

Viscosity *B*-Coefficients of Tetraalkylammonium Bromides and Iodides in Dimethylsulphoxide at 298.1, 308.1 and 318.1 K

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The relative viscosities of solutions of tetraalkylammonium bromides and iodides in dimethyl sulphoxide have been measured at 298, 308 and 318 K. The experimental results have been analyzed using the Jones-Dole equation. Ionic viscosity *B*-coefficients for the tetraalkyl salts have been analyzed on the basis of Einstein equation and structural contributions. Comparison of the ionic-*B*-coefficients based on Krumgalz's method has also been made. Transition state parameters for viscous flow have also been determined.

Die relativen Viskositäten der Lösungen von Tetraalkylammoniumbromid und Jodid in Dimethylsulfoxid wurden bei 298, 308 und 318 K gemessen und die Ergebnisse nach der Jones-Dole-Gleichung analysiert. Die Ionenviskositäten wurden nach der Einsteinschen Gleichung nach Strukturbeiträgen diskutiert und nach Krumgalz verglichen. Übergangsparameter für viskoses Fließen wurden bestimmt.

The potentiality of dimethylsulphoxide (DMSO) as solvent for use in non-aqueous batteries and its applications in organic synthesis [1, 2] and electrochemical [3] studies have been widely stressed. These necessitate the

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Table 1. *Solvent properties*

	298°K	308°K	348°K
density/g cm ⁻³	1.0941	1.08607	1.07830
dielectric constant	46.4	44.7	43.3
viscosity/10 ⁻³ kg ⁻¹ s ⁻¹	2.000	1.656	1.402

study of the transport properties of various ions in the dipolar aprotic solvent DMSO conductometrically and viscometrically. The viscometric method is known to give valuable information regarding ion-solvent interactions. Although a number of extensive viscometric studies [4–9] have been made in DMSO dealing mainly with the alkali metal halides, but literature provides no information regarding the viscometric studies of the tetraalkylammonium halides in DMSO. This led us to study the viscometric properties of tetraalkylammonium halides R₄NX (R = Me, Et, Pr, Bu; X = Br or I) in DMSO at 298.1, 308.1 and 318.1 K on which we report in this communication.

Experimental

Dimethylsulphoxide (Baker Analyzed Reagent) was dried over freshly ignited calciumoxide and was distilled twice under reduced pressure. The solvent properties are given in Table 1. The solutions were always prepared using freshly distilled DMSO.

The tetraalkylammonium bromides and iodides (R₄NX where R = Me, Et, Pr and Bu; X = Br or I) were of Fluka's puriss or purum grade. They were purified following the method suggested by Kay and Evans [10] and Conway *et al.* [11].

The kinematic viscosities were measured using a suspended Ubbelohde-viscometer [12] with a flow time of 538 s for water at 298.1 K.

The viscometer was calibrated using triply distilled water ($\eta = 0.8903$ cp at 298.1 K) by means of the Eq. (1),

$$\frac{\eta}{\rho} = Kt - \frac{L}{t} \quad (1)$$

where η is the absolute viscosity, ρ is the density and t is the efflux time of water. The values of the characteristic constants of the viscometer K and L were found to be 0.00167 and 5.50600 respectively. The calibration of the viscometer was periodically checked by measuring the flowtimes with water at three temperatures and the ratio K/L of the viscometer constants was found to be constant during the course of the work. Runs were repeated until three successive determinations were obtained within 0.1 s. The viscometer needs no correction for kinetic energy.

Densities were measured with an Ostwald-Sprengel type pycnometer (25 ml) calibrated with distilled water.

Both viscosity and density measurements were made in an oil-bath controlled to ± 0.01 .

A stock solution for each salt was prepared by weight and the working solutions were obtained by weight dilution. Due to low solubilities of the salts in DMSO, the concentration ranges of the working solutions were limited to $0.01 < M < 0.1$. The molar concentration of the solutions were calculated from molality and density values. The densities ρ of the working solutions were obtained from Eq. (2).

$$\rho = \rho_0 + \theta \bar{m} \quad [13, 14] \quad (2)$$

where \bar{m} is the concentration in moles per kilogram of solutions, ρ_0 is the solvent density and θ is an empirical constant determined by density measurement on most concentrated solution studied for each salt. The experimental densities agreed well with those calculated using the Eq. (2). The viscosities were calculated using the Eq. (1).

