

CHAPTER VII

SECTION A

VISCOSITIES AND ELECTRICAL CONDUCTANCES OF SOME TETRAALKYLAMMONIUM AND COMMON IONS IN AQUEOUS BINARY MIXTURES OF N,N-DIMETHYLACETAMIDE AT 298.15K.

The use of amide + water mixtures has attracted much attention as solvents in the study of various physico-chemical properties of electrolytic solution.¹⁻³ The present chapter is to study such a system through conductance and viscosity measurements which are very much useful to provide information regarding ion-ion and ion-solvent interactions.⁴⁻⁶ In chapter IV and V, we have reported the transport properties of some lithium and tetraalkylammonium salts in pure DMA from the measurements of their viscosities and conductances. The study has now been extended to binary mixtures with water as cosolvent, in order to understand the nature of ion-solvent interactions and other structural changes that may occur due to the addition of water to DMA.

Experimental

N,N-dimethylacetamide (G.R.E. Merck, India, >99.5%) was distilled twice in an all-glass distillation set as described earlier (chapter III). The purified solvent had a density of $0.93652 \text{ g.cm}^{-3}$, a coefficient of viscosity $0.9370 \text{ mPa}\cdot\text{s}$ and a specific conductance of about $1.01 \times 10^{-6} \text{ s}\cdot\text{cm}^{-1}$ at 298.15K. Triply distilled water with a specific conductance of less than $10^{-6} \text{ S}\cdot\text{cm}^{-1}$ was used for the preparation of

the mixtures. Freshly distilled solvents were always used, and the solvent mixtures were prepared immediately prior to use. Solvent mixtures, prepared by weight had a density of $0.99853 \text{ g.cm}^{-3}$, a coefficient of viscosity $3.318 \text{ mPa}\cdot\text{s}$, a specific conductance of about $3 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1}$ and a dielectric constant 59.92 at 298.15K.

The tetraalkylammonium bromides were of purum or puriss grade (Fluka) and were purified as described earlier (chapter III).

Conductance measurements were carried out on a Pye-Unicam PW9509 conductivity meter at a frequency of 2000Hz as described in chapter III. The kinematic viscosities were measured using a suspended-level Ubbelohde type viscometer and results were then converted into absolute viscosities by multiplying the former with the density values. Measurements were made in a thermostatic water bath maintained within specified temperature. Solutions were prepared by mass for viscosity and conductance runs, the molalities being converted to molarities using the densities measured with an Ostwald-Sprengel type Pycnometer of about 25 cm^3 capacity. Several independent solutions were prepared and the 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 (Λ) of electrolyte solutions as a function of molar concentration (c) at 298.15K are given in Table 1.

The conductance data have been analysed by the 1978 Fuoss conductance – concentration equation⁷ as given in chapter IV.

For computation, the initial Λ° values were obtained from Shedlovsky extrapolation of the data. In practice, calculations are made by finding the values of Λ° and σ which minimize the standard deviation, σ ,

$$\sigma^2 = \frac{\sum_{j=1}^n [\Lambda_j (\text{calc.}) - \Lambda_j^{\circ} (\text{obs.})]^2}{(n-2)} \quad (1)$$

for a sequence of R values and then plotting σ against R , the best-fit R corresponds to the minimum in σ 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 crystallographic radii and d is given by⁷

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

where M is the molecular weight of the solvent and ρ_0 its density.

The values of Λ° , K_A and R obtained by this procedure have been recorded in Table 2.

In absence of accurate transference data in the mixed solvent, we have to use the 'reference electrolyte' method for the division of Λ° into single-ion values. The Bu_4NBPh_4 has been used as the 'reference electrolyte', and the Λ° -value has been derived from the relation :

$$\Lambda_{\text{Bu}_4\text{NBPh}_4}^{\circ} = \Lambda_{\text{Bu}_4\text{NBr}}^{\circ} + \Lambda_{\text{NaBPh}_4}^{\circ} - \Lambda_{\text{NaBr}}^{\circ} \quad (3)$$

To obtain single ion values we have divided Λ° values of Bu_4NBPh_4 using the method similar to that proposed by Krumgalz⁸

$$\frac{\lambda_{\text{Bu}_4\text{N}^+}^\circ}{\lambda_{\text{Ph}_4\text{B}^-}^\circ} = \frac{\Gamma_{\text{Ph}_4\text{B}^-}}{\Gamma_{\text{Bu}_4\text{N}^+}} = \frac{5.35}{5.00} = 1.07 \quad (4)$$

The r-values have been taken from the works of Gill and Sekhri⁹. The limiting ionic conductances based on the above relationship are presented in Table 3.

