Annexure

Electrical Conductances of Tetrabutylammonium Bromide, Sodium Tetraphenylborate, and Sodium Bromide in Methanol-Water Mixtures at 298.15, 308.15, and 318.15 K

Introduction

In order to analyse the conductivity data of sodium carboxymethylcellulose in methanol-water mixed solvent media, the limiting ionic equivalent conductivities of sodium ion in relevant mixtures are essential. We have, therefore, performed electrical conductivity measurement on tetrabutylammonium bromide (Bu_4NBr), sodium tetraphenylborate ($NaBPh_4$) and sodium bromide (NaBr) in methanol-water mixtures at 298.15, 308.15, and 318.15 K in order to obtain precise temperature-dependent single-ion conductivities since these data are not available in the literature.

Experimental

Materials

Methanol (Acros Organics, 99.9% pure) was dried over molecular sieves and distilled fractionally. The middle fraction was collected and redistilled. The purified solvent had a density of 0.77728 $g.cm^{-3}$ and a coefficient of viscosity of 0.4747 mPa·s at 308.15 K; these values are in good agreement with the literature values.[1,2] 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 methanol-water mixed solvents used in this study at 298.15, 308.15, and 318.15 K are reported in Table 1. The relative permittivities of methanol-water mixtures at the experimental temperatures were obtained from literature.[3]

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

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

Data Analysis: Limiting Ionic Equivalent Conductances

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

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

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

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

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

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

$$K_A = K_R(1 + K_S) \quad (6)$$

where *RX* is the relaxation field effect, *EL* is the electrophoretic countercurrent, γ is the fraction of unpaired ions, and α 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, ε is the relative permittivity of the solvent, *e* is the protonic 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 β is twice the Bjerrum distance. The computations were performed on a computer using the program as suggested by Fuoss. The initial Λ^0 values for the iteration procedure were obtained from Shedlovsky extrapolation[9] of the data. Input for the program is the set (c_j, Λ_j; $j = 1, \ldots, n$), n, ε, η, T, initial value of Λ^0, and an instruction to cover a preselected range of *R* values.

In practice, calculations are made by finding the values of Λ^0 and α which minimize the standard deviation, σ,

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

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,for salts investigated here, sice a preliminary scan using incremental *R* values from 4 to 20 produced no significant minima in the σ vs. *R* curves, the R value was assumed to be $R = a + d$, where a is the sum of the ionic crystallographic radii and *d* is given by

$$d = 1.183(M/\rho_0)^{1/3} \quad (8)$$

where M is the molecular weight of the solvent and ρ_0 is its density.The values of Λ^0, K_A, and R obtained by this procedure are reported in Table 1.

Division of Limiting Equivalent Conductances: Limiting Ionic Equivalent Conductivities

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 Λ^0 values of Bu_4NBPh_4 using the following relationship:

$$\lambda^0(Bu_4N^+) = 0.517\,\Lambda^0(Bu_4NPh_4B) \qquad (9)$$

as described in the literature.[10,11]

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

$$\Lambda^0(Bu_4NBPh_4) = \Lambda^0(Bu_4NBr) + \Lambda^0(NaPh_4B) - \Lambda^0(NaBr) \qquad (10)$$

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

Ion Association Behaviour

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 298.15 to 318.15 K. This is expected because the relative parmittivities of the solvent mixtures are fairly high ($60.99 \leq \varepsilon \leq 75.09$).

The cosphere diameter (R) values for all the salts under study in the methanol-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: $\lambda^0_{Br^-} > \lambda^0_{Na^+} > \lambda^0_{Bu_4N^+} > \lambda^0_{Ph_4B^-}$ at each temperature indicating that the sizes of these ions as they exist in solutions follow the order: $Br^- < Na^+ < Bu_4N^+ < Ph_4B^-$. Another interesting observation is that the limiting ionic equivalent conductances of all ions decrease in going form 10 volume percent of methanol to 30 volume percent of methanol in the mixture at all temperatures investigated.

The limiting equivalent conductances of the electrolytes as well as the single-ion conductivity values increase appreciably with temperature.The effect of temperature on $\lambda^0_{Na^+}$ and $\lambda^0_{Br^-}$ ions is more pronounced as compaired to that as $\lambda^0_{Bu_4N^+}$ and $\lambda^0_{Ph_4B^-}$ in the present mixed solvent media.

