

## VISCOSITY STUDIES OF SOME ELECTROLYTES IN DIMETHYL SULFOXIDE AND *N,N*-DIMETHYLFORMAMIDE AT DIFFERENT TEMPERATURES

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The limiting molar conductivity  $\Lambda_0$  and the Jones–Dole viscosity coefficients  $A$  and  $B$  were measured for  $\text{Ph}_4\text{PBPh}_4$ ,  $\text{Bu}_4\text{NBPh}_4$ ,  $\text{Bu}_4\text{NClO}_4$ ,  $\text{Ph}_4\text{PBr}$ ,  $\text{Bu}_4\text{NBr}$ ,  $\text{NaBPh}_4$ ,  $\text{NaClO}_4$ ,  $\text{KClO}_4$ ,  $\text{LiClO}_4$  and  $\text{AgClO}_4$  in pure DMF and DMSO at 20, 30 and 40 °C. The experimental coefficients  $A$  are compared with the coefficients  $A_\eta$  calculated from the Falkenhagen–Vernon equation. The ionic viscosity coefficients  $B$ , which were obtained using  $\text{Ph}_4\text{PBPh}_4$  as the reference electrolyte, are discussed in terms of the contributions in the expression:  $B_{\text{ion}} = B_w + B_{\text{solv}} + B_{\text{ord}} + B_{\text{disord}} + B_{\text{shape}}$ .

Transport properties of electrolyte solutions provide useful information about ion–solvent interactions<sup>1–6</sup>. However, the majority of experimental studies accomplished in non-aqueous solvents refer to a single temperature. This is especially true at viscosity studies. Very few systematic viscosity studies have been performed over a temperature range<sup>7–13</sup>. In the present paper, viscosity studies of solutions of various electrolytes in pure dimethyl sulfoxide (DMSO) and *N,N*-dimethylformamide (DMF) were carried out at 20, 30 and 40 °C with a view to gaining a deeper insight into the ion–solvent interactions. Both DMSO and DMF are dipolar aprotic solvents possessing properties suitable for electrochemical studies<sup>14</sup>. Moreover, for the quantitative analysis of viscosity data, the conductance data of the electrolytes in DMSO and DMF at 20, 30 and 40 °C were also determined.

### EXPERIMENTAL

DMSO and DMF of AR grade were purified as described earlier<sup>2</sup>. Tetraphenylphosphonium tetraphenyl borate ( $\text{Ph}_4\text{PBPh}_4$ ) was prepared by mixing aqueous solutions containing stoichiometric amounts of

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tetraphenylphosphonium bromide ( $\text{Ph}_4\text{PBr}$ ) (Merck) and sodium tetraphenylborate ( $\text{NaBPh}_4$ ) (Merck). The precipitate was triply washed with distilled water and dried in a vacuum at 50 – 60 °C for several days (m.p. 279 – 282 °C)<sup>9</sup>. Tetrabutylammonium tetraphenylborate ( $\text{Bu}_4\text{NBPh}_4$ ) was prepared as reported earlier<sup>2</sup>. Tetrabutylammonium perchlorate ( $\text{Bu}_4\text{NClO}_4$ ) was prepared by slowly adding a dilute aqueous solution (17.5%) of perchloric acid (Merck) to a dilute aqueous solution (0.02 mol dm<sup>-3</sup>) of tetrabutylammonium hydroxide. The resulting precipitate was filtered out, washed with distilled water, and dried in a vacuum at 50 – 60 °C for 2 – 3 days (m.p. 214 – 216 °C)<sup>8</sup>. Silver perchlorate was prepared by adding aqueous solution of perchloric acid (35%) to an aqueous solution of silver carbonate (Merck). The mixture was filtered and evaporated carefully to dryness. The salt was recrystallized from distilled water, powdered and dried in a vacuum at 50 – 60 °C for 24 h. Sodium perchlorate and potassium perchlorate (both Merck), lithium perchlorate and tetrabutylammonium bromide ( $\text{Bu}_4\text{NBr}$ ) (both Fluka), and  $\text{NaBPh}_4$  and  $\text{Ph}_4\text{PBr}$  were dried in a vacuum at suitable temperatures and used without further purification.