The density (ρ) and viscosity (η) data for the electrolytes in the molarity range 0.008 – 0.20 mol dm⁻³ at 298.15K are given in Table 4.

The relative viscosity (η_r) data of the electrolytes in solution have been analysed with the Jones-Dole equation.¹⁰:

$$\eta_r = 1 + Ac^{1/2} + Bc \quad (5)$$

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

Plots of $(\eta_r - 1)/\sqrt{c}$ against \sqrt{c} for the electrolytes have been found to be linear and the experimental A values have been calculated using the least squares method. The A coefficients have also been calculated at 298.15K from the physical properties of the solvent by using Falkenhagen-Vernon equation:

$$A_{\text{theo}} = \frac{0.2577\Lambda^\circ}{\eta_o(\epsilon T)^{1/2}\lambda_o^+ \lambda_o^-} \left[1 - 0.6863 \left[\frac{\lambda_o^+ - \lambda_o^-}{\Lambda_o} \right]^2 \right] \quad (6)$$

The conductance data required in these calculations have been taken from the present work. A coefficients (A_{theo}) thus calculated from Eq. (6) are recorded in Table 5. These A_{theo} values have been used for the analysis of viscosity data.

Viscosity β -coefficients calculated by using the least squares method are also presented in Table 5. Viscosity β -coefficient values of the electrolytes have been divided into ionic components using similar method described above in equations (3) and (4) for division of the limiting molar conductances. The ionic β -coefficients obtained from these relationships are given in Table 6.

Ionic β -values have also been analysed⁴ on the basis of Einstein's equation and the corresponding ionic radii evaluated :

$$B_{\pm} = 2.5 (4/3) \pi \frac{R_{\pm}^3 N}{1000} \quad (7)$$

The number n_s of solvent molecules bound to the ion in the primary shell of solvation can be calculated by combining the Jones-Dole equation with that of Einstein:

$$B_{\pm} = (2.5/1000) (V_i + n_s V_s) \quad (8)$$

Where 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. Table 7 deals with the crystallographic radius (R_c), experimental ionic radii (R_{\pm}) and solvation number (n_s) of ions at 298.15K.

Table 2 shows that the limiting equivalent conductivities (Λ°) of tetraalkylammonium bromides decrease with increasing length of the alkyl chain and the difference becomes very small in cases of higher homologues. This is in agreement with our earlier findings in pure DMA as described in chapter V. 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. It is seen from Table 3 that for the tetraalkylammonium ions, the λ° values decrease in the following order : $\text{Et}_4\text{N}^+ > \text{Pr}_4\text{N}^+ > \text{Bu}_4\text{N}^+ > \text{Pen}_4\text{N}^+ > \text{Hex}_4\text{N}^+$ i.e. the limiting ionic conductivity values decrease with increasing size of these cations. The trends become similar with the earlier observation made by Ramanamurti et al¹¹ in this aqueous binary system at higher temperature and can be attributed to the size and structure forming effect of cations (anion Br^- , being the same). Size and structure forming effects (hydrophobic solvation) of cations increase in the order : $\text{Et}_4\text{N}^+ < \text{Pr}_4\text{N}^+ < \text{Bu}_4\text{N}^+ < \text{Pen}_4\text{N}^+ < \text{Hex}_4\text{N}^+$, so the mobility should be in the reverse order and this explains the order observed for limiting equivalent conductance. In cases of anions the λ° values decrease with increasing size of the ions i.e. $\text{Br}^- > [\text{B}(\text{Ph})_4]^-$. Table 2 clearly indicates that in almost all cases except tetraethylammonium bromide, association constants are less than 10, so little emphasis should be given to numerical values of K_A . This implies that a preponderant portion of each salt remains dissociated in this solvent medium. However, in solvent mixtures having dielectric constants less than 60, the value of K_A seems to decrease with increasing chain length of tetraalkylammonium bromide salts.¹¹ This is expected because the charge density of tetraalkylammonium ions decrease in the same order.

