

# CHAPTER V

## SECTION A

### ELECTRICAL CONDUCTANCE OF SOME TETRA-ALKYLAMMONIUM AND ALKALI SALTS IN N,N-DIMETHYLACETAMIDE AT 298.15K

Studies of the transport properties of electrolytes in different solvent media are of great importance to obtain information on the behaviour of ions in solution. The conductometric method is well-suited to investigate the ion-solvent and ion-ion interactions in electrolyte solutions.<sup>1,2</sup> Recently, we have studied the solvation and association behaviour of several 1:1 electrolytes in different non aqueous solvents from the measurements of various transport, thermodynamic, and spectroscopic properties.<sup>3-9</sup> In this section we report the conductance studies of some selected tetraalkylammonium bromides and some other alkali metal salts e.g., of tetraethylammonium bromide ( $\text{Et}_4\text{NBr}$ ), tetrapropylammonium bromide ( $\text{Pr}_4\text{NBr}$ ), tetrapentylammonium bromide ( $\text{Pen}_4\text{NBr}$ ), tetrahexylammonium bromide ( $\text{Hex}_4\text{NBr}$ ), tetraheptylammonium bromide ( $\text{Hep}_4\text{NBr}$ ), tetraoctylammonium bromide ( $\text{Oct}_4\text{NBr}$ ), sodium tetraphenylborate ( $\text{NaBPh}_4$ ) and potassium tetraphenylborate ( $\text{KBPh}_4$ ) in N,N-dimethylacetamide to unravel the nature of various types of interactions prevailing in these solutions.

## EXPERIMENTAL

The purification of salts and solvent and solution preparation have been described in chapter III. The conductance measurement has also been described in chapter III. Solutions were prepared by mass for the conductance runs, the molalities being converted to molarities by the use of densities measured with an Ostwald-Sprengel type pycnometer of about 25 cm<sup>3</sup> capacity. Several independent solutions were prepared and runs were performed to ensure the reproducibility of the results. Due correction was made for the specific conductance of the solvent.

## RESULTS AND DISCUSSION

The measured molar conductance ( $\Lambda$ ) of electrolyte solutions as a function of molar concentration ( $c$ ) at 298.15K are given in Table 1.

The conductance data have been analyzed by the 1978 Fuoss conductance-concentration as described earlier (chapter IV).

Calculations are made by finding the values of  $\Lambda^\circ$  and  $\sigma$  which minimize the standard deviation,  $\sigma$ ,

$$\sigma^2 = \sum_{j=1}^n [\Lambda_j(\text{calcd}) - \Lambda^\circ_j(\text{obsd})]^2 / (n - 2) \quad (1)$$

for a sequence of R values and then plotting  $\sigma$  against R; the best fit R corresponds to the minimum in  $\sigma$  vs. R curve. However, since a rough scan using unit increment of R values from 4 to 20 gave no significant minima in the  $\sigma(\%)$  vs. R curves, the R

value was assumed to be  $R = a + d$ , where  $a$  is the sum of the ionic crystallographic radii and  $d$  is given by

$$d = 1.183 (M / \rho_0)^{1/3} \quad (2)$$

where  $M$  is the molecular weight of the solvent and  $\rho_0$  its density.

The values of  $\Lambda^\circ$ ,  $K_A$ , and  $R$  obtained by this procedure are reported in Table II.

Table II shows that the limiting equivalent conductivities ( $\Lambda^\circ$ ) values of tetraalkylammonium bromides decrease with increasing length of the alkyl chain. This is in agreement with earlier findings in several pure and mixed solvents.<sup>1,5,10,11</sup>

The association constants ( $K_A$ ) of these electrolytes (cf. Table II) indicate that these salts are slightly associated in *N,N*-dimethylacetamide. This implies that a preponderant portion of each salt remains dissociated in this solvent medium. For all these tetraalkylammonium bromide salts the association constants are found to be very close to each other thus indicating these salts are almost similarly associated at any given concentration. Furthermore, the process of ionic association of these electrolytes do not exhibit the simple dependence upon ionic size predicted by electrostatic theory.

In order to investigate the specific behaviour of the individual ions comprising these electrolytes, it is necessary to split the limiting molar electrolyte conductances into their ionic components. In the absence of accurate transport

number data in this solvent medium, we have earlier used the "reference electrolyte" method with tetrabutylammonium tetraphenylborate ( $\text{Bu}_4\text{NBPh}_4$ ) as the "reference electrolyte" for the division of  $\Lambda^\circ$  into their ionic components. The limiting ion conductances ( $\lambda^\circ_{\pm}$ ) were estimated by using  $\lambda^\circ_{\text{Bu}_4\text{N}^+} = 22.99$  from our previous work. (Chapter IV, Section A). The  $\lambda^\circ_{\pm}$  values thus obtained are presented in Table III.