References

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Table 1. Derived Conductivity Parameters of Electrolytes in Methanol-Water Mixtures Containing 10, 20 and 30 Volume Percent of Methanol at 298.15, 308.15, and 318.15 K

T(K)	Λ^0 (S.cm^2.mol^{-1})	K_A /(dm^3.mol^{-1})	R / $\mathring{A}$	σ%[a]
		10 Vol. % of Methanol		
		Bu_4NBr		
298.15	81.16 ± 0.07	2.72 ± 0.06	9.99	0.10
308.15	95.30 ± 0.07	3.20 ± 0.05	10.09	0.08
318.15	114.75 ± 0.28	3.81 ± 0.18	10.18	0.27
		$NaPh_4B$		
298.15	66.87 ± 0.02	4.88 ± 0.04	9.50	0.01
308.15	75.45 ± 0.02	4.83 ± 0.05	9.59	0.01
318.15	91.86 ± 0.02	5.79 ± 0.03	9.68	0.01
		NaBr		
298.15	114.46 ± 0.04	1.41 ± 0.01	5.95	0.05
308.15	134.88 ± 0.05	1.50 ± 0.02	5.95	0.05
318.15	163.50 ± 0.07	1.61 ± 0.02	5.96	0.05
		20 Vol. % of Methanol		
		Bu_4NBr		
298.15	65.56 ± 0.05	2.74 ± 0.05	10.09	0.08
308.15	79.87 ± 0.06	2.34 ± 0.05	10.09	0.09
318.15	100.19 ± 0.09	2.40 ± 0.06	10.10	0.10
		$NaPh_4B$		
298.15	53.14 ± 0.02	4.87 ± 0.06	9.59	0.01
308.15	67.33 ± 0.19	4.16 ± 0.06	9.59	0.07
318.15	85.18 ± 0.02	5.30 ± 0.03	9.68	0.01
		NaBr		
298.15	93.85 ± 0.04	1.41 ± 0.02	6.04	0.05
308.15	118.20 ± 0.08	1.82 ± 0.03	6.04	0.08
318.15	153.22 ± 0.12	3.38 ± 0.04	6.05	0.08
		30 Vol. % of Methanol		
		Bu_4NBr		
298.15	59.94 ± 0.04	8.05 ± 0.06	10.18	0.05
308.15	71.05 ± 0.04	8.95 ± 0.05	10.18	0.04
318.15	93.08 ± 0.04	9.41 ± 0.04	10.19	0.03

Table 1. (contd..)

T(K)	Λ^0 (S.cm^2.mol^{-1})	K_A /(dm^3.mol^{-1})	R / $\mathring{A}$	σ%^{a}
		30 Vol. % of Methanol		
		$NaPh_4B$		
298.15	44.46 ± 0.02	6.25 ± 0.09	9.68	0.01
308.15	63.08 ± 0.05	6.44 ± 0.13	9.68	0.01
318.15	78.17 ± 0.03	6.28 ± 0.06	9.69	0.01
		NaBr		
298.15	83.67 ± 0.05	1.22 ± 0.03	6.13	0.07
308.15	106.55 ± 0.08	1.55 ± 0.04	6.13	0.08
318.15	142.04 ± 0.10	4.60 ± 0.04	6.14	0.07

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

Table 2. Limiting Ionic Conductances in Methanol-Water Mixtures Containing 10, 20 and 30 Vol. % of Methanol at 298.15, 308.15 and 318.15 K

T (*K*)	$\lambda^0_\pm$ (S.cm^2.mol^{-1})			
	Na^+	Bu_4N^+	Br^-	Ph_4B^-
		10 Vol. % of Methanol		
298.15	50.66	17.36	63.80	16.21
308.15	58.12	18.54	76.76	17.33
318.15	71.04	22.29	92.46	20.82
		20 Vol. % of Methanol		
298.15	41.14	12.85	52.71	12.00
308.15	53.32	14.99	64.88	14.01
318.15	69.65	16.62	83.57	15.53
		30 Vol. % of Methanol		
298.15	34.45	10.72	49.22	10.01
308.15	49.76	14.26	56.79	13.32
318.15	64.06	15.10	77.98	14.11