Results and calculations

It has been assumed that the relative viscosities of the electrolytes in non-aqueous solvents like DMSO may be represented by Jones-Dole equation [15]

$$(\eta/\eta_0^{-1})/\sqrt{C} = A + B\sqrt{C} \quad (3)$$

where η and η_0 are the viscosities of the solution and the solvent respectively, C is the molar concentration. A and B are characteristic constants specific to the ion and the solvent. The A -coefficient depends on the ion-ion interactions and can be calculated from physical properties of the solvent and the solution.

The B -coefficient represents the ion-solvent interactions conditioned by ion-size and cannot be calculated a priori.

We have not used the extended Jones-Dole equation including the DC^2 term as suggested by Desnoyers and Perron [16] and utilized recently by Bicknell *et al.* [9].

The $(\eta/\eta_0^{-1})/\sqrt{C}$, concentration C and density d values of the solutions of different electrolytes at different temperatures are reported in Table 2.

The plots of $(\eta/\eta_0^{-1})/\sqrt{C}$ against \sqrt{C} for the electrolytes were found to be linear without scatter in the concentration ranges studied. A typical plot is presented in Fig. 1. The intercepts were found to be positive contrary to the observations made by Yao and Benion [5].

Table 2. Concentration, C , $(\eta/\eta_0 - 1)/\sqrt{C}$ and density, d , values for several tetraalkylammonium halides at 298.1, 308.1 and 318.1 K in DMSO

$c/\text{mol dm}^{-3}$	$(\eta/\eta_0 - 1)/\sqrt{C}$	$d/\text{g cm}^{-3}$	$c/\text{mol dm}^{-3}$	$(\eta/\eta_0 - 1)/\sqrt{C}$	$d/\text{g cm}^{-3}$
Me ₄ NBr 298.1 K			Pr ₄ NBr 298.1 K		
0.0110	0.088709	1.09466	0.0110	0.105902	1.09433
0.0220	0.124804	1.09515	0.0220	0.145930	1.09457
0.0330	0.142103	1.09571	0.0331	0.166492	1.09480
0.0441	0.169880	1.09625	0.0555	0.214542	1.09525
0.0520	0.1764401	1.09662	0.0782	0.252501	1.09571
			0.1011	0.282459	
308.1 K			308.1 K		
0.0109	0.086604	1.08668	0.0109	0.104596	1.08619
0.0218	0.114961	1.08726	0.0218	0.132768	1.08632
0.0328	0.136612	1.08789	0.0329	0.162210	1.08645
0.0430	0.156356	1.08850	0.0551	0.220044	1.08670
0.0517	0.168591	1.08892	0.0551	0.220044	1.08670
318.1 K			318.1 K		
0.0108	0.071464	1.07857	0.0108	0.081259	1.07838
0.0216	0.102412	1.07882	0.0217	0.117257	1.07845
0.0325	0.125887	1.07909	0.0326	0.134376	1.07852
0.0434	0.138561	1.07935	0.0547	0.179829	1.07867
0.0512	0.145059	1.07953	0.0995	0.230841	1.07896
Et ₄ NBr 298.1 K			Me ₄ NI 298.1 K		
0.0100	0.097386	1.09457	0.0110	0.084126	1.09913
0.0303	0.151224	1.09576	0.0220	0.112216	1.09621
0.0509	0.195960	1.09686	0.0331	0.134245	1.09725
0.0718	0.228220	1.09791	0.0413	0.148176	1.09802
0.0931	0.253779	1.09906			
308.1 K			308.1 K		
0.0100	0.876583	1.08645	0.0109	0.076125	1.08701
0.0301	0.140147	1.08722	0.0219	0.104215	1.08798
0.0505	0.178496	1.08798	0.0329	0.12822	1.08893
0.0712	0.212946	1.08871	0.0410	0.13922	1.08962
0.0923	0.236519	1.08951			
318.1 K			318.1 K		
0.0099	0.060486	1.07867	0.0108	0.07212	1.07891
0.0299	0.142437	1.07939	0.0217	0.10621	1.07955
0.0501	0.159765	1.08011	0.0326	0.12010	1.08017
0.0711	0.194527	1.08686	0.0406	0.13432	1.08063
0.0916	0.207242	1.09155			
			Et ₄ NI 298.1 K		
			0.0110	0.08226	1.09486
			0.0331	0.145014	1.09638
			0.0556	0.182469	1.09788
			0.0784	0.216020	1.09936
			0.1014	0.23474	1.10083

