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The Viscosity of Tetraphenylphosphonium and -arsonium Halides in Water

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A viscometer, the inside of which was thoroughly coated by silicon grease, was prepared because it is difficult to measure precisely the viscosities of aqueous solutions of tetraphenylonium salts by means of a usual flow-type viscometer because of the characteristic peculiar to these solutions, that they make the glass wall water-repellent and water droplets tend to adhere to it. By comparing the relative viscosities on sucrose and $LaCl_3$ in water obtained by the coated viscometer with those found in the literature, it was confirmed that the viscometer operates adequately. The viscosities of Ph_4PCl, Ph_4PBr, Ph_4PNO_3, Ph_4AsCl, and Ph_4AsBr in water have been measured at 15, 25, and 35 °C. The ionic B-coefficients determined at 25 °C are 1.09 mol^{-1} for both cations, while the ionic activation energies for viscous flow are +4.98 and +5.02 kJ/mol for Ph_4P^+ and Ph_4As^+ respectively.

The viscosity measurement of electrolyte solutions has been widely used as an important experimental method to provide information concerning the nature of ion–solvent interactions. Although no satisfactory interpretation for the viscosity B-coefficient has yet been established, its sign and magnitude and its temperature dependence are usually regarded as measures of the effects arising from the size of the ion and ion–solvent interactions.[1–3] Especially with aqueous solutions which are recognized as partly structured liquids, the B-coefficient has been discussed in connection with the water structure and the effects of ions or of neutral solutes upon it.[4–11]

On the other hand, in the studies of aqueous solutions of hydrophobic solutes, differences between the water-solute interactions of alkyl- and aryl-substituted ions have been illustrated. In these studies, tetraphenyl ions, such as Ph_4P^+, Ph_4As^+, and BPh^-_4, have often been examined as typical and important ions containing phenyl groups.[12–19] Furthermore, some indications that BPh^-_4 and Ph_4P^+ or Ph_4As^+ interact differently with water have been obtained.[14b–19]

However, it should be noted that no studies of the viscosity of aqueous solutions of tetraphenylphosphonium and -arsonium salts have appeared, except one[17] which dealt with Ph_4AsCl only at 25 °C, and concerning the temperature dependence no data are available. This may be attributed to the peculiar characteristics of the aqueous solutions of these salts that the solutions make the glass surface water-repellent, presumably because of the preferential adhesion[20] of these large cations on the glass surface, and that the solution tends to form droplets on the glass surface.[21] Thus, in this case it is difficult to measure the viscosity precisely by means of a usual flow viscometer.

The basic conditions for assuring the precise measurement of the viscosity of fluid by means of a flow viscometer are that the flow rate on the boundary surface of the capillary be zero and the flow in the capillary be laminar. As is well known, the former is fulfilled in the case of the mercury-glass surface though the angle of contact is larger than 90°, *i.e.*, *ca.* 140° at room temperature. It can, therefore, be expected that the viscosity measurement for an aqueous solution of Ph_4MX may be possible provided that a viscometer is available which is coated by a suitable hydrophobic substance to prevent the adhesion of water droplets on the surface.

The purposes of this work are the preparation of such a viscometer, the examination of its properties as a viscometer, and the determination of the viscosities and the temperature dependence of aqueous solutions of tetraphenylphosphonium and -arsonium halides.

Experimental

Viscometer. The outline of the viscometer is shown in Fig. 1. The inside of the viscometer and all the paths for sample solutions are thoroughly coated by silicon grease film. The coating procedure is as follows: a hexane solution containing silicon grease (Dow Corning Co., Ltd.) (about 2 ppm) was filtered several times by a glass filter; each part of the viscometer was then filled up with the solution and was dried at room temperature after the solution has been removed. This procedure was repeated ten times or more. Finally the apparatus was dried at 120 °C for 24 h. The inner wall thus prepared is completely water-repellent, and the water introduced in the apparatus flows out thoroughly without leaving any droplets on the wall.