The experimental procedure for conductance and viscosity measurements was as reported earlier<sup>2</sup>. The precision of the conductance, viscosity and density measurements was  $\pm 0.2\%$ ,  $\pm 0.1\%$  and  $\pm 1 \cdot 10^{-4}$  g cm<sup>-3</sup>, respectively.

## RESULTS AND DISCUSSION

The viscosities of  $\text{Bu}_4\text{NBPh}_4$ ,  $\text{Bu}_4\text{NClO}_4$ ,  $\text{Ph}_4\text{PBr}$ ,  $\text{Bu}_4\text{NBr}$ ,  $\text{NaBPh}_4$ ,  $\text{NaClO}_4$ ,  $\text{KClO}_4$ ,  $\text{LiClO}_4$  and  $\text{AgClO}_4$  were measured in DMSO and DMF at 20, 30 and 40 °C over the concentration range of 8.5 to 78 mmol dm<sup>-3</sup>. Because of the low solubility of  $\text{Ph}_4\text{PBPh}_4$  in the two solvents, this electrolyte was only measured at 30 and 40 °C over the concentration range of 2 to 11 mmol dm<sup>-3</sup>.

Molar conductivities of the electrolytes (except for  $\text{Bu}_4\text{NBPh}_4$ ) in DMF and DMSO at 20, 30 and 40 °C were measured at concentrations of 0.4 to 6 mmol dm<sup>-3</sup>. The conductivity data were treated to derive the values of the limiting molar conductivity  $\Lambda_0$  (in S cm<sup>2</sup> mol<sup>-1</sup>) and the ion-association constant  $K_A$  (in dm<sup>3</sup> mol<sup>-1</sup>) using the least squares computer program for the Shedlovsky equation<sup>2</sup>. The data so obtained are summarized in Table I. Since conductivity data were not available in the literature for 20, 30 and 40 °C, a direct comparison of the present  $\Lambda_0$  values could not be made. The internal consistency of the limiting molar conductivities in DMSO and DMF, however, was checked by comparing the experimental  $\Lambda_0$  values of  $\text{Bu}_4\text{NBr}$  and  $\text{NaBPh}_4$  (Table I) with those calculated by using the relations

$$\Lambda_0(\text{Bu}_4\text{NBr}) = \Lambda_0(\text{Bu}_4\text{NBPh}_4) + \Lambda_0(\text{Ph}_4\text{PBr}) - \Lambda_0(\text{Ph}_4\text{PBPh}_4) \quad (1a)$$

and

$$\Lambda_0(\text{NaBPh}_4) = \Lambda_0(\text{NaClO}_4) - \Lambda_0(\text{Bu}_4\text{NClO}_4) + \Lambda_0(\text{Bu}_4\text{NBPh}_4) . \quad (1b)$$

The  $\Lambda_0$  values for  $\text{Bu}_4\text{NBPh}_4$  in DMSO and DMF at 20, 30 and 40 °C were taken from our earlier study<sup>2</sup>. The two sets of  $\Lambda_0$  values were identical to within  $\pm 1.0$  conductance unit.

The conductivity data give evidence that all the electrolytes are highly dissociated in DMSO and DMF, because none of the  $K_A$  values is significant (Table I). This brought us to analyze the entire viscosity data in terms of the Jones–Dole equation<sup>15</sup> in the form

$$\eta/\eta_0 = 1 + Ac^{1/2} + Bc \quad (2)$$

for unassociated electrolytes, rather than in the form<sup>12</sup> for associated electrolytes. In Eq. (2), the  $\eta/\eta_0$  ratio is the relative viscosity of the electrolyte solution with respect to the solvent,  $c$  is the molar concentration of the electrolyte, and  $A$  and  $B$  are constants characteristic of the electrolyte. Coefficient  $A$  represents the contribution of the inter-ionic electrostatic forces<sup>15</sup>, whereas coefficient  $B$  represents the ion–solvent interaction and serves as a measure of the order or disorder introduced by the ions into the solvent structure.