Table 2 (Continued)

$c/\text{mol dm}^{-3}$	$\frac{(\eta/\eta_0-1)}{\sqrt{C}}$	$d/\text{g cm}^{-3}$	$c/\text{mol dm}^{-3}$	$\frac{(\eta/\eta_0-1)}{\sqrt{C}}$	$d/\text{g cm}^{-3}$
Et ₄ Nl 308.1 K			Pr ₄ Nl 318.1 K		
0.0109	0.081977	1.08677	0.0108	0.076528	1.07895
0.0329	0.136694	1.08816	0.0327	0.132630	1.07903
0.0552	0.175426	1.08954	0.0548	0.179175	1.07951
0.0778	0.208548	1.09090	0.0773	0.208141	1.07998
0.1006	0.238725	1.09224	0.1001	0.236456	1.08045
318.2 K			Bu ₄ Nl 298.1 K		
0.0108	0.082142	1.07667	0.0110	0.10556	1.09420
0.0326	0.12992	1.07940	0.0332	0.17234	1.09438
0.0547	0.172126	1.08012	0.0558	0.219119	1.09458
0.0770	0.203047	1.08083	0.0767	0.271687	1.09476
0.0996	0.224162	1.08154	0.1019	0.28373	1.09495
Pr ₄ Nl 298.1 K			308.1 K		
0.0110	0.096905	1.09473	0.0109	0.102261	1.08641
0.0332	0.159283	1.09599	0.0360	0.168961	1.08707
0.0557	0.214382	1.09722	0.0554	0.216608	1.08773
0.0786	0.242066	1.09845	0.0782	0.254713	1.08837
0.1016	0.265394	1.09966	0.1014	0.280451	1.08901
308.1 K			318.1 K		
0.0109	0.08664	1.08654	0.0108	0.084561	1.07835
0.0329	0.152778	1.08749	0.0327	0.147337	1.07845
0.0553	0.201701	1.08842	0.0548	0.194915	1.07854
0.0780	0.234764	1.08934	0.0775	0.226287	1.07864
0.1010	0.262218	1.09025	0.1004	0.260178	1.07873

However, instead of determining *A*-values by the least square method, the *A*-values were theoretically calculated from the physical properties of the solvent and the limiting ionic equivalent conductances using the relation [17]

$$A_{\text{theor}} = \frac{0.2577 A_0}{\eta_0(\epsilon T)^{1/2} \lambda_0^+ \lambda_0^-} \left[1 - 0.6863 \left(\frac{\lambda_0^+ - \lambda_0^-}{A_0} \right)^2 \right] \quad (4)$$

The values of the *A*-coefficient, calculated from the dielectric constant of DMSO [18] and conductometric data for tetra-alkylammonium salts in DMSO at 298.1 K from the literature [19], have been recorded in Table 3.

The use of theoretical *A*-coefficients is valid only at low concentrations of the electrolytes. Attempts to improve *A*-values at concentrated solutions have not yet proved to be successful. Since our investigations are restricted to low concentrations of electrolytes, the *A*-values appear to be in order.