The sample solution is introduced into the bulb, B, from B_1 through three filters and the B_2 and B_3 bulbs. The B_3 bulb is an automatic buret, with a volume of about 40 cm^3; it is used to measure out a constant volume of the solution. It was confirmed that the reproducibility of the measured volume was within an error of ±5 mg by the weight of water,

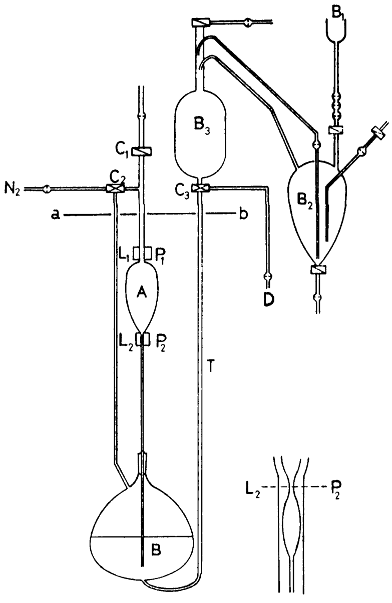

Fig. 1. The outline of the viscometer.

or 0.013%. The volume of the upper bulb, A, is about 20 cm^3; the length of the capillary, 18 cm; the diameter of the capillary, 0.06 cm.

The transit of the meniscus at each of the fixed points, P_1 and P_2 was detected as an electric pulse by means of a detector consisting of a small electric light (about 20 mW), a slit, and a phototransistor, PD 32H (NEC Co., Ltd.). The light was turned on for only a few seconds before and after the passing of the meniscus to minimize the heating. The pulse was introduced into a Takeda Riken universal counter, TR 5103, by which the flow time was recorded to the order of ms.

The viscometer was fixed in a stout frame made of brass, and, the main part was immersed in a thermostat maintaining its temperature within ± 0.0005 °C. The whole of the apparatus was mounted in air room, the temperature of which was controlled to within 0.1 °C. The thermostat consisted of inner and outer parts arranged concentrically. In the latter a cooling tube and a wire heater controlled automatically by a thermistor-regulator system were set, while in the former there was no heat source. The water in the bath was circulated between the two parts. Glass filters were set at all of the ends of the tubes of the apparatus opening to the atmosphere in order to keep the inside from dust.

The measured-out portion of the sample solution in B_3 is introduced slowly through the tube, T, into the bulb, B; the cock, C_3, is closed just when the meniscus passes C_3. The flow time was about 440 s for water at 25 °C. The reproducibility of the flow time is 10 ms, provided the variation in the bath temperature is kept within 0.0005 °C. After the timing, the inner solution is taken out thoroughly from an end, D, of the tube by suction. Since the removal of the solution is complete, there is no need to dry the inside after washing.

Density Measurements. The densities of the solutions at each temperature were measured by means of a pycnometer with a volume of 50 cm^3.

Chemicals. The tetraphenylphosphonium bromide was prepared by dissolving Ph_4PCl(Dotite TPPC) in dichloromethane and by shaking the solution with a 2 M aqueous solution of potassium bromide to change the chloride ion in the dichloromethane phase to the bromide ion. This extraction procedure was repeated with a fresh aqueous phase eight or more times. It was confirmed that the change of the anion from chloride to nitrate was completed by the time the process has been done five times. Considering the fact that the distribution ratio of Ph_4PBr is comparable to that of Ph_4PNO_3(200 or more) under the present conditions, the anion exchange is believed to be satisfactory. The organic phase was filtered with filter paper to remove the water, and then a small amount of ether was added to the filtrate to precipitate a small amount of a salt. The salt was filtered off from the organic solution. A crude Ph_4PBr was obtained from the solution by adding ether. The salt was recrystallized several times from dichloromethane by adding absolute ether to the solution. Ph_4AsBr was also prepared by a similar procedure. Ph_4PCl and Ph_4AsCl were purified by recrystallization.

