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Electrical Conductivity of a Semidilute Polyelectrolyte in Mixed Solvent Media

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Abstract

The electrical conductivity of solutions of sodium salt of polystyrenesulfonate in methanol-water mixed solvent media containing 8, 16, 25, and 34 weight per cent of methanol at 308.15, 313.15, 318.15 and 323.15 K was studied earlier. In that report, an attempt was made to interprete the results using the Manning Counterion condensation theory. Unfortunately, a major deviation of the theoretical prediction from the experimental results was noticed and the possible reasons for this discrepancy have been discussed. In this communication, the experimental conductivity have been analyzed on the basis of a new model for semi-dilute polyelectrolyte conductivity which takes into electrical conductivity of semi-dilute solutions of polyelectrolytes without added salt has been recently described by Colby *et al.*(1997) using the scaling description proposed by Dobrynin *et al.*(1995) for the configuration of a polyelectrolyte chain in semi-dilute solution. The predictions are found to be compared favorably well with the observed conductivity over the whole range of concentrations investigated.

Key Words: conductivity, counterion, condensation, semi-dilute, Manning theory

Introduction

Polyelectrolytes are polymers with ionizable groups. When they are dissolved in aqueous or mixed solvent these groups dissociate, leaving ions on the chain and counterions in the solution. The specific conductance and the equivalent conductivity, Λ, are experimentally determined parameters which are suitable to describe the electrolytic transport properties of polyelectrolyte solutions because these properties take into account the movement of any charged entity present in the system under the influence of an externally applied electric field.

Inspite of various attempts by different investigators, a completely satisfactory theory to describe the electrolytic conductivity of polyelectrolyte solutions has not yet been developed (Mandel 1988, Leeuven *et al.* 1991, Wandrey 1997).

However, the description of different electrical properties of polyions in aqueous solutions and of their interactions with counterions is generally based on the Manning counterion condensation theory (Manning a.b 1969, 1975, 1981) that, under some aspects, can be considered equivalent to the Poisson-Boltzmann cylindrical cell model (Katchalsky 1971, Stigter 1975, Mandel 1992, Le Bret & Zimm. 1984). Within this model, the polyion is represented as an infinitely long charged line, small ions (counterions) are assumed to form an ionic atmosphere whose density depends on the frame of the polyion and their interactions with the charged polyions groups are purely Coulombic, so that the screening effect extends over the Debye length. The uncondensed mobile ions are treated in the Debye-Hückel approximation. The solvent is assumed to be a continuous medium characterized by a spatially uniform dielectric constant. Interactions among polyions are neglected, the theory being addressed to highly diluted solutions. The basic idea is that if the charge density (ξ) of the rod exceeds a critical value, some charges on the chain can be partially neutralized by one of the free ions in the solution, which means that the repulsion Coulombic energy of two adjacent unit charges on the chain must be smaller than the thermal energy k_BT. On the basis of these assumptions, this approach has been successfully applied to different polyelectrolyte systems, and numerous experiments have strongly suggested the validity of this model (Shaaban *et al.* 1994, Penafiel & Litovitz 1992, Kuznetsov *et al.* 1991, Kwak & Hayes 1975, Szymczac *et al.* 1975, Kozak *et al.* 1971, Kwak *et al.* 1978).

According to the Manning counterion condensation theory, polyelectrolytes can be characterized by the linear charge density parameter defined by (Manning 1969, 1972, Oosawa 1971)

$$\xi = \frac{e^2}{bDk_BT} \tag{1}$$

where e is the protonic charge, D the relative permitivity of the medium, b the spacing between charged groups taken along the axis of the polyion chain, k_B the Boltzman constant and T the temperature in absolute scale. This theory states that if $\xi > 1$, enough counterions condense on to the polyion to yield the critical value $\xi = 1$. If, on the other hand, $\xi < 1$, ionization takes place to reach this critical value. A limiting law of electrical conductivity for a salt free polyelectrolyte solution is related to ξ by the following equation (Manning 1969, 1972, 1970)