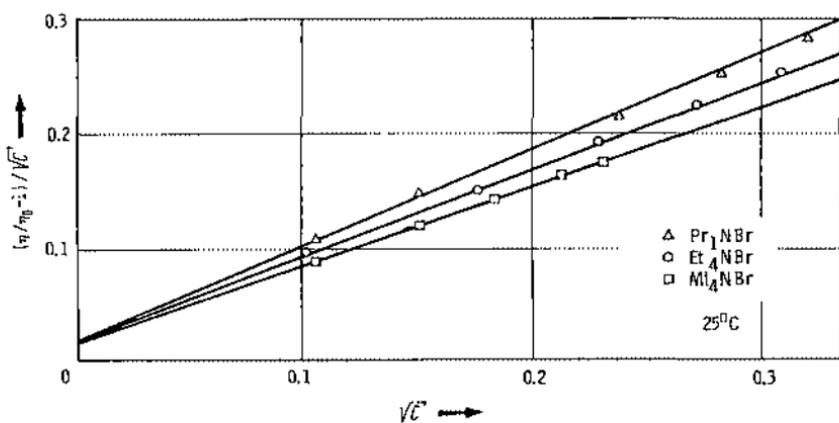


Fig. 1

Table 3. Theoretical A -values at 298.1 K

	A $\text{dm}^{3/2} \text{mol}^{-1/2}$	A $\text{dm}^{3/2} \text{mol}^{-1/2}$	Ionic A $\text{dm}^{3/2} \text{mol}^{-1/2}$
Me_4NBr	0.0104	Me_4NI	$(i\text{-Pr})_3\text{BuN}^+$ 0.0099
Et_4NBr	0.0108	Et_4NI	BPh_4^- 0.0099
			Na^+ 0.0075
Pr_4NBr	0.0121	Pr_4NI	K^+ 0.0073
		Bu_4NI	Rb^+ 0.0070
			CS^+ 0.0067
			Cl^- 0.0043
			Br^- 0.0043
			I^- 0.0044
			Me_4N^+ 0.0061
			Et_4N^+ 0.0065
			Pr_4N^+ 0.0078
			Et_4N^+ 0.0087

In view of weak temperature dependence [8, 9, 14] of the A -coefficients and non-availability of limiting ion-conductance values at different temperatures, the A -values at 298.1 K have been utilized at other temperatures namely 308.1 and 318.1 K.

Since $\lambda_0^+(\text{TAB}^+ \text{ or } \text{Ph}_4\text{AS}^+) = \lambda_0^-(\text{BPh}_4^-)$, the Eq. (4) reduces to

$$A_{\text{theor}}(\text{TABBPh}_4 \text{ or } \text{Ph}_4\text{ASBPh}_4) = \frac{0.2577 \times 2}{\eta_0(\epsilon T)^{1/2} \lambda_0^+} = \frac{\text{Constant}}{\eta_0 \epsilon^{1/2} \lambda_0^+} \quad (5)$$

(at constant temperature).

Table 4. *B*-coefficients of the tetraalkylammonium halides at different temperatures in DMSO

	298.1 K	308.1 K	318.1 K
Me ₄ NBr	0.710	0.672	0.631
Et ₄ NBr	0.775	0.748	0.697
Pr ₄ NBr	0.850	0.809	0.751
Me ₄ NI	0.670	0.643	0.612
Et ₄ NI	0.752	0.720	0.685
Pr ₄ NI	0.830	0.755	0.729
Bu ₄ NI	0.886	0.860	0.821

The equation can be utilized to calculate A_{theor} of TABBPh₄ or Ph₄ASBP₄ in any solvent if λ_0^+ (Ph₄AS⁺) is known or using Walden rule ($\lambda\eta = \text{constant}$). The *A*-values of TABBPh₄ or Ph₄ASBP₄ can be divided into equal parts and the ionic *A*-values can be calculated from additive properties of the respective ionic components. The ionic *A*-values, using data from the literature [9] and the present study, have been recorded in Table 3.

The *B*-coefficients of the salts, obtained as slopes of the straight lines using the least-square method with intercepts forced close to theoretical *A*-values, are shown in Table 4.