The salts thus obtained were dried over P_2O_5 under atmospheric pressure because the aqueous solutions prepared from the salts dried for several days under a reduced pressure at 50 °C, or even at room temperature, have sometimes shown turbidity, though these drying processes are found in the literature. Also, the drying of the salts at a high temparature, 120 °C or more, should be avoided because it produces a substance which abnormally enhances the conductivity of the aqueous solution at a low concentration range, as was confirmed by conductivity measurements.[22]

Potentiometric titration with a standard iodine solution[23] to form Ph_4MI_3 showed a purity of 99.9% with respect to the tetraphenylonium ion in Ph_4PCl, Ph_4PBr, Ph_4PNO_3, Ph_4AsBr, and Ph_4AsCl, while potentiometric titration with silver nitrate showed a purity of 99.99% for the chlorides and bromides. No halide was found with Ph_4PNO_3.

The potassium chloride used in this study was of a Merck Suprapur. The sucrose was a specially prepared reagent grade for density gradient determination (Nakarai Kagaku Co.), and the aqueous solution was used within a day after preparation. Lanthanum chloride of a reagent grade (Wako Pure Chemical Ind.) was used with no further purification, and the concentration of the aqueous solution was determined by titration with a standard EDTA solution.

All of the solutions were prepared by weight with conductivity water.

Results and Discussion

The Nature of the Coated Viscometer. The viscometer was calibrated by the use of the equation: $\eta/d = at - b/t$, where a and b are regarded as instrumental constants of the viscometer. These constants were determined from the known densities and viscosities of aqueous solutions of potassium chloride[24] in the concentration range from 0.01 to 0.2 M. Although water is usually employed as a standard liquid, the potassium chloride solution was chosen here for the reason to be described below. The kinetic energy term can be connected with a and b by this relation:[3]

$$\frac{b}{a} = \frac{mV^2}{\pi^2 R^4 h_m g} \tag{1}$$

where V is the volume of liquid in the bulb, A, in Fig. 1, h_m is the mean height of the liquid column, R is the radius of the capillary, and m is a numerical coefficient introduced to take account of the particular shape of the capillary ends. For the present viscometer, m was estimated to be about 1.7, which is somewhat larger than usual values,[26] 0.5 to 1.2, for conventional flow viscometers.

It should be noted that the flow time of pure water, t_0, was longer by about 50 ms than that extrapolated to a zero concentration of potassium chloride. This suggests the presence of some interfacial effect due to the silicon grease film. For the flow time for water, therefore, we preferred the extrapolated one, which was determined by a quadratic equation of the molal concentration, to the observed one.

The relative viscosities of aqueous solutions of potassium chloride were reproduced with a standard deviation of 0.000023, which amounts to 0.002% of the relative viscosities, by means of the Jones and Dole equation;

$$\eta_r = 1 + Ac^{1/2} + Bc \tag{2}$$

with $A = 0.0052_0$ and $B = 0.014$.[24] A plot of $(\eta_r - 1)/c^{1/2}$ against $c^{1/2}$ is shown in Fig. 2.

As a check, the viscosities of aqueous solutions of sucrose and lanthanum chloride were measured at 25 °C in the concentration region of 0.001 to 0.01 molar. The A- and B-coefficients determined by Eq. 2 are shown in Table 1, together with the values found in

TABLE 1. THE VISCOSITY A- AND B-COEFFICIENTS OF THE AQUEOUS SOLUTIONS OF SUCROSE AND $LaCl_3$

	A			B		
	Obsd	Ref.	Calcd	Obsd	p_B	Ref.
Sucrose	0	0[a]	0	0.89_0	0.004	0.878_6[a]
$LaCl_3$	0.031_6	0.0304[b]	0.0284	0.56_7	0.003	0.567_2[b]

a) Ref. 24. b) Ref. 25.

