## Appendix

# Electrical Conductances of Tetrabutylammonium Bromide, Sodium Tetraphenylborate, and Sodium Bromide in Acetonitrile-Water Mixtures at 308.15, 313.15, and 318.15 K: Determination of Limiting Ionic Equivalent Conductivities

## Introduction

In order to analyse the conductivity data of sodium polystyrenesulfonate (NaPSS) in acetonitrile-water mixed solvent media, the limiting equivalent conductivities of sodium ion in relevant mixture are essential. We have, therefore, performed electrical conductivity measurement on tetrabutylammonium bromide ($Bu_4NBr$), sodium tetraphenylborate ($NaBPh_4$) and sodium bromide (NaBr) in acetonitrile-water mixtures at 308.15, 313.15, and 318.15 K in order to obtain precise temperature-dependent single-ion conductivities since such data are practically nonexistent in mixed solvent media.

## Experimental

Acetonitrile (E. Merck, India, 99% pure) was distilled with phosphorus pentoxide and then redistilled over calcium hydride. The purified solvent had a density of 0.76570 $g{\cdot}cm^{-3}$ and a coefficient of viscosity of 0.3126 mPa·s at 308.15 K; these values are in good agreement with the literature values.[1] Triply distilled water with a specific conductance of less than $10^{-6}$ $S{\cdot}cm^{-1}$ at 308.15 K was used for the preparation of the mixed solvents. The physical properties of acetonitrile-water mixed solvents used in this study at 308.15, 313.15, and 318.15 K are reported in Table 1. The relative permittivities of acetonitrile-water mixtures at the experimental temperatures were obtained with the equations as described in the literature[2] using the literature density and relative permittivity data of the pure solvents[1,3] and the densities of the mixed solvents given in Table 1 of Chapter III .

All of these salts were of Fluka purum or puriss grade. Tetrabutylammonium bromide ($Bu_4NBr$) was purified by recrystallization from acetone and the recrystallized salt was dried in vacuo at 333.15 K for 48 h. Sodium tetraphenylborate ($NaBPh_4$) was recrystallized three times from acetone and then dried under vacuum at 353.15 K for 72 h. Sodium bromide (NaBr) was dried in vacuo for 72 h immediately prior to use and was used without further purification.

Conductance measurements were carried out on a Pye-Unicam PW 9509 conductivity meter at a frequency of 2000 Hz using a dip-type cell of cell constant 1.15 $cm^{-1}$ and having an uncertainty of 0.01 %. The cell was calibrated by the method of Lind and co-workers[4] using aqueous potassium chloride solutions. The measurements were made in a water bath maintained within ± 0.005 K of the desired temperature. The details of the experimental procedure have been described earlier[5,6] and also in Chapter II. 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 $cm^3$ 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 by subtracting the specific conductance of the relevant solvent medium from those of the salt solutions.

In order to avoid moisture pickup, all solutions were prepared in a dehumidified room with utmost care. In all cases, the experiments were performed at least in five replicates for each solution and at each temperature, and the results were averaged.

## Results and Discussion

The conductance data have been analyzed by the 1978 Fuoss conductance-concentration equation.[7,8] For a given set of conductivity values ($c_j$, $\Lambda_j$; $j = 1, \ldots, n$), three adjustable parameters - the limiting molar conductivity ($\Lambda^0$), association constant ($K_A$), and the association diameter ($R$), are derived from the following set of equations :

$$\Lambda = p[\Lambda^0(1 + RX + EL] \qquad (1)$$

$$p = 1 - \alpha(1 - \gamma) \qquad (2)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \qquad (3)$$

