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# Viscosities of Some Symmetrical Tetraalkylammonium Perchlorates in 2-Methoxyethanol + Water at 298.15, 308.15, and 318.15 K

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The viscosities of solutions of tetraethylammonium perchlorate ($Et_4NClO_4$), tetrapropylammonium perchlorate ($Pr_4NClO_4$), and tetrabutylammonium perchlorate ($Bu_4NClO_4$) in 2-methoxyethanol (1) + water (2) mixtures have been measured at 298.15, 308.15, and 318.15 K. The data have been analyzed by the Jones−Dole equation for the associated as well as unassociated electrolytes to evaluate viscosity *B* coefficients of the electrolytes. The resulting viscosity *B* coefficient and its dependence on temperature provide useful information with regard to changes in the solvent structure.

## Introduction

Recently, we have reported (Das and Hazra, 1996) the results of conductance measurements on three symmetrical tetraalkylammonium perchlorates, viz. $Et_4NClO_4$, $Pr_4NClO_4$, and $Bu_4NClO_4$ in 2-methoxyethanol (1) + water (2) mixtures ranging in the composition from 20 to 80 mass % of 2-methoxyethanol at 298.15 K. We have now extended this work to study the viscometric behavior of these electrolytes at three different temperatures in the same solvent mixtures at $x_1 = 0.056$, 0.136, 0.262, and 0.486, and the results are reported in this communication.

## Experimental Section

2-Methoxyethanol (ME; G.R. Merck, >99% pure) was distilled twice in an all-glass distillation set, and the middle fraction distilled between 397.15 to 398.15 K was collected. The fractionally distilled solvent had a specific conductance less than $(1-3) \times 10^{-7}$ S·cm$^{-1}$. Triply distilled water with a specific conductance less than $10^{-6}$ S·cm$^{-1}$ was used for the preparation of the mixtures. The physical properties of ME + water mixtures at three different temperatures are given in Table 1.

**Table 1. Densities ($\rho$) and Viscosities ($\eta_r$) of 2-Methoxyethanol (1) + Water (2) Mixtures at (298.15, 308.15, and 318.15) K**

| $x_1$ | $\rho$/g·cm$^{-3}$ | $\eta_0$/mPa·s |
|---|---|---|
| | 298.15 K | |
| 0.056 | 1.00240 | 1.5165 |
| 0.136 | 1.00690 | 2.3654 |
| 0.262 | 1.00233 | 2.8849 |
| 0.486 | 0.98672 | 2.5751 |
| 1.000 | 0.96002 | 1.5414 |
| | 308.15 K | |
| 0.056 | 0.99680 | 1.1533 |
| 0.136 | 1.00030 | 1.7280 |
| 0.262 | 0.99472 | 2.1510 |
| 0.486 | 0.97810 | 2.0213 |
| 1.000 | 0.95356 | 1.2579 |
| | 318.15 K | |
| 0.056 | 0.99267 | 0.9051 |
| 0.136 | 0.99327 | 1.2745 |
| 0.262 | 0.98657 | 1.5878 |
| 0.486 | 0.96960 | 1.6236 |
| 1.000 | 0.94715 | 1.0400 |

Tetraalkylammonium perchlorates were Fluka purum or puriss grade (purity >99%). These were recrystallized twice from conductivity water and dried in vacuo at 343.15 K for 24 h.

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 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 capillary of about 0.1 cm. The pycnometer was calibrated at (298.15, 308.15, and 318.15) K with doubly distilled water and benzene. The temperature of the bath was controlled to ±0.01 K. Details have been described earlier (Das and Hazra, 1993, 1995; Saha et al., 1995). The reproducibility of 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 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* 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 (Saha et al., 1995) were found to be $1.648 \times 10^{-5}$ cm$^2$·s$^{-2}$ and −0.023 316 47 cm$^2$, respectively. The estimated error of the viscosity measurements was ±0.2%.