The Walden products ( $\lambda^\circ_{\pm}\eta_0$ ) of the ions are also included in Table III. Walden products are usually employed to discuss the interactions of the ions with the solvent medium. From this table, we see that for the tetraalkylammonium ions Walden product decreases from the tetraethylammonium to tetraoctylammonium ion and for the electrolyte taken as a whole it follows the same sequence. This points out that the electrostatic ion-solvent interaction is very weak in these cases. On the other hand, the alkali-metal ions are small enough to possess high charge density, resulting in strong ion-solvent interactions.<sup>12</sup>

The starting point for most evaluations of ionic conductances is Stokes' law that contents that the limiting Walden product (the limiting ionic conductance – solvent viscosity product) for any singly charged, spherical ion is a function only of the ionic radius and thus, under normal conditions, is a constant. In Table III we have collected the Stokes' radii ( $r_s$ ) of the ions in N,N-dimethylacetamide. For sodium and potassium ions, the Stokes' radii are much higher than their crystallographic radii suggesting that these ions are significantly solvated in this

solvent medium. The Stokes' radii of the tetraalkylammonium ions are, however, found to be either very close to or smaller than their corresponding crystallographic radii. This observation indicates that these ions are scarcely solvated in N,N-dimethylacetamide solutions. This also supports our earlier contention derived from the Walden products of these ions that the electrostatic ion-solvent interaction is very weak in these cases

It may thus be concluded that all these tetraalkylammonium bromide salts and the two investigated alkali-metal salts remain slightly associated in N,N-dimethylacetamide solutions apparently due to the medium relative permittivity of the solvent. Sodium and potassium ions are found to be significantly solvated in this solvent medium while the tetraalkylammonium ions remain scarcely solvated.

## SECTION B

### VISCOSITIES OF SOME TETRAALKYLAMMONIUM AND ALKALI SALTS IN N,N-DIMETHYLACETAMIDE AT 298.15K

In previous section we have reported the results of conductance measurements on a number of tetraalkylammonium and alkali-metal salts e.g., tetrapropylammonium bromide ( $\text{Pr}_4\text{NBr}$ ), tetrabutylammonium bromide ( $\text{Bu}_4\text{NBr}$ ), tetrapentylammonium bromide ( $\text{Pen}_4\text{NBr}$ ), tetrahexylammonium bromide ( $\text{Hex}_4\text{NBr}$ ), tetraheptylammonium bromide ( $\text{Hep}_4\text{NBr}$ ), tetraoctylammonium bromide ( $\text{Oct}_4\text{NBr}$ ), tetrabutylammonium tetraphenylborate ( $\text{Bu}_4\text{NBPh}_4$ ), sodium tetraphenylborate ( $\text{NaBPh}_4$ ), and potassium tetraphenylborate ( $\text{KBPh}_4$ ) in N,N-dimethylacetamide at 298.15K. We have now extended this work to study the viscometric behaviour of these electrolyte solutions since viscometry is well-suited to provide information concerning the solvation of the ions and their effects on the structure of the solvent in the near environment of the solute particles.<sup>13</sup>

### EXPERIMENTAL

The kinematic viscosities were measured at  $298.15 \pm 0.01\text{K}$  using a suspended Ubbelohde-type viscometer with a precision of 0.05%. The kinematic viscosities were then converted into absolute viscosities by multiplying the former with the density values measured with an Ostwald-Sprengel type pycnometer having a bulb volume of  $25\text{ cm}^3$  and an internal diameter of the capillary of about 0.1 cm. The details of the experimental procedure have been described in chapter

III. The solutions were prepared by mass for the viscosity runs, the molalities being converted to molarities by the use of densities. In all cases the experiments were performed at least in five replicates for each solution and the results were averaged. Several independent solutions were prepared and the runs were performed to ensure the reproducibility of the results.

## RESULTS AND DISCUSSION

The measured relative viscosities ( $\eta_r$ ) and densities ( $\rho$ ) of electrolyte solutions as functions of molar concentrations ( $c$ ) at 298.15K are given in Table IV.

The relative viscosities of the electrolytes in solution are generally analysed by the Jones-Dole equation,<sup>14</sup>

$$\eta_r = 1 + Ac^{1/2} + Bc \quad (3)$$

Where A and B, the characteristic parameters for salt and solvent, depend on ion-ion and ion-solvent interactions, respectively.

As the electrolytes investigated here are found to be somewhat associated from our earlier conductivity measurements, the viscosity data have been analyzed by the following equation.<sup>15</sup>

$$\eta_r = 1 + A(\alpha c)^{1/2} + B\alpha c + B'(1-\alpha)c \quad (4)$$

Here A, B, and B' are the characteristic constants and  $\alpha$  is the degree of dissociation of the ion pair.

