

# Ionic Viscosity B-Coefficients of $(\text{CH}_3)_4\text{N}^+$ , $(\text{C}_2\text{H}_5)_4\text{N}^+$ , $(\text{C}_3\text{H}_7)_4\text{N}^+$ , $(\text{C}_4\text{H}_9)_4\text{N}^+$ , $\text{Na}^+$ , $\text{I}^-$ and $\text{Bph}_4^-$ in Aqueous Methanol at 298.15 K

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**Abstract:** Viscosities of  $\text{R}_4\text{NI}$  ( $\text{R} = \text{CH}_3$  to  $\text{C}_4\text{H}_9$ ),  $\text{NaI}$  and  $\text{NaBh}_4$  solutions in 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 mass % of methanol + water at 298.15 K were measured. The viscosity data have been analyzed with the help of Jones-Dole equation. The corresponding viscosity  $B$  coefficient is calculated. Ionic B coefficients of cations and anions have been determined using  $\text{Bu}_4\text{NBPh}_4$  as reference electrolyte.

**Keywords:** Density, Ionic viscosity, B-Coefficients

## Introduction

Measurements of viscosities of solutions in aqueous, pure non- aqueous and mixed solvents at various temperatures throw light on ion-ion and ion-solvent interactions. The structure breaking and structure making characters of the solute resulting in bond formation and disruption properties are correlated to changes in the viscosity of solution. We have investigated nature of ion-solvent interactions of some salt solutions from the measurements of viscosities and densities of solutions<sup>1-4</sup>. Although a number of extensive viscometric studies have been made in various solvents involving simple salts, the literature provides very little information regarding the viscometric properties of  $\text{R}_4\text{NI}$  solutions in aqueous methanol. This stimulated us to undertake the present investigations.

## Experimental

The salts used in the present investigations were  $(\text{CH}_3)_4\text{NI}$  (s.d.fine -chem., 99%),  $(\text{C}_2\text{H}_5)_4\text{NI}$  (SISCO, 99%),  $(\text{C}_3\text{H}_7)_4\text{NI}$  (Fluka, 98%),  $(\text{C}_4\text{H}_9)_4\text{NaI}$  (s.d.fine-chem., 99%),  $\text{NaBph}_4$  (E.Merck, 99.5%),  $\text{NaI}$  (s.d.fine chem., 99.8 %),  $\text{R}_4\text{NI}$  salts were used after recrystallisation<sup>5</sup>.  $\text{NaI}$  and  $\text{NaBph}_4$  were used as received. All salts were stored in a vacuum desiccator and dried at 60 to 80 °C in the vacuo for at least 2 days prior to use. Water was distilled in a Pyrex glass apparatus with traces of  $\text{KMnO}_4$ , followed by successive distillations<sup>2</sup>. The electric conductance of distilled water was between  $7 \times 10^{-6}$  to  $9 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$ . Methanol (Glaxo, Excel-R,

purity 99.5%) was directly used without further purification<sup>2</sup>. The purity of methanol was checked by comparing its observed density  $0.78665 \text{ g.cm}^{-3}$  with reported value ( $0.78662 \text{ g.cm}^{-3}$ )<sup>6</sup> at 298.15 K

Methanol + water mixtures of compositions of 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 mass % methanol were prepared by mixing an appropriate mass of water and methanol in glass stoppered flask. Comparison of densities of methanol (1) + water (2) mixtures at 298.15 K with those of literature values<sup>2,6</sup> is given in Table 1. Accurately weighed amounts of recrystallised salts were dissolved in a particular solvent to give a desired concentration. Salt concentration varied from 0.0022 to 0.0529 M. Each time freshly prepared solution was used for viscosity measurement. The exact concentration of the salt solution was obtained from measurement of halide ion concentration using Volahard's method or by gravimetric analysis<sup>7,8</sup>. Viscosities of solutions were determined by using suspended level Ubbelohde viscometer described elsewhere<sup>9</sup>. The viscometer was calibrated with water using viscosity and density values recommended by Marsh<sup>10</sup>.  $20 \text{ cm}^3$  of solution was added in the viscometer from the burette. Viscometer filled with air bubble free solution, was clamped exactly vertical in a transparent glass walled water bath with thermal stability of  $\pm 0.01 \text{ K}$  for 10–15 minutes to attain the thermal equilibrium. The reflux time of flow of solutions were recorded with an electronic stopwatch accurate to  $\pm 0.01 \text{ s}$ . Viscosity values of liquids were calculated by using the equation.