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 density ($\rho$) data for the electrolyte solutions as functions of molar concentration (*c*) in different solvent mixtures at (298.15, 308.15, and 318.15)

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**Table 2. Concentration ($c$), Density ($\rho$), and Relative Viscosity ($\eta_r$) of Tetraalkylammonium Perchlorates in 2-Methoxyethanol (1) + Water (2) Mixtures at (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$^{-3}$ | $\eta_r$ |
|---|---|---|---|---|---|
| | | $Et_4NClO_4$ at 298.15 K | | | |
| $x_1 = 0.056$ | $\Lambda_0{}^a = 78.2$ | $K_A{}^b = 3.49$ | $x_1 = 0.136$ | $\Lambda_0{}^a = 62.92$ | $K_A{}^b = 4.80$ |
| 0.011 01 | 1.003 32 | 1.0010 | 0.010 10 | 1.007 41 | 1.0019 |
| 0.020 12 | 1.004 08 | 1.0014 | 0.020 01 | 1.007 92 | 1.0033 |
| 0.025 11 | 1.004 49 | 1.0016 | 0.025 61 | 1.008 20 | 1.0042 |
| 0.030 00 | 1.004 90 | 1.0018 | 0.032 50 | 1.008 55 | 1.0051 |
| 0.041 01 | 1.005 82 | 1.0022 | 0.041 06 | 1.008 99 | 1.0064 |
| 0.052 51 | 1.006 78 | 1.0026 | 0.050 85 | 1.009 49 | 1.0077 |
| $x_1 = 0.262$ | $\Lambda_0{}^a = 57.95$ | $K_A{}^b = 9.00$ | $x_1 = 0.486$ | $\Lambda_0{}^a = 32.46$ | $K_A{}^b = 31.92$ |
| 0.010 92 | 1.002 62 | 1.0044 | 0.009 78 | 0.987 07 | 1.0060 |
| 0.020 08 | 1.002 86 | 1.0078 | 0.019 67 | 0.987 42 | 1.0112 |
| 0.024 96 | 1.002 99 | 1.0097 | 0.025 01 | 0.987 61 | 1.0139 |
| 0.030 41 | 1.003 13 | 1.0117 | 0.030 65 | 0.987 81 | 1.0168 |
| 0.041 02 | 1.003 41 | 1.0156 | 0.040 08 | 0.988 15 | 1.0215 |
| 0.051 20 | 1.003 68 | 1.0193 | 0.050 33 | 0.988 52 | 1.0266 |
| | | $Pr_4NClO_4$ at 298.15 K | | | |
| $x_1 = 0.056$ | $\Lambda_0{}^a = 67.87$ | $K_A{}^b = 3.93$ | $x_1 = 0.136$ | $\Lambda_0{}^a = 52.58$ | $K_A{}^b = 5.11$ |
| 0.010 12 | 1.003 62 | 1.0011 | 0.010 01 | 1.007 40 | 1.0022 |
| 0.020 00 | 1.004 80 | 1.0016 | 0.020 02 | 1.007 91 | 1.0039 |
| 0.025 00 | 1.005 40 | 1.0019 | 0.025 45 | 1.008 18 | 1.0048 |
| 0.030 00 | 1.006 00 | 1.0021 | 0.030 11 | 1.008 41 | 1.0056 |
| 0.040 99 | 1.007 32 | 1.0026 | 0.041 26 | 1.008 97 | 1.0074 |
| 0.055 01 | 1.009 01 | 1.0031 | 0.050 44 | 1.009 43 | 1.0089 |
| $x_1 = 0.262$ | $\Lambda_0{}^a = 51.63$ | $K_A{}^b = 9.74$ | $x_1 = 0.486$ | $\Lambda_0{}^a = 28.84$ | $K_A{}^b = 38.10$ |
| 0.011 06 | 1.002 62 | 1.0049 | 0.009 84 | 0.987 38 | 1.0073 |
| 0.021 20 | 1.002 89 | 1.0091 | 0.020 08 | 0.988 07 | 1.0132 |
| 0.025 14 | 1.002 99 | 1.0109 | 0.025 04 | 0.988 40 | 1.0159 |
| 0.030 62 | 1.003 14 | 1.0132 | 0.030 13 | 0.988 74 | 1.0185 |
