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# Viscosities of Some Symmetrical Tetraalkylammonium Salts in Acetonitrile at (288.15, 298.15, 308.15, and 318.15) K

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The viscosities of solutions of tetraethylammonium bromide ($Et_4NBr$), tetrapropylammonium bromide ($Pr_4NBr$), tetrabutylammonium bromide ($Bu_4NBr$), tetrapentylammonium bromide ($Pen_4NBr$), tetrahexylammonium bromide ($Hex_4NBr$), tetraheptylammonium bromide ($Hep_4NBr$), and tetrabutylammonium tetraphenylborate ($Bu_4NBPh_4$) have been measured at (288.15, 298.15, 308.15, and 318.15) K. The data have been analyzed by the Jones−Dole equation to evaluate the viscosity *B*-coefficients of the electrolytes. The resulting *B*-coefficient and its dependence on temperature provide useful information regarding ion−ion and ion−solvent interactions.

## Introduction

Viscometry has been widely used for the investigation of the behavior of ions in nonaqueous solvents.[1] Earlier studies on the viscosities of tetraalkylammonium bromides in acetonitrile were limited only to one or two temperatures. Moreover, in some cases where comparisons of the literature values are possible,[1−7] the disagreement is as high as 25%. To remove the disparities among the existing literature viscosity *B*-coefficients of these electrolytes, and some contradictions regarding temperature dependences of the *B*-values of tetrabutylammonium tetraphenylborate (an electrolyte often used as a "reference electrolyte" for the evaluation of ionic *B*-values), it seemed necessary to perform an extensive experimental investigation of tetraalkylammonium bromides along with tetrabutylammonium tetraphenylborate in acetonitrile as a function of temperature and to make a critical examination of published results.

We have, therefore, redetermined the viscosities of tetraethylammonium bromide ($Et_4NBr$), tetrapropylammonium bromide ($Pr_4NBr$), tetrabutylammonium bromide ($Bu_4NBr$), tetrapentylammonium bromide ($Pen_4NBr$), tetrahexylammonium bromide ($Hex_4NBr$), tetraheptylammonium bromide ($Hep_4NBr$), and tetrabutylammonium tetraphenylborate ($Bu_4NBPh_4$) in acetonitrile at (298.15 and 308.15) K. The study has also been extended to two other temperatures, viz. (288.15 and 318.15) K, in order to investigate the temperature dependence over a wide range of temperatures. Ionic viscosity *B*-values have been derived on the basis of the reference electrolyte $Bu_4NBPh_4$.

## Experimental Section

Acetonitrile is the same as that used in our earlier studies,[8,9] and its purification has been described there. Properties of the purified solvent at (288.15, 298.15, 308.15, and 318.15) K together with the available literature values[3,10−13] are reported in Table 1. Our values agree well with the literature data.

Tetraalkylammonium bromides were of purum or puriss grade (Fluka) and were purified as described earlier by us.[8] Tetrabutylammonium tetraphenylborate was prepared and purified as reported in the literature.[14]

**Table 1. Properties of Acetonitrile at (288.15, 298.15, 308.15, and 318.15) K**

| | $\rho$/g·cm$^{-3}$ | | $\eta_0$/mPa·s | |
|---|---|---|---|---|
| *T*/K | this work | lit. | this work | lit. |
| 288.15 | 0.787 35 | 0.7874[a] | 0.3770 | 0.375[a] |
| 298.15 | 0.776 86 | 0.7766[b] | 0.3446 | 0.341[a] |
| | | 0.77685[c] | | 0.341[b] |
| | | 0.7759[c] | | 0.344[c] |
| | | 0.77682[d] | | |
| 308.15 | 0.765 64 | 0.7663[a] | 0.3125 | 0.313[a] |
| | | 0.76581[b] | | 0.314[b] |
| | | 0.7662[c] | | 0.314[c] |
| | | 0.76560[e] | | |
| 318.15 | 0.754 98 | 0.75271[b] | 0.2893 | 0.293[b] |
| | | 0.7559[c] | | 0.289[c] |

[a] Reference 3. [b] Reference 10. [c] Reference 12. [d] Reference 11. [e] Reference 13.