Viscosity data have also been analysed on the basis of a transition state treatment of the relative viscosity of electrolytic solutions as suggested by Feakins *et al.* [20]. The *B*-coefficient is expressed by the equation

$$B = \frac{\bar{V}_1^0 - \bar{V}_2^0}{1000} + \frac{\bar{V}_1^0}{1000} \left(\frac{\Delta\mu_2^{\ddagger} - \Delta\mu_1^{\ddagger}}{RT} \right) \quad (6)$$

where \bar{V}_1^0 and \bar{V}_2^0 are the partial molar volumes of the solvent and solute respectively, $\Delta\mu_2^{\ddagger}$ is the contribution per mole of solute to the free energy of activation for viscous flow of the solution. $\Delta\mu_1^{\ddagger}$, the free energy of activation per mole of the pure solvent, is given by [21]

$$\Delta\mu_1^{\ddagger} = \Delta G_1^{\ddagger} = RT \ln \left(\frac{\eta_1 V_1}{\lambda N} \right). \quad (7)$$

The activation parameters for viscous flow for the electrolytes and pure solvent are presented in Table 5.

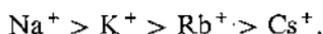
Enthalpies of activation of electrolytes have been calculated with the help of Gibb-Helmholtz equation since *B*-coefficients have been determined at three different temperatures. The results are recorded in Table 5.

Table 5. Activation parameters for viscous flow

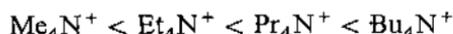
	Temp/K	Δ_f^\ddagger kJ mol ⁻¹	ΔH^\ddagger kJ mol ⁻¹	$T\Delta S^\ddagger$ kJ mol ⁻¹
Me ₄ NBr	298.1	35.24	49.40	14.16
	308.1	34.19		
	318.1	34.25		
Et ₄ NBr	298.1	35.66	54.28	18.62
	308.1	35.59		
	318.1	34.35		
Pr ₄ NBr	298.1	37.43	63.95	26.52
	308.1	36.79		
	318.1	35.65		
Me ₄ NI	298.1	31.46	40.55	9.09
	308.1	30.69		
	318.1	30.85		
Et ₄ NI	298.1	32.86	46.42	13.56
	308.1	32.29		
	318.1	31.95		
Pr ₄ NI	298.1	34.15	57.99	23.84
	308.1	33.39		
	318.1	32.55		
Bu ₄ NI	298.1	35.96	62.92	26.96
	308.1	34.69		
	318.1	34.15		
DMSO	298.1	14.56	13.22	-1.34
	308.1	14.59		
	318.1	14.65		

Discussion

The ionic A -values recorded in Table 3 indicate that ionic A -values decrease in the order.



for tetraalkylammonium ions the order is



whereas A -values of anions Cl^- , Br^- and I^- are almost the same. The results are in reasonable agreement with the limiting equivalent conductances of ions [19] i.e., the conductance of the alkali metal ion increases as the crystal radius increases and the conductance of R_4N^+ decreases as the size of R increases. It is apparent that cation-solvent interactions should decrease with increasing radius, the interactions between large R_4N^+ ions and the solvent would be small. The halide ions are unsolvated by DMSO which is consistent with the

Table 6. Ionic *B* (in $\text{dm}^3 \text{mol}^{-1}$) coefficients at different temperatures in DMSO

	298.1 K	308.1 K	318.1 K
Me_4N^+	0.405	0.395	0.375
Et_4N^+	0.478	0.471	0.445
Pr_4N^+	0.555	0.504	0.493
Bu_4N^+	0.614	0.609	0.583
Br^-	0.299	0.274	0.255
I^-	0.272	0.251	0.238

structure of DMSO molecules in which the positive ends of the dipoles are shielded by two methyl groups.

That *A* is not sensitive to temperature can be explained from Eq. (5). Though λ_0^+ or λ_0^- increase with temperature, ϵ and η_0 decrease with temperature, the net result being an almost independence of *A*-values with temperature.

The viscosity *B*-coefficients (Table 4) for the tetraalkylammonium halides are positive and large and increase as we go from tetramethyl ammonium halides to tetrabutylammonium halides. The *B*-coefficients show a strong temperature dependence in contrast to the weak temperature dependence of the *B*-values of NaClO_4 , NaSCN , NaBPh_4 and $(i\text{-Pr})_3\text{BuBPh}_4$ salts in DMSO [5] or of tetraalkylammonium halides in sulpholane [22]. However, a strong temperature dependence of alkali halides in DMSO has been reported by Bicknell *et al.* [9]. They compared the *B*-values of different electrolytes in DMSO reported by various authors. They noted appreciable variations in the results (even in spite of a recalculation using the orthogonal polynomial method incorporating DC^2 terms). The differences in the results have been attributed to variations in the dryness of the solvent and the solutions (from one laboratory to another) which make reproducible viscosity measurements difficult.