$$\Lambda = f(\lambda_c^0 + \lambda_p) \tag{2}$$

where λ_c^0 and λ_p are the limiting ionic equivalent conductivity of the counterion and the equivalent conductivity of the polyion at a finite concentration, respectively, and f is counterion–polyion interaction parameter given by(Manning 1969,1972,Oosawa 1971)

$$f = \frac{0.866}{\xi} \tag{3}$$

In contrast to Huizenga *et al.* 1950 where the counterions are regarded either as "bound" or as "free" implying that they are not influenced by the polyion, Manning assumed that while the condensed counterions, certainly qualify as bound, the fraction of such ions is $1-\xi^{-1} \neq 1-f$, the uncondensed counterions may, in no way, be thought of as free, being subjected to the Debye-Hückel potential of the polyions. Thus f does not have the significance of free counterions rather it represents the fraction of uncondensed counterions. Considering electrophoretic and relaxation contributions to the equivalent conductivity, λ_p has been derived theoretically for the cylinder model of polyelectrolyte (Manning 1975), and it follows for counterions with a charge of z_c

$$\lambda_p = \frac{279A|z_c|^{-1}|\ln \kappa a|}{1 + 43.2A(|z_c|\lambda_c^0)^{-1}|\ln \kappa a|} \tag{4}$$

where the parameter a is the radius of the polymer chain, while

$$A = \frac{Dk_BT}{3\pi\eta_0 e} \tag{5}$$

with η_0 being the coefficient of viscosity of the solvent. In eq. 4, κ is the Debye screening constant, which is defined by

$$\kappa^2 = \frac{4\pi . e^2}{Dk_BT}\xi^{-1} n_e |z_c| \tag{6}$$

where n_e is the stoichiometric equivalent polyion concentration (monovalent charged groups per unit volume).

Materials and Methods

Methanol (E. Merck, India, 99% pure) was distilled with phosphorous pentoxide and then redistilled over calcium hydride. The purified solvent had a density of 0.7772 g.cm^{-3} and a co-efficient of viscosity of 0.4742 mPa.s at 308.15 K; these values are in good agreement with the literature values (Moumouzias *et al.*1991). Triply distilled water with a specific conductance less than 10^{-6} S.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 308.15, 313.15, 318.15, and 323.15 K are reported in Table 1. The relative permittivity of methanol-water mixtures at the experimental temperatures were obtained by regressing the relative permittivity data as function of solvent composition from the literature (Albright & Gasting 1946) and are included in Table 1.

Sodium polystyrenesulphonate (NaPSS) employed in these investigations was purchased from Aldrich Chemical Company, Inc. The average molecular weight (M_w) of the sample was *ca*. 70,000.

Table 1. Properties of Methanol-Water Mixtures Containing 8, 16, 25, and 34 Weight Per Cent of Methanol at 308.15, 313.15, 318.15, and 323.15 K and the Corresponding λ_c^0 Values of the Sodium Ion

T/*K*	ρ_0 /g.cm^{-3}	η_0 / mPa.s	**D**	λ_c^0 / S.cm^2.mol^{-1}
		8 per cent methanol		
308.15	0.9797	0.8665	71.57	58.12
313.15	0.9780	0.7752	69.99	63.86
318.15	0.9760	0.7017	68.18	71.06
323.15	0.9741	0.6375	66.45	79.52
		16 per cent methanol		
308.15	0.9663	1.0217	68.14	53.32
313.15	0.9641	0.9091	66.63	60.88
318.15	0.9616	0.8075	64.80	69.65
323.15	0.9588	0.7300	63.15	76.78
		25 per cent methanol		
308.15	0.9516	1.1418	64.25	49.76
313.15	0.9490	1.0084	62.81	57.01
318.15	0.9463	0.8957	60.99	64.06
323.15	0.9433	0.8052	59.41	73.55
		34 per cent methanol		
308.15	0.9310	1.2034	60.34	47.52
313.15	0.9300	1.0503	58.94	52.85
318.15	0.9254	0.9309	57.18	59.20
323.15	0.9234	0.8288	55.62	66.02