| 0.040 10 | 1.003 39 | 1.0172 | 0.041 12 | 0.989 48 | 1.0240 |
| 0.051 04 | 1.003 68 | 1.0217 | 0.050 20 | 0.990 09 | 1.0284 |
| | | $Bu_4NClO_4$ at 298.15 K | | | |
| $x_1 = 0.056$ | $\Lambda_0{}^a = 66.67$ | $K_A{}^b = 5.22$ | $x_1 = 0.136$ | $\Lambda_0{}^a = 51.82$ | $K_A{}^b = 9.58$ |
| 0.009 63 | 1.003 77 | 1.0017 | 0.010 45 | 1.007 79 | 1.0025 |
| 0.020 19 | 1.005 27 | 1.0025 | 0.020 11 | 1.008 61 | 1.0044 |
| 0.024 48 | 1.005 88 | 1.0028 | 0.027 01 | 1.009 20 | 1.0056 |
| 0.031 26 | 1.006 84 | 1.0033 | 0.032 70 | 1.009 68 | 1.0067 |
| 0.041 01 | 1.008 23 | 1.0039 | 0.041 18 | 1.010 40 | 1.0082 |
| 0.052 14 | 1.009 81 | 1.0045 | 0.050 60 | 1.011 20 | 1.0099 |
| $x_1 = 0.262$ | $\Lambda_0{}^a = 50.61$ | $K_A{}^b = 23.66$ | $x_1 = 0.486$ | $\Lambda_0{}^a = 28.14$ | $K_A{}^b = 83.71$ |
| 0.010 20 | 1.002 67 | 1.0052 | 0.009 89 | 0.987 19 | 1.0080 |
| 0.020 03 | 1.003 01 | 1.0099 | 0.020 16 | 0.987 67 | 1.0146 |
| 0.025 33 | 1.003 19 | 1.0123 | 0.025 04 | 0.987 90 | 1.0176 |
| 0.030 21 | 1.003 35 | 1.0145 | 0.030 01 | 0.988 14 | 1.0206 |
| 0.040 54 | 1.003 70 | 1.0193 | 0.041 00 | 0.988 66 | 1.0269 |
| 0.050 96 | 1.004 05 | 1.0240 | 0.050 06 | 0.989 09 | 1.0320 |
| | | $Et_4NClO_4$ at 308.15 K | | | |
| | $x_1 = 0.056$ | | | $x_1 = 0.136$ | |
| 0.010 95 | 0.997 62 | 1.0011 | 0.010 03 | 1.000 69 | 1.0023 |
| 0.020 00 | 0.998 29 | 1.0017 | 0.019 87 | 1.001 06 | 1.0042 |
| 0.024 96 | 0.998 66 | 1.0019 | 0.025 43 | 1.001 28 | 1.0053 |
| 0.029 82 | 0.999 08 | 1.0022 | 0.032 27 | 1.001 54 | 1.0066 |
| 0.040 77 | 0.999 84 | 1.0027 | 0.040 77 | 1.001 87 | 1.0082 |
| 0.052 19 | 1.000 71 | 1.0033 | 0.050 48 | 1.002 24 | 1.0100 |
| | $x_1 = 0.262$ | | | $x_1 = 0.486$ | |
| 0.010 84 | 0.995 51 | 1.0056 | 0.009 70 | 0.978 85 | 1.0069 |
| 0.019 95 | 0.996 17 | 1.0100 | 0.019 51 | 0.979 61 | 1.0126 |
| 0.024 80 | 0.996 52 | 1.0124 | 0.024 82 | 0.980 02 | 1.0156 |
| 0.030 22 | 0.996 72 | 1.0150 | 0.030 42 | 0.980 45 | 1.0186 |
| 0.040 79 | 0.997 69 | 1.0201 | 0.039 80 | 0.981 17 | 1.0235 |
| 0.050 93 | 0.998 42 | 1.0249 | 0.050 00 | 0.981 96 | 1.0286 |
| | | $Pr_4NClO_4$ at 308.15 K | | | |
| | $x_1 = 0.056$ | | | $x_1 = 0.136$ | |
| 0.010 12 | 1.003 62 | 1.0011 | 0.009 94 | 1.000 62 | 1.0027 |
| 0.020 00 | 1.004 80 | 1.0016 | 0.019 88 | 1.000 95 | 1.0051 |
| 0.025 00 | 1.005 40 | 1.0019 | 0.025 27 | 1.001 12 | 1.0063 |
| 0.030 00 | 1.006 00 | 1.0021 | 0.029 90 | 1.001 27 | 1.0073 |
| 0.040 99 | 1.007 32 | 1.0026 | 0.040 96 | 1.001 64 | 1.0098 |
| 0.055 01 | 1.009 01 | 1.0031 | 0.050 07 | 1.001 93 | 1.0117 |