The Walden products ($\lambda^\circ_{\pm} \eta_0$) of the ions are also included in Table 3. 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, the value of the Walden product decreases from tetraethylammonium ion to tetrahexylammonium ion. This points out that the electrostatic ion-solvent interaction is very weak in these cases. Such type of behaviour is also found in pure DMA as reported earlier. In comparison to the Walden product values of these electrolytes in pure DMA it is observed that except tetraethylammonium ion the other tetraalkylammonium ion maintains nearly same value in this present aqueous binary mixture. The phenomena can be explained by the hydrophobic dehydration of cations by the cosolvent (DMA) which is responsible for the similarity of the Walden product. Further, the hydrophobic dehydration effect will be more in the case of an ion which is more hydrophobic in nature. This hydrophobic character of cations varies in the order: $\text{Hex}_4\text{N}^+ > \text{Pen}_4\text{N}^+ > \text{Bu}_4\text{N}^+ > \text{Pr}_4\text{N}^+ > \text{Et}_4\text{N}^+$. Due to the greater hydrophobic dehydration effect of higher homologues of tetraalkylammonium cation the ability to promote the structure of water becomes reduced and as a result of it the Walden product remains the same value. The Stokes radii (Table 3) of the tetraalkylammonium cations are, however, found to be either close to or smaller than their corresponding crystallographic radii. This observation indicates that these ions are scarcely solvated in this medium.

In addition to conductance measurements the result of the viscosity measurements of different tetraalkylammonium salts from Et_4NBr to Pen_4NBr and some common salts except Hex_4NBr (solubility too low to perform viscosity experiments) are also reported.

The viscosity β -coefficients which represents solute – solvent interactions shown in Table 5 are positive for all the electrolytes studied. The β -values for the tetraalkylammonium bromides increase regularly as we go from tetraethylammonium bromide to tetrapentylammonium bromide. The same kind of behaviour has also been found for these electrolytes in Ethyl – methyl ketone and Ethyl – methyl ketone + Dimethylformamide mixtures.¹²

In order to make further investigation for the specific behaviour of the individual ions the viscosity β -coefficients values of electrolyte resolved into ionic β_{\pm} coefficients by using “reference electrolyte” method and are given in Table 6. The table shows that the viscosity β – coefficients for all cations and anions are positive and are also large with the exception of bromide ion. The observed order may be attributed to greater electrostatic ion-solvent interaction and resistance to the movement of ion due to large size of cation. In case of Br^- ion the very low viscosity β -coefficient value indicates that the viscosity of the solvent mixture is very little modified by its presence due to the poor solvation of the ion and this is also supported by the conductance data. The other anion, Ph_4B^- , however, is found to be very efficient in modifying the solvent viscosity as manifested by its large and positive viscosity β value. The A – coefficients reported in Table 5 are small and positive for all the electrolytes indicating the presence of weak ionic interactions. The A values, calculated theoretically from the physical parameters of the solvent and the limiting ionic equivalent conductances using Falkenhagen and Vernon

equation given in Table 5 are almost similar with the experimental A-value. The values of crystallographic radius (R_c), Ionic radii (R_{\pm}) and solvation number (n_s) shown in Table 7 can provide us important information regarding the solvation of some tetraalkylammonium, Na^+ , Br^- and Ph_4B^- ions in this present aqueous binary mixture. With the exception of Na^+ , Br^- and Ph_4B^- ions, the R_{\pm} values for the other ions are always found to be less than R_c values of the ions indicating that they are not so solvated in this mixture. Although the negative values of solvation number have no physical significance, it seems to an indication of the poor solvation of these ions. For Na^+ and Br^- ions, the greater value of ionic radii (R_{\pm}) than crystallographic radii (R_c) and positive solvation number clearly demonstrate that these ions are significantly solvated in this solvent medium. The results obtained from viscosity measurements are found to be in good agreement with the conductometric investigation.