Table 2. Best Fitted '*A*' in Methanol-Water Mixtures at 308.15, 313.15, 318.15 K, and 323.15K; respective standard deviation value (sd)

wt% of methanol	*T* = 308.15 K		*T* = 313.15 K		*T* = 318.15 K		*T* = 323.15 K	
	sd	best fitted"A"	sd	best fitted"A"	sd	best fitted"A"	sd	best fitted"A"
8	2.4446	3.86	3.6811	4.30	2.4888	4.18	3.7284	4.00
16	2.9481	3.95	3.7697	4.25	3.1757	4.19	3.7563	4.21
25	2.3839	4.15	2.4309	4.35	3.2640	4.40	3.0669	4.42
34	1.1401	4.22	2.0968	4.43	2.2782	4.53	1.9132	4.71

Conductance measurements were carried out on a Pye-Unicam PW 9509 conductivity meter at a frequency of 2000 Hz using a dip-type cell with a cellconstant of 1.15 cm^{-1} and having an uncertainty of 0.01%. The cell was calibrated by the method of Lind and co-workers (Lind *et al.* 1957) using aqueous potassium chloride solution. 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 (Das & Hazra 1992, 1995).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 polyelectrolyte 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 three replicates.

Results and Discussion

It is noteworthy that the Manning theory does not contain any adjustable parameter, and despite its simplicity, the main results based on this model (Manning a, b 1969, Mandel *et al.*1984, de Gennes 1980) are fairly well satisfied by the experimental data mainly for colligative properties, although they are valid only at infinite dilution. Since the Manning theory applies, as stated above, to highly diluted systems where polyion-polyion interactions are assumed to be absent and to polyions modeled as a linear array of point charges, its validity is limited to very low concentration regimes of polyelectrolyte solutions. Up to now, the electrical conductivity has been repeatedly measured for a great variety of polyelectrolytes (Bhattarai *et al.* 2006, Nagasawa *et al.* 1972, Kwak *et al.* 1975, Kwak and Johnston, 1975, Szymczak *et al.* 1975, Kwak *et al.* 1978, Vink 1984, Rios *et al.* 1993, Abramovic and Klofutar 1997, Rios 2001, Liu *et al.*1999, Wandrey 1999). In most of these cases, the concentrations are far from being very dilute and primarily the semidilute solutions ($c > c^*$) have been studied. The application of the Manning model to these systems is, however, less straightforward because these semi-dilute macroions do not assume a fully stretched conformation in solution. Even then some studies (Kwak & Hayes1975) reported close agreement between experiment and the Manning theory in the semi-dilute regime. However, these surprising results should not be over interpreted, since the underlying reason is nothing but a fortuitous cancellation of two opposing contributions of approximately the same size, which are not contained in the limiting law. Careful measurements (Bhattarai *et al.* 2006, Kwak and Hayes 1975, Szymczak *et al.* 1975, Rios *et al.* 1993, Abramovic and Klofutar 1997, Rios 2001, Liu *et al.* 1999) of the electrical conductivity of aqueous salt-free polyelectrolyte solutions demonstrated a major deviation of the experimental results from the Manning theory.

A new model for the electrical conductivity of semidilute solutions of polyelectrolytes without added salt has been recently proposed by (Colby *et al.* 1997) using the scaling description proposed by (Dobrynin *et al.* 1995) for the configuration of a polyelectrolyte chain in semi-dilute solution.

In the semi-dilute solutions, the polyion chain is modeled as a random walk of N_ξ correlation blobs of size ξ_0, each of them containing g monomers. Each blob bears an electric charge $q_\xi = zefg$ (z being the counterion valence and e is the electronic charge) and the complete chain, of contour length $L = N_\xi\, \xi_0$, bears a charge $Q_p = N_\xi\, q_\xi = zefg\, N_\xi$. Due to the strong electrostatic interactions within each correlation blob, the chain is a fully extended conformation of g_e electrostatic blobs of size ξ_e. This means that for length scales less than ξ_0, the electrostatic interactions dominate (and the chain is a fully extended conformation of electrostatic blobs of size ξ_e), and for length scales greater than ξ_0, the hydrodynamic interactions are screened and the chain is a random walk of correlation blobs of size ξ_0.

