

Chapter IV-A

Conductance of Sodium Carboxymethylcellulose in Acetonitrile-Water Mixed Solvent Media: An Analysis using the Scaling Theory Approach

Introduction

It has been shown in the previous chapter that the conductivity behaviour of NaCMC in acetonitrile-water mixed solvent media could not be explained by the Manning counterion condensation model. The deviation points out that this theory predicts too-large values for the fraction of uncondensed counterions for the present system. Possible reasons for the observed deviations have also been discussed. A thorough analysis, however, provided very important conclusions concerning the structures of the polyion and its counterions.

A new model for the electrical conductivity of semidilute solutions of polyelectrolytes without added salt has been recently proposed by Colby *et. al.*¹ using the scaling description proposed by Dobrynin *et. al.*² for the configuration of a polyelectrolyte chain in semidilute solution. It would be of interest to apply this model for the analysis of the conductivity data which are in the semidilute concentration region since the application of the Manning model to these systems is, however, less straightforward because these semidilute macroions do not assume a fully stretched conformation in solution.

In the semidilute 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 of $q_\xi = zefg$ (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 of $Q_p = N_\xi q_\xi = zefgN_\xi$. 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 semidilute solution is given by

$$\lambda_p = \frac{Fzefg \ln(g/g_e)}{3\pi\eta_0\xi_0} \quad (1)$$

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. (1) reduces to

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

The equivalent conductance of the polyelectrolyte solution is then given by

$$\Lambda = \frac{1}{A} \left[\lambda_c^0 + \frac{Fzefc\xi_0^2 \ln(\xi_0/\xi_e)}{3\pi\eta_0} \right] \quad (3)$$

The above expression given by Colby *et. al.*¹ is derived taking into account the scaling arguments proposed by Dobrynin *et. al.*² 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 (adjustable) parameter A , 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 $\xi = \lambda_b/b$, Eq. (3) can be applied to more concentrated systems,

up to the concentration c_D , where the electrostatic blobs begin to overlap and the electrostatic length equals the electrostatic blob size.

This new model for semidilute polyelectrolyte conductivity has been applied, so far, to a limited number of aqueous polyelectrolytes^{1,3,4} and good agreement with the experiment was observed. This model, however, has not been applied to polyelectrolyte solutions in solvents besides water with the exception of an attempt by one of us for sodium polystyrenesulfonate in acetonitrile-water mixed solvent media.⁵

Results and Discussion

Graphical representation of the experimental Λ values (points), and the Manning predictions (solid lines) are shown in Figures 1–3 at 308.15, 313.15, and 318.15 K in acetonitrile-water mixtures. The experimentally obtained equivalent conductivities have always been found to be considerably lower than the theoretical values calculated following the Manning model. Possible reasons for the deviation and their implication for the elucidation of the structure of the polyelectrolyte solutions have been amply discussed in the previous chapter. The deviation probably arises from the fact that the polyelectrolyte solutions investigated here are different from the model that underlies the Manning counterion condensation 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 equation⁶

$$c^* = \frac{1}{N_A L^2 a} \quad (4)$$

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 semidilute regime ($c_p > c^* \approx 0.0001 \text{ eqv.l}^{-1}$) where the Manning limiting law does not apply.

We, therefore, have made an attempt to analyze the present conductivity data using the scaling theory approach as proposed by Colby *et. al.*¹ for semidilute polyelectrolyte solutions.

Since the present acetonitrile-water mixtures are poor solvent for the uncharged polymer carboxymethylcellulose, the electrostatic blob is collapsed into a dense globule, we use a value of $7A^0$ as the effective monomer size (b) as suggested by Colby *et. al.*¹ while analyzing the data on the basis of the Colby model.

Under poor solvent condition, the electrostatic blob size (ξ_e) and the correlation blob size (ξ_0) are given by¹

$$\xi_e = b \left(\frac{A^2 b}{\lambda_B} \right)^{1/3} \quad (5)$$

and

$$\xi_0 = (cb)^{-1/2} \left(\frac{A^2 b}{\lambda_B} \right)^{1/3} \quad (6)$$

Therefore, Eq. (3) in conjunction with Eqs. (5) and (6) gives an estimate of polyelectrolyte equivalent conductivity in the semidilute regime.