SECTION B

ULTRASONIC VELOCITIES AND ISENTROPIC COMPRESSIBILITIES OF SOME SYMMETRICAL TETRAALKYLAMMONIUM AND ALKALI-METAL SALTS IN *N,N*-DIMETHYLACETAMIDE-WATER MIXTURE AT 298.15 K

The thermodynamic properties are generally convenient parameters for interpreting solute-solute, and solute-solvent interactions occurring in solution phase. Fundamental properties such as enthalpy, entropy, and Gibbs energy represent the macroscopic state of a system as an average of numerous microscopic states at a given temperature and pressure. An interpretation of these macroscopic properties in terms of molecular phenomena is generally difficult. Higher derivatives of these properties, however, can be interpreted in terms of molecular interactions. The compressibility behaviour of solutes, which is the second derivative of the Gibbs energy, is a very sensitive indicator of molecular interactions and can provide useful information about these phenomena.¹³⁻¹⁸ In Chapter V, Section C we have reported the results of our compressibility measurements on some selected symmetrical tetraalkylammonium bromides in *N,N*-dimethylacetamide at 298.15 K. The present work reports the study of the apparent molar isentropic compressibility behaviour of some tetraalkylammonium and alkali salts in *N,N*-dimethylacetamide + water (50% v/v) mixture at 298.15 K to elucidate the nature of interactions prevailing in these salt solutions.

Experimental

For the preparation of the solution of each salt, a different batch of solvent was used and the properties of the mixed solvent used in each case are recorded in Table 8.

In order to minimize the moisture contaminations, all solutions were prepared in a dehumidified room with utmost care. A stock solution for each salt was prepared by mass and the working solutions were prepared by mass dilution from the stock. The conversion of molality to molarity was performed using the density values.

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 interferometer was calibrated with water, methanol and benzene. The temperature stability was maintained within ± 0.01 K by circulating thermostated water around the measuring cell.

Results and Discussion

Adiabatic compressibility coefficients were derived from the following equation

$$\kappa_s = \frac{1}{u^2 \rho} \quad (9)$$

where ρ is the density and u is the velocity of sound in the solution. The apparent

molar isentropic compressibility (κ_ϕ) of the electrolyte solutions was then calculated from the relationship

$$\kappa_\phi = \frac{M\kappa_s^0}{\rho_0} + \frac{1000(\kappa_s\rho_0 - \kappa_s^0\rho)}{m\rho\rho_0} \quad (10)$$

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

The molality (m), the density (ρ), the sound velocity (u), and the apparent molar isentropic compressibility (κ_ϕ) of the electrolyte solutions at 298.15 K are reported in Table 8.

The limiting apparent molar isentropic compressibility (κ_ϕ^0) have been obtained by extrapolating the linear plots of κ_ϕ versus the square root of the molal concentration of the solutes to zero concentration by the method of least-squares

$$\kappa_s = \kappa_s^0 + S_K \sqrt{m} \quad (11)$$

where S_K is the experimental slope. The values of the limiting apparent molar isentropic compressibilities (κ_ϕ^0), and the experimental slopes (S_K) are listed in Table 9.

The limiting apparent molar isentropic compressibilities (κ_ϕ^0) of the tetraalkylammonium salts investigated here are found to increase in the order:



It is also interesting to note that the κ_{ϕ}^0 values of Et_4NBr and NaBr are negative while those of the other three tetraalkylammonium bromides and NaBPh_4 are found to be positive.

The negative κ_{ϕ}^0 values of the electrolytes can be interpreted in terms of loss of compressibility of the solvent due to the presence of these solutes in solution. The positive κ_{ϕ}^0 values, on the other hand, indicate an increase in the compressibility of the solution compared to the pure solvent.

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

The bromide ion is found to remain unsolvated in the mixed *N,N*-dimethylacetamide + water system under investigation from our conductivity study. Moreover, it is not a molecular ion, thus ruling out the possibility of having intrinsic compressibility. This ion, therefore, does not influence the compressibility of the medium. The sodium ion, however, is found to be solvated from conductivity study. This ion will, therefore, cause a loss of solvent compressibility resulting from the electrostriction of the solvent molecules around the ion.

Most of the interpretations of the limiting apparent molar isentropic compressibilities in terms of solvation effects¹⁹⁻²³ assume κ_{ϕ}^0 of unsolvated ions is negligibly small, although Conway and Verral²⁴ recognized that large organic ions could have some intrinsic compressibility due to the intermolecular free space which

makes the medium more compressible. This could also be expected for the unsolvated large tetraalkylammonium and tetraphenylborate ions investigated in this study.