Eq(4) can be rearranged to give

$$[\eta_r - 1 - A(\alpha c)^{1/2}] / \alpha c = B + B'(1 - \alpha)/\alpha \quad (5)$$

For the evaluation of B coefficients from eq.(5), the method suggested earlier by us<sup>16</sup> was followed. The values of  $\alpha$  were calculated from the conductance data of previous section using the equations described in the literature.<sup>15</sup> The A values were calculated theoretically from the physical parameters of the solvent and the limiting ionic equivalent conductances using the Falkenhagen and Vernon equation.<sup>17</sup>

$$A = \frac{0.2577 \Lambda^\circ}{\eta_0(\epsilon T)^{1/2} \lambda_+^\circ \lambda_-^\circ} \left[ 1 - 0.6863 \left( \frac{\lambda_+^\circ - \lambda_-^\circ}{\Lambda^\circ} \right)^2 \right] \quad (6)$$

where  $\eta_0$  is the coefficient of viscosity of the solvent,  $\epsilon$  is its relative permittivity, T is the temperature in absolute scale, and  $\Lambda^\circ$ ,  $\lambda_+^\circ$  and  $\lambda_-^\circ$  are the limiting equivalent conductivities of the electrolyte, cation, and anion respectively. The values of the A coefficients thus obtained are recorded in Table II. These have been used for the analysis of the data. The viscosity B coefficients have also been included in Table V.

The viscosity data have also been analyzed on the basis of the transition-state treatment of the relative viscosity of electrolyte solutions, as suggested by Feakins et.al.<sup>18</sup>

$$B = \frac{\bar{V}_1^\circ - \bar{V}_2^\circ}{1000} + \frac{\bar{V}_1^\circ}{1000} \left[ \frac{\Delta\mu_2^{\circ\#} - \Delta\mu_1^{\circ\#}}{RT} \right] \quad (7)$$

In the above equation  $\bar{V}_1^\circ$  and  $\bar{V}_2^\circ$  are the partial molar volumes of the solvent and solute, respectively.  $\Delta\mu_2^{\circ\#}$  the contribution per mole of solute to the free energy of activation for viscous flow of the solution, has been determined from the above relationship and is reported in Table V. the free energy of activation per mole of the pure solvent,  $\Delta\mu_1^{\circ\#}$  is given by the equation,<sup>19</sup>

$$\Delta\mu_1^{\circ\#} = \Delta G_1^{\circ\#} = RT \ln \left[ \frac{\eta_0 \bar{V}_1^\circ}{\eta N} \right] \quad (8)$$

where N is the Avogadro's number and the other symbols have their usual significance.

The activation parameters for viscous flow for the electrolytes obtained from equation (7) are given table V.

The viscosity  $\beta$  coefficients shown in Table V are large and positive for all the electrolytes studied. The B values for the tetraalkylammonium bromides increase regularly as we go from tetrapropylammonium bromide through tetraoctylammonium bromide. From this table we see that  $\Delta\mu_2^{\circ\#}$  values for all the electrolytes are also large and positive, and they follow the same pattern as the B values.

In order to investigate the specific behaviour of the individual ions comprising these electrolytes, it is necessary to split the viscosity B coefficients of

the electrolytes into their ionic components. The ionic B values were calculated using tetrabutylammonium tetraphenylborate ( $\text{Bu}_4\text{NBPh}_4$ ) as the "reference electrolyte" from the following equations.<sup>20,21</sup>

$$B(\text{Bu}_4\text{NBPh}_4) = B(\text{Bu}_4\text{N}^+) + B(\text{Ph}_4\text{B}^-) \quad (9)$$

$$\frac{B_{\text{Ph}_4\text{B}^-}}{B_{\text{Bu}_4\text{N}^+}} = \frac{r_{\text{Ph}_4\text{B}^-}^3}{r_{\text{Bu}_4\text{N}^+}^3} = \left[ \frac{5.35}{5.00} \right]^3 \quad (10)$$

The  $r$  - values for the  $\text{Bu}_4\text{N}^+$  and  $\text{Ph}_4\text{B}^-$  ions were taken from the literature<sup>21</sup>

The ionic B coefficients obtained from the above relationships are given in the Table VI. This table shows that the viscosity B coefficients for all cations and anions are positive and are also very high with the exception of bromide ion. The observed order of the ionic B values for the tetraalkylammonium ions,  $\text{Oct}_4\text{N}^+ > \text{Hep}_4\text{N}^+ > \text{Hex}_4\text{N}^+ > \text{Pen}_4\text{N}^+ > \text{Bu}_4\text{N}^+ > \text{Pr}_4\text{N}^+$ , shows that the obstruction of the solvent viscous flow increases with an increase of size of these species in solution. In case of  $\text{Br}^-$  ion, it might be that the viscosity of the solvent is very little modified by its presence in solution resulting in a very low viscosity B coefficient for this ion. The other anion,  $\text{Ph}_4\text{B}^-$ , however, is found to be very efficient in modifying the solvent viscosity as manifested by its large and positive viscosity B value. Among the two alkali metal ions investigated,  $\text{K}^+$  ion is found to cause greater obstruction of the solvent viscous flow compared to the  $\text{Na}^+$  ion in N, N - dimethylacetamide.