In Figures 1-3, the predictions of the Colby model (dashed lines) for the semidilute regime have been compared with the experimental data. The dashed lines in the Figures. 1-3 display the results of the calculation using the optimum values of A . The best fit A values which describe the experimental results best along with the respective standard deviations of fits are given in Table 1. We have, thus, been able to quantitatively describe the electrical conductivity data of NaCMC in acetonitrile-water mixed solvent media with the help of the scaling concept of polyelectrolyte solutions.

References

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Table 1. Best Fitted A Values for NaCMC in Water and Acetonitrile-Water Mixtures at 308.15, 313.15, and 318.15 K and the Respective Standard Deviations (sd)

T= 308.15 K		T= 313.15 K		T= 318.15 K	
Best Fitted A	sd	Best Fitted A	sd	Best Fitted A	sd
0 Vol% Acetonitrile					
3.03	0.7004	3.21	1.1265	3.32	1.2470
10 Vol% Acetonitrile					
2.94	0.7229	3.11	2.5152	3.18	1.5645
20 Vol% Acetonitrile					
3.21	0.5857	3.18	0.8773	3.28	1.0328
40 Vol% Acetonitrile					
3.72	0.5690	4.24	0.6990	4.70	1.3327

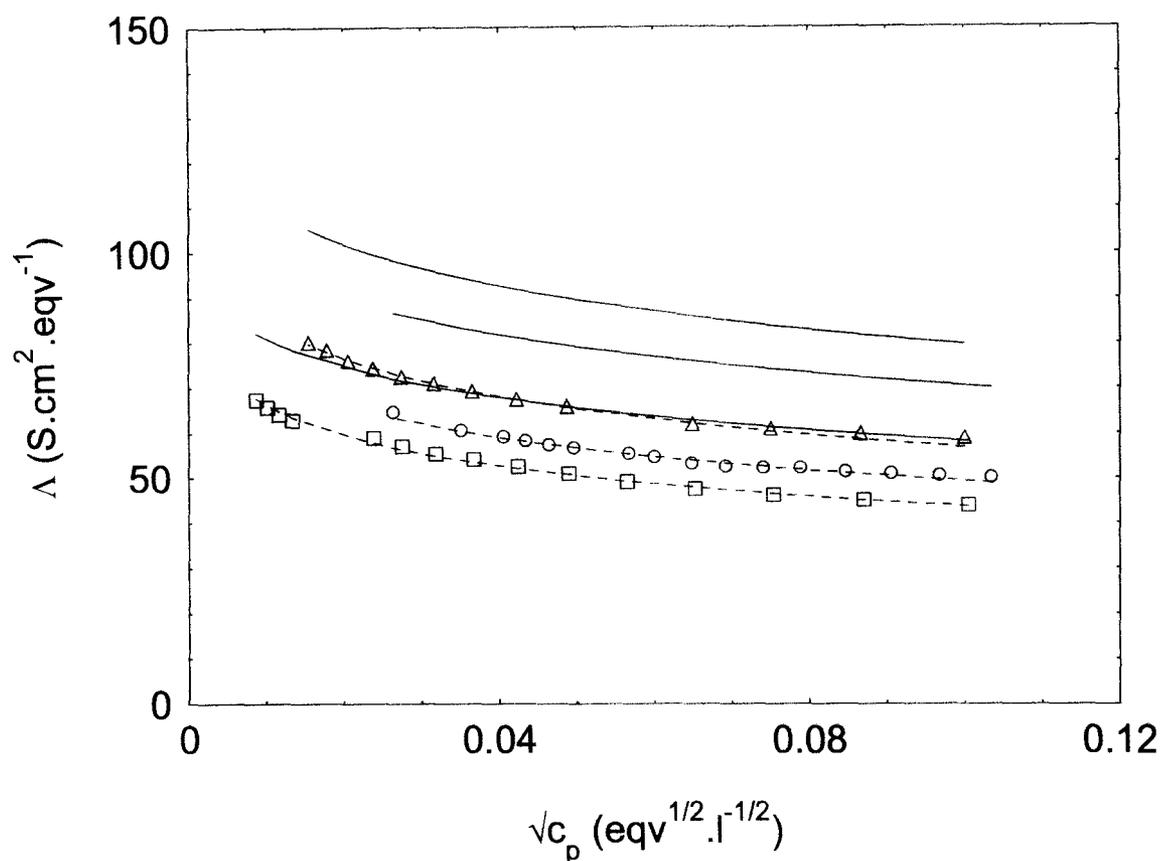


Figure 1. Comparison of the experimental values of the equivalent conductivity (Λ) of solutions of NaCMC with those predicted by Colby theory at 308.15 K: Experimental values: 10 volume percent acetonitrile, Triangles; 20 volume percent acetonitrile, Circles; 40 volume percent acetonitrile, Squares; Calculated with structural ξ : solid lines for 10 20 and 40 volume percent acetonitrile respectively from top to bottom; Calculated with best fitted ξ : broken lines.

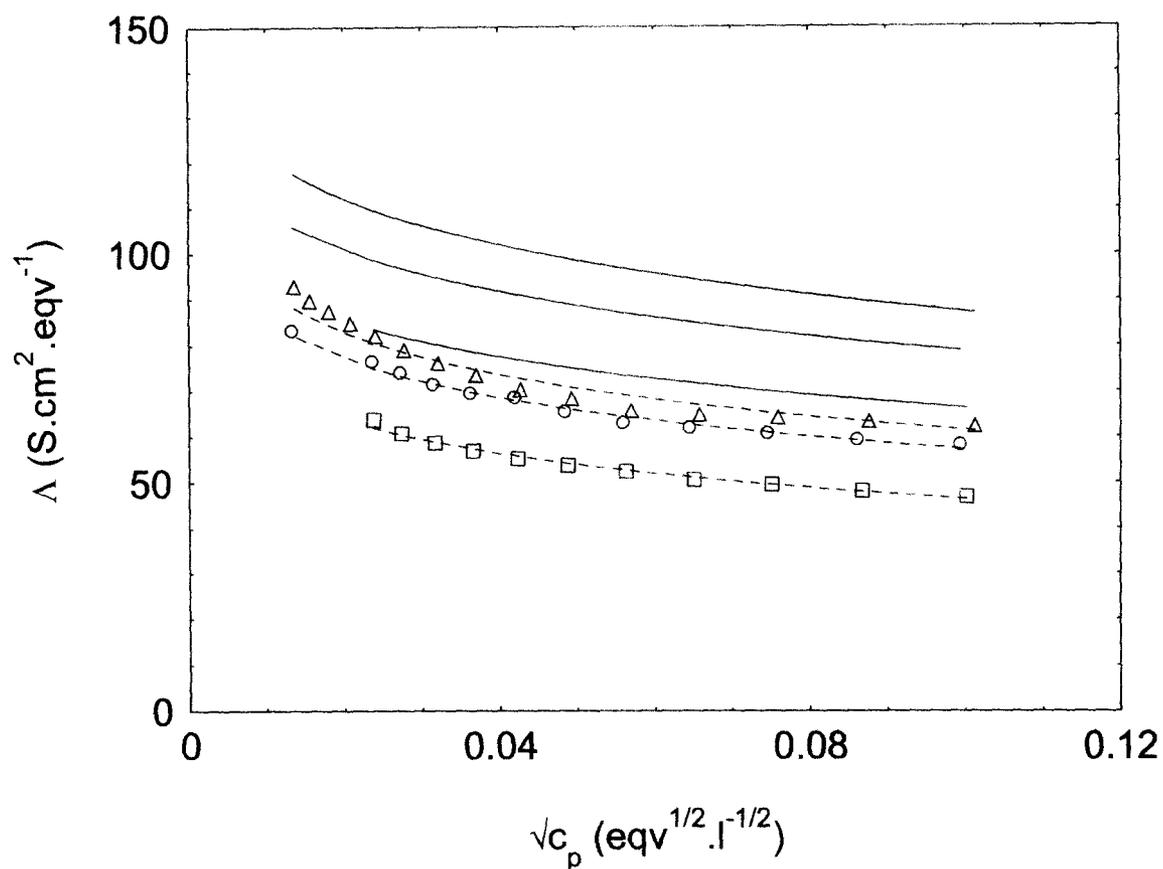


Figure 2. Comparison of the experimental values of the equivalent conductivity (Λ) of solutions of NaCMC with those predicted by Colby theory at 313.15 K: Experimental values: 10 volume percent acetonitrile, Triangles; 20 volume percent acetonitrile, Circles; 40 volume percent acetonitrile, Squares; Calculated with structural ξ : solid lines for 10 20 and 40 volume percent acetonitrile respectively from top to bottom; Calculated with best fitted ξ : broken lines.