In order to obtain better insight, the division of *B*-values and activation parameter is desirable. Of the various methods, the most widely used is based on "reference electrolyte" method [5, 9, 22, 23]. We have taken the values of B_{Br^-} or B_{I^-} reported by Bicknell [9] *et al.* based on corrected *B*-values for $(i\text{-Pr})_3\text{Bu}_4\text{NBPh}_4$ and NaBPh_4 of Yao and Benion [5]. Slight discrepancies in the B_+ values of tetraalkylammonium ions are noted based on B_{Br^-} or B_{I^-} ions. We have reported the average B_+ values obtained by using B_{Br^-} and B_{I^-} ions. The B_+ and B_- values and the ionic enthalpies and entropies of activation for viscous flow obtained in the same way based on the values of Bromide and Iodide ions [9] have been recorded in Tables 6 and 7.

It is expected that the value of the ion-solvent interaction parameter is determined by a sum of terms in which the solvent structure plays the pivotal role. This problem has been extensively treated by Feakins and co-workers [9].

Table 7. Ionic enthalpy and entropy of activation for viscous flow at 298.1 K

Ion	$\Delta\mu^{\theta*}/$ kJ mol ⁻¹	$\Delta H^{\theta*}/$ kJ mol ⁻¹	$T\Delta S^{\theta*}/$ kJ mol ⁻¹
Me ₄ N ⁺	15.65 (± 2.24)	-0.42 (± 1.59)	-16.05 (± 0.06)
Et ₄ N ⁺	16.56 (± 1.55)	4.95 (± 0.89)	-11.61 (± 0.47)
Pr ₄ N ⁺	18.09 (± 1.89)	15.57 (± 0.45)	-12.52 (± 1.66)
Bu ₄ N ⁺	18.56 (± 0.00)	20.82	+12.26
Br ⁻	18.0	48.7	30.7
I ⁻	17.4	42.1	24.7

Table 8. Ionic radii R_{\pm} (Å^0) calculated by Einstein's equation and solvation number n_s by viscometric data in DMSO at different temperatures

	298 K	R_+ 308 K	38 K	298 K	n_s 308 K	38 K
Me ₄ N ⁺	4.00	3.97	3.90	0.7994	0.7371	0.6213
Et ₄ N ⁺	4.23	4.21	4.13	0.4208	0.3811	0.2347
Pr ₄ N ⁺	4.45	4.30	4.27	0.1403	-0.4228	-0.4805
Bu ₄ N ⁺	4.60	4.58	4.52	-0.8331	-0.8696	-0.9913

The ionic B -coefficients are quite large and increase continuously from Me₄N⁺ to Bu₄N⁺. The B_{ion} can be analyzed in the way described by Stokes and Mills [24] and Krungalz [25].

$$B_{\text{ion}} = B_{\text{ion}}^{\text{Einst}} + B_{\text{ion}}^{\text{Orient}} + B_{\text{ion}}^{\text{Str}} + B_{\text{ion}}^{\text{reinf}} \quad (9)$$

where $B_{\text{ion}}^{\text{Einst}}$ is the positive increment arising from the obstruction to the viscous flow of the solvent caused by the shape and size of the ions; $B_{\text{ion}}^{\text{Orient}}$ is the positive increment arising from the structure making action of the electric field of the ion on the dipoles of the solvent molecules. $B_{\text{ion}}^{\text{Str}}$ is the increment related to the destruction of the solvent structure in the region of ionic co-sphere arising from the opposing tendencies of the ion to orientate the molecules round itself centrosymmetrically and of the solvent to keep its own structure [22]. $B_{\text{ion}}^{\text{reinf}}$ is the positive increment conditioned by the effect of "reinforcement of the water structure" by the large tetraalkylammonium ions due to hydrophobic hydration, a phenomenon absent in DMSO. Due to very small surface charge density of the tetraalkylammonium ions, $B_{\text{ion}}^{\text{orient}}$ can also be neglected in the present case. Thus,

$$B_{\text{ion}} = B_{\text{ion}}^{\text{Einst}} + B_{\text{ion}}^{\text{Str}} \quad (9)$$