Within this model, in absence of added salt, the equivalent conductivity of a polyion in a semi-dilute solution is given by

$$\lambda_p = \frac{Fzefg \ln(g/g_e)}{3\pi\eta_0\xi_0} \tag{7}$$

where F is the Faraday number and η_0 is the coefficient of viscosity of solvent.

Under the condition of $g/g_e = \xi_0/\xi_e$ and making use of the fact that the electrostatic blobs are space filling ($g = c\xi_0^3$, c being the number density of monomers) Eq. 7 reduces to

$$\lambda_p = \frac{Fzefc\xi_0^2 \ln(\xi_0/\xi_e)}{3\pi\eta_0} \tag{8}$$

The equivalent conductance of the polyelectrolyte solution is then given by

$$\Lambda = f\left[\lambda_c{}^0 + \frac{Fzefc\xi_0^2 \ln(\xi_0 / \xi_e)}{3\pi\eta_0}\right] \tag{9}$$

The above expression given by (Colby *et al.* 1997) is derived taking into account the scaling arguments proposed by (Dobrynin *et al.* 1995) neglecting the hydrodynamic interactions (Kirkwood model) between the single structural units i.e., the correlation blobs and neglecting the asymmetry field effect. As can be seen the above model has a single free parameter *f,* the fraction of uncondensed counterions that defines the degree of the effectively ionized groups along the chain, in the scheme of the Manning counterion condensation theory. Whereas the Manning theory applies to polyelectrolyte solutions in the highly diluted regime and predicts a fraction of condensed counterions independent of the polymer concentration given by the value of the charge-density parameter $\xi = \lambda_B / b$. This model, which is based on the scaling theory approach, has been applied, so far, to a limited number of aqueous polyelectrolytes(Bordi *et al.* 2004) and the good agreement with the experimental conductivity results is very encouraging.

Here we present a study on the electrical conductivity of the semi-dilute solutions of sodium polystyrenesulfonate in methanol-water mixed solvent media at four different temperatures keeping in mind the failure of the Manning model in explaining our experimental findings (Bhattarai *et al.* 2006) we analyzed our experimental data according to the model derived from the scaling concept. This is, in fact, the first report on the application of the scaling theory approach to semi-dilute polyelectrolyte conductivity in mixed solvent media. The influence of concentration, medium, and temperature on the mobility of the polyelectrolyte species will also be investigated.

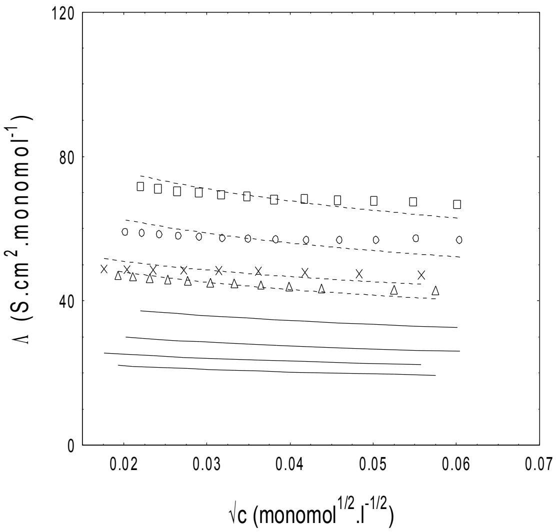

Fig.1. Comparison of the experimental values of the equivalent conductivity (Λ) of solutions of sodium polystyrenesulphonate with those predicted on the basis of the Manning counterion condensation theory and on the basis of the scaling theory at 308.15 K: Experimental values: squares, 8 per cent methanol; circles, 16 per cent methanol; crosses, 25 per cent methanol, triangles, 34 per cent methanol; Manning theory : solid lines for 8, 16, 25 and 34 per cent methanol respectively from top to bottom; Scaling theory with best fitted A: broken lines.