The ionic free energies of activation for viscous flow,  $\Delta\mu_2^{\text{of}}$  (ion) based on the division of tetrabutylammonium tetraphenylborate have been presented in Table VI. The values of  $\Delta\mu_2^{\text{of}}$  for tetraalkylammonium ions in *N,N*-dimethylacetamide decrease in the order  $\text{Oct}_4\text{N}^+ > \text{Hep}_4\text{N}^+ > \text{Hex}_4\text{N}^+ > \text{Pen}_4\text{N}^+ > \text{Bu}_4\text{N}^+ > \text{Pr}_4\text{N}^+$ , those for the alkali metal ions decrease in order  $\text{K}^+ > \text{Na}^+$ , and those for anions in the order  $\text{Ph}_4\text{B}^- > \text{Br}^-$ . However, these values are always found to be positive, and hence the formation of the transition state is made less favourable in the presence of these ions.

The ionic viscosity B-coefficients have also been analyzed on the basis of Einstein's equation<sup>22</sup>

$$B_{\pm} = 2.5 \frac{4}{3} \pi \frac{R_{\pm}^3 N}{1000} \quad (11)$$

where  $R_{\pm}$  is the radius of the ion assumed to be rigid sphere moving in a continuum and 2.5 is the shape factor for a sphere. The values of  $R_{\pm}$  are shown in Table VI.

A comparison of the  $R_{\pm}$  value with the sum of the ionic crystallographic radius and the radius of the solvent molecule can provide important information regarding the solvation of ions in solution. With the exception of  $\text{Na}^+$  and  $\text{K}^+$  ions, the  $R$  values for the other ions are always found to be much less than the sum of the radii of the ion<sup>23</sup> and the solvent molecule ( $r_{\text{solvent}} = 2.78^{\circ}\text{A}$ ). This indicates that the bromide, tetraphenylborate, and tetraalkylammonium ions are only scarcely solvated in *N,N*-dimethylacetamide. For  $\text{Na}^+$ , and  $\text{K}^+$  ions, however, the  $R_{\pm}$  values are found

to be much higher than the sum of the radii of the ion<sup>3</sup> and the solvent molecule which clearly demonstrates that these alkali-metal ions are significantly solvated in this solvent medium.

It may thus be concluded that the bromide, tetraphenylborate, and tetraalkylammonium ions remain only scarcely solvated in N,N-dimethylacetamide. The sodium and potassium ions, on the other hand, are found to be significantly solvated in this medium. The viscosity of the solvent is greatly modified by the presence of all the ions investigated here with the exception of the bromide ion.

## SECTION C

### ULTRASONIC VELOCITIES AND ISENTROPIC COMPRESSIBILITIES OF SOME SYMMETRICAL TETRAALKYLAMMONIUM SALTS IN N,N-DIMETHYLACETAMIDE AT 298.15K.

In previous section of this chapter we have described the results of conductance and viscosity measurements on a number of tetraalkylammonium salts. Here we described the findings of the compressibility behaviour of this electrolyte solutions to unravel the nature of various types of interactions prevailing in these solutions.

#### EXPERIMENTAL

The purification of salts and solvent have been described earlier. For the preparation of the solutions of each salt, a different batch of solvent was used and the properties of the pure solvent used in each case is recorded in Table VII.

The velocities of sound were measured with an accuracy of 0.3%, using a single-crystal variable path ultrasonic interferometer (Mittal Enterprises, New Delhi, India) operating at 4 MHz. The details of experimental procedure have been given in chapter III.

## RESULTS AND DISCUSSION

Adiabatic compressibility coefficients were derived from the following equation –

$$\kappa_s = 1/u^2\rho \quad (12)$$

where  $\rho$  is the density and  $u$  is the velocity of sound in the solution. The apparent molar isentropic compressibility  $\kappa_\phi$  of the electrolyte solutions was calculated from

$$\kappa_\phi = \frac{1000}{m\rho\rho_0} (\kappa_s\rho_0 - \kappa_s^0\rho) + \kappa_s^0 \frac{M}{\rho_0} \quad (13)$$

where  $m$  is the molal concentration of the solution and the other symbols have their usual significance.

The molality  $m$ , the density  $\rho$ , the sound velocity  $u$  and the apparent molar isentropic compressibility  $\kappa_\phi$  of the electrolyte solutions at 298.15K are given in Table VII.