This B_{ion} can be equated to [26]

$$B_{\text{ion}} = 2.5 \bar{V} = 2.5 \times \frac{4}{3} \pi \frac{R_{\pm}^3 N}{1000} \quad (10)$$

assuming that the ion behaves like a rigid sphere with an effective radius R_{\pm} moving in a continuum. The number n_s of solvent molecules bound to the ion in the primary shell of solvation can easily be calculated by combining the Jones-Dole equation with Einstein's [27]

$$B_{\text{ion}} = \frac{2.5}{1000} (V_i + n_s V_s) \quad (11)$$

where

$$B_{\text{ion}}^{\text{Einst}} = \frac{2.5}{1000} V_i = \frac{2.5}{1000} \times \frac{4}{3} \pi r_c^3 N \quad (12)$$

and

$$B_{\text{ion}}^{\text{Str}} = \frac{2.5}{1000} n_s V_s \quad (13)$$

V_i represents the bare ion molar volume and is related to the crystallographic radius r_c of the ion. V_s is the solvent molar volume.

Obviously, R_{\pm} should be greater than the crystallographic radius of the R_4N^+ ion. It is apparent that the values of $B_{\text{ion}}^{\text{Einst}}$ and n_s would depend on the choice of the radii values. The r_c values from different sources are

	(a) [28]	(b) [28]	(c) [28]	(d) [35]
Me_4N^+	2.83	3.47	3.2	2.16
Et_4N^+	3.39	4.00	4.00	2.80
Pr_4N^+	3.81	4.52	4.60	3.35
Bu_4N^+	(4.15)	4.94	5.00	3.85

We have calculated n_s values based on the radii given in (b), but the choice of r_c values from other sources would obviously change the n_s values. The values of R_{\pm} and n_s are shown in Table 8.

It is observed that due to cation-solvent interactions (which decrease as we go from Me_4N^+ to Bu_4N^+), the solvent molecules are bound to the ions and the obstruction to the stream-lines caused by the resulting complex determines the magnitude of the structural contribution ($B_{\text{ion}}^{\text{Str}}$) to B_{ion} values. The $B_{\text{ion}}^{\text{Str}}$ actually determine the B -values of alkali metal ions whereas $B_{\text{ion}}^{\text{Einst}}$ which increases with increasing radius determines the magnitude of the B_{ion} value in case of tetraalkylammonium ions, $B_{\text{ion}}^{\text{Str}}$, though dependent on the surface charge density, is essentially dependent on the polarizability and other solvent properties. Thus, the formulation of Krumgalz [25] that $B_{\text{ion}}^{\text{Str}}$ is a function of the radius of an ion appears to be defective.

From the results, it appears that the solvation number n_s based on B_{ion} is not reliable particularly when the radii from different sources are so widely divergent.

The Table 9 contains $\frac{dB_+}{dT}$ values of ions to have more insight on ion-solvent interactions. The negative values of $\frac{dB_+}{dT}$ and $B_+ > 0$ [29] represent

Table 9. $-dB^{\pm}/dT$ of ions in DMSO

Me_4N^+	0.0015	Li^+	0.0022
Et_4N^+	0.0017	Na^+	0.0025
Pr_4N^+	0.0031	K^+	0.0021
Bu_4N^+	0.0016	Rb^+	0.0017
		Cs^+	0.0017
		Cl^-	0.0021
		Br^-	0.0022
		I^-	0.0022
		$(i\text{-Pr})_3\text{BuN}^+$	0.0042
		BPh_4^-	0.0042

the structure making behaviour of tetraalkylammonium ions in DMSO arising from the interactions of alkyl groups and solvent molecules similar to the observations made by Sacco *et al.* in DMS [22]. The structure making character passes through a maximum at Pr_4N^+ which means that solvation character may well change beyond Pr_4N^+ in conformity with the observation that solvation of large tetraalkylammonium ions ceases in organic solvents [25]. In case of alkali metal ions, the structure making character passes through a maximum at Na^+ and becomes effectively constant beyond Rb^+ [9]. The structure making character appears to be equal in case of halide ions and almost equal to that of Li^+ . This is contrary to the observations that the anions interact less strongly with a solvent than the cations. It is also strange to note that the structure making character appears to be maximum in case of BPh_4^- and $(i\text{-Pr})_3\text{BuN}^+$ [9] ions though these ions are regarded to be least solvated.

