

Chapter X

Concluding Remarks

Polyelectrolytes show numerous interesting properties that are now being actively investigated in many laboratories. Many important information and concepts on aqueous polyelectrolyte solutions both in absence and in presence of low molar-mass electrolytes have been derived from studies on their electrical conductivity, viscosity and density. Moreover, studies on polyelectrolytes in presence of surfactants provide important information on polyelectrolyte-surfactant interactions. However, very little attention has been paid to polyelectrolyte solutions in absence as well as in presence of electrolytes and surfactants in mixed solvent media despite that fact that the study of polyelectrolytes in these media is important in the sense that such studies can offer insights into the understanding of fundamentals of polyelectrolytes; the effect of electrostatic interactions on the solution behaviour of polyelectrolytes can be investigated conveniently by varying the composition of the mixed solvent media and this is important in understanding the characteristic behaviour of polyelectrolytes. We have, therefore, investigated some transport and thermodynamic properties of sodium polystyrenesulfonate in acetonitrile-water mixed solvent media using the techniques mentioned above with special reference to polyelectrolyte-salt and polyelectrolyte-surfactant interactions with a view to obtain a precise information on the behavior of polyelectrolytes in such solutions.

Electrical conductivities provided valuable information on the condensation of counterions onto the polyion chain in salt-free solutions. A model put forward by Colby *et. al.* [*J. Polym. Sci. Part B: Polym. Phys.*, **35**, 2951 (1997)] using the scaling description proposed by Dobrynin *et. al.* [*Macromolecules*, **28**, 1859 (1995)] for the configuration of a polyelectrolyte chain in semidilute solution offered a sharp improvement over the Manning counterion condensation model. Electrical conductivities of the polyelectrolyte in presence of salts underlined the importance of various factors namely, electrophoretic countercurrent, solvodynamic interactions, salt-induced conformational changes in the polyion structure and hence a concomitant change in the apparent charge of the polyion *etc.* in polyelectrolyte solutions. The method of isoionic dilution has been successfully employed for determining the intrinsic viscosity and the Huggins constant of sodium in acetonitrile-water mixed solvent media. These were also obtained in presence of an excess of an added electrolyte where neutral polymer behaviour could be recovered. Viscosity studies shed light on the

coiling/expansion of the polyion chains in solvents with varying relative permittivities. The roles of electrostriction, solvophobicity and counterions condensation and their desolvation have been conveniently assessed from the partial molar volume studies. Studies on the influence of the solvent medium on the complexation of the present polyelectrolyte with a cationic surfactant, cetyltrimethylammonium bromide, and the aggregation of the surfactant molecules induced by the polyelectrolyte using conductometry and tensiometry provided important information on the polyelectrolyte-surfactant complexation and polyelectrolyte-induced aggregation behaviour.

However, it is necessary to remember that interactions in solutions containing polyelectrolytes are very complex in nature because of the coupling of the macromolecular properties with the electrolyte properties of these species. Investigation in mixed solvent media provide the opportunity to study the behaviour of polyelectrolyte solutions from a more general point of view compared to those in aqueous solutions since use of a series of mixed solvents corresponds to a gradual change in the relative permittivity of the media and hence in the interactions prevailing in these solutions. More extensive studies on the different thermodynamic and transport properties of a variety of polyelectrolytes both in absence and in presence of salts and surfactants in different mixed solvent media will be of immense help in understanding the nature of various interactions in polyelectrolyte solutions. A multi-method attack to this intricate problem - like the one presented here - might be very helpful in this regard.

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 $0.76570 \text{ g}\cdot\text{cm}^{-3}$ and a coefficient of viscosity of $0.3126 \text{ mPa}\cdot\text{s}$ 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 $10^{-6} \text{ S}\cdot\text{cm}^{-1}$ 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 literature² 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-workers⁴ using aqueous potassium chloride solutions. The measurements were made in a water bath maintained within $\pm 0.005 \text{ K}$ 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 (κ_j , Λ_j ; $j = 1, \dots, n$), 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 :

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

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

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

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

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

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

where R_X 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 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 β is twice the Bjerrum distance. The computations were performed on a computer using the program as suggested by Fuoss. The initial A^0 values for the iteration procedure were obtained from Shedlovsky extrapolation⁹ of the data. Input for the program is the set $(c_j, A_j; j = 1, \dots, n)$, n , ϵ , η , T , initial value of A^0 , and an instruction to cover a preselected range of R values.

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

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

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.