The limiting apparent molar isentropic compressibilities  $\kappa_\phi^0$  were obtained<sup>3,4</sup> by extrapolating the linear plots of  $\kappa_\phi$  versus the square root of the molal concentration of the solutes to zero concentration by the method of least-squares :

$$\kappa_\phi = \kappa_\phi^0 + S_k \sqrt{m} \quad (14)$$

where  $S_k$  is the experimental slope. The  $\kappa_\phi^\circ$  and  $S_k$  values are listed in Table VIII. The limiting apparent molar isentropic compressibilities ( $\kappa_\phi^\circ$ ) of the electrolytes investigated here are found to increase in the order :

$\text{Pr}_4\text{NBr} < \text{Bu}_4\text{NBr} < \text{Pen}_4\text{NBr} < \text{Hex}_4\text{NBr} < \text{Hep}_4\text{NBr} < \text{Oct}_4\text{NBr}$ . It is also interesting to note that the  $\kappa_\phi^\circ$  values of  $\text{Pr}_4\text{NBr}$ ,  $\text{Bu}_4\text{NBr}$ ,  $\text{Pen}_4\text{NBr}$  are negative while those of the next three higher homologues are found to be positive.

The negative  $\kappa_\phi^\circ$  values of the electrolytes can be interpreted in terms of loss of compressibility of the solvent N,N-dimethylacetamide due to the presence of these solutes in solution. The positive  $\kappa_\phi^\circ$  values, on the other hand, indicates an increase in the compressibility of the solution compared to the pure solvent.

Several factors may contribute to the compressibility of the solution and we will now examine the important factors in order to elucidate the effects of the solutes on the solvent structure and their role as compressibility.

The bromide has been shown to remain unsolvated in N,N-dimethylacetamide from our earlier conductivity and viscosity study. Moreover, it is not a molecular ion, thus ruling out the possibility to have intrinsic compressibility. This ion, therefore, does not influence the compressibility of the medium.

Most of the interpretations of  $\kappa_\phi^\circ$  in terms of solvation effects<sup>24-26</sup> assume that  $\kappa_\phi^\circ$  of unsolvated ions is negligible, although Conway and Verral recognized that large organic ions could have some intrinsic compressibility due to the

intermolecular free space which makes the solution more compressible. This could be expected for the unsolvated tetraalkylammonium ions in our study also.

Another effect that is possible for large organic ions is the penetration of the solvent molecules into the intramolecular free space. This is the result of the interaction of the positively charged nitrogen central atom of the tetraalkylammonium ions with the neighbouring solvent molecules. This is essentially an electrostriction effect and causes constriction in the solution volumes, resulting in a more compact and, hence, a less compressible medium.

In view of the above factors, it can be concluded that since bromide ion has no effect on the compressibility of the solution, the interplay of the other two factors actually controls the compressibility of the solution.

The negative  $\kappa_{\phi}^{\circ}$  values for  $\text{Pr}_4\text{NBr}$ ,  $\text{Bu}_4\text{NBr}$ , and  $\text{Pen}_4\text{NBr}$  solutions can be attributed to the predominance of the effect of the intrinsic compressibility of the tetraalkylammonium ions over the penetration effect.

$\text{Hex}_4\text{NBr}$ ,  $\text{Hep}_4\text{NBr}$  and  $\text{Oct}_4\text{NBr}$ , on the other hand, the penetration effect overrides the effect of intrinsic compressibility of these ions.

In order to investigate the behaviour of the individual ions comprising these electrolytes, it is necessary to split the limiting apparent molar isentropic compressibilities into their ionic components. However, there are no reliable methods for the division of  $\kappa_{\phi}^{\circ}$  values into ionic contributions. Miller<sup>27</sup> has suggested dividing the limiting partial molar volumes of  $\text{Ph}_4\text{As}^+\text{Ph}_4\text{B}^-$  into ionic

components, but such a method cannot be used here since we do not know the ratio of the compressibilities of the pure (solid as gaseous) ions. The extrapolation method as suggested by Conway *et.al*<sup>18</sup> can also not be used for the division of  $\kappa_{\phi}^{\circ}$  values since the variation of the limiting apparent molar isentropic compressibilities of these salts with the formula weight of the tetraalkylammonium ions is not linear. The method<sup>29</sup> used for acetonitrile, which assumes  $\kappa_{\phi}^{\circ}(\text{Ph}_4\text{B}^+) = 0$  is also not appropriate as the  $\text{Ph}_4\text{B}^+$  ion is large ( $r = 0.535$  nm), and therefore, its intrinsic compressibility contribution cannot be taken as zero.

Under these circumstances and also in view of the compressibility behaviour of bromide in N,N-dimethylacetamide as discussed above, the choice of  $\kappa_{\phi}^{\circ}(\text{Br}^-) = 0$  seems to be the best at the moment. Ionic  $\kappa_{\phi}^{\circ}$  values based on this assumption are given in Table VIII which seem to fit quite well with the discussion made above on the basis of the  $\kappa_{\phi}^{\circ}$  values of the electrolytes as a whole.