$$-\ln f = \frac{\beta k}{2(1 + kR)} \qquad (4)$$

$$\beta = \frac{e^2}{\varepsilon k_B T} \qquad (5)$$

$$K_A = K_R(1 + K_S) \tag{6}$$

where *RX* is the relaxation field effect, *EL* is the electrophoretic countercurrent, $\gamma$ is the fraction of unpaired ions, and $\alpha$ is the fraction of contact-pairs, $K_A$ is the overall pairing constant evaluated from the association constants of contact-pairs, $K_S$, of solvent-separated pairs, $K_R$, $\varepsilon$ is the relative permittivity of the solvent, *e* is the electronic charge, $k_B$ is the Boltzmann constant, $k^{-1}$ is the radius of the ion atmosphere, *c* is the molarity of the solution, *f* is the activity coefficient, *T* is the temperature in absolute scale, and $\beta$ is twice the Bjerrum distance. The computations were performed on a computer using the program as suggested by Fuoss. The initial $\Lambda^0$ values for the iteration procedure were obtained from Shedlovsky extrapolation[9] of the data. Input for the program is the set ($c_j$, $\Lambda_j$; $j = 1, \ldots, n$), $n$, $\varepsilon$, $\eta$, $T$, initial value of $\Lambda^0$, and an instruction to cover a preselected range of *R* values.

In practice, calculations are made by finding the values of $\Lambda^0$ and $\alpha$ which minimize the standard deviation, $\sigma$,

$$o^2 = \sum[\Lambda_j(\text{calcd}) - \Lambda_j(\text{obsd})]^2/(n-2) \tag{7}$$

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.

The values of $\Lambda^0$, $K_A$, and *R* obtained by this procedure are reported in Table 1.

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

The limiting ionic conductivities have been evaluated from the division of the $\Lambda^0$ values of $Bu_4NBPh_4$ using the following relationship:

$$\lambda^0(Bu_4N^+) = 0.517\,\Lambda^0(Bu_4NPh_4B) \tag{8}$$

as described in the literature.[10,11]

The limiting molar conductivity ($\Lambda^0$) of the "reference electrolyte" $Bu_4NBPh_4$ was obtained by considering the Kohlrausch rule that allows the calculation of the $\Lambda^0$ value for a given electrolyte by the appropriate combination of others. The $\Lambda^0$ values of $Bu_4NBr$, $NaBPh_4$ and NaBr obtained in the present solvent media have been used to obtain the $\Lambda^0$ value of $Bu_4NBPh_4$ through the following equation:

$$\Lambda^0(\mathrm{Bu_4NBPh_4}) = \Lambda^0(\mathrm{Bu_4NBr}) + \Lambda^0(\mathrm{NaPh_4B}) - \Lambda^0(\mathrm{NaBr}) \qquad (9)$$

The limiting ionic conductances calculated from the above equations are recorded in Table 2.

The association constants ($K_A$) listed in Table 1 for all these systems are practically negligible (*i.e.*, $K_A < 10$). So, the numerical values of $K_A$ should not be taken seriously.[12] One can only conclude that all of these three electrolytes exist as free ions in both the solvent mixtures in the temperature range 308.15 to 318.15 K. This is expected because the relative parmittivities of the solvent mixtures are fairly high ($57.32 \le \varepsilon \le 67.94$).

The cosphere diameter ($R$) values for all the salts under study in the acetonitrile-water mixtures are also reported in Table 2. No systematic trend in $R$ values for the salts studied has been observed. Since the best fit conductivity parameters are reproduced equally well over a wide range of arbitrarily chosen $R$ values, a comprehensive correlation of the cosphere diameter of the studied systems could not be made in the present situation. This type of behavior has also been reported earlier.[11,13,14]

In both the mixed solvent media, the limiting ionic equivalent conductances decreases in the order: $\lambda^0_{\mathrm{Br^-}} > \lambda^0_{\mathrm{Na^+}} > \lambda^0_{\mathrm{Bu_4N^+}} > \lambda^0_{\mathrm{Ph_4B^-}}$ at each temperature indicating that the sizes of these ions as they exist in solutions follow the order: $\mathrm{Br^-} < \mathrm{Na^+} < \mathrm{Bu_4N^+} < \mathrm{Ph_4B^-}$. Another interesting observation is that the limiting ionic equivalent conductances of $Na^+$ and $Br^-$ ions decrease in going form 20 volume percent of acetonitrile to 40 volume percent of acetonitrile in the mixture at all temperatures investigated, whereas those for $Bu_4N^+$ and $Ph_4B^-$ ions exhibit an increase in going form 20 to 40 volume prcent of acetonitrile in the mixture. This indicates that besides the relative permittivity and the viscosity of the media, specific interaction of the ions with the solvent media has a profound influence on their mobilities.