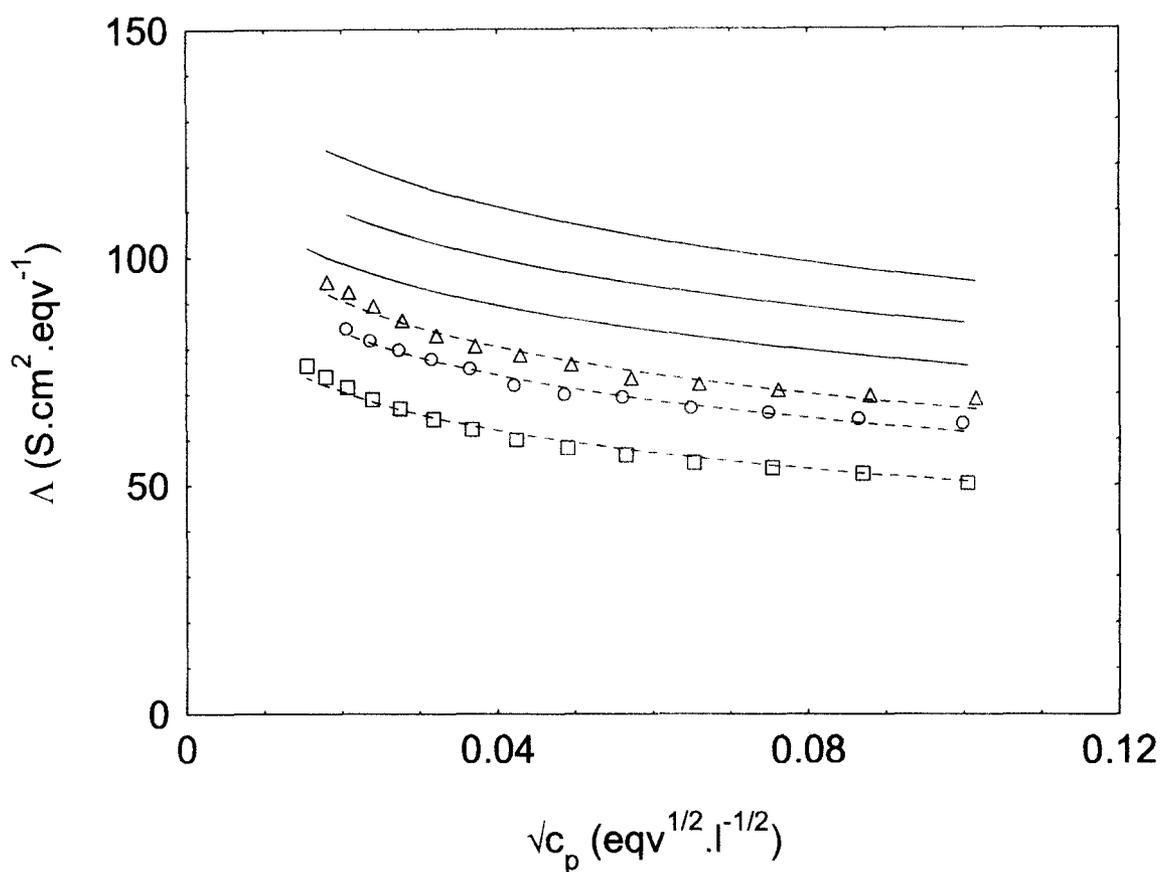


Figure 3. Comparison of the experimental values of the equivalent conductivity (Λ) of solutions of NaCMC with those predicted by Colby theory at 318.15 K: Experimental values: 10 volume percent acetonitrile, Triangles; 20 volume percent acetonitrile, Circles; 40 volume percent acetonitrile, Squares; Calculated with structural ξ : solid lines for 10 20 and 40 volume percent acetonitrile respectively from top to bottom; Calculated with best fitted ξ : broken lines.