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**Table 1 : Equivalent Conductances and corresponding Molarities of Electrolytes in N,N-Dimethylacetamide at 298.15 K.**

$10^4 c$ mol-dm <sup>-3</sup>	$\Lambda$ s-cm <sup>2</sup> -mol <sup>-1</sup>	$10^4 C$ mol-dm <sup>-3</sup>	$\Lambda$ s-cm <sup>2</sup> -mol <sup>-1</sup>
	Et <sub>4</sub> NBr		Pr <sub>4</sub> NBr
135.258	56.48	140.322	50.33
125.930	57.19	130.64	51.08
116.602	58.01	120.967	51.88
107.273	58.78	111.290	52.66
97.945	59.62	101.613	53.49
88.617	60.47	91.935	54.45
79.289	61.40	82.258	55.31
69.961	62.39	72.580	56.38
	Pen <sub>4</sub> NBr		Hex <sub>4</sub> NBr
130.642	45.38	135.722	44.12
120.593	46.09	126.028	44.73
110.543	46.77	116.333	45.49
100.494	47.21	106.639	46.20
90.445	48.30	96.944	46.92
80.395	49.12	87.250	47.69
70.346	50.57	77.554	48.54
60.296	50.98	67.861	49.44
50.247	51.98	58.166	50.38

Contd...

$10^4 c$ mol-dm <sup>-3</sup>	$\Lambda$ s-cm <sup>2</sup> -mol <sup>-1</sup>	$10^4 C$ mol-dm <sup>-3</sup>	$\Lambda$ s-cm <sup>2</sup> -mol <sup>-1</sup>
	Hep <sub>4</sub> NBr		Oct <sub>4</sub> NBr
140.779	42.88	128.189	44.76
130.723	43.54	119.033	45.34
120.668	44.23	109.176	45.95
110.612	44.91	100.720	46.17
100.556	45.33	91.564	47.33
90.501	46.55	82.407	48.14
80.445	47.43	73.251	48.80
70.389	48.36	64.095	49.63
60.334	49.32	54.938	50.49
49.837	57.22		
	NaBPh <sub>4</sub>		KBPh <sub>4</sub>
140.479	36.84	138.328	35.65
130.444	37.28	128.788	36.06
120.410	37.80	119.284	36.55
110.376	38.31	109.708	36.98
100.342	38.82	100.169	37.38
90.308	39.42	90.629	38.02
80.273	40.01	81.009	38.52
70.239	40.66	71.549	39.17
60.205	41.34		

**Table II : Conductivity Parameters of Electrolytes in N,N-Dimethylacetamide at 298.15K.**

Salt	$\Lambda^\circ$ S-cm <sup>2</sup> -mol <sup>-1</sup>	$K_A$ dm <sup>3</sup> -mol <sup>-1</sup>	R °A	$\sigma\%$
Et <sub>4</sub> NBr	76.98± 0.20	47.78 ± 0.76	11.16	0.06
Pr <sub>4</sub> NBr	72.03±0.27	58.31±1.13	11.68	0.08
Bu <sub>4</sub> NBr	69.27±0.20	45.63±0.88	12.10	0.08
Pen <sub>4</sub> NBr	62.30±0.66	51.03±3.29	12.45	0.28
Hex <sub>4</sub> NBr	61.69±0.21	53.64±1.04	12.76	0.10
Hep <sub>4</sub> NBr	61.35±0.46	58.15±2.33	13.04	0.21
Oct <sub>4</sub> NBr	61.32±0.53	51.60±2.74	13.20	0.27
NaBPh <sub>4</sub>	49.27±0.09	41.80±0.50	11.33	0.06
KBPh <sub>4</sub>	48.38±0.18	44.64±1.07	11.65	0.09
Bu <sub>4</sub> NBPh <sub>4</sub>	44.47±0.09	30.97±0.44	14.50	0.08

Table III. Limiting Ionic Conductances and Ionic Stokes' Radii in N,N-Dimethylacetamide at 298.15K

Ion	$\lambda_{\pm}^{\circ}$ S-cm <sup>2</sup> -mol <sup>-1</sup>	$r_s$ °A	ion	$\lambda_{\pm}^{\circ}$ S-cm <sup>2</sup> -mol <sup>-1</sup>	$r_s$ °A
Et <sub>4</sub> N <sup>+</sup>	30.70	2.18	Hep <sub>4</sub> N <sup>+</sup>	15.07	4.43
Pr <sub>4</sub> N <sup>+</sup>	25.75	2.60	Oct <sub>4</sub> N <sup>+</sup>	15.03	4.46
Bu <sub>4</sub> N <sup>+</sup>	22.99	2.91	Na <sup>+</sup>	27.79	2.41
Pen <sub>4</sub> N <sup>+</sup>	16.02	4.18	K <sup>+</sup>	26.90	2.49
Hex <sub>4</sub> N <sup>+</sup>	15.41	4.34	Br <sup>-</sup>	46.28	1.45