The values of A^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 A^0 values of Bu_4NBPh_4 using the following relationship:

$$\lambda^0(\text{Bu}_4\text{N}^+) = 0.517 A^0(\text{Bu}_4\text{NPh}_4\text{B}) \quad (8)$$

as described in the literature.^{10,11}

The limiting molar conductivity (A^0) of the "reference electrolyte" Bu_4NBPh_4 was obtained by considering the Kohlrausch rule that allows the calculation of the A^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:

$$\Lambda^0(\text{Bu}_4\text{NBPh}_4) = \Lambda^0(\text{Bu}_4\text{NBr}) + \Lambda^0(\text{NaPh}_4\text{B}) - \Lambda^0(\text{NaBr}) \quad (9)$$

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 permittivities of the solvent mixtures are fairly high ($57.32 \leq \epsilon \leq 67.94$).

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: $\lambda_{\text{Br}^-}^0 > \lambda_{\text{Na}^+}^0 > \lambda_{\text{Bu}_4\text{N}^+}^0 > \lambda_{\text{Ph}_4\text{B}^-}^0$ at each temperature indicating that the sizes of these ions as they exist in solutions follow the order: $\text{Br}^- < \text{Na}^+ < \text{Bu}_4\text{N}^+ < \text{Ph}_4\text{B}^-$. Another interesting observation is that the limiting ionic equivalent conductances of Na^+ and Br^- ions decrease in going from 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 from 20 to 40 volume percent 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

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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

$T(\text{K})$	$\Lambda^0 (\text{S cm}^2 \text{ mol}^{-1})$	$K_{\Lambda} / (\text{dm}^3 \text{ mol}^{-1})$	R / Λ^0	$\sigma\%$ ^a
20 Vol Percent of Acetonitrile				
Bu ₄ NBr				
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 ₄ B				
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

Table 1. continued

Table 1. continued

40 Vol Percent of Acetonitrile**Bu₄NBr**

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

NaPh₄B

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

$$^a \sigma \% = 100\sigma / A^0$$

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)	λ_{\pm}^0 (S cm ² mol ⁻¹)			
	Na ⁺	Bu ₄ N ⁺	Br ⁻	Ph ₄ B ⁻
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

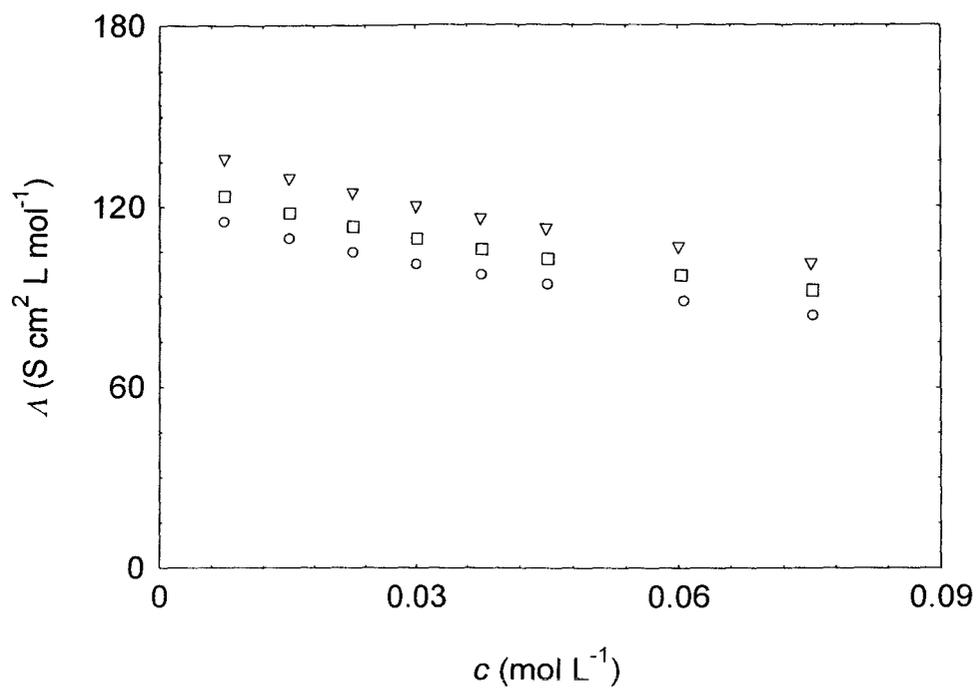


Figure 1. Concentration dependence of the equivalent conductance of tetrabutylammonium bromide (Bu_4NBr) in 20 volume percent acetonitrile-water mixture at different temperatures: (○) 308.15 K; (□) 313.15 K; (▽) 318.15 K.

