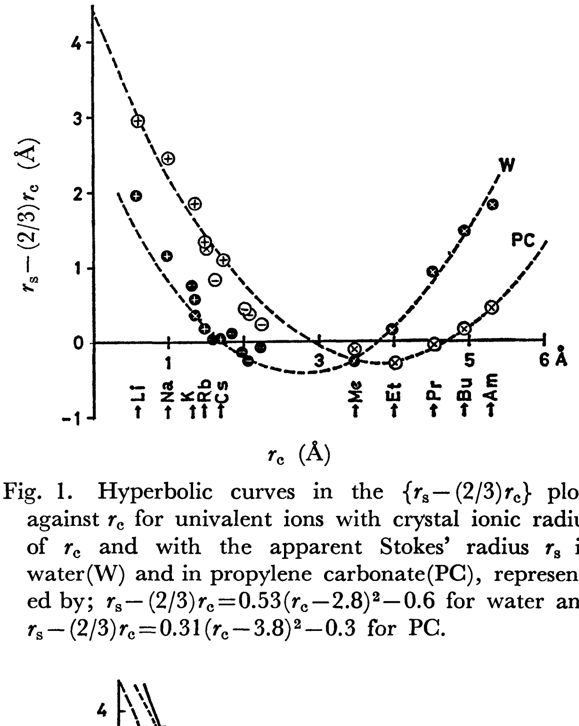

Fig. 1. Hyperbolic curves in the $\{r_s - (2/3)r_c\}$ plots against r_c for univalent ions with crystal ionic radius of r_c and with the apparent Stokes' radius r_s in water(W) and in propylene carbonate(PC), represented by; $r_s - (2/3)r_c = 0.53(r_c - 2.8)^2 - 0.6$ for water and $r_s - (2/3)r_c = 0.31(r_c - 3.8)^2 - 0.3$ for PC.

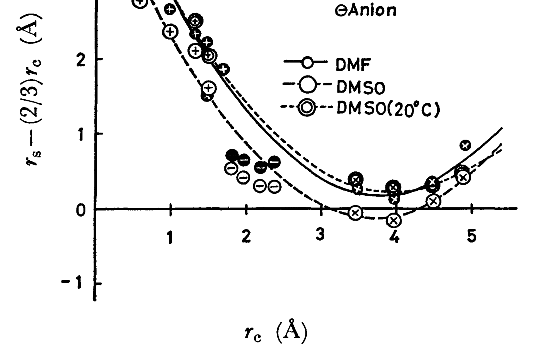

Fig. 2. Similar curves as Fig. 1 in DMF(dimethylformamide) and DMSO(dimethyl sulfoxide) represented by; $r_s - (2/3)r_c = 0.32(r_c - 3.75)^2 + 0.2$ for DMF and $r_s - (2/3)r_c = 0.33(r_c - 3.7)^2 - 0.2$ for DMSO.

Table 2. Parameters employed for the formulation of Stokes' radii by Eq. (6) from the plots shown in Figs. 1 and 2

Solvent	k $Å^{-1}$	r_0 Å	$r_s{}^0$ Å	σ_s Å	$1/\sigma_s$ $Å^{-1}$	Donor Number
PC	0.31	3.80	−0.3	3.23	0.31	15.1
DMF	0.32	3.75	+0.2	3.13	0.32	26.6
DMSO	0.33	3.70	−0.2	3.05	0.33	29.8
Water[a]	0.53	2.80	−0.6	1.93	0.52	18.0

a) From the data of ionic conductance in aqueous system well established and available to be referred in the Hand-book (Landolt Bernstein Tabellen, II. Band, 7. Teil, 259, pp. 266 (1960)).

The correction r_s° is too small to affect greatly the accuracy in the predicted k and r_0 values which are required for the formulation. The parameters k and r_0 could be determined by application of least squares rule to the average values, $\sqrt{r_s-(2/3)\ r_c-r_s^\circ/r_c}$. The results are given in Table 2.