A stock solution for each salt was prepared by mass, and the working solutions were obtained by mass dilution. The conversion of the molality into molarity was done using the density values.

The densities, $\rho$, were measured with an Ostwald−Sprengel type pycnometer having a bulb volume of 25 cm$^3$ and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at (288.15, 298.15, 308.15, and 318.15) K with triply distilled water and benzene. The temperature of the bath was controlled to ±0.01 K. Details have been described earlier.[15−17] The reproducibility of the density measurements was $\pm(3 \times 10^{-5})$ g·cm$^{-3}$.

The kinematic viscosities, $\nu$, were measured by means of a suspended Ubbelohde viscometer. The time of efflux was measured with a stopwatch to ±0.1 s. The viscometer was kept in a vertical position in a water thermostat controlled to ±0.01 K. The absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge. The efflux time for water at 298.15 K was about 540 s. The kinematic viscosity ($\nu$) and the absolute viscosity ($\eta$) are given by the following equations:

$$\nu = Ct - K/t \qquad (1)$$

$$\eta = \nu\rho \qquad (2)$$

where $t$ is the efflux time, $\rho$ is the density, and $C$ and $K$

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**Table 2. Concentration ($c$), Density ($\rho$), and Relative Viscosity ($\eta_r$) of Tetraalkylammonium Bromides and Tetrabutylammonium Tetraphenylborate in Acetonitrile at (288.15, 298.15, 308.15, and 318.15) K**