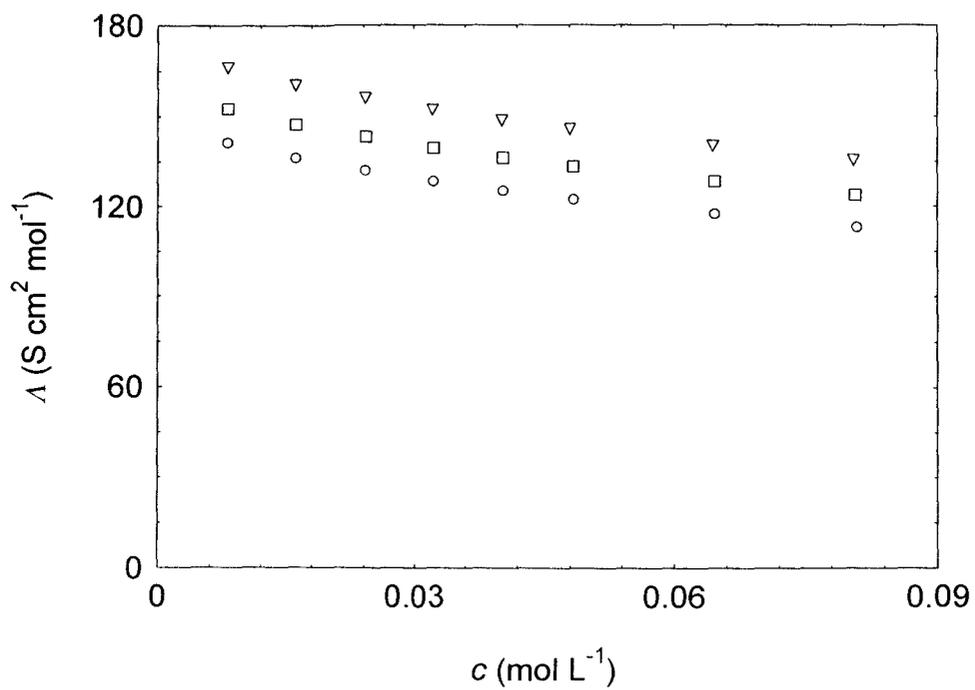


Figure 2. Concentration dependence of the equivalent conductance of sodium bromide (NaBr) in 20 volume percent acetonitrile-water mixture at different temperatures: (○) 308.15 K; (□) 313.15 K; (▽) 318.15 K.

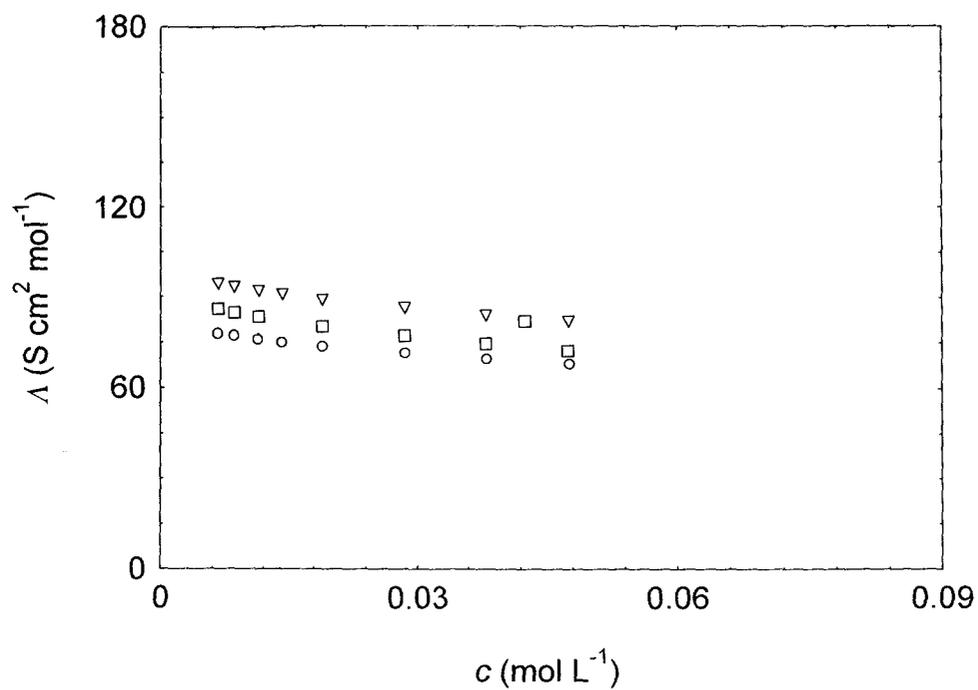


Figure 3. Concentration dependence of the equivalent conductance of sodium tetrphenylborate (NaPh_4B) in 20 volume percent acetonitrile-water mixture at different temperatures: (○) 308.15 K; (□) 313.15 K; (▽) 318.15 K.