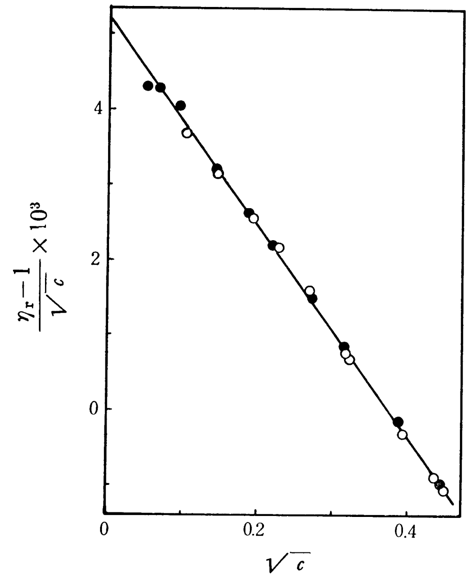

Fig. 2. Calibration of the coated viscometer with KCl in water at 25 °C.

○: Present data, ●: G. Jones and S. K. Talley.[24)]

the literature. The probable errors expected in the B-coefficients, which are designated as P_B in the table, are 0.004 and 0.003 for sucrose and lanthanum chloride respectively. The agreement is fairly well, although with sucrose the present B-coefficient is slightly larger, beyond the probable error, than that found in the literature.[25)]

Thus, it may be concluded that the coated viscometer can be used to determine the viscosities of aqueous solutions, provided that the extrapolated value for t_0 is used. One advantage of the present viscometer over the usual ones is that, since the sample solutions can be exchanged without removing the viscometer from the support, as has been described above, this viscometer is free from any error arising from the removal and resetting.

The Viscosities of Ph_4MX. The densities of aqueous solutions were calculated by Eq. 3, assuming a linearity of the density against the molal concentration of the salts;

$$d = d_0 + \alpha m \tag{3}$$

where m is the molality and α is a constant for a given salt at a given temperature. The linearity was confirmed for Ph_4AsCl and Ph_4AsBr at 25 °C, at least in the low concentration range below 0.015 m, which was the highest concentration for the viscosity measurement. Table 2 lists the values of α for all of the salts and temperatures examined. The molar concentrations of the solutions were calculated from the molality and the density.

TABLE 2. DENSITY COEFFICIENTS OF Ph_4MX IN WATER AT 15, 25, AND 35 °C; α, IN Eq. 3

	Temp (°C)		
	15	25	35
Ph_4PCl	0.072_1	0.065_5	0.058_2
Ph_4PBr	0.108_1	0.098_1	0.088_1
Ph_4PNO_3	0.090_6	0.083_4	0.076_2
Ph_4AsCl	0.111_6	0.102_7	0.094_8
Ph_4AsBr	0.144_5	0.137_4	0.130_2

TABLE 3. THE RELATIVE VISCOSITIES OF THE AQUEOUS SOLUTIONS OF TETRAPHENYLONIUM BROMIDES AT 15, 25, AND 35 °C

Temp(°C) $c(10^{-3}$ M)	15 η_r	$c(10^{-3}$ M)	25 η_r	$c(10^{-3}$ M)	35 η_r
		Ph_4PBr			
0.092_6	1.000210	0.799_2	1.001094	0.797_8	1.001017
0.569_7	1.000862	1.584_1	1.001982	1.595_6	1.001814
1.491_1	1.001996	2.461_4	1.003027	2.499_4	1.002826
2.836_0	1.003730	4.144_0	1.004707	4.007_5	1.004430
4.570_6	1.005875	6.301_6	1.007191	6.080_6	1.006461
7.531_3	1.009590	8.848_7	1.010156	8.036_2	1.008330
12.43_7	1.015526	10.61_3	1.011981	10.12_9	1.010524
		Ph_4AsBr			
0.801_2	1.001244	0.808_2	1.001081	0.781_2	1.001017
1.727_3	1.002361	1.622_3	1.002099	2.388_9	1.002668
2.525_6	1.003340	2.530_3	1.003094	4.021_3	1.004259
4.240_1	1.005620	4.275_1	1.005004	6.595_5	1.007078
6.568_0	1.008303	6.653_6	1.007664	8.813_6	1.009153
8.694_1	1.011168	9.171_3	1.010400	10.78_1	1.011089
11.25_2	1.014140	11.47_9	1.012991		