The viscosity coefficients  $A$  and  $B$  were obtained by least squares treatment from the plots of  $(\eta/\eta_0 - 1)/c^{1/2}$  vs  $c^{1/2}$ , which were linear over the entire concentration range of the electrolytes. The values so obtained are listed in Tables II and III, respectively. In

TABLE I

Values of the limiting molar conductivity  $\Lambda_0$  ( $\text{S cm}^2 \text{ mol}^{-1}$ ) of the studied electrolytes in DMSO and DMF solutions at different temperatures

Electrolyte	DMSO			DMF		
	20 °C	30 °C	40 °C	20 °C	30 °C	40 °C
$\text{Ph}_4\text{PBPh}_4$	19.4	24.0	29.1	46.6	52.2	59.0
$\text{Bu}_4\text{NCIO}_4$	34.8	40.7	48.9	73.6	83.7	95.3
$\text{Ph}_4\text{PBr}$	33.0	40.0	47.1	72.6	80.7	90.0
$\text{Bu}_4\text{NBr}$	34.0	41.0	49.0	74.9	83.8	93.1
$\text{NaBPh}_4$	22.7	27.9	33.9 <sup>a</sup>	51.9	59.9	69.5
$\text{NaClO}_4$	37.4	44.0	52.0	76.8	88.0	102.0
$\text{KClO}_4$	37.2	44.0	53.0	77.8	91.0	103.8
$\text{LiClO}_4$	34.4	40.3	48.0	72.7	85.6	102.8
$\text{AgClO}_4$	39.1	46.0	54.5	82.3	92.8	105.0 <sup>b</sup>

<sup>a</sup>  $K_A = 16 \text{ dm}^3 \text{ mol}^{-1}$ . <sup>b</sup>  $K_A = 15 \text{ dm}^3 \text{ mol}^{-1}$ . The remaining  $K_A$  values are lower than  $10 \text{ dm}^3 \text{ mol}^{-1}$  and are considered insignificant<sup>4</sup>.

TABLE II  
 Values of the viscosity coefficients  $A \cdot 10^2$  and  $A_\eta \cdot 10^2$  ( $\text{dm}^{3/2} \text{mol}^{-1/2}$ ) of the electrolytes in DMSO and DMF solutions at different temperatures

Electrolyte	DMSO						DMF					
	20 °C		30 °C		40 °C		20 °C		30 °C		40 °C	
	A	$A_\eta$	A	$A_\eta$	A	$A_\eta$	A	$A_\eta$	A	$A_\eta$	A	$A_\eta$
Ph <sub>4</sub> PBPh <sub>4</sub>	–	2.04	2.2	2.03	2.1	2.01	–	2.45	2.3	2.49	2.5	2.52
Bu <sub>4</sub> NBPh <sub>4</sub>	2.0	1.90	1.8	1.90	1.9	1.90	2.4	2.32	2.2	2.36	2.4	2.37
Bu <sub>4</sub> NClO <sub>4</sub>	1.4	1.20	1.1	1.25	1.3	1.25	1.6	1.58	1.5	1.61	1.7	1.61
Ph <sub>4</sub> PBr	1.2	1.28	1.4	1.29	1.2	1.31	1.6	1.65	1.3	1.69	1.7	1.72
Bu <sub>4</sub> NBr	1.2	1.22	1.2	1.47	1.2	1.25	1.5	1.58	1.6	1.61	1.5	1.65
NaBPh <sub>4</sub>	1.7	1.76	1.8	1.72	1.7	1.73	2.4	2.21	2.4	2.20	2.5	2.15
NaClO <sub>4</sub>	1.3	1.10	1.1	1.13	1.1	1.16	1.6	1.52	1.4	1.52	1.4	1.48
KClO <sub>4</sub>	1.2	1.10	1.0	1.13	1.2	1.14	1.5	1.49	1.5	1.46	1.4	1.45
LiClO <sub>4</sub>	1.4	1.22	1.2	1.28	1.3	1.28	1.6	1.63	1.5	1.57	1.5	1.47
AgClO <sub>4</sub>	1.1	1.03	1.1	1.07	1.0	1.10	1.4	1.40	1.4	1.43	1.4	1.43