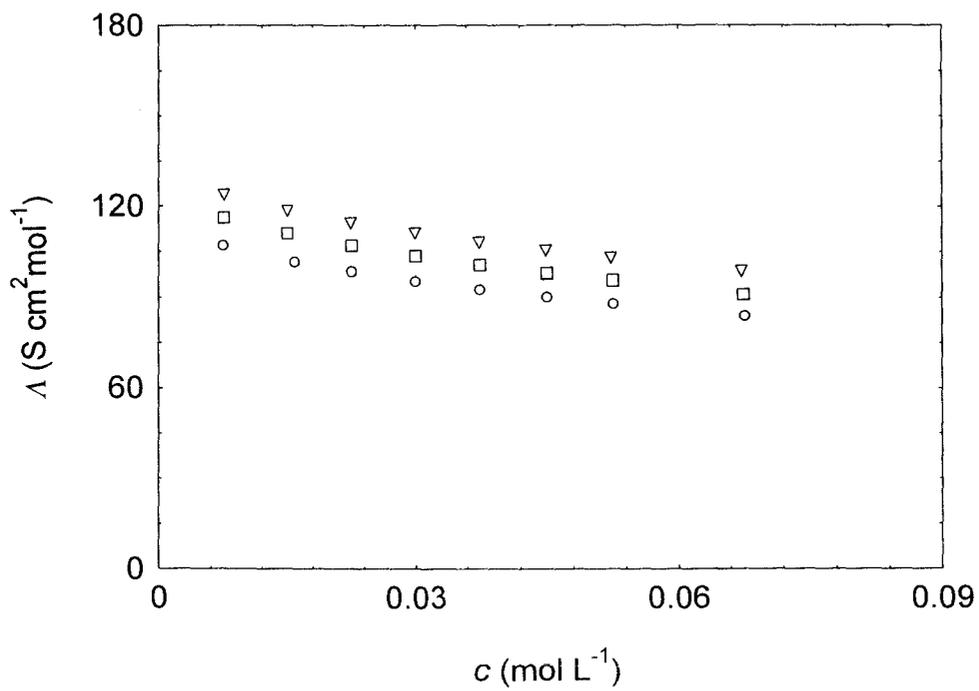


Figure 4. Concentration dependence of the equivalent conductance of tetrabutylammonium bromide (Bu_4NBr) in 40 volume percent acetonitrile-water mixture at different temperatures: (○) 308.15 K; (□) 313.15 K; (▽) 318.15 K.