Although the association constants of the electrolytes do not vary significantly as a function of temperature, the limiting equivalent conductances of the electrolytes as well as the single-ion conductivity values increase appreciably with temperature.

## References

1. G. Moumouzias, D. K. Panopoulos, and G. Ritzoulis, *J. Chem. Eng. Data*, **36**, 20 (1991).
2. M. Pal and S. Bagchi, *J. Chem. Soc., Faraday Soc. 1*, **81**, 961 (1985).
3. R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, 2nd ed., Butterworths, London (1959).
4. J. E. Lind, Jr., J. J. Zwolenik, and R. M. Fuoss, *J. Am. Chem. Soc.*, **81**, 1557 (1959).
5. B. Das and D. K. Hazra, *Bull. Chem. Soc. Jpn.*, **65**, 3470 (1992).
6. B. Das and D. K. Hazra, *J. Phys. Chem.*, **99**, 269 (1995).
7. R. M. Fuoss, *Proc. Natl. Acad. Sci., U.S.A.*, **75**, 16 (1978).
8. R. M. Fuoss, *J. Phys. Chem.*, **82**, 2427 (1978).
9. R. M. Fuoss and T. Shedlovsky, *J. Am. Chem. Soc.*, **71**, 1496 (1949).
10. B. Das and D. K. Hazra, *J. Solution Chem.*, **27**, 1021 (1998).
11. P. K. Muhuri and D. K. Hazra, *Z. Phys. Chem.*, **190**, 111 (1995).
12. L. Bahadur and M. V. Ramanamurti, *Can. J. Chem.*, **62**, 1051 (1984).
13. N. Islam, A. B. S. Zaidi, A. A. Ansari, *Bull. Chem. Soc. Jpn.*, **62**, 309 (1989).
14. A. K. Srivastava and R. A. Samant, *J. Chem. Eng. Data*, **39**, 358 (1994).

**Table 1.** Derived Conductivity Parameters of Electrolytes in Acetonitrile-Water Mixtures Containing 20 and 40 Volume Percent of Acetonitrile at 308.15, 313.15, and 318.15 K

| **$T$(K)** | **$\Lambda^0$ (S cm$^2$ mol$^{-1}$)** | **$K_A$ /(dm$^3$ mol$^{-1}$)** | $R / \overset{0}{A}$ | $\sigma\%^{a}$ |
|---|---|---|---|---|
| **20 Vol Percent of Acetonitrile** | | | | |
| $Bu_4NBr$ | | | | |
| 308.15 | 125.96 ± 0.07 | 9.24 ± 0.04 | 16.47 | 0.05 |
| 313.15 | 135.50 ± 0.06 | 8.30 ± 0.03 | 14.77 | 0.03 |
| 318.15 | 149.27 ± 0.06 | 8.46 ± 0.03 | 14.85 | 0.03 |
| $NaPh_4B$ | | | | |
| 308.15 | 84.16 ± 0.01 | 3.65 ± 0.01 | 11.24 | 0.02 |
| 313.15 | 94.05 ± 0.08 | 5.59 ± 0.08 | 12.11 | 0.03 |
| 318.15 | 102.92 ± 0.02 | 3.80 ± 0.02 | 11.50 | 0.03 |
| NaBr | | | | |
| 308.15 | 152.27 ± 0.04 | 5.51 ± 0.01 | 10.76 | 0.02 |
| 313.15 | 164.80 ± 0.02 | 4.97 ± 0.01 | 10.20 | 0.01 |
| 318.15 | 179.96 ± 0.02 | 4.81 ± 0.01 | 10.07 | 0.01 |