| $c$/mol·dm$^{-3}$ | $\rho$/g·cm$^{-3}$ | $\eta_r$ | $c$/mol·dm$^{-3}$ | $\rho$/g·cm$^{-3}$ | $\eta_r$ | $c$/mol·dm$^{-3}$ | $\rho$/g·cm$^{-3}$ | $\eta_r$ | $c$/mol·dm$^{-3}$ | $\rho$/g·cm$^{-3}$ | $\eta_r$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 288.15 K | | | | | | | | | | | |
| | $Et_4NBr$ | | | $Pr_4NBr$ | | | $Bu_4NBr$ | | | $Pen_4NBr$ | |
| 0.009 90 | 0.788 36 | 1.0088 | 0.010 75 | 0.788 43 | 1.0103 | 0.009 06 | 0.788 31 | 1.0102 | 0.009 90 | 0.788 44 | 1.0121 |
| 0.019 12 | 0.789 29 | 1.0159 | 0.020 01 | 0.789 35 | 1.0182 | 0.019 82 | 0.789 44 | 1.0217 | 0.019 98 | 0.789 54 | 1.0237 |
| 0.022 01 | 0.789 58 | 1.0181 | 0.024 97 | 0.789 84 | 1.0223 | 0.025 37 | 0.790 02 | 1.0272 | 0.025 32 | 0.790 12 | 1.0293 |
| 0.029 81 | 0.790 36 | 1.0241 | 0.029 54 | 0.790 29 | 1.0261 | 0.029 88 | 0.790 49 | 1.0316 | 0.030 12 | 0.790 64 | 1.0347 |
| 0.034 73 | 0.790 85 | 1.0281 | 0.035 55 | 0.790 88 | 1.0311 | 0.035 94 | 0.791 12 | 1.0379 | 0.035 58 | 0.791 23 | 1.0404 |
| 0.040 36 | 0.791 41 | 1.0322 | 0.039 84 | 0.791 30 | 1.0348 | 0.040 46 | 0.791 59 | 1.0426 | 0.040 31 | 0.791 74 | 1.0455 |
| | $Hex_4NBr$ | | | $Hep_4NBr$ | | | $Bu_4NBPh_4$ | | | | |
| 0.010 57 | 0.788 49 | 1.0140 | 0.009 62 | 0.788 38 | 1.0154 | 0.009 34 | 0.788 54 | 1.0157 | | | |
| 0.020 21 | 0.789 52 | 1.0261 | 0.019 31 | 0.789 41 | 1.0296 | 0.019 80 | 0.789 86 | 1.0313 | | | |
| 0.024 45 | 0.789 97 | 1.0308 | 0.025 45 | 0.790 06 | 1.0387 | 0.027 61 | 0.790 84 | 1.0429 | | | |
| 0.029 53 | 0.790 51 | 1.0372 | 0.029 52 | 0.790 49 | 1.0443 | 0.033 37 | 0.791 56 | 1.0515 | | | |
| 0.035 20 | 0.791 11 | 1.0438 | 0.035 02 | 0.791 07 | 1.0523 | 0.040 43 | 0.792 44 | 1.0617 | | | |
| 0.040 98 | 0.791 72 | 1.0510 | 0.039 20 | 0.791 51 | 1.0583 | 0.044 37 | 0.792 93 | 1.0679 | | | |
| 298.15 K | | | | | | | | | | | |
| | $Et_4NBr$ | | | $Pr_4NBr$ | | | $Bu_4NBr$ | | | $Pen_4NBr$ | |
| 0.009 96 | 0.777 85 | 1.0083 | 0.010 15 | 0.777 87 | 1.0090 | 0.010 02 | 0.777 89 | 1.0110 | 0.009 85 | 0.777 89 | 1.0115 |
| 0.020 05 | 0.778 84 | 1.0157 | 0.019 91 | 0.778 83 | 1.0172 | 0.020 04 | 0.778 91 | 1.0212 | 0.020 19 | 0.778 96 | 1.0226 |
| 0.024 97 | 0.779 32 | 1.0192 | 0.025 03 | 0.779 33 | 1.0213 | 0.024 98 | 0.779 41 | 1.0262 | 0.024 94 | 0.779 45 | 1.0272 |
| 0.029 91 | 0.779 80 | 1.0228 | 0.030 06 | 0.779 82 | 1.0250 | 0.030 14 | 0.779 93 | 1.0309 | 0.030 01 | 0.779 97 | 1.0329 |
| 0.034 97 | 0.780 29 | 1.0267 | 0.035 00 | 0.780 30 | 1.0290 | 0.035 00 | 0.780 42 | 1.0358 | 0.035 08 | 0.780 47 | 1.0379 |
| 0.040 06 | 0.780 78 | 1.0303 | 0.040 16 | 0.780 80 | 1.0328 | 0.040 09 | 0.780 93 | 1.0409 | 0.039 98 | 0.780 99 | 1.0432 |
| | $Hex_4NBr$ | | | $Hep_4NBr$ | | | $Bu_4NBPh_4$ | | | | |
| 0.009 88 | 0.777 90 | 1.0130 | 0.010 07 | 0.777 94 | 1.0152 | 0.010 90 | 0.778 28 | 1.0167 | | | |
| 0.020 05 | 0.778 96 | 1.0248 | 0.020 03 | 0.779 00 | 1.0292 | 0.019 11 | 0.779 34 | 1.0281 | | | |
| 0.025 06 | 0.779 48 | 1.0310 | 0.025 04 | 0.779 53 | 1.0360 | 0.025 88 | 0.780 21 | 1.0378 | | | |
| 0.030 09 | 0.780 00 | 1.0368 | 0.030 06 | 0.780 06 | 1.0431 | 0.029 47 | 0.780 67 | 1.0429 | | | |
| 0.035 03 | 0.780 51 | 1.0424 | 0.034 90 | 0.780 47 | 1.0495 | 0.036 67 | 0.781 59 | 1.0531 | | | |