$$\frac{\eta_1}{\eta_2} = \frac{Q_1 t_1}{Q_2 t_2} \quad (1)$$

Where  $\eta_1, \rho_1, t_1$  and  $\eta_2, \rho_2, t_2$  are the viscosity, density and flow time of the solvent and solution respectively. For viscosity measurements a viscometer was selected having a flow time more than 250 s for triply distilled water at 298.15 K. The uncertainty in the experimental values of viscosities was  $\pm 0.001 \text{ mPa.s}$  comparisons of measured densities and viscosities of 0 - 100 mass % methanol + water at 298.15 K is included in Table 1.

**Table 1.** Comparison of measured densities ( $\rho$ ) and Viscosities ( $\eta$ ) of Methanol + Water at 298.15 K

Mass % methanol	$\rho \times 10^{-3} / \text{kg.m}^{-3}$ observed	$\rho \times 10^{-3} / \text{kg.m}^{-3}$ Literature	$\eta / \text{mPa.s}$ observed	$\eta / \text{mPa.s}$ Literature
0	0.99707	0.99705 <sup>a</sup> , 0.99706 <sup>b</sup>	0.8903	0.8949 <sup>a</sup> , 0.8944 <sup>b</sup> , 0.8903 <sup>c</sup>
10	0.98035	0.97973 <sup>a</sup> , 0.97984 <sup>b</sup>	1.1443	1.158 <sup>a</sup> , 1.1635 <sup>b</sup>
20	0.96444	0.96451 <sup>a</sup> , 0.96431 <sup>b</sup>	1.3724	1.400 <sup>a</sup> , 1.3817 <sup>b</sup>
30	0.94878	0.94869 <sup>a</sup> , 0.94886 <sup>b</sup>	1.5265	1.531 <sup>a</sup> , 1.5393 <sup>b</sup>
40	0.93140	0.93134 <sup>a</sup> , 0.93156 <sup>b</sup>	1.5682	1.593 <sup>a</sup> , 1.5870 <sup>b</sup>
50	0.91213	0.91185 <sup>a</sup> , 0.91192 <sup>b</sup>	1.5176	1.510 <sup>a</sup> , 1.5201 <sup>b</sup>
60	0.89049	0.89013 <sup>a</sup> , 0.89041 <sup>b</sup>	1.3868	1.403 <sup>a</sup> , 1.3855 <sup>b</sup>
70	0.86737	0.86706 <sup>a</sup> , 0.86718 <sup>b</sup>	1.2017	1.190 <sup>a</sup> , 1.2040 <sup>b</sup>
80	0.84258	0.84217 <sup>a</sup> , 0.84244 <sup>b</sup>	0.9972	1.006 <sup>a</sup> , 0.9984 <sup>b</sup>
90	0.81541	0.81528 <sup>a</sup> , 0.81546 <sup>b</sup>	0.7739	0.767 <sup>a</sup> , 0.7759 <sup>b</sup>
100	0.78665	0.78662 <sup>a</sup> , 0.78662 <sup>b</sup>	0.5481	0.541 <sup>a</sup> , 0.5490 <sup>b</sup>

<sup>a</sup> from ref 6, <sup>b</sup> from ref 2, <sup>c</sup> from ref 17

## Results and Discussion

The relative viscosities ( $\eta_r$ ) of electrolyte solutions under investigation at temperature 298.15 K are analysed with the help of Jones – Dole equation<sup>11</sup>.