Table1. continued

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|---|---|---|---|---|
| | | **40 Vol Percent of Acetonitrile** | | |
| | | $Bu_4NBr$ | | |
| 308.15 | 117.52 ± 0.01 | 7.40 ± 0.01 | 12.11 | 0.01 |
| 313.15 | 128.59 ± 0.01 | 7.31 ± 0.01 | 11.97 | 0.01 |
| 318.15 | 137.35 ± 0.05 | 6.13 ± 0.02 | 11.09 | 0.03 |
| | | $NaPh_4B$ | | |
| 308.15 | 84.06 ± 0.06 | 3.64 ± 0.03 | 10.55 | 0.04 |
| 313.15 | 93.26 ± 0.04 | 3.29 ± 0.03 | 10.50 | 0.05 |
| 318.15 | 101.79 ± 0.06 | 2.38 ± 0.04 | 10.47 | 0.07 |
| | | NaBr | | |
| 308.15 | 133.97 ± 0.07 | 1.92 ± 0.03 | 9.11 | 0.03 |
| 313.15 | 148.54 ± 0.08 | 2.29 ± 0.03 | 9.13 | 0.06 |
| 318.15 | 163.69 ± 0.10 | 2.27 ± 0.03 | 9.19 | 0.07 |

[a] $\sigma\% = 100\sigma / \Lambda^0$

**Table 2.** Limiting Ionic Conductances in Acetonitrile-Water Mixtures Containing 20 and 40 Volume Percent of Acetonitrile at 308.15, 313.15, and 318.15 K

| $T$ (K) | $\lambda_{\pm}^{0}$ (S cm$^2$ mol$^{-1}$) | | | |
|---|---|---|---|---|
| | $Na^+$ | $Bu_4N^+$ | $Br^-$ | $Ph_4B^-$ |
| | **20 Vol Percent of Acetonitrile** | | | |
| 308.15 | 56.21 | 29.90 | 96.06 | 27.95 |
| 313.15 | 62.77 | 33.47 | 102.03 | 31.28 |
| 318.15 | 68.03 | 37.34 | 111.93 | 34.89 |
| | **40 Vol Percent of Acetonitrile** | | | |
| 308.15 | 51.40 | 34.95 | 82.57 | 32.66 |
| 313.15 | 57.84 | 37.89 | 90.70 | 35.42 |
| 318.15 | 65.34 | 39.00 | 98.35 | 36.45 |

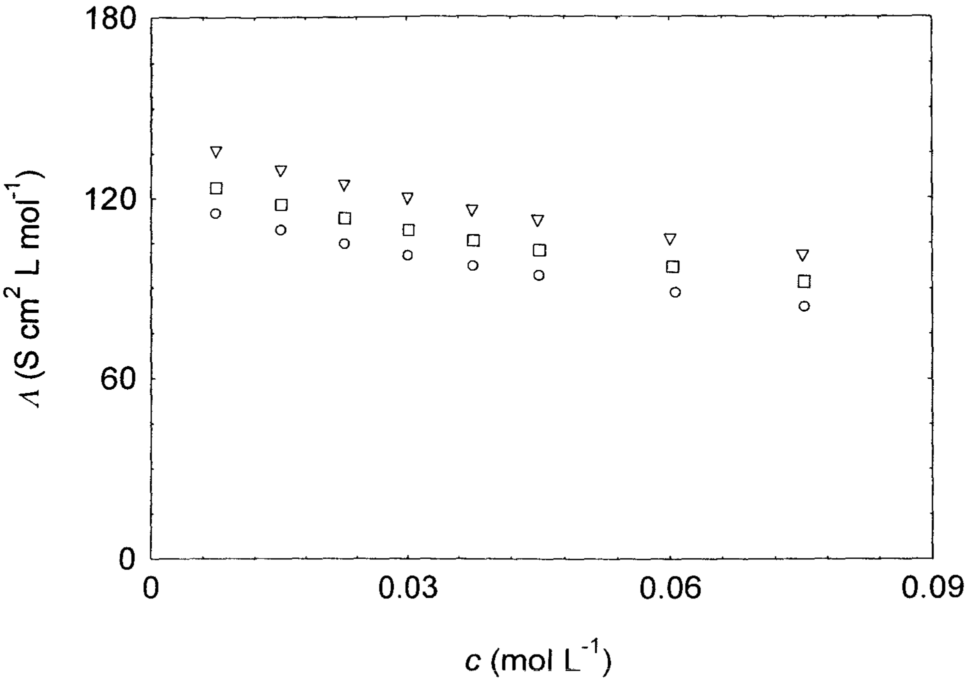

**Figure 1.** Concentration dependence of the equivalent conductance of tetrabutylammonium bromide ($Bu_4NBr$) in 20 volume percent acetonitrile-water mixture at different temperatures: (○) 308.15 K; (□) 313.15 K; (∇) 318.15 K.