The ionic $\Delta\mu^{\theta\pm}$, enthalpy and entropy values of R_4N^+ are much less than those of alkali metal ions where ion-solvent interactions are strong. It appears that Me_4N^+ undergoes strong interactions with DMSO leading to solvation. This causes a slight negative enthalpy and a large negative entropy of viscous-flow. The solvation gradually diminishes leading to positive $\Delta H^{\theta\pm}$ and increasing $\Delta S^{\theta\pm}$ values. $\Delta H^{\theta\pm}$ and $\Delta S^{\theta\pm}$ values of Bu_4N^+ are fairly positive. This is similar to the observations of Yao and Benion that the interaction of symmetrical R_4N^+ ions with the DMSO dipole is weak. Ions present a hydrodynamic obstruction to the solvent flow plane which increases with increasing ion-size leading to an increase in viscosity and concomitant, an increase of entropy.

It is to be noted that the single ion B or $\Delta\mu_2^{\theta\pm}$ etc. values as given here are based on the equal division of B -values of large molecules like $(i\text{-Pr})_3\text{BuNBPh}_4$ or $(i\text{-Am})_3\text{BuNBPh}_4$. The method, however, has been strongly criticized by Krumgalz [25]. According to him, equality of the dimensions of $(i\text{-Am})_3\text{BuN}^+$ or $(i\text{-Pr})_3\text{BuN}^+$ and Ph_4B^- does not necessarily imply equality of B -coefficients of these ions as they are likely to be both solvent and ion-structure dependent.

Krumgalz supposed that the large tetraalkylammonium cations are not solvated in organic solvents in the normal sense involving significant electrostatic interactions. Thus, for tetraalkylammonium ions with a common anion, he proposed the following methods to calculate B_{ion} :

$$\text{i) } B_{R_4NX} = a + br^3_{R_4N^+} \quad (14)$$

where $a = B_{Br^-}$ or B_{I^-} and b is a constant dependent on temperature and solvent nature or

$$\text{ii) } B_{R_4N^+} - B_{R_4N^+} = B_{R_4NX} - B_{R_4NX} \quad (15)$$

$$\frac{B_{R_4N^+}}{B_{R_4N^+}} = \frac{r^3_{R_4N^+}}{r^3_{R_4N^+}} \quad (16)$$

Recently, Gill [30] also used the method (ii) to calculate single ion values. Thus, a and b can easily be calculated from the knowledge of B and r values of different tetraalkyl halides.

The ionic B_{\pm} values based on $r_{R_4N^+}$ values (c and d) and $B_{\text{ion}}^{\text{Einst}}$ calculated using Eq. (12) based on $r_{R_4N^+}$ (d) are given below

	(c)	(d)	$B_{\text{ion}}^{\text{Einst}}$ (d)
Me_4N^+	0.075	0.048	0.206
Et_4N^+	0.148	0.130	0.403
Pr_4N^+	0.225	0.280	0.613
Bu_4N^+	0.306	0.264	0.787
Br^-	0.639	0.659	0.047 ($r = 1.95 \text{ \AA}$)
I^-	0.589	0.622	0.064 ($r = 2.17 \text{ \AA}$)

The result also suggests $B_{\text{ion}}^{\text{Str}}$ of tetraalkylammonium ions would be negative similar to the observation made by Krumgalz in case of $B_{\text{ion}}^{\text{Str}}$ of R_4N^+ ions in DMF. However, the method would suggest high positive values of $B_{\text{ion}}^{\text{Str}}$ of halide ions.

The values are widely at variance with the values reported by other workers. The results predict strong anion solvent interactions rather than cation-solvent interactions.

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