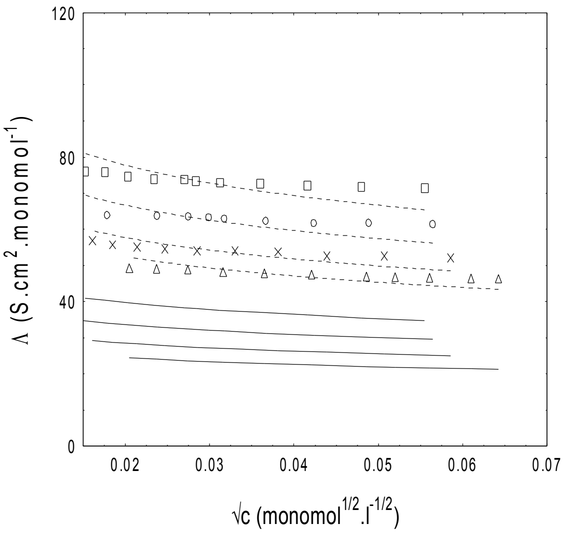

Fig. 2. Comparison of the experimental values of the equivalent conductivity (Λ) of solutions of sodium polystyrenesulphonate with those predicted on the basis of the Manning counterion condensation theory and on the basis of the scaling theory at 313.15 K: Experimental values: squares, 8 per cent methanol; circles, 16 per cent methanol; crosses, 25 per cent methanol, triangles, 34 per cent methanol; Manning theory : solid lines for 8, 16, 25 and 34 per cent methanol respectively from top to bottom; Scaling theory with best fitted A: broken lines.

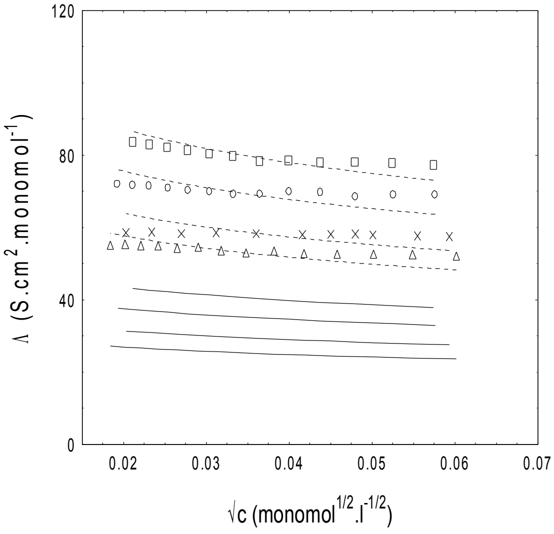

Fig. 3. Comparison of the experimental values of the equivalent conductivity (Λ) of solutions of sodium polystyrenesulphonate with those predicted on the basis of the Manning counterion condensation theory and on the basis of the scaling theory at 318.15 K: Experimental values: squares, 8 per cent methanol; circles, 16 per cent methanol; crosses, 25 per cent methanol, triangles, 34 per cent methanol; Manning theory : solid lines for 8, 16, 25 and 34 per cent methanol respectively from top to bottom; Scaling theory with best fitted A: broken lines.

Graphical representation of the experimental *Λ* values (points), the Manning predictions (solid lines) and calculated values based on Colby model values (broken lines) are included in Figures 1– 4 at 308.15, 313.15, 318.15 and 323.15 K in methanol-water mixtures. The experimentally obtained equivalent conductivities have always been found to be considerably higher than the theoretical values calculated following the Manning model. The reason for the failure of the Manning model can be understood if one estimates the overlap concentration (c*) for the polymer chain investigated using the following equation (Wandrey and Langmuir 1999)

$$c^* = \frac{1}{N_A L^2 a} \qquad (10)$$

where L is the contour length and the other symbols have their usual significance. It is observed that the polymer solutions in the present study are essentially in the semi-dilute regime where the Manning limiting law does not apply.