**Table 2 (Continued)**

| $c$/mol·dm$^{-3}$ | $\rho$/g·cm$^{-3}$ | $\eta_r$ | $c$/mol·dm$^{-3}$ | $\rho$/g·cm$^{-3}$ | $\eta_r$ |
|---|---|---|---|---|---|
| | | $Pr_4NClO_4$ at 308.15 K | | | |
| | $x_1 = 0.262$ | | | $x_1 = 0.486$ | |
| 0.010 98 | 0.995 16 | 1.0064 | 0.009 75 | 0.978 85 | 1.0088 |
| 0.021 05 | 0.995 57 | 1.0121 | 0.019 91 | 0.979 64 | 1.0162 |
| 0.024 96 | 0.995 73 | 1.0143 | 0.024 83 | 0.980 02 | 1.0196 |
| 0.030 40 | 0.995 95 | 1.0176 | 0.029 88 | 0.980 41 | 1.0230 |
| 0.039 82 | 0.996 33 | 1.0226 | 0.040 78 | 0.981 25 | 1.0300 |
| 0.050 69 | 0.996 77 | 1.0286 | 0.049 79 | 0.981 95 | 1.0355 |
| | | $Bu_4NClO_4$ at 308.15 K | | | |
| | $x_1 = 0.056$ | | | $x_1 = 0.136$ | |
| 0.009 63 | 1.003 77 | 1.0017 | 0.010 38 | 1.001 27 | 1.0029 |
| 0.020 19 | 1.005 27 | 1.0025 | 0.019 98 | 1.002 17 | 1.0054 |
| 0.024 48 | 1.005 88 | 1.0028 | 0.026 84 | 1.002 82 | 1.0071 |
| 0.031 26 | 1.006 84 | 1.0033 | 0.032 49 | 1.003 35 | 1.0086 |
| 0.041 01 | 1.008 23 | 1.0039 | 0.040 92 | 1.004 14 | 1.0095 |
| 0.052 14 | 1.009 81 | 1.0045 | 0.050 29 | 1.005 01 | 1.0131 |
| | $x_1 = 0.262$ | | | $x_1 = 0.486$ | |
| 0.010 13 | 0.995 32 | 1.0070 | 0.009 81 | 0.978 98 | 1.0102 |
| 0.019 89 | 0.995 91 | 1.0134 | 0.020 00 | 0.979 89 | 1.0190 |
| 0.025 15 | 0.996 22 | 1.0169 | 0.024 85 | 0.980 32 | 1.0230 |
| 0.030 00 | 0.996 51 | 1.0200 | 0.029 79 | 0.980 76 | 1.0271 |
| 0.040 27 | 0.997 12 | 1.0268 | 0.040 71 | 0.981 74 | 1.0357 |
| 0.050 64 | 0.997 74 | 1.0334 | 0.049 73 | 0.982 54 | 1.0425 |
| | | $Et_4NClO_4$ at 318.15 K | | | |
| | $x_1 = 0.056$ | | | $x_1 = 0.136$ | |
| 0.010 90 | 0.993 38 | 1.0013 | 0.009 96 | 0.993 60 | 1.0027 |
| 0.019 92 | 0.993 97 | 1.0019 | 0.019 73 | 0.993 92 | 1.0051 |
| 0.024 85 | 0.994 29 | 1.0022 | 0.025 25 | 0.994 10 | 1.0064 |
| 0.029 69 | 0.994 61 | 1.0026 | 0.032 04 | 0.994 32 | 1.0080 |
| 0.040 58 | 0.995 32 | 1.0033 | 0.040 47 | 0.994 60 | 1.0099 |
| 0.051 95 | 0.996 06 | 1.0039 | 0.050 12 | 0.994 91 | 1.0122 |
| | $x_1 = 0.262$ | | | $x_1 = 0.486$ | |
| 0.010 76 | 0.987 90 | 1.0067 | 0.009 62 | 0.970 68 | 1.0078 |