| 0.039 99 | 0.781 02 | 1.0483 | 0.040 14 | 0.781 12 | 1.0569 | 0.040 20 | 0.782 04 | 1.0580 | | | |
| 308.15 K | | | | | | | | | | | |
| | $Et_4NBr$ | | | $Pr_4NBr$ | | | $Bu_4NBr$ | | | $Pen_4NBr$ | |
| 0.009 85 | 0.766 60 | 1.0078 | 0.009 87 | 0.766 62 | 1.0088 | 0.009 83 | 0.766 64 | 1.0108 | 0.009 65 | 0.766 64 | 1.0113 |
| 0.019 74 | 0.767 55 | 1.0146 | 0.019 65 | 0.767 58 | 1.0167 | 0.019 78 | 0.767 64 | 1.0203 | 0.019 88 | 0.767 69 | 1.0217 |
| 0.024 76 | 0.768 03 | 1.0183 | 0.024 67 | 0.768 07 | 1.0205 | 0.024 67 | 0.768 13 | 1.0251 | 0.024 58 | 0.768 17 | 1.0267 |
| 0.029 70 | 0.768 50 | 1.0216 | 0.029 62 | 0.768 55 | 1.0242 | 0.029 69 | 0.768 63 | 1.0299 | 0.029 50 | 0.768 67 | 1.0315 |
| 0.034 56 | 0.768 96 | 1.0252 | 0.034 57 | 0.769 03 | 1.0280 | 0.034 51 | 0.769 11 | 1.0346 | 0.034 53 | 0.769 18 | 1.0369 |
| 0.039 65 | 0.769 44 | 1.0286 | 0.039 65 | 0.769 52 | 1.0319 | 0.039 55 | 0.769 61 | 1.0395 | 0.039 27 | 0.769 66 | 1.0416 |
| | $Hex_4NBr$ | | | $Hep_4NBr$ | | | $Bu_4NBPh_4$ | | | | |
| 0.009 75 | 0.766 67 | 1.0120 | 0.009 83 | 0.766 70 | 1.0146 | 0.009 71 | 0.766 93 | 1.0154 | | | |
| 0.019 79 | 0.767 72 | 1.0237 | 0.019 77 | 0.767 76 | 1.0281 | 0.020 20 | 0.768 31 | 1.0304 | | | |
| 0.024 69 | 0.768 23 | 1.0288 | 0.024 75 | 0.768 29 | 1.0347 | 0.024 63 | 0.768 89 | 1.0366 | | | |
| 0.029 70 | 0.768 75 | 1.0346 | 0.029 66 | 0.768 81 | 1.0412 | 0.031 91 | 0.769 84 | 1.0468 | | | |
| 0.034 53 | 0.769 25 | 1.0396 | 0.034 48 | 0.769 32 | 1.0476 | 0.034 83 | 0.770 22 | 1.0508 | | | |
| 0.039 38 | 0.769 75 | 1.0453 | 0.039 50 | 0.769 85 | 1.0542 | 0.039 91 | 0.770 88 | 1.0579 | | | |
| 318.15 K | | | | | | | | | | | |
| | $Et_4NBr$ | | | $Pr_4NBr$ | | | $Bu_4NBr$ | | | $Pen_4NBr$ | |
| 0.009 60 | 0.755 91 | 1.0076 | 0.009 57 | 0.755 93 | 1.0084 | 0.009 63 | 0.755 96 | 1.0106 | 0.009 48 | 0.755 97 | 1.0103 |
| 0.019 45 | 0.756 85 | 1.0145 | 0.019 26 | 0.756 88 | 1.0155 | 0.019 57 | 0.756 96 | 1.0200 | 0.019 64 | 0.757 02 | 1.0205 |
| 0.024 41 | 0.757 32 | 1.0181 | 0.024 19 | 0.757 36 | 1.0193 | 0.024 37 | 0.757 44 | 1.0247 | 0.024 21 | 0.757 49 | 1.0248 |
| 0.029 28 | 0.757 78 | 1.0213 | 0.029 03 | 0.757 83 | 1.0231 | 0.029 28 | 0.757 93 | 1.0294 | 0.029 10 | 0.757 99 | 1.0295 |
| 0.034 07 | 0.758 23 | 1.0245 | 0.034 00 | 0.758 31 | 1.0269 | 0.034 01 | 0.758 40 | 1.0337 | 0.033 99 | 0.758 49 | 1.0345 |
| 0.039 07 | 0.758 70 | 1.0279 | 0.038 98 | 0.758 79 | 1.0305 | 0.038 95 | 0.758 89 | 1.0386 | 0.038 61 | 0.758 96 | 1.0390 |
| | $Hex_4NBr$ | | | $Hep_4NBr$ | | | $Bu_4NBPh_4$ | | | | |
| 0.009 63 | 0.756 01 | 1.0116 | 0.009 66 | 0.756 04 | 1.0135 | 0.009 25 | 0.756 24 | 1.0142 | | | |
| 0.019 56 | 0.757 06 | 1.0228 | 0.019 51 | 0.757 11 | 1.0265 | 0.020 00 | 0.757 69 | 1.0293 | | | |
| 0.024 30 | 0.757 56 | 1.0278 | 0.024 41 | 0.757 64 | 1.0329 | 0.024 62 | 0.758 31 | 1.0357 | | | |
| 0.029 26 | 0.758 08 | 1.0332 | 0.029 24 | 0.758 16 | 1.0391 | 0.030 00 | 0.759 03 | 1.0431 | | | |
| 0.034 03 | 0.758 58 | 1.0381 | 0.033 98 | 0.758 67 | 1.0453 | 0.038 25 | 0.760 13 | 1.0544 | | | |
| 0.038 82 | 0.759 08 | 1.0435 | 0.038 91 | 0.759 20 | 1.0517 | 0.042 01 | 0.760 63 | 1.0595 | | | |