It should be noted that the parameter k is a constant varying inversely with the size of a solvent molecule, σ_s, defined by $\sqrt[3]{(3/4\pi)V_s^\circ}$, where V_s° is the molar volume of solvent at 25 °C. In order to see if this observation on k values is right, works on conductance are extended to many other non-aqueous solvents whose data are available in literature. In a similar way to our treatment stated before, calculated Stokes' radii of univalent cations were formulated by a second order linear equation in a more general form of $a\cdot r_c^2+b\cdot r_c+c=r_s$, where a, b, and c are constants and a is identical with the constant k.

The results are given in Table 3 for a dozen solvents. In is interesting to see that a linear relationship between the molarvolume radius σ_s and the coefficient a or parameter k exsists in satisfactory agreement. Furthermore, the coefficient b has a value approximately equal to −2 and another constant coefficient c is proportional to the molecular radius of solvent, σ_s. The constant c

Table 3. Coefficients of a second order linear function of r_c (crystal ionic radius) employed for formulation of apparent Stokes' radius, r_s at 25 °C

	Solvent	Molar Volume Radius Å		Coefficients in $r_s=ar_c{}^2+br_c+c$		Stokes' Radius Å	Reference
		σ_s	a ($Å^{-1}$)	b (Å)	c (Å)	$(n\text{-Bu})_4N^+$	
1	Water	1.93	0.53	−2.30	3.56	4.77	a, b
2	Formamide	2.51	0.40	−1.97	4.06	3.80	c
3	Methanol	2.52	0.40	−2.13	5.08	3.85	d
4	Acetonitrile	2.75	0.36	−2.07	4.39	3.88	e, f, g, h, i
5	Ethanol	2.85	0.35	−2.13	5.55	3.84	j, p
6	NMF[1]	2.85	0.70	−3.81	6.17	4.83	k
7	DMSO[2]	3.05	0.33	−1.78	4.32	3.73	l, m
8	Acetone	3.08	0.29	−1.55	4.60	4.02	n, o
9	Propanol	3.10	0.32	−2.02	5.85	3.92	p
10	NMA[3]	3.12	0.34	−1.93	4.50	3.39	q (35 °C)
11	Pyridine	3.18	0.31	−1.79	4.80	3.87	s
12	DMF[4]	3.13	0.32	−1.84	4.70	3.69	r
13	PC[5]	3.23	0.31	−1.84	4.67	3.55	t, u
14	Butanol	3.31	0.28	−1.80	6.02	4.04	v
15	NMP[6]	3.34	0.25	−1.70	5.00	2.6	w
16	Nitrobenzene	3.46	0.31	−1.79	4.80	3.80	x, y, z
			Average:	−2.03			

1 *N*-Methyl formamide, 2 Dimethyl sulfoxide, 3 *N*-Methylacetamide, 4 Dimethylformamide, 5 Propylene carbonate, 6 *N*-Methylpropionamide.

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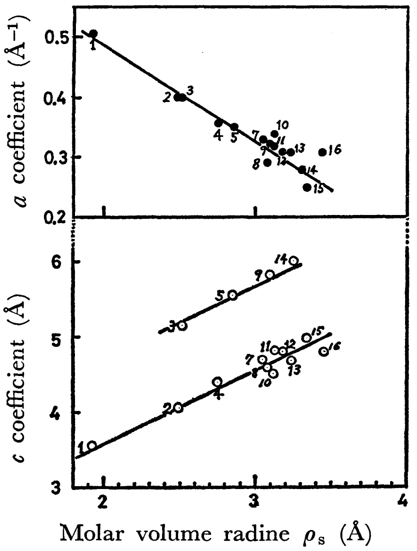

(Solvent number refers to Table 3)

Fig. 3. A linear correlation between molar-volume radius σ_s of solvents and constant coefficients, a and c in the second order linear equation of r_c for representation of apparent Stoke's radius r_s. Solvent numbers refered to Table 3.