| 0.019 80 | 0.989 02 | 1.0121 | 0.019 36 | 0.971 78 | 1.0142 |
| 0.024 63 | 0.989 61 | 1.0149 | 0.024 62 | 0.972 37 | 1.0174 |
| 0.030 02 | 0.990 28 | 1.0181 | 0.030 19 | 0.973 00 | 1.0207 |
| 0.040 54 | 0.991 58 | 1.0243 | 0.039 51 | 0.974 04 | 1.0260 |
| 0.050 65 | 0.992 82 | 1.0303 | 0.049 65 | 0.975 18 | 1.0315 |
| | | $Pr_4NClO_4$ at 318.15 K | | | |
| | $x_1 = 0.056$ | | | $x_1 = 0.136$ | |
| 0.010 02 | 0.993 72 | 1.0014 | 0.009 87 | 0.993 46 | 1.0034 |
| 0.019 80 | 0.994 74 | 1.0022 | 0.019 74 | 0.993 65 | 1.0062 |
| 0.024 75 | 0.995 26 | 1.0026 | 0.025 09 | 0.993 76 | 1.0077 |
| 0.029 70 | 0.995 78 | 1.0029 | 0.029 67 | 0.993 84 | 1.0090 |
| 0.040 57 | 0.996 92 | 1.0037 | 0.040 65 | 0.994 06 | 1.0121 |
| 0.054 43 | 0.998 37 | 1.0047 | 0.049 68 | 0.994 23 | 1.0146 |
| | $x_1 = 0.262$ | | | $x_1 = 0.486$ | |
| 0.010 89 | 0.987 22 | 1.0079 | 0.009 67 | 0.970 42 | 1.0103 |
| 0.020 88 | 0.987 82 | 1.0149 | 0.019 74 | 0.971 27 | 1.0194 |
| 0.024 77 | 0.988 06 | 1.0176 | 0.024 62 | 0.971 69 | 1.0235 |
| 0.030 17 | 0.988 38 | 1.0213 | 0.029 62 | 0.972 11 | 1.0278 |
| 0.039 52 | 0.988 94 | 1.0277 | 0.040 44 | 0.973 03 | 1.0367 |
| 0.050 32 | 0.989 59 | 1.0352 | 0.049 37 | 0.973 79 | 1.0438 |
| | | $Bu_4NClO_4$ at 318.15 K | | | |
| | $x_1 = 0.056$ | | | $x_1 = 0.136$ | |
| 0.009 54 | 0.993 96 | 1.0020 | 0.010 31 | 0.994 35 | 1.0037 |
| 0.019 99 | 0.995 37 | 1.0033 | 0.019 85 | 0.995 35 | 1.0069 |
| 0.024 24 | 0.995 94 | 1.0037 | 0.026 66 | 0.996 06 | 1.0093 |
| 0.030 95 | 0.996 85 | 1.0044 | 0.032 23 | 0.996 65 | 1.0112 |
| 0.040 60 | 0.998 15 | 1.0054 | 0.040 66 | 0.997 53 | 1.0140 |
| 0.051 61 | 0.999 63 | 1.0064 | 0.049 96 | 0.998 51 | 1.0172 |
| | $x_1 = 0.262$ | | | $x_1 = 0.486$ | |
| 0.010 05 | 0.987 83 | 1.0088 | 0.009 73 | 0.971 19 | 1.0123 |
| 0.019 75 | 0.989 04 | 1.0170 | 0.019 86 | 0.972 84 | 1.0234 |
| 0.024 99 | 0.989 70 | 1.0214 | 0.024 68 | 0.973 63 | 1.0282 |
| 0.029 82 | 0.990 30 | 1.0256 | 0.029 59 | 0.974 43 | 1.0331 |
| 0.040 05 | 0.991 69 | 1.0342 | 0.040 48 | 0.976 21 | 1.0440 |
| 0.050 39 | 0.992 88 | 1.0429 | 0.049 48 | 0.977 68 | 1.0527 |