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

Where,  $\eta$  and  $\eta_0$  are the viscosities of solution and solvent respectively.  $C$  is molar concentration.  $A$  is measure of long – range coulombic forces between ions.  $B$  measures ion – solvent interactions. The plots of  $\eta_r - 1/c^{1/2}$  versus  $c^{1/2}$  for all solutions at 298.15 K are linear with intercepts equal to  $A$  and slopes give the viscosity coefficients  $B$ . The values of  $A$  and  $B$  for all systems at 298.15 K are given in Table 2. The representative plot of  $(\eta_r - 1/c^{1/2})$  versus  $c^{1/2}$  for  $(CH_3)_4NI$  solutions in all solvent mixtures at 298.15 K are linear. Similar plots were obtained for other systems.  $B$  coefficients were obtained by a computerized least – square method.

**Table 2.** Parameters of Jones-Dole Equation  $A$  and  $B$  for  $R_4NI$ ,  $NaI$  and  $NaBH_4$  in methanol + water at 298.15 K

Electrolyte	Mass % methanol	$A/\text{dm}^{3/2}.\text{mol}^{-1/2}$	$B/\text{dm}^3.\text{mol}^{-1}$
$(CH_3)_4NI$	0	0.0101	0.0501 (0.049) <sup>b,c</sup>
	10	0.0114	0.0644
	20	0.0127	0.0788
	30	0.0140	0.0932
	40	0.0153	0.1078
	50	0.0166	0.1220
	60	0.0179	0.1364
	70	0.0192	0.1508
	80	0.0250	0.1652
	90	0.0214	0.1796
$(C_2H_5)_4NI$	100	0.0231	0.1941
	0	0.0275	0.3121, (0.31) <sup>b,c</sup>
	10	0.0302	0.3402
	20	0.0356	0.3684
	30	0.0383	0.3966
	40	0.0410	0.4248
	50	0.0431	0.4530
	60	0.0437	0.4812
	70	0.0464	0.5094
	80	0.0491	0.5376
$(C_3H_7)_4NI$	90	0.0518	0.5658
	100	0.0546	0.5940
	0	0.0591	0.7741, (0.77) <sup>b,c</sup>
	10	0.0672	0.7611
	20	0.0753	0.7503
	30	0.0834	0.7373
	40	0.0915	0.7254
	50	0.0995	0.7125
	60	0.1077	0.7015
	70	0.1158	0.6905
	80	0.1239	0.6777
	90	0.1319	0.6658
	100	0.1401	0.6549

Contd.....

(C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> NI	0	0.0872	1.1862 , (1.19 ) <sup>b,c</sup>
	10	0.0991	1.1327
	20	0.1106	1.0956
	30	0.1208	1.0594
	40	0.1326	1.0223
	50	0.1437	0.9849
	60	0.1545	0.9484
	70	0.1658	0.9107
	80	0.1761	0.8743
	90	0.1876	0.8376
	100	0.1986	0.8007, (0.8) <sup>b</sup>
NaI	0	0.0012,(0.005) <sup>d</sup>	0.0191, (0.017) <sup>c</sup> , (0.018) <sup>d</sup>
	10	0.0073	0.0298
	20	0.0135	0.0405
	30	0.0196	0.0513
	40	0.0258	0.0620
	50	0.0313	0.0725
	60	0.0381	0.0832
	70	0.0442	0.0941
	80	0.0504	0.1047
	90	0.0565	0.1154
	100	0.0627	0.1262
NaBPh <sub>4</sub>	0	0.0200, (0.0264) <sup>e</sup>	1.1985 ,(1.210) <sup>e</sup>
	10	0.0260	1.2597
	20	0.0320	1.3094
	30	0.0380	1.3591
	40	0.0440	1.4088
	50	0.0500	1.4486
	60	0.0560	1.5082
	70	0.0619	1.5580
	80	0.0682	1.6078
	90	0.0736	1.6574
	100	0.0798	1.7072 ,(1.7072) <sup>b</sup>

<sup>b</sup> from ref 12, <sup>c</sup> from ref 13, <sup>d</sup> from ref 14, <sup>e</sup> from ref 15