Another effect which is possible for large organic ions is the penetration of the solvent molecules within the intraionic free space. This is the result of the interaction of the positively charged nitrogen central atom of the tetraalkylammonium ions (or of the negatively charged boron central atom in the case of the tetraphenylborate ion) with the neighboring solvent molecules. This is essentially an electrostriction effect and causes constriction of the solution volumes, thus resulting in a more compact and, hence, a less compressible medium.

In view of the factors delineated above which control the compressibility of the electrolyte solutions, it can be concluded that since the bromide ion has no influence on the compressibility of the solution, the interplay of the other factors would actually determine the overall compressibility of the solution.

The negative limiting apparent molar isentropic compressibility value for Et_4NBr solution can be attributed to the predominance of the penetration effect over the effect of the intrinsic compressibility of the tetraethylammonium ions. For Pr_4NBr , Bu_4NBr , and Pen_4NBr solutions exhibiting positive κ_p^0 values, on the other hand, the effect of intrinsic compressibility of the large tetraalkylammonium ions overrides the penetration effect. This observation is quite expected since the extent of penetration of the solvent molecules should be maximum for tetraethylammonium ion with the lowest crystal radius and hence the highest surface charge density

among the tetraalkylammonium ions studied here. For higher homologues, the surface charge density decreases with the radius, thus lowering the possibility of penetration.

For NaBr solution, however, the negative κ_{ϕ}^0 value arises from the loss of solvent compressibility caused by the sodium ions.

The positive κ_{ϕ}^0 value for NaBPh₄ solution indicates that the intrinsic compressibility of the tetraphenylborate ion is playing the major role as compared to the penetration effect of this ion and the electrostriction effect of the sodium ion.

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 exist no reliable method for the division of κ_{ϕ}^0 values into ionic contributions. Millero²³ has suggested a method for the division of the limiting partial molar volumes of the "reference electrolyte" tetraphenylarsonium tetraphenylborate (Ph₄As⁺Ph₄B⁻) into ionic parts, but such a method cannot be used here since we do not know the ratio of the compressibilities of the pure (solid or gaseous) ions. A similar model based on another "reference electrolyte" tetrabutylammonium tetraphenylborate (Bu₄N⁺Ph₄B⁻) originally used for the splitting of the viscosity *B*-coefficients of electrolytes into the contributions from individual ions was attempted²⁵ to split the κ_{ϕ}^0 values. But, this approach is inappropriate since it assumes that the ratio of the volumes of these ions is equal to the ratio of their compressibilities which is not possible since the

compressibilities of these large ions are not a simple function of their volumes. The extrapolation method as suggested by Conway et. al.²⁶ for volumes can also not be used for the division of the κ_{ϕ}^0 values in view of the large contribution of the compressibilities of the tetraalkylammonium ions which does not seem to be a simple function of the size of the ion. Interestingly, we tried both the extrapolation method and the "reference electrolyte" method using tetrabutylammonium tetraphenylborate ($\text{Bu}_4\text{N}^+\text{Ph}_4\text{B}^-$) to perform the division of the κ_{ϕ}^0 values into ionic components. But, unfortunately, the results obtained by these two methods differ appreciably. The method used by Davidson et. al.¹³ for acetonitrile, which assumes the limiting ionic compressibility of the tetraphenylborate ion to be zero is also not appropriate as the tetraphenylborate ion is large (its crystal radius is 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 ion in the mixed solvent system under study as discussed above, the choice of $\kappa_{\phi}^0(\text{Br}^-) = 0$ seems to be the best at this moment. Ionic κ_{ϕ}^0 values based on this assumption are given in Table 3, which fit quite well with the discussion made above on the basis of the κ_{ϕ}^0 values of the electrolytes as whole thus substantiating the present protocol for the division of limiting apparent molar isentropic compressibilities of these electrolytes in *N,N*-dimethylacetamide + water mixed solvent system.