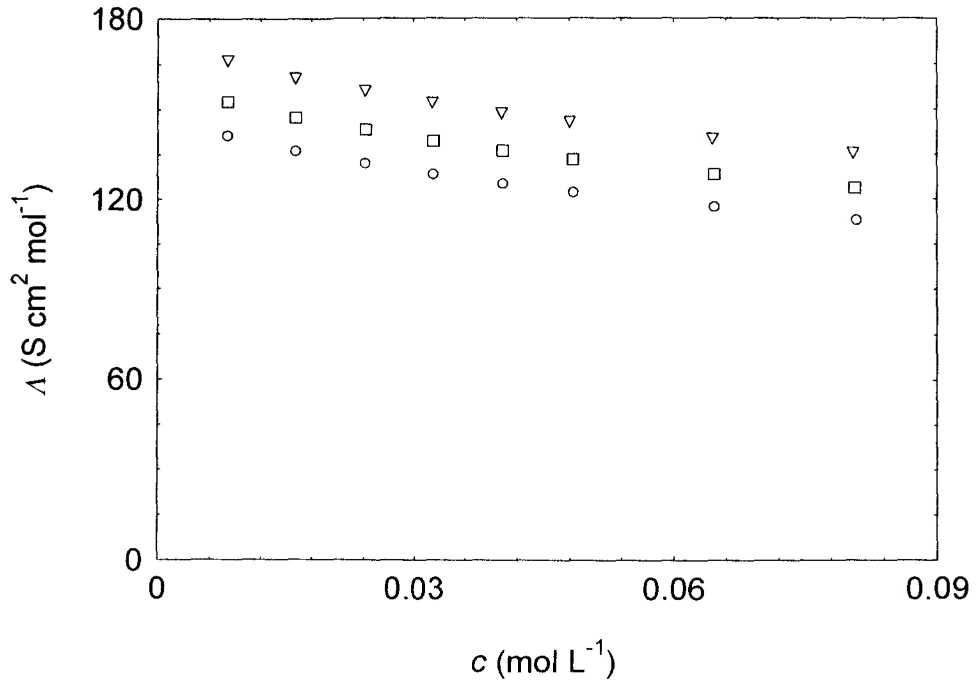

**Figure 2.** Concentration dependence of the equivalent conductance of sodium bromide (NaBr) in 20 volume percent acetonitrile-water mixture at different temperatures: (○) 308.15 K; (□) 313.15 K; (∇) 318.15 K.