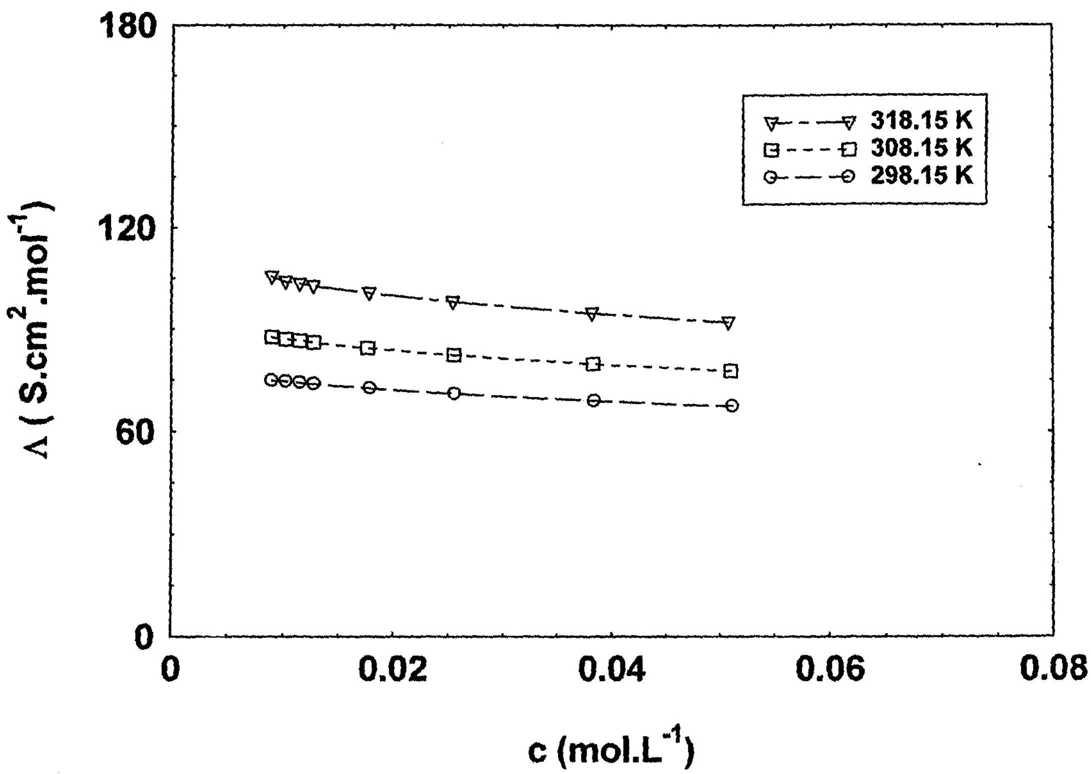

Fig. 1. Concentration dependence of the equivalent conductance of tetrabutylammonium bromide (Bu_4NBr) in methanol-water mixture containing 10 vol. % methanol at different temperatures.