Thus the above study shows the effect of penetration of the solvent molecules into the intraionic free space of the tetraethylammonium ions to predominate over the effect of their intrinsic compressibility for tetraethylammonium bromide solution. For sodium bromide solution, however, the negative κ_{ϕ}^0 value arises from the loss of solvent compressibility caused by the sodium ions. For tetrapropylammonium bromide, tetrabutylammonium bromide, and tetrapentylammonium bromide solutions exhibiting positive κ_{ϕ}^0 values, on the other hand, the effect of intrinsic compressibility of the large tetraalkylammonium ions overrides the penetration effect. The positive κ_{ϕ}^0 value for sodium tetraphenylborate solution indicates that the intrinsic compressibility of the tetraphenylborate ion is playing the major role as compared to the penetration effect of this ion and the electrostriction effect of the sodium ion.

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Table 1 - Equivalent conductances and corresponding molarities of electrolytes in aqueous binary mixture of N,N-dimethyl acetamide at 298.15K.

$10^4 c$ (mol dm ⁻³)	\wedge (S cm ² mol ⁻¹)	$10^4 c$ (mol dm ⁻³)	\wedge (S cm ² mol ⁻¹)
	Et ₄ NBr	Pr ₄ NBr	
442.48	24.25	435.51	21.57
411.96	24.60	405.47	21.83
381.44	24.98	375.44	22.09
350.93	25.39	345.40	22.33
320.41	25.78	315.37	22.62
290.00	26.21	285.34	22.92
259.40	26.67	255.30	23.23
228.87	27.14	225.26	23.54
	Bu ₄ NBr	Pen ₄ NBr	
435.90	21.14	434.23	20.47
405.84	21.33	404.29	20.64
375.78	21.55	374.34	20.85
345.72	21.77	344.39	21.05
315.65	21.98	314.44	21.28
285.59	22.13	284.50	21.50
255.53	22.42	254.55	21.77
225.47	22.68	224.60	22.01

contd....

$10^4 c$ (mol dm ⁻³)	\wedge (S cm ² mol ⁻¹)	$10^4 c$ (mol dm ⁻³)	\wedge (S cm ² mol ⁻¹)
Hex ₄ NBr		NaBr	
436.55	19.57	436.72	31.41
406.44	19.72	406.60	31.59
376.33	19.89	376.48	31.78
346.22	20.08	346.36	31.95
316.12	20.24	316.24	32.14
286.01	20.43	286.12	32.33
255.90	20.62	256.01	32.55
225.80	20.72	225.89	32.78
Na[B(Ph) ₄]			
436.50	20.00		
406.40	20.10		
376.29	20.20		
346.19	20.29		
316.09	20.40		
285.98	20.50		
255.88	20.62		
225.78	20.75		

Table 2 - Conductivity parameters of electrolytes in aqueous binary mixture of N,N-dimethylacetamide at 298.15K.

Salt	\wedge_{∞} (S cm ² mol ⁻¹)	K _A (dm ³ mol ⁻¹)	R (°A)	$\sigma\%$
Et ₄ NBr	34.74± 0.15	18.12± 0.41	5.80	0.09
Pr ₄ NBr	27.34±0.03	9.31±0.08	18.40	0.04
Bu ₄ NBr	25.54±0.08	6.86±0.20	16.00	0.10
Pen ₄ NBr	25.43±0.03	8.50±0.10	8.00	0.04
Hex ₄ NBr	23.40±0.11	6.19±0.30	7.40	0.16
NaBr	35.76±0.02	3.88±0.04	8.00	0.02
Na[B(Ph) ₄]	25.52±0.01	3.12±0.03	6.00	0.02

Table 3 - Limiting ionic conductances (λ_{\pm}°), Walden products ($\lambda_{\pm}^{\circ} \eta_0$) and Ionic Stokes' Radii (r_s) in aqueous binary mixture of N,N-dimethylacetamide at 298.15K.

Ion	λ_{\pm}° (S cm ² mol ⁻¹)	$\lambda_{\pm}^{\circ} \eta_0$ (S cm ² mol ⁻¹ P _{a.s})	r_s (\AA)
Et ₄ N ⁺	17.11	0.056	1.44
Pr ₄ N ⁺	9.71	0.032	2.55
Bu ₄ N ⁺	7.91	0.026	3.13
Pen ₄ N ⁺	7.80	0.025	3.17
Hex ₄ N ⁺	5.76	0.019	4.30
Na ⁺	18.13	0.060	1.36
Br ⁻	17.63	0.058	1.40
[B(Ph) ₄] ⁻	7.39	0.024	3.35

Table 4 - Concentration (c), density (ρ) and relative viscosity (η_r) of electrolytes in aqueous binary mixture at 298.15K.