The vscosities of the aqueous solutions of Ph_4PCl, Ph_4PBr, Ph_4PNO_3, Ph_4AsBr, and Ph_4AsCl were measured at 15, 25, and 35 °C in the concentration range from 0.0005 to 0.012 M. The relative viscosities of aqueous solutions of these bromides are given in Table 3. Recently, it was stressed[20)] that an extra term in c^2 should be added to the Jones and Dole equation in order to determine the B-coefficient precisely. In the present study, however, the Jones and Dole equation was employed to analyze the viscosity data. Taking account of the facts that the tetraphenyl ions have considerably large B-coefficients and that the measurement was carried out in a low concentration range below 0.012 M, no significant error will be introduced into the results by neglecting the extra term. As an example, the plots for Ph_4PBr at three temperatures are shown in Fig. 3. The A- and B-coefficients of Eq. 2 are obtainable from the intercept and the slope, as usual.

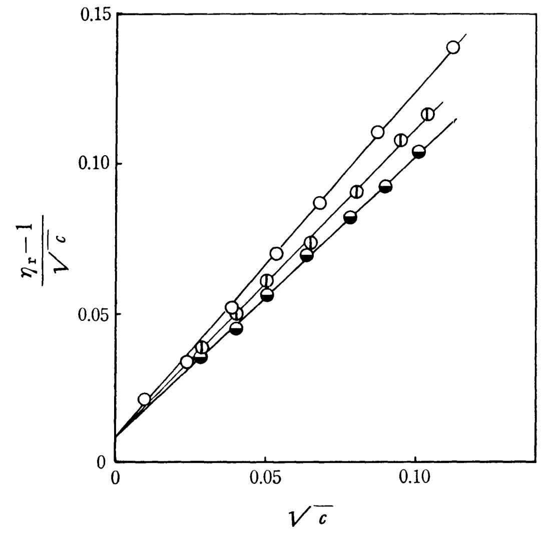

Fig. 3. Evaluation of the limiting slopes for relative viscosity of Ph_4PBr in water at 15°, 25°, and 35 °C. ○: 15 °C, ⦶: 25 °C, ◒: 35 °C.

These coefficients were determined by the method of least squares and are listed in Table 3. The uncertainty in the B-coefficients is expected to be less than 0.02 mol^{-1}, as is shown in the column headed by p_B, which is the probable error. The A-coefficients found agree fairly well with the predicted ones, which are given in terms of the ionic equivalent conductivities by means of the relation derived by Falkenhagen and Vernon.[27] The splitting of the B-coefficient into the ionic components was carried out by the use of the scales introduced by Gurney[1] and by Kaminsky.[2] The ionic B-coefficients for the bromide ion at some temperatures were taken from the data by Kay, Vituccio, Zawoyski and Evans.[7] The ionic B-coefficients, B_i, thus obtained are given in the last column of Table 4. The consistency among the values of B_i for each cation obtained from different salts is satisfactory. No previous data to be compared with the present results are found in the literature except for one on Ph_4AsCl at 25 °C reported by Jolicoeur, Philip, Perron, Leduc, and Desnoyers,[17] this value is 1.08 mol^{-1}, the same as the value obtained here, though their value is based on a somewhat different equation, as has been mentioned above.

Table 4. The viscosity A- and B-coefficients of the aqueous solutions of tetraphenylonium halides

		A		B	p_B	B_i
		Obsd	Calcd			
15 °C	Ph_4PCl	0.0088	0.0089	1.20	0.015	1.22
	Ph_4PBr	0.0086	0.0087	1.17	0.014	1.22
	Ph_4AsCl	0.0085	0.0089	1.20	0.015	1.22
	Ph_4AsBr	0.0091	0.0087	1.17	0.014	1.23
25 °C	Ph_4PCl	0.0098	0.0091	1.08	0.013	1.09
	Ph_4PBr	0.0083	0.0090	1.05	0.014	1.09
	Ph_4PNO_3	0.0065	0.0094	1.04	0.014	1.08
	Ph_4AsCl	0.0085	0.0091	1.08	0.012	1.09
	Ph_4AsBr	0.0089	0.0090	1.04	0.003	1.08
35 °C	Ph_4PCl	0.010	0.0093	0.98	0.014	0.98
	Ph_4PBr	0.0085	0.0092	0.95	0.010	0.98
	Ph_4AsCl	0.0090	0.0093	0.98	0.013	0.98
	Ph_4AsBr	0.0092	0.0092	0.94	0.013	0.97