[a] Units: $\Lambda_0$/S·cm$^2$·mol$^{-1}$. [b] Units: $K_A$/dm$^{-3}$·mol$^{-1}$.

**Table 3. Theoretical $A$/dm$^{3/2}$ mol$^{-1/2}$ Coefficients of Electrolytes in 2-Methoxyethanol (1) + Water (2) at 298.15 K**

| salt | $x_1$ = 0.056 | $x_1$ = 0.136 | $x_1$ = 0.262 | $x_1$ = 0.486 | $x_1$ = 1.000 |
|---|---|---|---|---|---|
| $Et_4NClO_4$ | 0.0064 | 0.0054 | 0.0055 | 0.0143 | 0.0198 |
| $Pr_4NClO_4$ | 0.0082 | 0.0068 | 0.0063 | 0.0170 | 0.0224 |
| $Bu_4NClO_4$ | 0.0085 | 0.0070 | 0.0064 | 0.0177 | 0.0238 |

K are given in Table 2. The $\Lambda_0$ and $K_A$ values (Das and Hazra, 1996) for the electrolytes at 298.15 K have also been included in this table. At 0.056, 0.136, and 0.262 mole fractions of ME in ME + water mixtures, $Et_4NClO_4$ and $Pr_4NClO_4$ are almost in an unassociated state whereas $Bu_4NClO_4$ remains unassociated at 0.056 and 0.136 mole fractions of ME in the mixture. At the higher percentages, however, all these salts are found to be moderately associated. The viscosity data in cases where the electrolytes were found to be in an unassociated state were analyzed by the Jones−Dole equation as described earlier by us (Muhuri and Hazra, 1993)

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

whereas for the electrolytes in an associated state the data were analyzed (Crudden et al., 1986; Das and Hazra, 1992) with the help of eq 4.

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

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

For the evaluation of $B$ coefficients from eq 3, the plots of $(\eta_r - 1)/c^{1/2}$ versus $c^{1/2}$ were constructed and were found to be linear in all cases over the whole concentration range of the electrolytes studied. The $B$ coefficients for the electrolytes were evaluated from these plots by the least-squares treatment. For the evaluation of $B$ coefficients from eq 4, the method suggested earlier by us (Das and Hazra, 1992) was followed. The values of $\alpha$ were calculated from the conductance data (Das and Hazra, 1996) using the equation as described in the literature (Crudden et al., 1986). The $A$ values were calculated theoretically from the physical parameters of the solvent and the limiting ionic equivalent conductances (Das and Hazra, 1996) using Falkenhagen and Vernon equation and are given in Table 3. These $A$ values have been used for the analysis of the data. In view of the weak temperature dependence of the $A$ coefficients, the $A$ values at 298.15 K were utilized at the other two temperatures, viz., at 308.15 and 318.15 K.

## Discussion

The viscosity $B$ coefficients for the tetraalkylammonium perchlorates in mixed solvents (Table 4) are all found to be positive. The $B$ values increase as the alkyl chain length increases. For all electrolytes, the $B$ values increase up to 0.486 mole fraction of 2-methoxyethanol in the mixture followed by a decrease in pure 2-methoxyethanol. The results must be due to increase in hydrophobic interactions and consequent structural changes that occur in solution. At 0.056 mole fraction of 2-methoxyethanol, the $B$ coefficients are very small. In such cases, it might be that the viscosity of the solvent is very little modified by the presence of these solutes in solution. According to Gurney (Gurney, 1962), this can happen when the cosphere of the cation causes a local increase in viscosity while that of the anion causes a nearly equal decrease in the viscosity or vice versa. Furthermore, the d$B$/d$T$ values are positive, indicating the structure-breaking properties of these solutes in ME + water mixtures.

**Table 4. Viscosity $B$ Coefficients (dm$^3$·mol$^{-1}$) of Tetraalkylammonium Perchlorates in 2-Methoxyethanol (1) + Water (2) at $T$ = (298.15, 308.15, and 318.15) K**