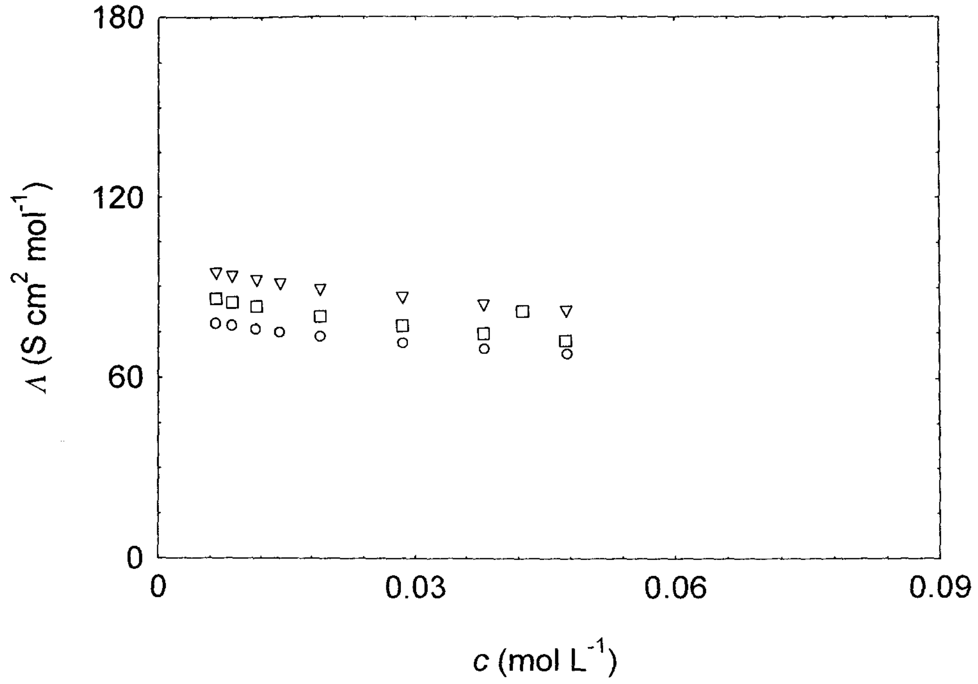

**Figure 3.** Concentration dependence of the equivalent conductance of sodium tetraphenylborate ($NaPh_4B$) in 20 volume percent acetonitrile-water mixture at different temperatures: (○) 308.15 K; (□) 313.15 K; (∇) 318.15 K.

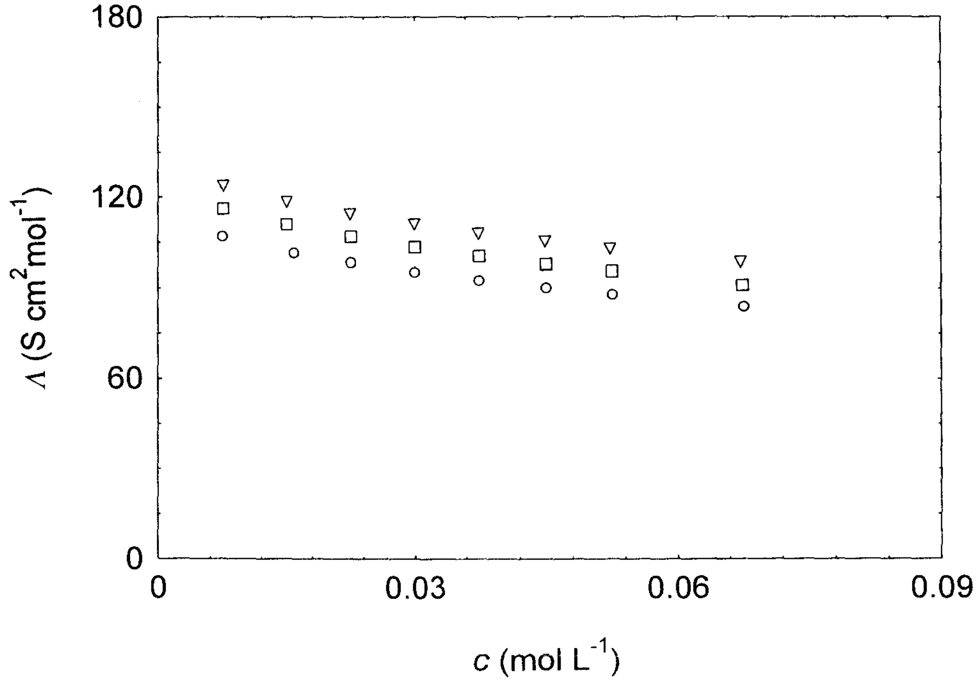

**Figure 4.** Concentration dependence of the equivalent conductance of tetrabutylammonium bromide ($Bu_4NBr$) in 40 volume percent acetonitrile-water mixture at different temperatures: (○) 308.15 K; (□) 313.15 K; (∇) 318.15 K.