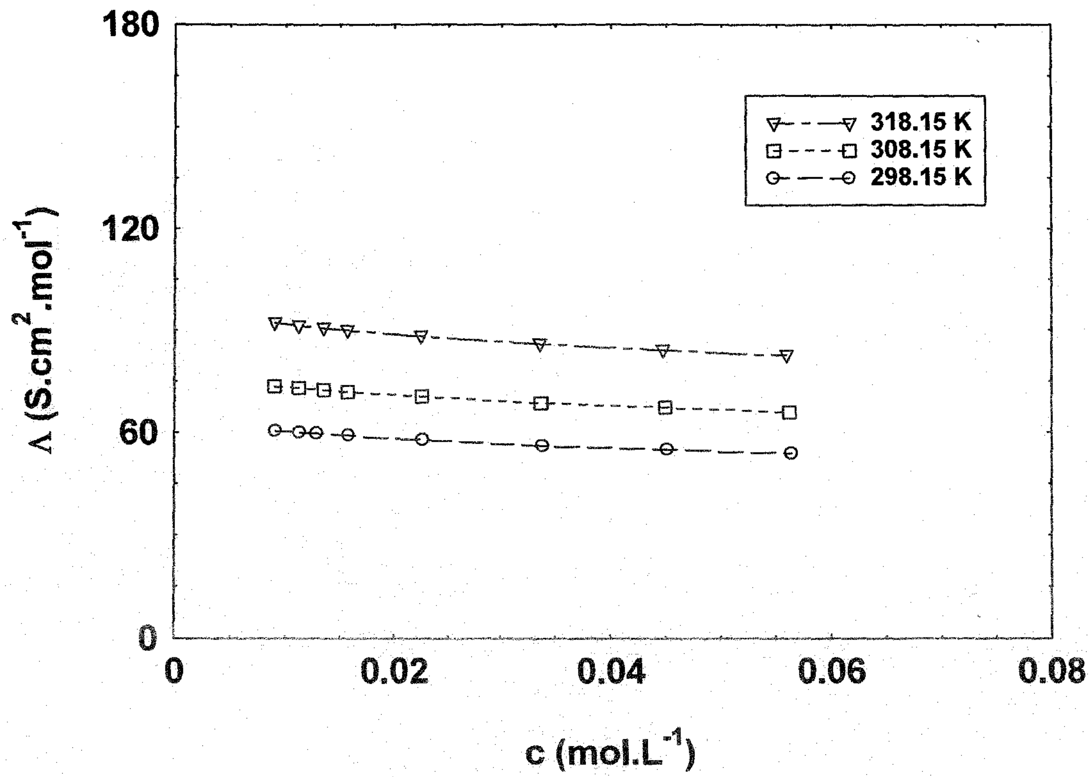

Fig. 2. Concentration dependence of the equivalent conductance of tetrabutylammonium bromide (Bu_4NBr) in methanol-water mixture containing 20 vol. % methanol at different temperatures.

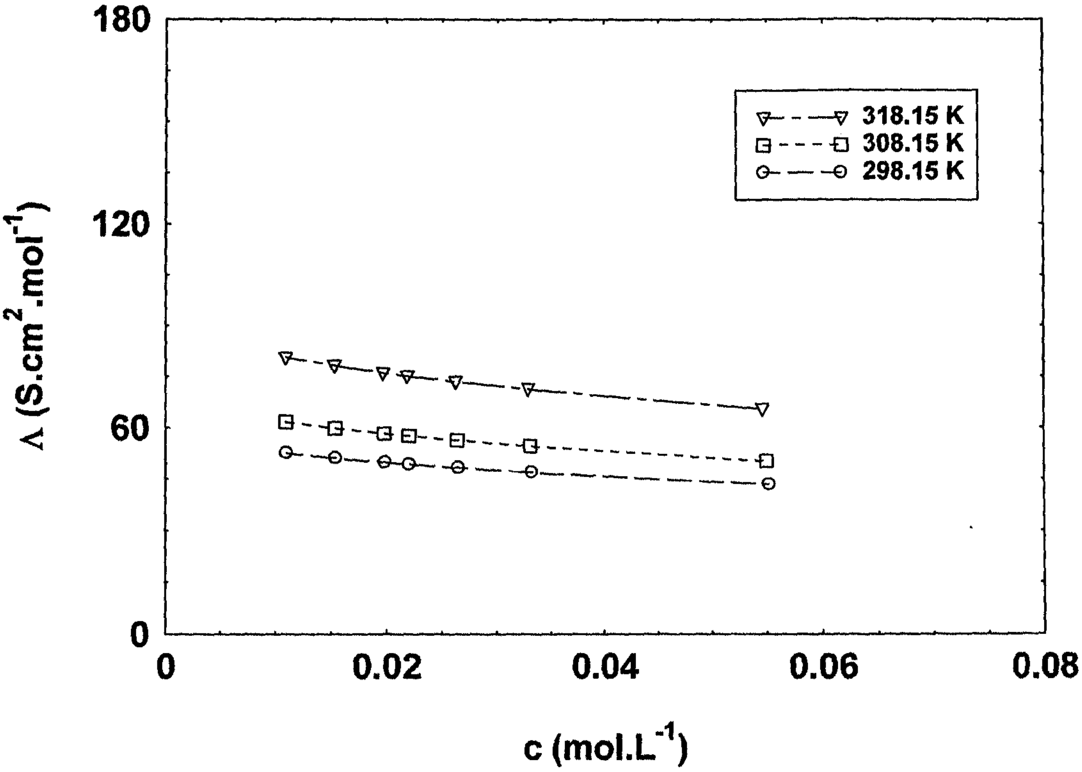

Fig. 3. Concentration dependence of the equivalent conductance of tetrabutylammonium bromide (Bu_4NBr) in methanol-water mixture containing 30 vol. % methanol at different temperatures.