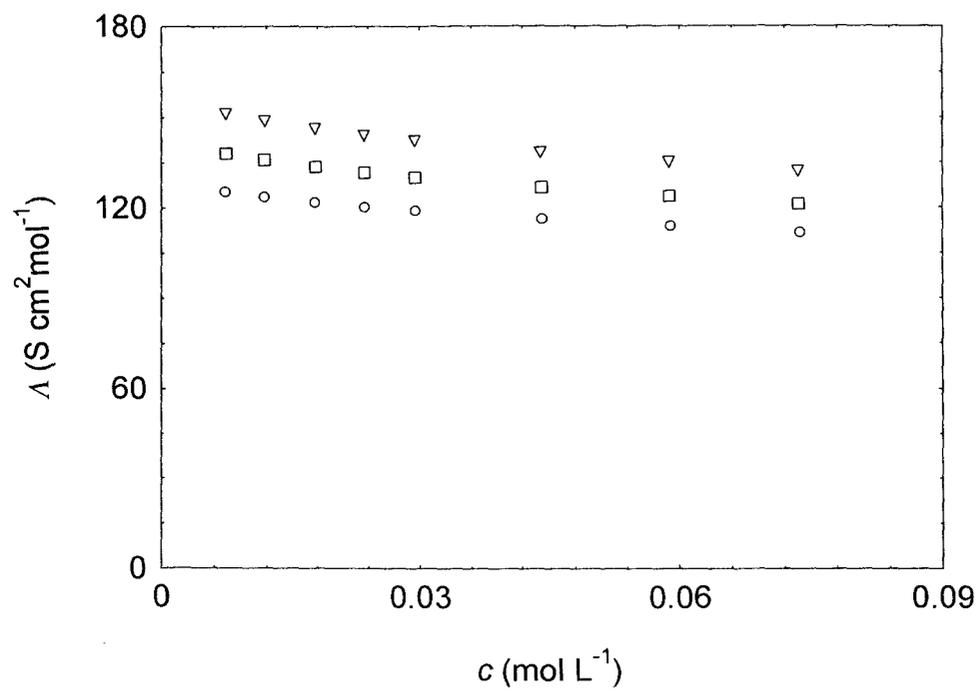


Figure 5. Concentration dependence of the equivalent conductance of sodium bromide (NaBr) in 40 volume percent acetonitrile-water mixture at different temperatures: (○) 308.15 K; (◻) 313.15 K; (◂) 318.15 K.

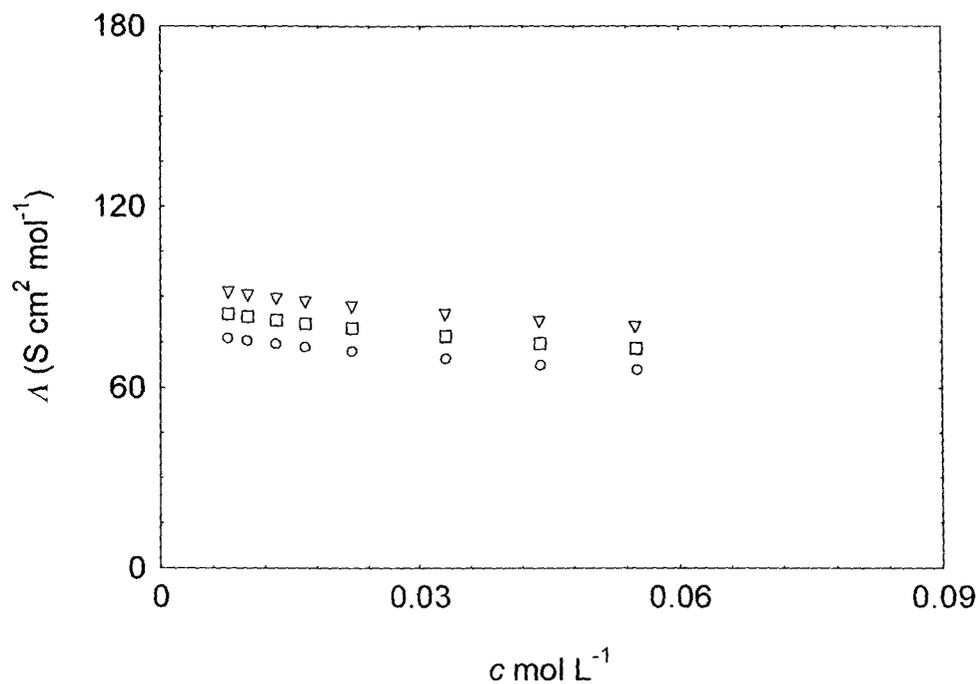


Figure 6. Concentration dependence of the equivalent conductance of sodium tetrphenylborate (NaPh_4B) in 40 volume percent acetonitrile-water mixture at different temperatures: (○) 308.15 K; (□) 313.15 K; (▽) 318.15 K.

Publications

List of Papers Published

1. Electrical Conductances of Tetrabutylammonium Bromide, Sodium Tetraphenylborate, and Sodium Bromide in Acetonitrile-Water Mixtures at 308.15, 313.15, and 318.15K , D. Ghosh and B. Das, *J. Chem. Eng. Data*, **49**, 1771 (2004).
2. Electrical Conductivity of Sodium Polystyrenesulfonate in Acetonitrile-Water Mixed Solvent Media: Experiment and Data Analysis Using the Manning Counterion Condensation Model and the Scaling Theory Approach, D. Ghosh, A. Bhattarai, and B. Das, *Colloid Polym. Sci.*, 287,1005 (2009).