**Table IV : Molar Concentration(c), Densities( $\rho$ ) and Relative Viscosities ( $\eta_r$ ) of Some Tetraalkylammonium and Alkali-Metal Salts in N,N-Dimethylacetamide at 298.15**

c mol-dm <sup>-3</sup>	$\rho$ g-cm <sup>-3</sup>	$\eta_r$	c mol-dm <sup>-3</sup>	$\rho$ g-cm <sup>-3</sup>	$\eta_r$
	Pr <sub>4</sub> NBr			Bu <sub>4</sub> NBr	
0.01205	0.93749	1.0132	0.01322	0.93768	1.0163
0.02789	0.93876	1.0291	0.03247	0.93871	1.0381
0.04946	0.94033	1.0503	0.05727	0.93987	1.0659
0.07420	0.94211	1.0745	0.07930	0.94076	1.0904
0.09897	0.94388	1.0985	0.10131	0.94155	1.1147
0.11155	0.94478	1.1107	0.12773	0.94240	1.1439
	Pen <sub>4</sub> NBr			Hex <sub>4</sub> NBr	
0.01887	0.93813	1.0247	0.01184	0.93712	1.0187
0.05031	0.94003	1.0626	0.03154	0.93802	1.0459
0.08180	0.94184	1.1000	0.05126	0.93888	1.0724
0.11010	0.94340	1.1334	0.07096	0.93971	1.0986
0.15100	0.94556	1.1814	0.09066	0.94050	1.0247
0.22015	0.94902	1.2623	0.11431	0.94143	1.1557
	Hep <sub>4</sub> NBr			Oct <sub>4</sub> NBr	
0.01930	0.93715	1.0342	0.01142	0.93676	1.1903
0.03858	0.93814	1.0635	0.03045	0.93770	1.1571
0.06003	0.93918	1.0952	0.04951	0.93858	1.1234
0.07930	0.94010	1.1232	0.06854	0.93942	1.0923
0.09860	0.94098	1.1511	0.08952	0.94032	1.0600
0.12001	0.94193	1.1817	0.11042	0.94118	1.0235

Contd...

$c$ mol-dm <sup>-3</sup>	$\rho$ g-cm <sup>-3</sup>	$\eta_r$	$c$ mol-dm <sup>-3</sup>	$\rho$ g-cm <sup>-3</sup>	$\eta_r$
	Bu <sub>4</sub> NBPh <sub>4</sub>			NaBPh <sub>4</sub>	
0.00957	0.93680	1.0229	0.01115	0.93838	1.0228
0.02152	0.93739	1.0501	0.02972	0.94030	1.0566
0.04068	0.93816	1.0887	0.04831	0.94203	1.0889
0.05006	0.93848	1.1072	0.06687	0.94361	1.1207
0.05978	0.93878	1.1261	0.08550	0.94508	1.1525
0.08369	0.93938	1.1724	0.10778	0.94670	1.1902
	KBPh <sub>4</sub>				
0.00714	0.93768	1.0166			
0.00919	0.93791	1.0208			
0.01533	0.93860	1.0332			
0.02133	0.93924	1.0447			
0.02553	0.93965	1.0526			
0.03576	0.94062	1.0716			

**Table V. Theoretical A-Coefficients, the Viscosity B-Coefficients and the Free Energies of Activation for Viscous Flow of Electrolytes in N,N-Dimethylacetamide at 298.15K**

Electrolyte	A $\text{dm}^{3/2}\text{-mol}^{-1/2}$ ;	B $\text{dm}^3\text{-mol}^{-1}$ ;	$\Delta\mu_2^{0\#}$ $\text{kJ}\text{-mol}^{-1}$
Pr <sub>4</sub> NBr	0.0150	0.988	43.33
Bu <sub>4</sub> NBr	0.0158	1.117	49.73
Pen <sub>4</sub> NBr	0.0186	1.217	53.12
Hex <sub>4</sub> NBr	0.0189	1.491	62.41
Hep <sub>4</sub> NBr	0.0191	1.854	73.62
Oct <sub>4</sub> NBr	0.0192	2.121	82.41
Bu <sub>4</sub> NBPh <sub>4</sub>	0.0238	2.311	88.12
NaBPh <sub>4</sub>	0.0215	1.947	70.46
KBPh <sub>4</sub>	0.0219	2.220	77.62

**Table VI : Ionic Viscosity B-coefficients, Ionic Free Energies of Activation for Viscous Flow and Ionic Radii in N,N-Dimethylacetamide at 298.15K.**