C (mol dm ⁻³)	ρ (g cm ⁻³)	η_r	C (mol dm ⁻³)	ρ (g cm ⁻³)	η_r
Et ₄ NBr			Pr ₄ NBr		
0.10186	1.0032	1.0395	0.10233	1.0027	1.0615
0.07276	1.0021	1.0280	0.07309	1.0017	1.0444
0.05238	1.0012	1.0206	0.05262	1.0010	1.0322
0.03201	1.0003	1.0129	0.03216	1.0002	1.0204
0.02037	0.9998	1.0084	0.02046	0.9997	1.0130
0.00873	0.992	1.0037	0.00877	0.9992	1.0063
Bu ₄ NBr			Pen ₄ NBr		
0.10470	1.0016	1.0743	0.10235	0.99942	1.0832
0.07479	1.0009	1.0535	0.07310	0.99929	1.0601
0.05385	1.0003	1.0390	0.05264	0.99914	1.0436
0.03290	0.9997	1.0240	0.03217	0.99893	1.0268
0.02094	0.9993	1.0156	0.02047	0.99877	1.0174
0.00897	0.9989	1.0070	0.00877	0.99858	1.0076
NaBr			Na[B(Ph) ₄]		
0.10954	1.0065	1.0322	0.10386	1.0022	1.1049
0.07824	1.0044	1.0233	0.07418	1.0013	1.0729
0.05633	1.0028	1.0169	0.05341	1.0006	1.0544
0.03442	1.0012	1.0105	0.03264	0.9998	1.0337
0.02191	1.0002	1.0069	0.02077	0.9994	1.0217
0.00939	0.9991	1.0031	0.00890	0.9989	1.0096

Table 5 - Theoretical and experimental A-coefficients and viscosity B-coefficients for the electrolytes in aqueous binary mixture of N,N-dimethylacetamide at 298.15K.

Salt	A_{theo} ($\text{dm}^{3/2}\text{mol}^{-1/2}$)	$A_{\text{expt.}}$ ($\text{dm}^{3/2}\text{mol}^{-1/2}$)	B ($\text{dm}^3\text{mol}^{-1}$)	σ
Et ₄ NBr	0.0068	0.0062	0.366	0.03
Pr ₄ NBr	0.0086	0.0132	0.558	0.04
Bu ₄ NBr	0.0096	0.0088	0.683	0.05
Pen ₄ NBr	0.0099	0.0082	0.790	0.06
NaBr	0.0064	0.0052	0.279	0.01
Na[B(Ph) ₄]	0.0110	0.0113	0.964	0.08

Table 6 - Ionic B-values in aqueous binary mixture of N,N-dimethylacetamide at 298.15K.

Ions	B_{\pm} ($\text{dm}^3 \text{mol}^{-1}$)
Et_4N^+	0.298
Pr_4N^+	0.490
Bu_4N^+	0.615
Pen_4N^+	0.722
Na^+	0.211
Br^-	0.068
Ph_4B^-	0.753

Table 7 - Theoretical and experimental Ionic radii (R_{\pm}) and solvation numbers (n_s) of ions in aqueous binary mixture of N,N-dimethylacetamide at 298.15K.

Ions	R_c (°A)	R_{\pm} (°A)	n_s
Et ₄ N ⁺	4.00	3.60	-0.358
Pr ₄ N ⁺	4.52	4.20	-0.345
Bu ₄ N ⁺	4.94	4.60	-0.236
Pen ₄ N ⁺	5.29	4.80	-0.303
Na ⁺	1.17	3.20	0.968
Br ⁻	1.80	2.20	0.465
Ph ₄ B ⁻	4.80	4.90	-0.075