are the characteristic constants of the viscometer. The values of the constants $C$ and $K$ determined by using the density and viscosity values of water and benzene[17] were found to be $1.648 \times 10^{-5}$ cm$^2$·s$^{-2}$ and $-0.023\,316\,47$ cm$^2$, respectively. The calibration constants were also checked with acetonitrile used in this study. The estimated error of the viscosity measurements was ±0.1%.

In all cases the experiments were performed at least in five replicates for each composition and at each temperature, and the results were averaged.

## Results

The relative viscosity ($\eta_r$) and the density ($\rho$) data for the electrolyte solutions as functions of molar concentration ($c$) in acetonitrile at (288.15, 298.15, 308.15, and 318.15) K are given in Table 2. The viscosity data of the electrolytes were analyzed by the Jones−Dole equation as described in the literature[18]

$$\eta_r = 1 + Ac^{1/2} + Bc \tag{3}$$

where $A$ and $B$, the characteristic parameters for salt and solvent, depend on ion−ion and ion−solvent interactions, respectively.

The plots of $(\eta_r - 1)/c^{1/2}$ versus $c^{1/2}$ were found to be linear in all cases over the whole concentration range of the electrolytes studied. This indicates that ion pairing is not occurring to any great extent in these salt solutions. This

**Table 3. Theoretical *A*-Coefficients of Electrolytes in Acetonitrile at 298.15 K**

| electrolyte | $A$/dm$^{3/2}$ mol$^{-1/2}$ |
|---|---|
| $Et_4NBr$ | 0.0155 |
| $Pr_4NBr$ | 0.0170 |
| $Bu_4NBr$ | 0.0181 |
| $Pen_4NBr$ | 0.0189 |
| $Hex_4NBr$ | 0.0197 |
| $Hep_4NBr$ | 0.0203 |
| $Bu_4NBPh_4$ | 0.0240 |

is in agreement with our earlier investigation on the behavior of these salts in acetonitrile.[8,9,19]