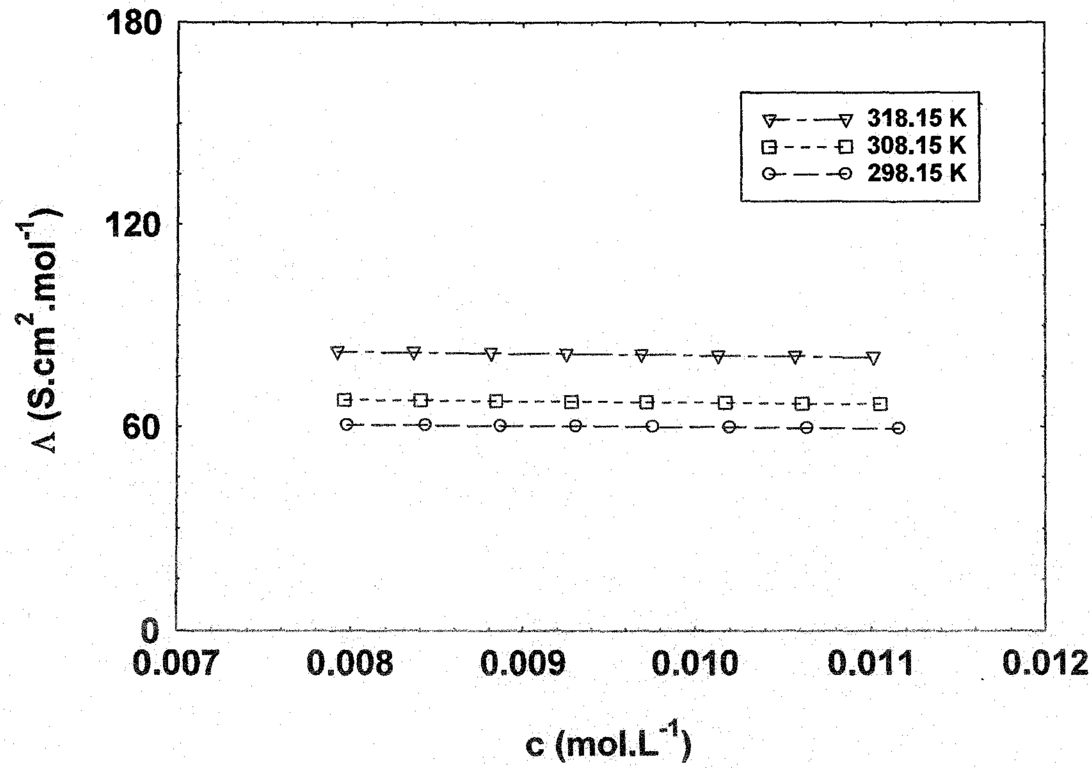

Fig. 4. Concentration dependence of the equivalent conductance of sodium tetraphenylborate ($NaPh_4B$) in methanol-water mixture containing 10 vol. % methanol at different temperatures.