| salt | $T$/K | $x_1$ = 0.056 | $x_1$ = 0.136 | $x_1$ = 0.262 | $x_1$ = 0.486 | $x_1$ = 1.000 |
|---|---|---|---|---|---|---|
| $Et_4NClO_4$ | 298.15 | 0.015<br>(±0.001) | 0.124<br>(±0.003) | 0.356<br>(±0.002) | 0.480<br>(±0.001) | 0.191<br>(±0.003) |
| | 308.15 | 0.030<br>(±0.002) | 0.173<br>(±0.001) | 0.466<br>(±0.002) | 0.615<br>(±0.002) | 0.360<br>(±0.005) |
| | 318.15 | 0.040<br>(±0.003) | 0.219<br>(±0.002) | 0.576<br>(±0.002) | 0.739<br>(±0.001) | 0.523<br>(±0.005) |
| $Pr_4NClO_4$ | 298.15 | 0.018<br>(±0.002) | 0.142<br>(±0.001) | 0.416<br>(±0.002) | 0.643<br>(±0.002) | 0.286<br>(±0.003) |
| | 308.15 | 0.036<br>(±0.001) | 0.203<br>(±0.003) | 0.548<br>(±0.002) | 0.812<br>(±0.002) | 0.541<br>(±0.004) |
| | 318.15 | 0.046<br>(±0.002) | 0.254<br>(±0.003) | 0.675<br>(±0.002) | 0.966<br>(±0.002) | 0.785<br>(±0.004) |
| $Bu_4NClO_4$ | 298.15 | 0.020<br>(±0.002) | 0.158<br>(±0.002) | 0.455<br>(±0.003) | 0.735<br>(±0.002) | 0.383<br>(±0.004) |
| | 308.15 | 0.039<br>(±0.002) | 0.243<br>(±0.004) | 0.628<br>(±0.003) | 0.980<br>(±0.005) | 0.731<br>(±0.005) |
| | 318.15 | 0.059<br>(±0.002) | 0.331<br>(±0.002) | 0.807<br>(±0.003) | 1.217<br>(±0.003) | 1.070<br>(±0.004) |

The reason for the observed change in the viscosity and other properties may be attributed to structural changes and changed ion−solvent interactions in ME + water mixtures. Intermolecular hydrogen bonding gives water a distinct geometrical structure in the form of three-dimensional arrays. The addition of ME to water first strengthens the three-dimensional structure of water. Further addition of ME causes depolymerization of water structure, but intermolecular interactions between ME and water lead to the formation of ME−water complexes with a bigger hydrodynamic entity. Viscosity thus increases up to 0.262 mole fraction of ME after which the ME−water structure breaks down, leading to a decrease in viscosity in this region.

Tetraalkylammonium ions are large and tend to enhance the "cagelike" structure of water owing to hydrophobic interactions. The disruption of the ME−water structure by tetraalkylammonium ions may lead to the decrease in structure, but ultimate formation of a strong ME−tetraalkylammonium ion complex with a large solvodynamic entity increases the viscosity.

## Literature Cited

Crudden, J.; Delaney, G. M.; Feakins, D.; O'Reilley, P. J.; Waghorne, W. E.; Lawrence, K. G. The Viscosity and Structure of Solutions. Part 2. Measurements of B Coefficient of Viscosity of Alkali Metal Chlorides in Propan-1-ol-Water Mixtures at 25 and 35 °C. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 2195−2206.

Das, B.; Hazra, D. K. Studies on the Viscosities, Conductances and Adiabatic Compressibilites of Some Tetraalkylammonium Perchlorates in 2-Methoxyethanol. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 3470−3476.

Das, B.; Hazra, D. K. Viscosities and Excess Molar Volumes for 2-Methoxyethanol + Water at Different Temperatures. *J. Chem. Eng. Data* **1993**, *38*, 361−363.

Das, B.; Hazra, D. K. Apparent and Partial Molar Volumes of Some Symmetrical Tetraalkylammonium Perchlorates in 2-Methoxyethanol at 25, 35, and 45 °C. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 734−737.

Das, B.; Hazra, D. K. Ionic Association and Conductances of Some Symmetrical Tetraalkylammonium Perchlorates in 2-Methoxyethanol + Water at 298.15 K. *J. Chem. Eng. Data* **1996**, *41*, 1470−1472.

Gurney, R. W. *Ionic Processes in Solution*; Dover Publications: New York, 1962.

Muhuri, P. K.; Hazra, D. K. Viscosity B Coefficients of Some Tetraalkylammonium Bromides, Lithium Tetrafluoroborate and Tetrabutylammonium Tetraphenylborate in Propylene Carbonate. *Z. Naturforsch.* **1993**, *48a*, 523−528.

Saha, N.; Das, B.; Hazra, D. K. Viscosities and Excess Molar Volumes for Acetonitrile + Methanol at 298.15, 308.15, and 318.15 K. *J. Chem. Eng. Data* **1995**, *40*, 1264−1266.

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