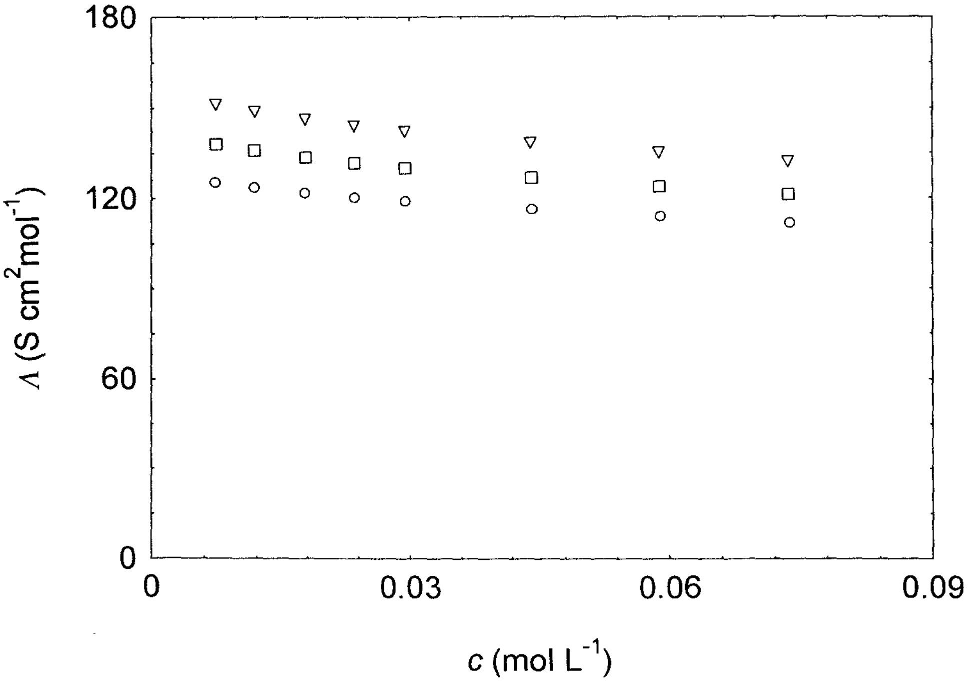

**Figure 5.** Concentration dependence of the equivalent conductance of sodium bromide (NaBr) in 40 volume percent acetonitrile-water mixture at different temperatures: (○) 308.15 K; (□) 313.15 K; (∇) 318.15 K.

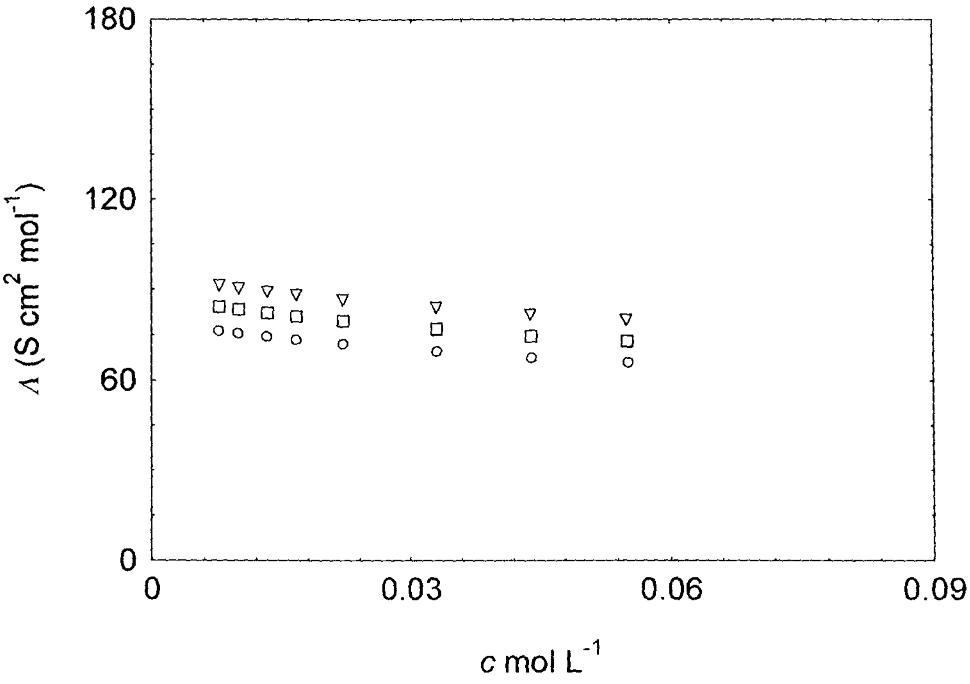

**Figure 6.** Concentration dependence of the equivalent conductance of sodium tetraphenylborate ($NaPh_4B$) in 40 volume percent acetonitrile-water mixture at different temperatures: (○) 308.15 K; (□) 313.15 K; (∇) 318.15 K.