Table II, the experimental values of the viscosity coefficients  $A$  are compared with the  $A_\eta$  values calculated from the Falkenhagen–Vernon equation<sup>16</sup>

$$A_\eta = \frac{0.2577\Lambda_0}{(DT)^{1/2}\eta_0\lambda_1^0\lambda_2^0} \left[ 1 - 0.6863 \left( \frac{\lambda_1^0 - \lambda_2^0}{\Lambda_0} \right)^2 \right]. \quad (3)$$

The relevant solvent properties such as the viscosity  $\eta_0$  and dielectric constant  $D$  as well as the  $\Lambda_0$  values for  $\text{Bu}_4\text{NBPh}_4$  were taken from our earlier study<sup>2</sup>, the remaining  $\Lambda_0$  values are those in Table I. The limiting ionic conductivities  $\lambda_i^0$  required for the analysis of the coefficient  $A_\eta$  were obtained as follows, using  $\text{Ph}_4\text{PBPh}_4$  as the reference electrolyte. According to Lawrence and Sacco<sup>9</sup>,  $\text{Bu}_4\text{NBBu}_4$  and  $\text{Ph}_4\text{PBPh}_4$  as reference electrolytes are preferred to  $\text{Bu}_4\text{NBPh}_4$  because their cations and anions are symmetrical in shape and their interactions with the solvent dipoles are very similar. The coefficients  $B$  for each reference salt can thus be divided into the cation and anion contributions in the same ratio as the van der Waals volumes  $V_w$  of the ions:

$$\frac{B(\text{Bu}_4\text{N}^+)}{B(\text{Bu}_4\text{B}^-)} = \frac{V_w(\text{Bu}_4\text{N}^+)}{V_w(\text{Bu}_4\text{B}^-)} \quad \text{and} \quad \frac{B(\text{Ph}_4\text{P}^+)}{B(\text{Ph}_4\text{B}^-)} = \frac{V_w(\text{Ph}_4\text{P}^+)}{V_w(\text{Ph}_4\text{B}^-)}. \quad (4)$$

TABLE III

Values of the viscosity coefficient<sup>a</sup>  $B$  ( $\text{dm}^3 \text{mol}^{-1}$ ) of the electrolytes in DMSO and DMF solutions at different temperatures

Electrolyte	DMSO			DMF		
	20 °C	30 °C	40 °C	20 °C	30 °C	40 °C
$\text{Ph}_4\text{PBPh}_4$	1.76 <sup>b</sup>	1.66	1.60	1.87 <sup>b</sup>	1.78	1.74
$\text{Bu}_4\text{NBPh}_4$	1.33	1.22	1.13	1.48	1.37	1.30
$\text{Bu}_4\text{NClO}_4$	0.76	0.70	0.65	1.05	0.86	0.82
$\text{Ph}_4\text{PBr}$	1.38	1.29	1.25	1.37	1.31	1.27
$\text{Bu}_4\text{NBr}$	0.96	0.88	0.80	0.96	0.90	0.83
$\text{NaBPh}_4$	1.31	1.22	1.18	1.32	1.27	1.23
$\text{NaClO}_4$	0.74	0.72	0.69	0.89	0.82	0.78
$\text{KClO}_4$	0.80	0.71	0.68	0.91	0.82	0.79
$\text{LiClO}_4$	0.74	0.69	0.66	0.87	0.78	0.74
$\text{AgClO}_4$	0.84	0.84	0.82	0.94	0.89	0.86

<sup>a</sup> The maximum uncertainty in the  $B$  values reported in this table is  $\pm 0.01 \text{ dm}^3 \text{mol}^{-1}$ . <sup>b</sup> Obtained by extrapolation from experimental values at 30 and 40 °C.