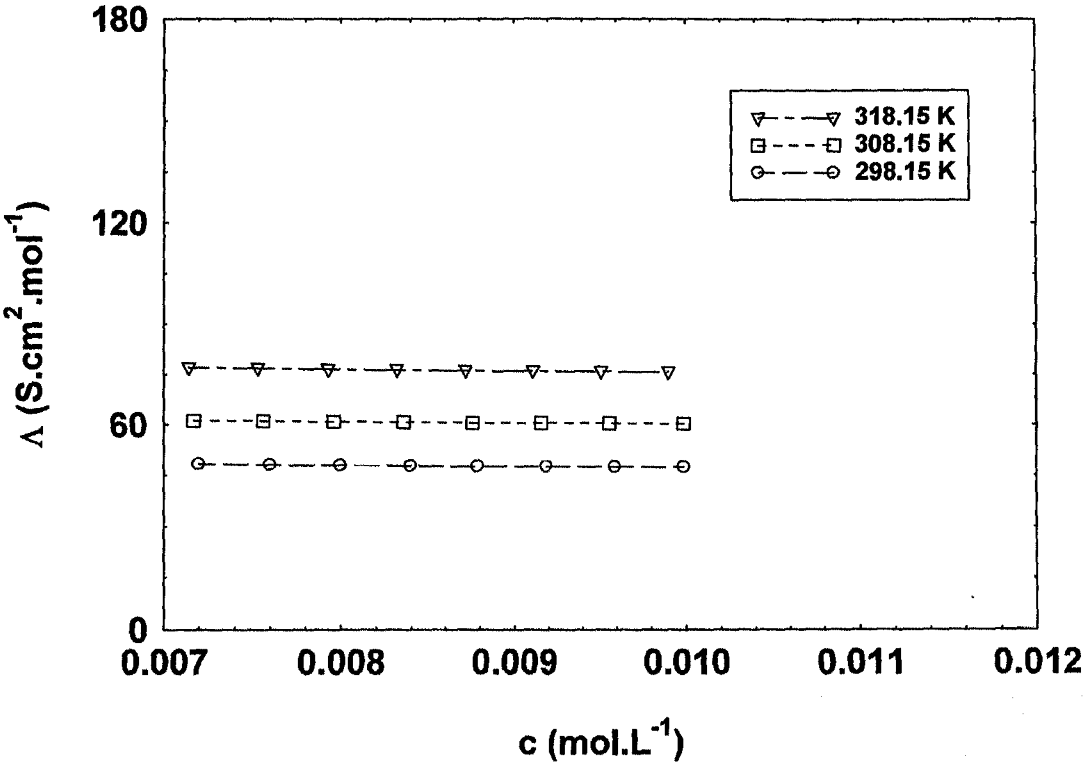

Fig. 5. Concentration dependence of the equivalent conductance of sodium tetraphenylborate ($NaPh_4B$) in methanol-water mixture containing 20 vol. % methanolat different temperatures.

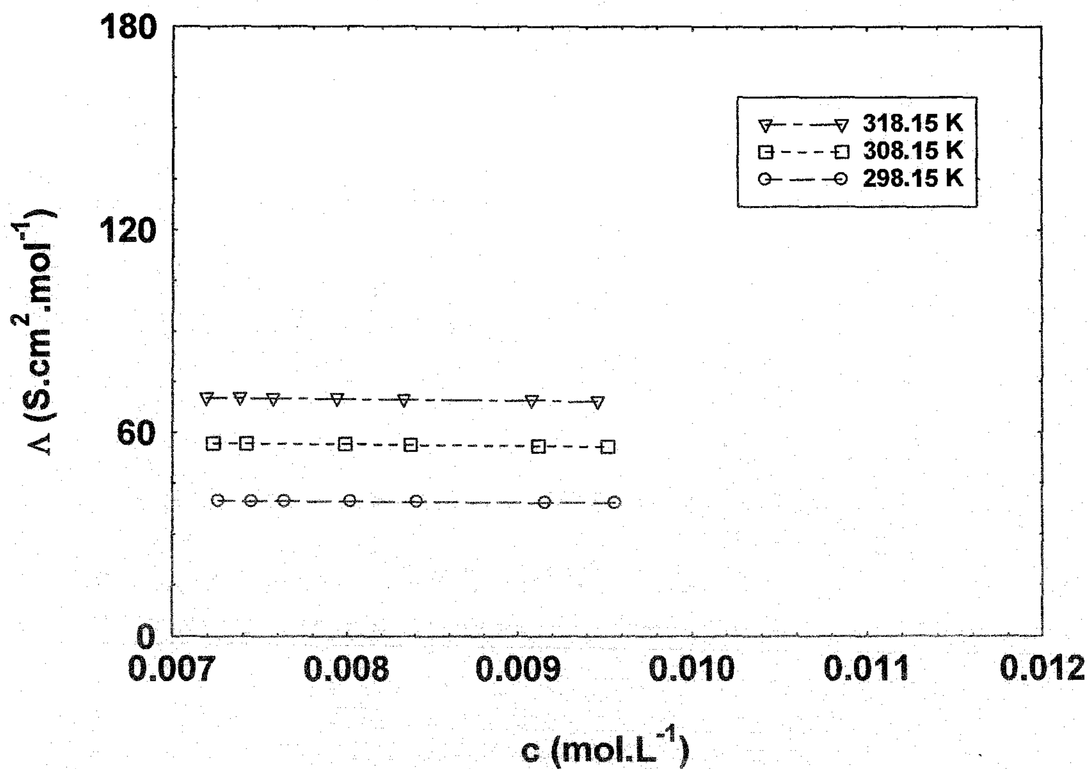

Fig. 6. Concentration dependence of the equivalent conductance of sodium tetraphenylborate ($NaPh_4B$) in methanol-water mixture containing 30 vol. % methanol at different temperatures.