Table 8. Concentration (c), density (ρ), ultrasonic velocity (u), and apparent molar isentropic compressibility (κ_ϕ) of the electrolyte solutions in N,N -dimethylacetamide + water mixture (50% v/v) at 298.15 K

c mol.dm ⁻³	ρ g.cm ⁻³	u cm.s ⁻¹	$10^{10}\kappa_\phi$ cm ³ .mol ⁻¹ .bar ⁻¹	c mol.dm ⁻³	ρ g.cm ⁻³	u cm.s ⁻¹	$10^{10}\kappa_\phi$ cm ³ .mol ⁻¹ .bar ⁻¹
Et ₄ NBr				Pr ₄ NBr			
0.00000	0.99877	173938	-	0.00000	0.99877	173938	-
0.00873	0.99922	174058	-12.74	0.00877	0.99919	174032	19.90
0.02037	0.99979	174177	-6.36	0.02046	0.99970	174130	24.28
0.03201	1.00030	174284	-1.50	0.03216	1.00020	174208	28.09
0.05238	1.00120	174423	4.62	0.05262	1.00100	174326	32.94
0.07276	1.00210	174517	9.80	0.07309	1.00170	174424	37.04
0.10186	1.00320	174624	15.85	0.10233	1.00270	174513	41.97
Bu ₄ NBr				Pen ₄ NBr			
0.00000	0.99854	173818	-	0.00000	0.99841	173770	-
0.00897	0.99888	173880	52.07	0.00877	0.99858	173840	81.68
0.02094	0.99930	173954	56.77	0.02047	0.99877	173929	84.24
0.03290	0.99969	174020	59.55	0.03217	0.99893	174010	86.49
0.05385	1.00030	174117	63.68	0.05264	0.99914	174139	89.79
0.07479	1.00090	174189	66.87	0.07310	0.99929	174253	92.61
0.10470	1.00160	174274	70.87	0.10235	0.99942	174400	95.79

Table 8. contd..

c/l mol.dm ⁻³	ρ/l g.cm ⁻³	u/l cm.s ⁻¹	$10^{10} \kappa_\phi/l$ cm ³ .mol ⁻¹ .bar ⁻¹	c/l mol.dm ⁻³	ρ/l g.cm ⁻³	u/l cm.s ⁻¹	$10^{10} \kappa_\phi/l$ cm ³ .mol ⁻¹ .bar ⁻¹
	NaBPh ₄				NaBr		
0.00000	0.99853	173696	-	0.00000	0.99831	173842	-
0.00890	0.99891	173575	137.77	0.00939	0.99915	173815	-13.64
0.02077	0.99939	173381	144.30	0.02191	1.00020	173781	-12.28
0.03264	0.99984	173168	149.14	0.03442	1.00120	173752	-11.43
0.05341	1.00060	172753	155.93	0.05633	1.00280	173720	-10.41
0.07418	1.00130	172300	161.48	0.07824	1.00440	173683	-9.57
0.10386	1.00220	171611	168.17	0.10954	1.00650	173648	-8.55

Table 9. Limiting apparent molar isentropic compressibilities (κ_ϕ^0), and the experimental slopes (S_K) of the electrolyte solutions in *N,N*-dimethylacetamide + water mixture (50% v/v) at 298.15 K

Electrolyte	$10^{10} \kappa_\phi^0 / \text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{bar}^{-1}$	$10^{10} S_K / \text{cm}^3 \cdot \text{mol}^{-3/2} \cdot \text{kg}^{1/2} \cdot \text{bar}^{-1}$
Et ₄ NBr	-24.41 ± 0.20	125.63 ± 0.92
Pr ₄ NBr	10.49 ± 0.20	98.16 ± 0.93
Bu ₄ NBr	44.72 ± 0.29	81.21 ± 1.31
Pen ₄ NBr	75.40 ± 0.31	63.30 ± 1.41
NaBPh ₄	124.83 ± 0.83	134.44 ± 0.38
NaBr	-15.09 ± 0.01	19.73 ± 0.05

Table 10. Ionic standard apparent molar isentropic compressibilities ($\kappa_{\phi\pm}^0$) in *N,N*-dimethyl-acetamide + water mixture (50% v/v) at 298.15 K

ion	$10^{10} \kappa_{\phi\pm}^0 / \text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{bar}^{-1}$	ion	$10^{10} \kappa_{\phi\pm}^0 / \text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{bar}^{-1}$
Et ₄ N ⁺	-24.41	Na ⁺	-15.09
Pr ₄ N ⁺	10.49	Ph ₄ B ⁻	139.92
Bu ₄ N ⁺	44.72	Br ⁻	0.00
Pen ₄ N ⁺	75.40		