Since coefficient  $B$  is an additive property of the ions of the strong electrolyte at a given temperature<sup>17</sup> i.e.  $B(\text{Ph}_4\text{PBPh}_4) = B(\text{Ph}_4\text{P}^+) + B(\text{Ph}_4\text{B}^-)$ ,  $B(\text{Ph}_4\text{B}^-)$  can be determined as

$$B(\text{Ph}_4\text{B}^-) = B(\text{Ph}_4\text{PBPh}_4) \left( 1 + \frac{V_w(\text{Ph}_4\text{P}^+)}{V_w(\text{Ph}_4\text{B}^-)} \right). \quad (5)$$

A similar expression can be derived for  $\text{Bu}_4\text{NBBu}_4$ . On the basis of Krumgalz assumption, Lawrence and Sacco<sup>9</sup> further suggested that

$$\frac{B(\text{Ph}_4\text{P}^+)}{B(\text{Ph}_4\text{B}^-)} = \frac{r^3(\text{Ph}_4\text{P}^+)}{r^3(\text{Ph}_4\text{B}^-)} = \frac{\lambda_{(\text{Ph}_4\text{B}^-)}^0}{\lambda_{(\text{Ph}_4\text{P}^+)}^0}, \quad (6)$$

where  $r$  is the Stokes' law radius and  $\lambda_i^0$  is the limiting ionic conductivity.

Again, since  $B(\text{Ph}_4\text{PBPh}_4) = B(\text{Ph}_4\text{B}^-) + B(\text{Ph}_4\text{P}^+)$ , one can also obtain  $B(\text{Ph}_4\text{B}^-)$  from Eq. (6) as

$$B(\text{Ph}_4\text{B}^-) = B(\text{Ph}_4\text{PBPh}_4) \left[ 1 + \left( \frac{\lambda_{(\text{Ph}_4\text{B}^-)}^0}{\lambda_{(\text{Ph}_4\text{P}^+)}^0} \right)^3 \right]. \quad (7)$$

Combining Eqs (5) and (7) we get:

$$\frac{\lambda_{(\text{Ph}_4\text{B}^-)}^0}{\lambda_{(\text{Ph}_4\text{P}^+)}^0} = \left( \frac{V_w(\text{Ph}_4\text{P}^+)}{V_w(\text{Ph}_4\text{B}^-)} \right)^{1/3}. \quad (8)$$

Since  $\Lambda_0(\text{Ph}_4\text{PBPh}_4) = \lambda_{(\text{Ph}_4\text{P}^+)}^0 + \lambda_{(\text{Ph}_4\text{B}^-)}^0$ ,  $V_w(\text{Ph}_4\text{P}^+) = 192.3 \text{ cm}^3 \text{ mol}^{-1}$  and  $V_w(\text{Ph}_4\text{B}^-) = 186.8 \text{ cm}^3 \text{ mol}^{-1}$  (the  $V_w$  values were taken from ref.<sup>9</sup>). The  $\lambda_i^0$  values so obtained for the  $\text{Ph}_4\text{B}^-$  ion in DMSO and DMF at 20, 30 and 40 °C are given in Table IV. Using these  $\lambda_i^0$  values, the  $\Lambda_0$  values summarized in Table I were separated into the  $\lambda_i^0$  values for the  $\text{Ph}_4\text{P}^+$ ,  $\text{Bu}_4\text{N}^+$ ,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ag}^+$ ,  $\text{ClO}_4^-$  and  $\text{Br}^-$  ions in terms of Kohlrausch's law. These  $\lambda_i^0$  values are also given in Table IV.