An analysis of data from Table 2 reveals that 'A' values which are measure of ion - ion interactions, are positive for all electrolytes in all solvent mixtures at 298.15 K. Small positive 'A' values suggest weak ion-ion interactions in the solutions. The higher values of 'A' in high region of the methanol content of solution suggest that lower dielectric constant of solvent favors ion-ion interactions. B values are positive with comparatively large magnitudes, indicating strong ion solvent interactions through hydrogen bonding, exhibiting structure making tendency of all added electrolytes. The B values of R<sub>4</sub>NI solutions in all solvent mixtures increase with increase of ionic size of R<sub>4</sub>N<sup>+</sup> ions. The higher B values in methanol than in water can be explained on preferential solvation of ions by methanol molecules. To have a better understanding of ion – solvent interactions, it is advised to split the viscosity B coefficients into the individual ionic B values. This has been done in the present study using Bu<sub>4</sub>NBh<sub>4</sub><sup>3</sup>. As the reference electrolyte assuming

$$\frac{B(\text{BPh}_4^-)}{B(\text{Bu}_4\text{N}^+)} = \frac{r^3(\text{BPh}_4^-)}{r^3B(\text{Bu}_4\text{N}^+)} = (5.35 / 5.00)^3 \quad (3)$$

$$B(\text{Bu}_4\text{NBPh}_4) = B(\text{BPh}_4^-) + B(\text{Bu}_4\text{N}^+) \quad (4)$$

Owing the low solubility of  $\text{Bu}_4\text{NBh}_4$  in aqueous methanol at low temperature an attempt was made to obtain its B coefficient from the relationship<sup>3</sup>.

$$B(\text{Bu}_4\text{NBPh}_4) = B(\text{Bu}_4\text{NI}) + B(\text{NaBPh}_4) - B(\text{NaI}) \quad (5)$$

The B coefficients of  $\text{Bu}_4\text{NBh}_4$  are obtained using equation 5. The ionic B coefficients for all cations and anions are tabulated in Table 3. It is seen from Table 3 that ionic B values of  $\text{R}_4\text{N}^+$ ,  $\text{Na}^+$ ,  $\text{BPh}_4^-$  are higher in methanol than in water and can reasonably be attributed to preferential ion- solvent interactions through dipole – dipole interactions. The ionic B values of  $\text{I}^-$  have a tendency to decrease with increase with methanol suggesting preferential solvation of  $\text{I}^-$  ions in water rich region.

**Table 3.** Ionic B – coefficients of  $\text{R}_4\text{N}^+$ ,  $\text{Na}^+$ ,  $\text{I}^-$ ,  $\text{BPh}_4^-$  at temperature 298.15 K

Mass % methanol	$\text{Na}^+$	$\text{I}^-$	$\text{BPh}_4^-$	$(\text{CH}_3)_4\text{N}^+$	$(\text{C}_2\text{H}_5)_4\text{N}^+$	$(\text{C}_3\text{H}_7)_4\text{N}^+$	$(\text{C}_4\text{H}_9)_4\text{N}^+$
0	-0.1039, (-0.1047) <sup>f</sup>	0.1230	1.3024 (1.3165) <sup>f</sup>	-0.0729 (-0.0791) <sup>f</sup>	0.1891 (0.161) <sup>f</sup>	0.6511 (0.6695) <sup>f</sup>	1.0632 (1.0747) <sup>f</sup>
10	-0.0411	0.0709	1.3008	-0.0065	0.2693	0.6902	1.0618
20	0.0076	0.0329	1.3018	-0.0459	0.3355	0.7173	1.0627
30	0.0558	0.0045	1.3033	0.0977	0.4011	0.7418	1.0639
40	0.1045	-0.0425	1.3043	0.1503	0.4673	0.7679	1.0648
50	0.1532	-0.0807	1.3504	0.2027	0.5337	0.7932	1.0656
60	0.2015	-0.1183	1.3067	0.2547	0.5995	0.8198	1.0667
70	0.2506	-0.1565	1.3074	0.3073	0.6659	0.8470	1.07672
80	0.2989	-0.1942	1.3089	0.3594	0.7318	0.8719	1.0685
90	0.3473	-0.2319	1.3101	0.4115	0.7977	0.8977	1.0695
100	0.3959	-0.2697	1.3113	0.4638	0.8637	0.9246	1.0704

<sup>f</sup>from ref 16

## Conclusion

Positive values of ‘A’ shows weak ion-ion interaction and positive values of ‘B’ shows strong ion-solvent interaction.

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