The $A$ values can be calculated theoretically from the physical parameters of the solvent and the limiting ionic equivalent conductances using the Falkenhagen and Vernon equation

$$A_{\mathrm{theo}} = \frac{0.2577\Lambda^0}{\eta_0(\epsilon T)^{0.5}\lambda_+^0\lambda_-^0}\left[1 - 0.6863\left(\frac{\lambda_+^0 - \lambda_-^0}{\Lambda^0}\right)^2\right] \qquad (4)$$

as described earlier by us.[20] The $A_{\mathrm{theo}}$ values at 298.15 K reported in Table 3 were calculated according to eq 3 using $\epsilon = 35.95$ and conductometric data from our earlier work.[9,19]

The viscosity $B$-coefficients were obtained by the method of least-squares from eq 3 using the theoretical $A$ values. In view of the weak temperature dependence of the $A$-coefficients in many solvents[21,22] including acetonitrile[3] and the nonavailability of limiting ionic conductances at different temperatures, the $A$ values at 298.15 K have been utilized at other temperatures. The viscosity $B$-coefficients obtained at various temperatures are given in Table 4. The literature data[1−7] for $B$-coefficients are also included in this table for comparison.

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.[23]

$$B = \frac{\bar{V}_1^0 - \bar{V}_2^0}{1000} + \frac{\bar{V}_1^0}{1000}\left(\frac{\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq}}{RT}\right) \qquad (5)$$

In the above equation $\bar{V}_1^0$ and $\bar{V}_2^0$ are the partial molar volumes of solvent and solute, respectively. $\Delta\mu_2^{0\neq}$, 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 5. $\Delta\mu_1^{0\neq}$, the free energy of activation per mole of pure solvent is given by the equation[24]

$$\Delta\mu_1^{0\neq} = \Delta G_1^{0\neq} = RT\ln(\eta_0\bar{V}_1{}^0/hN) \qquad (6)$$

where $N$ is Avogadro's number.

## Discussion

The viscosity $B$-coefficients (Table 4) for all the electrolytes are large and positive, and increase in acetonitrile as we go from tetraethylammonium bromide through tetraheptylammonium bromide at all the temperatures investigated. As can be seen from Table 4, our experimental $B$ values, in general, show fair agreement with the available literature data. It needs to be pointed out that the salts $Bu_4NBr$ and $Bu_4NBPh_4$, for which a number of $B$ values are available from different sources, exhibit significant scatter among the literature $B$ values.

The $B$-coefficients show moderate temperature dependence, and the values decrease with an increase of temperature, as observed earlier in some dipolar aprotic solvents such as sulfolane,[21] dimethyl sulfoxide,[25] propylene carbonate,[18] dimethylformamide,[14] and so forth. Furthermore, from Table 4 we see that, although $\mathrm{d}B/\mathrm{d}T$ is small, it is negative in sign for all the electrolytes, indicating that these behave as structure makers in this solvent medium. It is interesting to note that for $Bu_4NBPh_4$, while the data from Lawrence et al.[6] show a weak positive temperature dependence of the $B$ values, those from other sources[3,4] reveal clear negative $\mathrm{d}B/\mathrm{d}T$ values—though differing from each other very much.

The ionic $B$ values were calculated using $Bu_4NBPh_4$ as the "reference electrolyte" from the following equation[20]

$$B(\mathrm{Bu_4NBPh_4}) = B(\mathrm{Bu_4N^+}) + B(\mathrm{Ph_4B^-}) \qquad (7)$$

$$B(\mathrm{Ph_4B^-})/B(\mathrm{Bu_4N^+}) = (5.35/5.00)^3 \qquad (8)$$

The ionic $B$ values obtained from the above relationships are given in Table 6. This table shows that the viscosity $B$-coefficients for cations and anions are positive and are also very high. The observed order of the ionic $B$ values, $Hep_4N^+ > Hex_4N^+ > Pen_4N^+ > Bu_4N^+ > Pr_4N^+ > Et_4N^+$, shows that the obstruction of the solvent viscous flow increases with a decrease of the ion charge density and with a decrease of the size of the hydrodynamic entity by solvation.