In order to calculate the viscosity coefficients  $A_\eta$  in DMF (ref.<sup>11</sup>) and hexamethylphosphotriamide<sup>10</sup> (HMPT) at 25 and 35 °C in the absence of conductivity data for  $\text{Ph}_4\text{PBPh}_4$ , Lawrence et al. assumed that the limiting ionic conductivity terms are equal. Perusal of Table IV reveals that  $\lambda_{(\text{Ph}_4\text{P}^+)}^0 = \lambda_{(\text{Ph}_4\text{B}^-)}^0$  in DMSO and DMF over the entire temperature range studied. This confirms the validity of the assumption of Lawrence et al.

The viscosity coefficients  $B$  reported in Table III could not be compared directly due to the unavailability of the viscosity data at 20, 30 and 40 °C in the literature.

The consistency of the present viscosity data was checked by comparing the  $B(\text{Bu}_4\text{NBPh}_4)$  and  $B(\text{NaBPh}_4)$  values in Table III with those calculated according to the principle of additivity of the viscosity coefficients  $B$  of the ions: (i)  $B(\text{Bu}_4\text{NBPh}_4) = B(\text{Bu}_4\text{NBr}) - B(\text{Ph}_4\text{PBr}) + B(\text{Ph}_4\text{PBPh}_4)$ , calculated: 1.34, 1.25 and 1.15  $\text{dm}^3 \text{mol}^{-1}$  in DMSO and 1.46, 1.37 and 1.30  $\text{dm}^3 \text{mol}^{-1}$  in DMF at 20, 30 and 40 °C, respectively; (ii)  $B(\text{NaBPh}_4) = B(\text{NaClO}_4) - B(\text{Bu}_4\text{NClO}_4) + B(\text{Bu}_4\text{NBPh}_4)$ , calculated: 1.31, 1.24 and 1.17  $\text{dm}^3 \text{mol}^{-1}$  in DMSO and 1.30, 1.27 and 1.26  $\text{dm}^3 \text{mol}^{-1}$  in DMF, respectively. The experimental and calculated  $B$  values are in a mutual agreement to within  $\pm 0.03 \text{ dm}^3 \text{ mol}^{-1}$  over the entire temperature range.

Separation of the viscosity coefficients  $B$  into the ionic components  $B_{\pm}$  was achieved by using Eq. (7), employing the  $\lambda_i^0$  values for the  $\text{Ph}_4\text{B}^-$  and  $\text{Ph}_4\text{P}^+$  ions from Table IV. Using these  $B(\text{Ph}_4\text{B}^-)$  values, the  $B$  values in Table III were separated into the  $B_{\pm}$  components based on the additivity principle. The ionic  $B$  values thus obtained are summarized in Table V.

Whereas the ionic  $B$  value primarily characterizes the solvated ion as a kinetic entity, information concerning the role of the ion-solvent interaction in enhancing or diminishing the structure of the solution can be derived from the temperature dependence of the ionic coefficient  $B$ .

According to Lawrence et al.<sup>9</sup>, the ionic coefficient  $B$  can be written as the sum of several terms, each of which has the dimension of molar volume and represents the various influences of the ion on its environment in the solution:

TABLE IV  
Values of limiting molar conductivities of ions  $\lambda_i^0$  ( $\text{S cm}^2 \text{mol}^{-1}$ ) in DMSO and DMF solutions at different temperatures

Ion	DMSO			DMF		
	20 °C	30 °C	40 °C	20 °C	30 °C	40 °C
$\text{Ph}_4\text{P}^+$	9.7	11.9	14.5	23.2	26.0	29.4
$\text{Ph}_4\text{B}^-$	9.7	11.9	14.5	23.2	26.0	29.4
$\text{Bu}_4\text{N}^+$	10.7	12.9	16.4	25.2	29.1	32.5
$\text{ClO}_4$	24.1	27.8	32.5	48.1	54.6	62.8
$\text{Br}^-$	23.3	28.1	32.6	49.4	54.7	60.6
$\text{Li}^+$	10.3	12.5	15.5	24.6	31.0	40.0
$\text{Na}^+$	13.3	16.2	19.5	28.7	33.4	39.2
$\text{K}^+$	13.1	16.2	20.3	29.7	36.4	41.0
$\text{Ag}^+$	15.0	18.2	22.0	34.2	38.2	42.2

$$B_{\text{ion}} = B_{\text{w}} + B_{\text{solv}} + B_{\text{shape}} + B_{\text{ord}} + B_{\text{disord}} \quad (9)$$