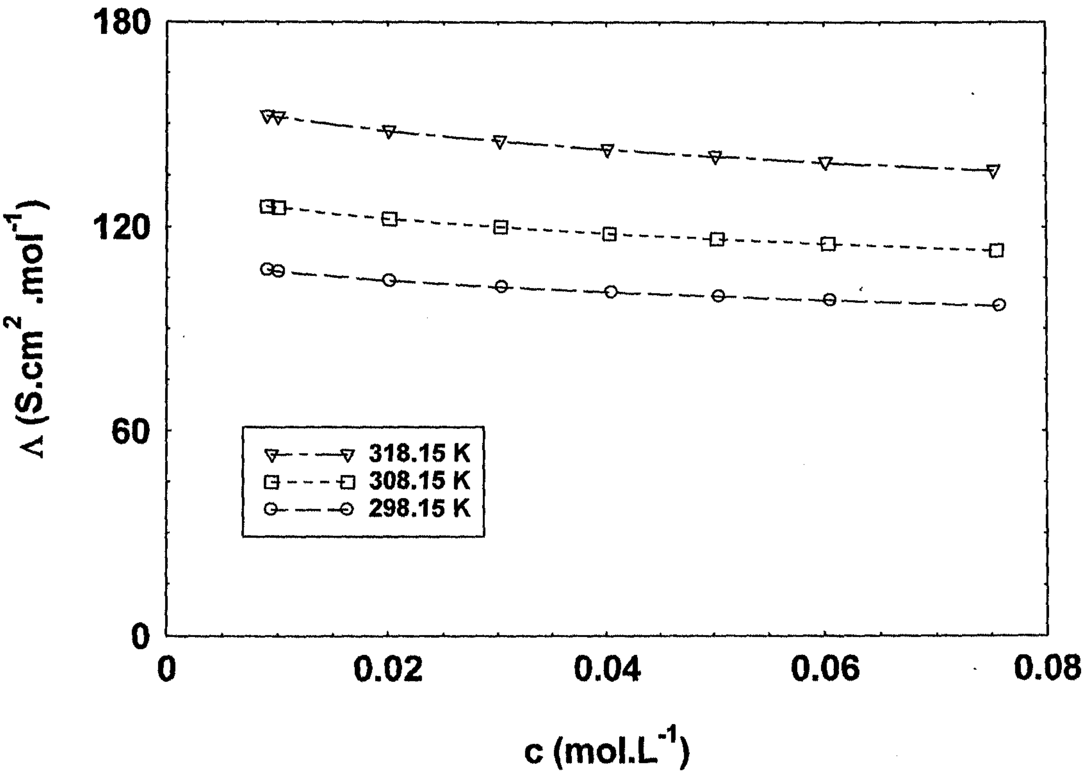

Fig. 7. Concentration dependence of the equivalent conductance of sodium bromide (NaBr) in methanol-water mixture containing 10 vol. % methanol at different temperatures.