There is so far no report on the temperature dependence of the ionic $B$ values for the ions investigated here, with the exception of $Bu_4N^+$ and $Ph_4B^-$ ions.[1] The $\mathrm{d}B_\pm/\mathrm{d}T$ values of the cations and anions in this study (cf. Table 6) are generally found to be negative (structure-making). The behavior of tetraalkylammonium ions in acetonitrile, arising mainly from the interaction of alkyl groups and solvent molecules, is similar to that observed in sulfolane[21] and in propylene carbonate.[18]

The values of $\Delta\mu_2^{0\neq}$ for tetraalkylammonium ions in acetonitrile (Table 6) decrease in the order $Hep_4N^+ > Hex_4N^+ > Pen_4N^+ > Bu_4N^+ > Pr_4N^+ > Et_4N^+$, and those for anions decrease in the order $Ph_4B^- > Br^-$. However, these values are found to be positive, and hence the formation of the transition state is made less favorable in the presence of these ions.

**Table 4. Viscosity *B*-Coefficients (dm$^3$ mol$^{-1}$) of Electrolytes in Acetonitrile at (288.15, 298.15, 308.15, and 318.15) K**

| | $B$ | | | |
|---|---|---|---|---|
| electrolyte | 288.15 K | 298.15 K | 308.15 K | 318.15 K |
| $Et_4NBr$ | 0.714 | 0.684 (0.650,[a] 0.690[f]) | 0.653 (0.640[a]) | 0.638 |
| $Pr_4NBr$ | 0.778 | 0.745 (0.706[a]) | 0.713 (0.704[a]) | 0.697 |
| $Bu_4NBr$ | 0.979 | 0.935 (0.839,[a] 0.74,[b] 0.91,[c] 0.93[f]) | 0.900 (0.829[a]) | 0.881 |
| $Pen_4NBr$ | 1.033 | 0.990 (0.984[a]) | 0.953 (0.952[a]) | 0.931 |
| $Hex_4NBr$ | 1.153 | 1.103 (1.100[a]) | 1.059 (1.091[a]) | 1.028 |
| $Hep_4NBr$ | 1.375 | 1.321 (1.309[a]) | 1.257 (1.313[a]) | 1.222 |
| $Bu_4NBPh_4$ | 1.398 (1.52,[d] 1.50[e]) | 1.336 (1.330,[a] 1.32,[c] 1.35,[d] 1.43,[e] 1.35[f]) | 1.319 (1.353,[a] 1.25,[d] 1.41[e]) | 1.307 |

[a] Reference 6. [b] Reference 5. [c] Reference 2. [d] Reference 3. [e] Reference 4. [f] Reference 7.

**Table 5. $\Delta\mu_2^{0\neq}$/kJ mol$^{-1}$ Values of Electrolytes in Acetonitrile at (288.15, 298.15, 308.15, and 318.15) K**

| | $\Delta\mu_2^{0\neq}$/kJ mol$^{-1}$ | | | |
|---|---|---|---|---|
| electrolyte | 288.15 K | 298.15 K | 308.15 K | 318.15 K |
| $Et_4NBr$ | 45.98 | 45.67 | 45.15 | 45.30 |
| $Pr_4NBr$ | 52.28 | 51.92 | 51.75 | 51.64 |
| $Bu_4NBr$ | 64.50 | 64.03 | 63.71 | 64.06 |
| $Pen_4NBr$ | 70.00 | 69.90 | 69.63 | 69.94 |
| $Hex_4NBr$ | 78.92 | 78.55 | 78.07 | 78.11 |
| $Hep_4NBr$ | 92.46 | 92.05 | 90.90 | 90.99 |
| $Bu_4NBPh_4$ | 96.15 | 95.32 | 96.40 | 97.65 |