In this sum,  $B_{\text{w}}$  and  $B_{\text{solv}}$  account for the viscosity increase attributed to by the van der Waals volume and volume of solvation of the ion,  $B_{\text{ord}}$  and  $B_{\text{disord}}$  represent the viscosity increase and decrease, respectively, due to the enhancement or disruption of the inherent solvent structure, and  $B_{\text{shape}}$  is a term accounting for the effect of shear at the surface of ions of different shapes.

Now, let us discuss the ionic  $B$  values reported in Table V on the basis of the various terms in Eq. (9). The term  $B_{\text{disord}}$  influences the  $B_{\text{ion}}$  value significantly in solvents which possess a three-dimensional network, such as water and glycerol. A significant contribution from  $B_{\text{ord}}$  is likely, however, to occur in highly associated solvents. The  $B_{\text{shape}}$  term, which accounts for the effect of the different shapes of ions during viscous flow processes will not contribute appreciably to the  $B_{\text{ion}}$  value of simple ions.

Like many other dipolar aprotic solvents, DMSO and DMF do not possess a structure as such, they are, however, known to be highly associated<sup>18</sup>. Therefore, it is reasonable to ascribe the ionic  $B$  values for  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ag}^+$  and  $\text{Br}^-$  ions to the sum of  $B_{\text{solv}}$  and  $B_{\text{ord}}$ . However, the fact that  $B(\text{Br}^-)$  is higher than  $B(\text{M}^+)$  ( $\text{M}^+ = \text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$ ) both in DMSO and DMF over the entire temperature range reflects the relatively larger contributions of  $B_{\text{ord}}$  to  $B(\text{Br}^-)$  than to  $B(\text{M}^+)$ , because, in dipolar aprotic solvents which cannot form hydrogen bonds, anion solvation is known to be very weak<sup>18</sup>.

TABLE V

Values of the viscosity coefficients<sup>a</sup>  $B$  of ions in DMSO and DMF solutions at different temperatures

Ion	DMSO			DMF		
	20 °C	30 °C	40 °C	20 °C	30 °C	40 °C
$\text{Ph}_4\text{P}^+$	0.88	0.83	0.80	0.94	0.89	0.87
$\text{Ph}_4\text{B}^-$	0.88	0.83	0.80	0.94	0.89	0.87
$\text{Bu}_4\text{N}^+$	0.45	0.39	0.33	0.54	0.48	0.43
$\text{ClO}_4$	0.31	0.31	0.32	0.49	0.45	0.43
$\text{Br}^-$	0.51	0.49	0.47	0.43	0.41	0.40
$\text{Li}^+$	0.43	0.37	0.34	0.36	0.33	0.31
$\text{Na}^+$	0.43	0.39	0.38	0.38	0.37	0.35
$\text{K}^+$	0.49	0.39	0.36	0.40	0.37	0.36
$\text{Ag}^+$	0.53	0.52	0.50	0.43	0.44	0.43

<sup>a</sup> Maximum uncertainty estimated for ionic  $B$  values reported here is  $\pm 0.02 \text{ dm}^3 \text{ mol}^{-1}$ .



Furthermore, the observation that  $B(\text{Br}^-)$  is greater in DMSO than in DMF suggests that the contribution of  $B_{\text{ord}}$  to  $B(\text{Br}^-)$  is higher in the former solvent than in the latter. This is consistent with the fact that, owing to dipole–dipole interactions, DMSO is relatively associated<sup>13</sup>. This conclusion is in agreement with the work of Lawrence et al.<sup>9</sup>.