Addendum / Corrigendum in the Thesis entitled "Studies on the Behaviour of Polyelectrolytes & their Interaction with Small Ion and Surfactant in Mixed Solvent" Submitted by Sri Debapratim Ghosh, M.Sc. of the Department of Chemistry, University of North Bengal, Darjeeling 734 013, India for the Degree of Doctor of Philosophy (Science) of the University of North Bengal

A. General Observations:

1. Chapter I presents a brief account of the works done in this dissertation while Chapter II provides an in-depth introduction and informative review of the subject matter of the thesis. Chapter IV describes a study on the conductivities of sodium polystyrenesulfonate (NaPSS) in salt-free acetonitrile-water mixed solvent media and their *quantitative* description by the present-day available model for semidilute polyelectrolyte conductivity, whereas Chapter V presents an analysis of the conductivity of NaPSS-NaCl-acetonitrile-water system on the basis of the so-called "*phenomenological*" approach to provide *qualitative* guidelines to the polyion-counterion interactions in presence of a salt. Chapter VI employs the method of *isoionic dilution* to maintain the intermolecular interactions at a constant level for the determination of the intrinsic viscosity of NaPSS, whilst Chapter VII revealed how the intermolecular interactions could be eliminated completely by adding an excess of an electrolyte to allow the determination of intrinsic viscosities. For better clarity of presentations, the pair of chapters (I and II), (IV and V), and (VI, VII) have been presented separately since each one of a pair deals with different aspects. The chapters have been written as self-sufficient articles maintaining at the same time their federal existence in the dissertation and, that is why each has its own experimental section. Analyses of the conductivity data of the NaPSS in absence and in the presence of a salt (*cf.* Chapters IV and V) require information on the limiting ionic equivalent conductances of the counterion in acetonitrile-water mixtures and the latter have been obtained from a separate measurement of the electrical conductances of appropriate salts in acetonitrile-water mixtures and analysis using suitable equations applicable for salt solutions (Annexure I). Since the present dissertation deals with the behaviour of polyelectrolytes, studies on the electrical conductances of salts in acetonitrile-water mixtures have been reported separately as an annexure so that it would not hamper the spirit and the continuity of the results presented for the polyelectrolyte system under investigation.
2. Equivalent conductivities of salt-free NaPSS in water have been referred to and compared with the data presented here in the mixed solvent media (*cf.* page 61, lines 9-16). The conductivity results with the same molecular weight of NaPSS as that used within the premises of the present dissertation are not, however, available in the literature in aqueous NaCl solutions. Moreover, the viscosity and density data with appropriate molecular weight of NaPSS are also not available in the literature in aqueous or in brine solutions. The available values of the *cmc*s of aqueous CTAB have been shown (page 144, lines 1-2) and due reference has been made to the literature sources.

3. In Chapters VI and VII, all basic viscosity data (from which all other parameters were evaluated) have been shown in the Figures.
4. All information on the molecular interactions obtained from the variations of the Huggins constants has been reported in the text of Chapter IX (page 100, lines 24-26; page 101, lines 2-5; page 101, lines 15-17) based on the concept described in the literature (reference 19 of Chapter IX).

B. Some Critical Comments:

1. There have been some inadvertent mistakes in the dissertation. The precisions of the temperature and density measurements would be one order of magnitude higher than those reported. The precision of the viscosity measurements was always within two percent. Although the viscosity values are, in a large number of cases, reported upto three decimal places, studies reporting the viscosity values upto four decimal places are not uncommon [e.g., *Z. Phys. Chem.*, **138**, 185 (1983); *J. Chem. Soc., Faraday Trans. 1*, **84**, 3877 (1988); *J. Chem. Soc., Faraday Trans. 1*, **85**, 4227 (1989); *J. Chem. Soc., Faraday Trans. 1*, **86**, 2225 (1990); *J. Chem. Eng. Data*, **44**, 6 (1999)].
2. Page 67, Table 1: The large departure of the experimental equivalent conductances from those calculated according to the Manning model is amply signified by the very high values of the standard deviations reported within the parentheses.
3. The *cmc* values of CTAB in acetonitrile-water systems have not been reported earlier and hence a comparison of the values reported here with the literature values is not possible. It may be noted that the *cmc* values obtained in the present study have been reported upto two decimal places (*cf.* page 150, Chapter IX, Table 1). The *cmc* values (reported upto three decimal places) shown in line 1 of page 144 are those taken from the literature (the value of 1.0900 should be read as 1.090; it has been a typographical error) [reference 11 of Chapter IX]. The effect of the presence of acetonitrile in water and its role in the process of aggregation of CTAB induced by NaPSS in mixed solvents has been described at length (page 146, lines 16-28).

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