The temperature dependence of the viscosity can reasonably be expressed in terms of the activation energy for viscous flow, $\Delta E^{\ast}$.[9,28] Assuming that the contribution of the salt to the $\Delta E^{\ast}$ is the sum of the activation energies for ionic components, it is possible to determine the ionic values for the 1 : 1 electrolyte by this equation:[9,28]

$$\Delta E^{\ast} - \Delta E^{\ast}_{0} = \Delta E^{\ast}_{+} + \Delta E^{\ast}_{-} \qquad (4)$$

where $\Delta E^{\ast}_{+}$ and $\Delta E^{\ast}_{-}$ stand for the cationic and anionic activation energies respectively, and where $\Delta E^{\ast}_{0}$ is that for a pure solvent. With chloride and bromide ions,[9,28] values of −0.92 and −1.00 kJ/mol respectively for $\Delta E^{\ast}_{-}$ at a concentration of 1 M are assigned. The ionic activation energies thus obtained are listed in Table 5, together with those for other cations found in the literature, for comparison.

A widely accepted explanation for the viscosity B-coefficient of electrolytes, as summarized by Stokes and Mills,[3] is that the B-coefficient is a measure of the effects of (a) the size and shape of the ions, (b) the ordering of solvent molecules in the vicinity of ions as a result of the ionic field, and (c) the distortion of the solvent structure, leading to greater fluidity. The first two effects result in increasing the viscosity. One more effect is added with large hydrophobic ions such as tetraalkylammonium ions; that is, the "ice-like" structure of water at a distance from these ions is increased by their presence.[4,5] The size and sign of the B-coefficient can be determined as a result of the competition of these factors. Although the evaluation of each contribution of these effects is impossible at present, the effect of ionic size is usually estimated by the Einstein equation,[29] which was derived in the case of rigid spheres suspended in a viscous continuum. This effect results in a positive contribution to the B-coefficient by an amount of 0.0025 V,[3] where V is the hydrodynamic volume of the ion which may be equated with the standard partial molal volume of the ion, V_i^0($cm^3\,mol^{-1}$), at lower concentrations. The ionic

Table 5. Ionic activation energies of some tetra-substituted ions for viscous flow in water at 25 °C

	$\bar{V}_i^{\circ}$ (cm^3/mol)	B_i (mol^{-1})	ΔB_i	$\Delta E_i^{\ast}$ (kJ/mol)
Ph_4P^+	286.3[a]	1.09	0.37	4.98
Ph_4As^+	295.3[b]	1.09	0.35	5.02
		1.09[a]		
BPh_4^-	283.0[b]	1.12[a]	0.41	4.31[e]
Pr_4N^+	209.0[b]	0.86[c]	0.33	4.35[c]
		1.092[d]	0.57	2.60[d]
		0.780[f]	0.26	
Bu_4N^+	270.3[b]	1.28[c]	0.57	5.65[c]
		1.396[d]	0.71	5.15[d]
		1.168[f]	0.49	

a) Ref. 17. b) Ref. 31. c) Ref. 7. d) Ref. 9.
e) Ref. 11. f) Ref. 20.

difference[20)], $B_i-0.0025\ V_i^0$, is considered as a measure of the effects arising from ion–solvent interactions other than the size effect, provided that it is reasonable to assume the ions to be spheres. These differences for tetraphenyl ions and some tetraalkylammonium ions are listed in the column designated as ΔB_i in Table 5. The ΔB_i values decrease in this order: $Bu_4N^+ > BPh^-_4 > Ph_4P^+ > Ph_4As^+ > Pr_4N^+$.