An interesting result revealed by Table V is that the  $B(\text{Ag}^+)$  values in DMSO and DMF are virtually independent of temperature and, in addition, the value in DMSO is larger than in DMF. In one of our recent papers<sup>2</sup> we found that the magnitude of the effective ionic radius of  $\text{Ag}^+$  ion is the same in DMSO and DMF and is independent of temperature. This has been explained in terms of the  $\text{Ag}^+$  ion being involved in a specific interaction with the  $\pi$ -bond system of these solvents. The identical  $B(\text{Ag}^+)$  values in DMSO and DMF are therefore interpreted so that a significant interaction occurs between the  $\text{Ag}^+$  ion and the DMSO and DMF molecules, and also that the viscous flow process is influenced or modified by structural effects due to solvent–solvent interactions which are relatively prevalent in DMSO (ref.<sup>13</sup>).

A contrast between the ionic  $B$  values for the  $\text{ClO}_4^-$  ion in DMSO and DMF is another important feature which is seen in Table V. It is the more striking that the molar volumes are fairly close to each other (0.071, 0.072 and 0.072  $\text{dm}^3 \text{mol}^{-1}$  for DMSO and 0.077, 0.078 and 0.077  $\text{dm}^3 \text{mol}^{-1}$  for DMF at 20, 30 and 40 °C, respectively). Moreover, anion solvation in dipolar aprotic solvents is known to be poor<sup>18</sup>. From these observations we conclude that the  $\text{ClO}_4^-$  ion affects the viscous flow processes of DMSO and DMF differently. This can be ascribed primarily to the shape of the ion and the solvent.

However, following the arguments suggested by Yao and Bennion<sup>7</sup>, the tetrahedral geometry of the  $\text{ClO}_4^-$  ion fits well into the pyramidal structure of DMSO. During this process the  $\text{ClO}_4^-$  ion disrupts the molecular association of DMSO and predominates to a sufficient extent to cause a net decrease in the viscosity of the solvent. Moreover, as can be seen from Table V,  $B(\text{ClO}_4^-)$  in DMSO is independent of temperature whereas in DMF it decreases with increasing temperature. This suggests that with a temperature increase, the DMSO molecules “freed” from molecular association interact with  $\text{ClO}_4^-$  ions more effectively. Such arrangement thus appears to be typical for the  $\text{ClO}_4^-$  ion in DMSO but less developed in DMF. This view is consistent with the negative activation parameters for the viscous flow of DMSO in the presence of the  $\text{ClO}_4^-$  ion<sup>7</sup>. It is, therefore, further concluded that the contributions of the term  $B_{\text{shape}}$  to  $B(\text{ClO}_4^-)$  are different in DMSO and DMF; in DMSO the effect of  $B_{\text{shape}}$  is apparently destructive, whereas in DMF it is constructive towards the structure of the solvent. Another evidence testifying to the effect of  $B_{\text{shape}}$  on the  $B$  value of the  $\text{ClO}_4^-$  ion can be obtained by comparing the  $B(\text{ClO}_4^-)$  and  $B(\text{Br}^-)$  values for DMF and DMSO. Since the ionic sizes of the  $\text{ClO}_4^-$  and  $\text{Br}^-$  ions are very close to each other<sup>18</sup> (0.195 and 0.200 nm, respectively), the larger  $B(\text{ClO}_4^-)$  value in DMF and smaller in DMSO as compared to the  $B(\text{Br}^-)$  values in the two solvents can be regarded as a consequence of the effect of the  $B_{\text{shape}}$  term.

Similarly, due to the large size and small surface charge density of the  $\text{Ph}_4\text{P}^+$ ,  $\text{Ph}_4\text{B}^-$  and  $\text{Bu}_4\text{N}^+$  ions, their ionic  $B$  values in DMSO and DMF are unlikely to be affected by the  $B_{\text{solv}}$ ,  $B_{\text{ord}}$  and  $B_{\text{disord}}$  terms. Thus the different ionic  $B$  values for these reference ions in DMSO and DMF reflect the different viscous flow patterns of DMSO and DMF around these complex ions. Thus the contribution of the  $B_{\text{shape}}$  term emerges as the most significant as far as the viscous flow processes of complex ion solutions are concerned.

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