Ion	$B_{\pm}$ $\text{dm}^3\text{-mol}^{-1}$	$\Delta\mu_2^{0\#}$ (ion), $\text{kJ}\text{-mol}^{-1}$	$R_{\pm}$ $^{\circ}\text{A}$ .
$\text{Pr}_4\text{N}^+$	0.910	33.20	5.24
$\text{Bu}_4\text{N}^+$	1.039	39.60	5.48
$\text{Pen}_4\text{N}^+$	1.139	42.99	5.65
$\text{Hex}_4\text{N}^+$	1.413	52.28	6.07
$\text{Hep}_4\text{N}^+$	1.776	63.49	6.55
$\text{Oct}_4\text{N}^+$	2.043	72.28	6.87
$\text{Na}^+$	0.675	21.94	4.74
$\text{K}^+$	0.948	29.10	5.32
$\text{Ph}_4\text{B}^-$	1.272	48.52	5.86
$\text{Br}^-$	0.078	10.13	2.31

**Table VII : Concentration (c ), density( $\rho$ ), ultrasonic velocity (u) and apparent molar isentropic compressibility ( $\kappa_\phi$ ) of the electrolyte solutions in N,N-dimethylacetamide at 298.15K.**

$C/\text{mol.dm}^{-3}$	$\rho/\text{g cm}^{-3}$	$u/\text{cm.s}^{-1}$	$\kappa_\phi \times 10^{10}$ $\text{cm}^3.\text{mol}^{-1}.\text{bar}^{-1}$	$c/\text{mol.dm}^{-3}$	$\rho/\text{g.cm}^{-3}$	$U/\text{cm.s}^{-1}$	$\kappa_\phi \times 10^{10}$ $\text{cm}^3.\text{mol}^{-1}.\text{bar}^{-1}$
Pr <sub>4</sub> NBr				Bu <sub>4</sub> NBr			
0.00000	0.93670	1460.35	-	0.00000	0.93686	1459.50	-
0.02789	0.93876	1465.82	-69.99	0.01322	0.93768	1461.87	-16.58
0.04946	0.94033	1468.44	-46.74	0.03247	0.93871	1464.42	8.27
0.07420	0.94211	1470.27	-25.64	0.05727	0.93987	1466.69	30.96
0.09897	0.94388	1471.07	-7.81	0.07930	0.94076	1468.02	47.10
0.11155	0.94478	1471.13	0.31	0.10131	0.94155	1468.80	60.87
				0.12773	0.94240	1469.03	75.68
Pen <sub>4</sub> NBr				Hex <sub>4</sub> NBr			
0.00000	0.93692	1461.09	-	0.00000	0.93654	1459.50	-
0.01887	0.93813	1464.26	22.55	0.01184	0.93712	1461.62	57.65
0.05031	0.94003	1468.05	43.73	0.03154	0.93802	1464.32	78.28
0.08180	0.94184	1470.82	58.60	0.05126	0.93888	1466.43	92.90
0.11010	0.94340	1472.45	70.63	0.07096	0.93971	1467.86	104.92
0.15100	0.94556	1474.09	84.00	0.09066	0.94050	1469.02	115.23
0.22015	0.94902	1474.43	103.57	0.11431	0.94143	1469.79	126.43
Hep <sub>4</sub> NBr				Oct <sub>4</sub> NBr			
0.00000	0.93610	1456.48	-	0.00000	0.93617	1458.54	-
0.01930	0.93715	1459.63	93.26	0.01142	0.93677	1460.87	98.93
0.03858	0.93814	1462.01	109.04	0.03045	0.93770	1463.98	117.86
0.06003	0.93918	1464.05	122.06	0.04951	0.93858	1466.58	131.30
0.07930	0.94010	1465.40	133.06	0.06854	0.93943	1468.68	142.30
0.09860	0.94098	1466.40	142.32	0.08952	0.94032	1470.58	152.78
0.12001	0.94193	1466.99	152.27	0.11042	0.94118	1472.08	162.04

**Table VIII : Limiting Apparent Molar Isentropic Compressibilities ( $\kappa_{\phi}^{\circ}$ ), the Experimental Slopes ( $S_k$ ) and the Standard Deviations for the Electrolyte Solutions in N,n-Dimethylacetamide at 298.15K.**

Electrolyte	$10^{10}(\kappa_{\phi}^{\circ})/$ $\text{Cm}^3\text{-mol}^{-1}\text{-bar}^{-1}$	$10^{10}S_k$ $\text{cm}^3\text{-mol}^{-3/2}\text{-kg}^{1/2}\text{-bar}^{-1}$	$\sigma$
Pr <sub>4</sub> NBr	-140.37± 0.09	421.23	0.29
Bu <sub>4</sub> NBr	-60.33±0.18	380.93	0.34
Pen <sub>4</sub> NBr	-11.07±0.39	244.65	0.29
Hex <sub>4</sub> NBr	25.00±0.12	299.90	0.25
Hep <sub>4</sub> NBr	53.37±0.89	283.66	0.22
Oct <sub>4</sub> NBr	69.00±0.01	280.00	0.23