The ionic activation energies of tetraphenylonium ions for the viscous flow at 25 °C are given in Table 5, together with other tetrasubstituted ions. The $\Delta E_i^\ddagger$ values are all positive, since the sign of dB_i/dT is opposite to that of $\Delta E_i^\ddagger$; this means that the dB_i/dT are all negative, and fairly large compared with most of the simple inorganic ions[9)]. The order of the temperature dependence of the B-coefficient is somewhat uncertain because of the experimental errors, and more acculate data are required, but it is probably safe to speculate that the order is $Bu_4N^+ > Ph_4M^\pm > Pr_4N^+$.

The conclusion is reached that tetraphenyl ions, independent of the sign of the ionic charge, are classified into net "structure-makers" in water by reason of their positive and large values for ΔB_i[20)] and the negative dependence of the B-coefficients on the temperature.[7−10)] However, it will be necessary here to refer to the concept of the "structure" being made or broken by the solutes introduced in the water. The information found in the literature is contradictory if an attempt is made to classify the solutes into "structure-maker" and "-breaker" based on only the results obtained from a specific experimental technique. With respect to Ph_4P^+ and Ph_4As^+, a structure-breaking effect for the water structure has been inferred from osmotic coefficient measurements[13)], while the reverse was suggested by a NMR study[15)] and by an inspection of the partial molal heat capacities in water.[17)] A marked effect on the water structure by Ph_4AsCl was not found in the near IR spectra.[16)] Also, for the tetraphenylborate ion a similar situation holds. By the criterion[30)] of the classification of solutes which is based on a thermodynamic relation, $(\partial \bar{C}_p/\partial p)_T = -T(\partial^2 \bar{V}_2/\partial T^2)_p$, both Ph_4AsCl and $NaBPh_4$ are "structure-breakers" because of the negative sign[32)] of $(\partial^2 \bar{V}_2^0/\partial T^2)_p$ for them.

This inconsistency is not strange; as has already been mentioned by some authors,[30,31,33,34)] it arises because we are still unable to define the structure as being either made or broken by solutes or to measure quantitatively the degree of the structure; also, the ion-water interactions are too complicated to explain in terms of structure-making or -breaking, though the concept has proven to be useful in some cases. Thus, it is inadequate to classify the tetraphenyl ions as either structure-makers or -breakers; at least the "structure" assumed in the present case should be different from the "iceberg" which is considered to be promoted by larger tetraalkylammonium ions.

To apply the Einstein equation to tetraphenyl ions (and also probably to R_4N^+ with long-chain alkyl groups) seems to be of doubtful value because tetraphenyl ions have a fairly open structure[15)]; to regard them as a sphere can be only a very rough approximation. The specific interactions of water molecules with phenyl groups in Ph_4As^+, Ph_4P^+ and BPh^-_4 were indicated by a NMR study[15)], and those with Ph_4As^+, by a laser-Raman study.[35)] The authors of the latter pointed out the possibility that this ion is pentacordinate in water, with water entering the fifth coordination site, while in methanol it is tetracoordinate. Also by this coordination model the viscosity behavior of the tetraphenyl ions in water appears to be explicable, although it will be necessary to accumulate more precise and varied information in order to understand their states in water wholly.

References

1) R. W. Gurney, "Inoic Processes in Solution," McGraw-Hill Book Co., New York (1953).

2) M. Kaminsky, *Discuss. Faraday Soc.*, **24**, 171 (1957).

3) R. H. Stokes and R. Mills, "Viscosity of Electrolytes and Related Properties," Pergamon Press, New York (1965).

4) H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).

5) H. S. Frank and W. Y. Wen, *Discuss. Faraday Soc.*, **24**, 133 (1957); H. S. Frank, *Proc. Roy. Soc.*, *A*, **247**, 481 (1958).

6) H. S. Frank, "Chemical Physics of Ionic Solutions," ed. by B. E. Conway and R. G. Barradas, John Wiley & Sons, New York (1966), p. 53.