**Table 6. Ionic Viscosity *B*-Coefficients (dm$^3$ mol$^{-1}$) and $\Delta\mu_2^{0\neq}$/kJ mol$^{-1}$ Values in Acetonitrile at (288.15, 298.15, 308.15, and 318.15) K**

| | $T$ = 288.15 K | | $T$ = 298.15 K | | $T$ = 308.15 K | | $T$ = 318.15 K | |
|---|---|---|---|---|---|---|---|---|
| ion | $B$ | $\Delta\mu_2^{0\neq}$ | $B$ | $\Delta\mu_2^{0\neq}$ | $B$ | $\Delta\mu_2^{0\neq}$ | $B$ | $\Delta\mu_2^{0\neq}$ |
| $Et_4N^+$ | 0.363 | 24.69 | 0.349 | 24.48 | 0.346 | 24.77 | 0.344 | 25.13 |
| $Pr_4N^+$ | 0.427 | 30.99 | 0.410 | 30.73 | 0.406 | 31.37 | 0.403 | 31.47 |
| $Bu_4N^+$ | 0.628 | 43.21 | 0.600 | 42.84 | 0.593 | 43.33 | 0.587 | 43.89 |
| $Pen_4N^+$ | 0.684 | 48.71 | 0.655 | 48.71 | 0.646 | 49.25 | 0.637 | 49.77 |
| $Hex_4N^+$ | 0.799 | 57.63 | 0.768 | 57.36 | 0.752 | 57.69 | 0.734 | 57.94 |
| $Hep_4N^+$ | 1.023 | 71.17 | 0.986 | 70.86 | 0.950 | 70.52 | 0.928 | 70.82 |
| $Br^-$ | 0.351 | 21.29 | 0.335 | 21.19 | 0.307 | 20.38 | 0.294 | 20.17 |
| $Ph_4B^-$ | 0.770 | 52.94 | 0.736 | 52.48 | 0.726 | 53.07 | 0.720 | 53.76 |

**Table 7. Ionic Radii ($R_\pm$) in Acetonitrile at 298.15 K**

| ion | $r_c$[a]/nm | $R_\pm$/nm |
|---|---|---|
| $Et_4N^+$ | 0.400 | 0.381 |
| $Pr_4N^+$ | 0.452 | 0.402 |
| $Bu_4N^+$ | 0.500 | 0.456 |
| $Pen_4N^+$ | 0.529 | 0.470 |
| $Hex_4N^+$ | 0.560 | 0.496 |
| $Hep_4N^+$ | 0.586 | 0.539 |
| $Ph_4B^-$ | 0.535 | 0.489 |
| $Br^-$ | 0.195 | 0.376 |

[a] Crystallographic radii.

Ionic *B*-coefficients have also been analyzed on the basis of Einstein's equation as described earlier[20]

$$B_\pm = 2.5\frac{4}{3}\pi\frac{R_\pm^3 N}{1000} \tag{9}$$

where $R_\pm$ is the radius of the ion assumed to be a 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 7.

The $R_\pm$ values for tetraalkylammonium ions are found to be in reasonable agreement with the crystallographic radii of these ions (Table 7). The results indicate these ions are scarcely solvated in acetonitrile and behave as spherical entities. However, the $R_-$ value of bromide ion is found to be much higher compared to its crystallographic radius, indicating that it is solvated in acetonitrile by ion−dipole interactions. Similar results have also been obtained from our earlier conductometric[9,19] and volumetric[8] measurements on these systems. Thus, it appears that the large sizes of the tetraalkylammonium ions and their low surface charge density coupled with the medium relative permittivity of acetonitrile render these ions to be free, unassociated, and almost unsolvated in this medium within the investigated temperature range.

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