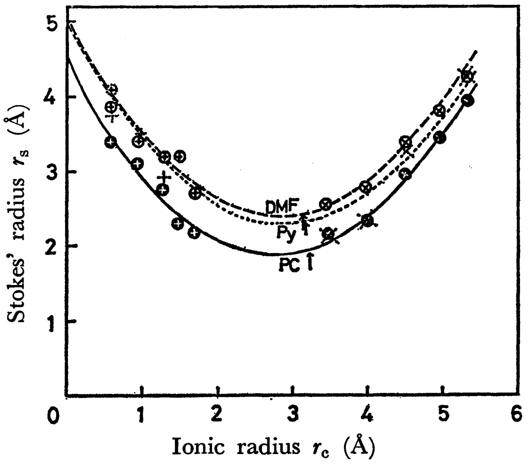

Fig. 4. Stokes' radius representation by crystal ionic radius in $a\cdot r_c^2+b\cdot r_c+c$ with constant coefficients a,b and c (in the Table 3), broken line with open circle for DMF, dotted line with cross for Pyridine and full line with black circle for PC.

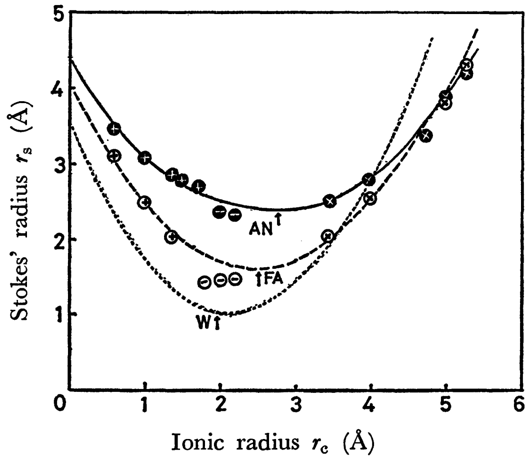

Fig. 5. Similar curves as Fig. 4. Full line for acetonitrile(AN), broken line for formamide and dotted line for water (Stokes' radius omitted).

is a distance measured from the center of point charge, that is r_s at $r_c=0$, to a solvent molecule in a kinetically restricted movement, designated by $\sqrt{\mu\cdot e/\varepsilon kT}$, where μ and ε are the dipole moment and dielectric constant respectively, of solvent at T K. A linear dependence of c on σ_s can be understood from the fact that the solvation sphere of a point charge ion has a distance proportional to the molar-volume radius of solvent, σ_s. Figure 3 shows the plots of a (or k) and c against σ_s. A close correlation can be seen between the apparent Stokes' radii or Walden products and the molecular size of the solvent. One exceptional case was observed in a system of *N*-methylformamide whose unusually high association by hydrogenbond could be responsible.

Stokes' radii of Bu_4N^+ion (Table 3) have essentially the same value of 3.8, indicating that the Walden product rule holds in a large number of non-aqueous solvents, as far as this particular ion is concerned. The only exception is seen in *N*-methylformamide and its homologue, probably due to their strong hydrogen bonded association. In our formulation of r_s, the curves plotted against r_c differ very slightly among the solvents with an appreciable change of dielectric constant. For example, pyridine ($\varepsilon=12.3$, $\sigma_s=3.18$ Å), DMF ($\varepsilon=36.1$, $\sigma_s=3.13$ Å) and PC ($\varepsilon=64$, $\sigma_s=3.23$ Å), yield three very close curves (Fig. 4). On the other hand, there is a large difference in the shape of curves and the location of the minimum point discriminating one solvent from another between acetonitrile, formamide and water (Fig. 5). It seems likely that the donor number of the solvent is also no influential factor in the ionic transport, although it is a good measure of the medium effect of non-aqueous solvent.[7] From the second order linear equation a minimum Stokes' radius appears at r_c (minimum)$=-b/2a$, which can be regarded, to first approximation, as $1/a$ or k since the value of $-b$ is close upon 2 (Table 3). This is the reason why a minimum Stokes' radius appears when the ion radius fits well with the molar-volume radius of the solvent. These facts lead to the conclusion that there should be a contribution of a structure cavity or a free-volume space in the solvent medium to the ionic transport depending on the size of moving ions relative to the size of solvent molecules.

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