7) R. L. Kay, T. Vituccio, C. Zawoyski, and D. F. Evans, *J. Phys. Chem.*, **70**, 2336 (1966).

8) D. F. Evans, G. P. Cunningham, and R. L. Kay, *J. Phys. Chem.*, **70**, 2974 (1966).

9) E. R. Nightingale, Jr., "Chemical Physics in Ionic Solutions," ed. by B. E. Conway and R. G. Barradas, John Wiley & Sons, New York (1966), p. 87.

10) W. Y. Wen, "Water and Aqueous Solutions," ed. by R. A. Horne, Wiley-Interscience, New York (1972), p. 613.

11) R. L. Kay, "Water," Vol. 3, ed. by F. Franks, Plenum Press, New York and London (1973), p. 173.

12) J. F. Skinner and R. M. Fuoss, *J. Phys. Chem.*, **68**, 1882 (1964).

13) G. Kalfoglou and L. H. Bowen, *J. Phys. Chem.*, **73**, 2728 (1969).

14) (a) C. V. Krishnan and H. L. Friedman, *J. Phys. Chem.*, **73**, 3934 (1969); (b) C. V. Krishnan and H. L. Friedman, *ibid.*, **75**, 3606 (1971).

15) J. F. Coetzee and W. R. Sharpe, *J. Phys. Chem.*, **75**, 3141 (1971).

16) C. Jolicoeur, N. D. The, and A. Cabana, *Can. J. Chem.*, **49**, 2008 (1971).

17) C. Jolicoeur, P. R. Philip, G. Perron, P. A. Leduc, and J. E. Desnoyers, *Can. J. Chem.*, **50**, 3167 (1972).

18) H. L. Friedman and C. V. Krishnan, "Water," Vol. 3, ed. by F. Franks, Plenum Press, New York and London (1973), p. 1.

19) C. Jolicoeur and H. L. Friedman, *J. Phys. Chem.*, **75**, 165 (1971); *Ber. Bunsenges. Physik. Chem.*, **75**, 248 (1971).

20) J. E. Desnoyers and G. Perron, *J. Solution Chem.*, **1**, 199 (1972).

21) J. S. Fok, Z. Z. Hugus, and E. B. Sandell, *Anal. Chim. Acta*, **48**, 243 (1969).

22) Unpublished work; *cf.* the results in A. I. Popov and R. E. Humphrey, *J. Am. Chem. Soc.*, **81**, 2043 (1959).

23) H. H. Willard and G. M. Smith, *Ind. Eng. Chem., Anal. Ed.*, II, 186 (1939).

24) G. Jones and S. K. Talley, *J. Am. Chem. Soc.*, **55**, 624 (1933).

25) G. Jones and R. E. Stauffer, *J. Am. Chem. Soc.*, **62**,

335 (1940).

26) G. Barr, "A Monograph of Viscometer," Humphrey Milford, London (1931), p. 20.

27) H. Falkenhagen and E. L. Vernon, *Z. Phys.*, **33**, 140 (1932).

28) E. R. Nightingale, Jr., and R. F. Benck, *J. Phys. Chem.*, **63**, 1777 (1959).

29) A. Einstein, *Ann. Phys.*, **19**, 289 (1906).

30) L. G. Hepler, *Can. J. Chem.*, **47**, 4613 (1969).

31) F. J. Millero, "Water and Aqueous Solutions," ed. by R. H. Horne, Wiley-Interscience, New York (1972), p. 519.

32) F. J. Millero, *J. Chem. Eng. Data*, **15**, 562 (1970).

33) A. Ben-Naim, "Water," Vol. 2, ed. by F. Franks, Plenum Press, New York and London (1973), p. 585.

34) A. Holtzer and M. F. Emerson, *J. Phys. Chem.*, **73**, 261 (1969).

35) J. B. Orenberg, M. D. Morris, and T. V. Long, *Inorg. Chem.*, **10**, 933 (1971).