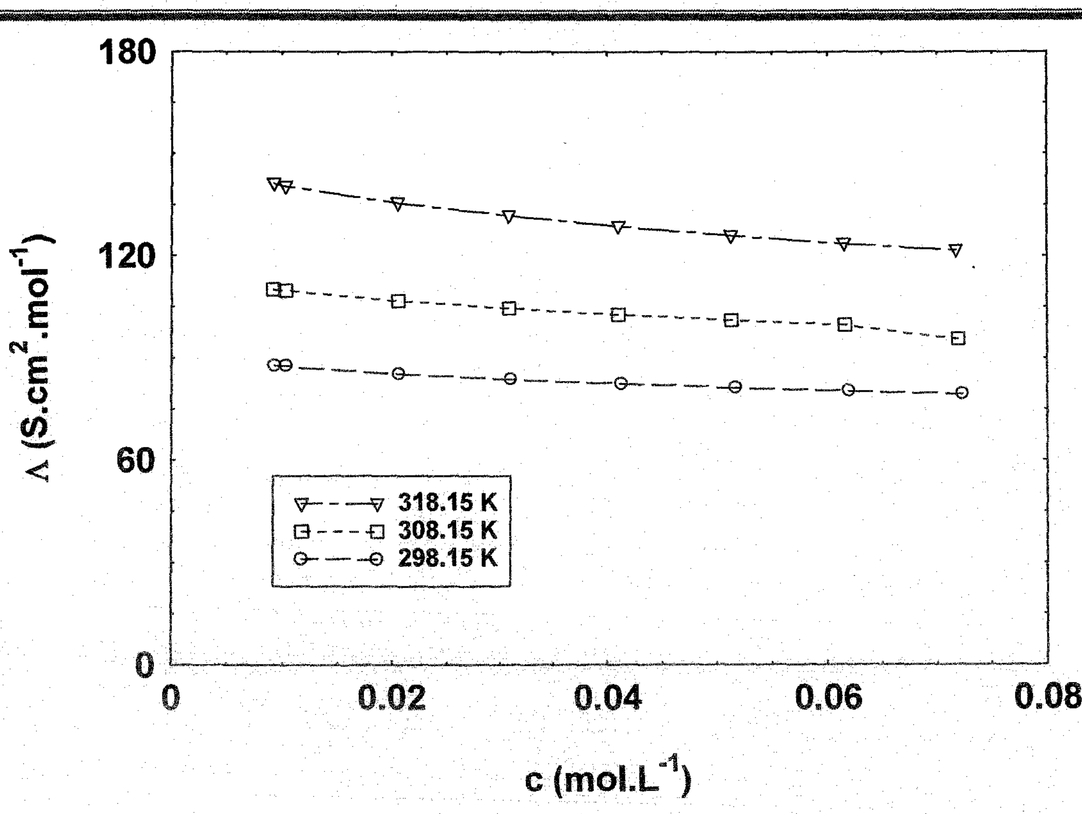

Fig. 8. Concentration dependence of the equivalent conductance of sodium bromide (NaBr) in methanol-water mixture containing 20 vol. % methanol at different temperatures.

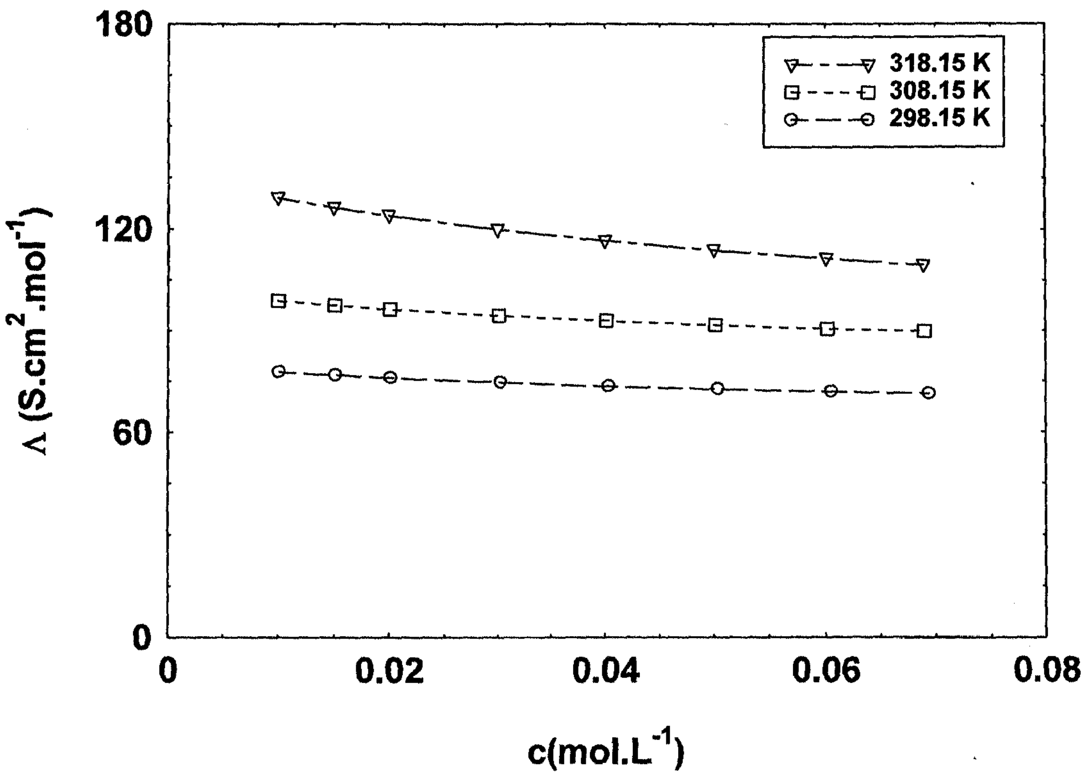

Fig. 9. Concentration dependence of the equivalent conductance of sodium bromide (NaBr) in methanol-water mixture containing 30 vol. % at different temperatures.