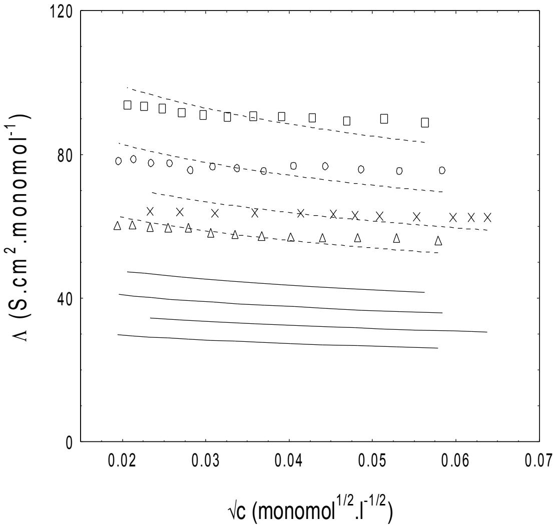

Fig. 4. Comparison of the experimental values of the equivalent conductivity (Λ) of solutions of sodium polystyrenesulphonate with those predicted on the basis of the Manning counterion condensation theory and on the basis of the scaling theory at 323.15 K: Experimental values: squares, 8 per cent methanol; circles, 16 per cent methanol; crosses, 25 per cent methanol, triangles, 34 per cent methanol; Manning theory : solid lines for 8, 16, 25 and 34 per cent methanol respectively from top to bottom; Scaling theory with best fitted A: broken lines.

We, therefore, have taken the recourse of the approach proposed by (Colby *et al.* 1997) for semi-dilute polyelectrolyte solutions, for analysis of our conductivity data.

Since the present methanol-water mixtures are poor solvent for the uncharged polymer sodium polystyrenesulfonate, the electrostatic blob is collapsed into a dense globule, we use a value of $8A^0$ as the effective monomer size (b) as suggested by (Colby *et al.* 1997) while analyzing the data on the basis of the Colby model (Colby *et al.* 1997).

Under poor solvent condition, the electrostatic blob size (ξ_e) and the correlation blob size (ξ_0) are given by (Colby *et al.* 1997)

$$\xi_e = b\left(\frac{A^2 b}{\lambda_B}\right)^{1/3} \qquad (11)$$

and

$$\xi_0 = (cb)^{-1/2} \left(\frac{A^2 b}{\lambda_B} \right)^{1/3} \tag{12}$$

It is interesting to note that the equivalent conductivity calculated here is found to be highly sensitive on the change in 'A' value in equation 11 and a very good agreement with the experimental result is obtained for an optimum value of '*A*'. The best fit '*A*' values which describe the experimental results best along with the respective standard deviation of fits are given in Table 2. We have, thus, been able to quantitatively describe the electrical conductivity data of the Sodium polystyrenesulfonate in methanol-water mixed solvent media with the help of the scaling concept of polyelectrolyte solutions.

An investigation on electrical conductivity of salt-free solution of an anionic polyelectrolyte sodium polystyrenesulfonate in methanol-water mixed solvent media has been presented as a function of polymer concentration and temperature. The equivalent conductivities are found to increase with increasing temperature over the entire concentration range in a given mixed solvent medium whereas these values are found to decrease as the relative permittivity of the medium decreases. The conductivity theory, proposed by Manning, for salt-free polyelectrolyte solutions was applied previously to analyze the experimental data. The measured values of equivalent conductivity could not be quantitatively described by this theory. A recent model proposed by Colby *et al*. based on scaling approach for the configuration of a polyelectrolyte chain in semidilute solution has also been tested and the results derived from this model are found to be quantitatively consistent with the experimental observations. The influences of temperature and the relative permittivity of the medium on the equivalent conductivity were also investigated.

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