Corrigendum and Addendum to the Thesis entitled "Polyelectrolyte-Surfactant Interactions in Mixed Solvent Media" Submitted by Sri Ajaya Bhattarai, 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 on 02.09.2010

1. **Chapter III:**

   Poor solubility of NaPSS in methanol-water mixtures in the methanol-rich region prevented us to perform studies in methanol-rich region.

2. **Chapter IV:**

   (i) Theoretical predictions according to the Manning theory are not shown in Figures 1-4 (Chapter IV) by mistake. The corrected figures with the theoretical predictions shown as solid lines are included herewith (please see below).

   (ii) We have considered the influences of *two* different parameters, namely, temperature and relative permittivity of the medium, on the fractions of uncondensed counterions (*f*).

   The influences of the relative permittivity and temperature on the fractions of uncondensed counterions (*f*) are coupled, and with the currently-available theories of polyelectrolyte conductivity, it is not yet possible to perform the separation of these two opposing effects. A qualitative analyses, however, provided useful guidelines as to the relative importance of these two effects. Such studies are expected to help develop theories to separate influences of various factors on the fractions of uncondensed counterions.

   The standard deviations of the fits of the experimental equivalent conductances following the scaling theory approach (shown in Figures 1-4) *have been listed* in *Table II* of *Chapter IV* and these indicate the quality of fits.

   (iii) On page 82, line number 2 from bottom, please read "higher" in place of "lower". The fitted values of f' (which represent the fractions of *uncondensed* counterions) indicate a lower fractions of uncondensed counterions (and hence a *higher counterion condensation*, the fraction of which being $1-f'$) in the presence of electrolyte (please see pages 72, 82 and 85). Addition of NaCl to NaPSS solution will result in a more counterion condensation onto the polyion chain due to the shifting of the following equilibrium:

   $$\text{NaPSS} \rightleftharpoons \text{Na}^+ + \text{PSS}^-$$

   to the left. That means higher counterion condensation takes place in presence of NaCl. Or, in other words, there will be lower amount of uncondensed counterion. This is, obviously, *in agreement* with the common ion effect.

3. **Chapter VIII:**

   The values of γ and κ for the pure methanol-water mixtures have been provided in Table 1 (please see below).

The radius of the assumedly rod-like polymer cylinder (*a*) is the minimum distance of contact of the polyion and the counterions.[1-3] The symbol *b* (p. 66), on the other hand, stands for the effective monomer size. These two parameters represent two entirely different aspects of polyelectrolytes in solution. It may, however, be pointed out that a polyion chain remains in a fairly extended state in very dilute salt-free solutions, and addition of salts leads a screening of the polyion charges and hence a reduction in the size of the polyion.

General Comments:

Chapter IV has been derived from our published paper,[4] but while incorporation into the thesis, some *more new calculations* on the basis of the scaling theory approach were performed in order to describe the experimental equivalent conductivity values more closely and the entire chapter has been rewritten.

References

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2. T. Alfrey, P.W. Berg, and H. Morawetz, *J. Polym. Sci.*, **7**, 543 (1951).
3. M. Le Bret, and B.H. Zimm, *Biopolymers*, **23**, 287 (1984).
4. A. Bhattarai, P. Nandi, and B. Das, *J. Polym. Res.*, **13**, 475 (2006).

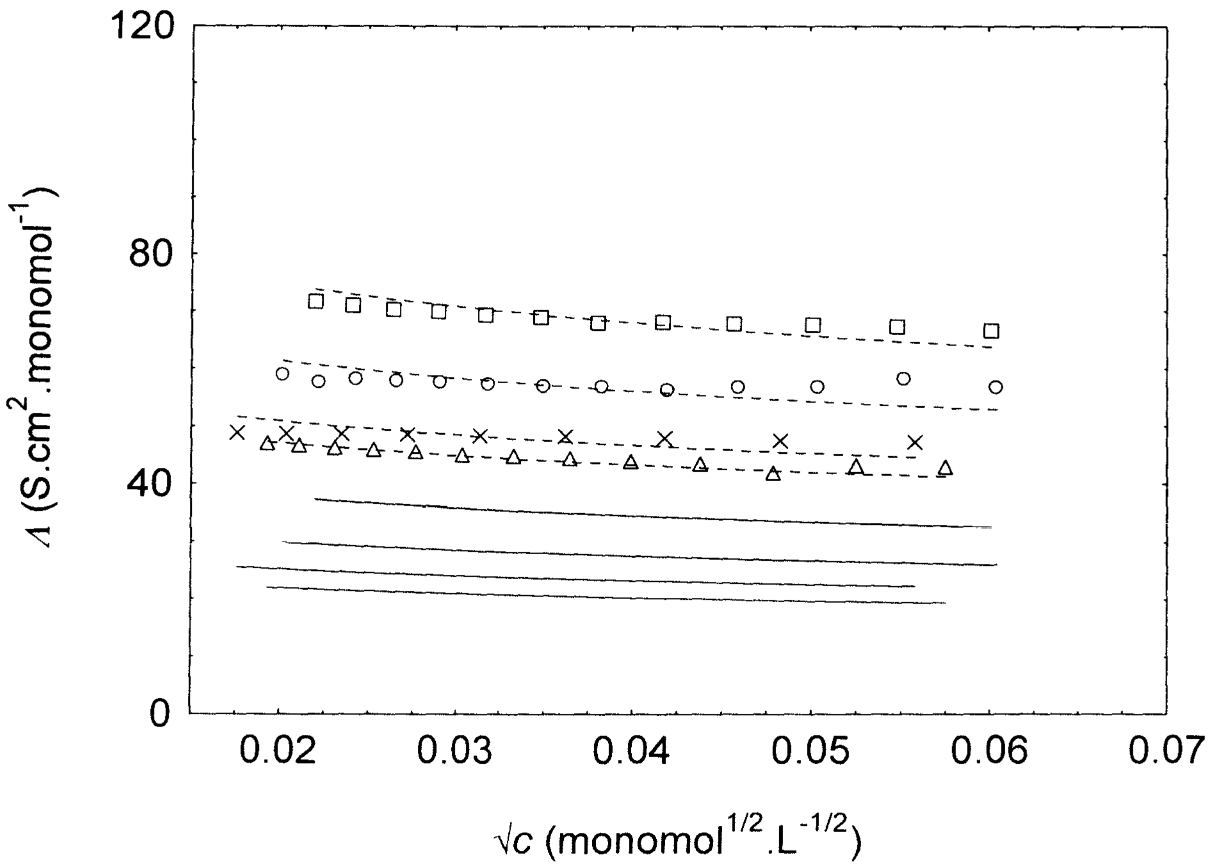

Figure 1. Comparison of the experimental values of the equivalent conductivity (Λ) of solutions of NaPSS with those predicted on the basis of the Manning counterion condensation theory and on the basis of the scaling (Colby) theory at 308.15 K. Experimental: 8 mass% methanol (*squares*), 16 mass% methanol (*circles*), 25 mass% methanol (*crosses*), 34 mass% methanol (*triangles*). Manning theory: *solid lines* for 8, 16, 25 and 34 mass% methanol respectively from top to bottom. Scaling theory: *dashed lines*.

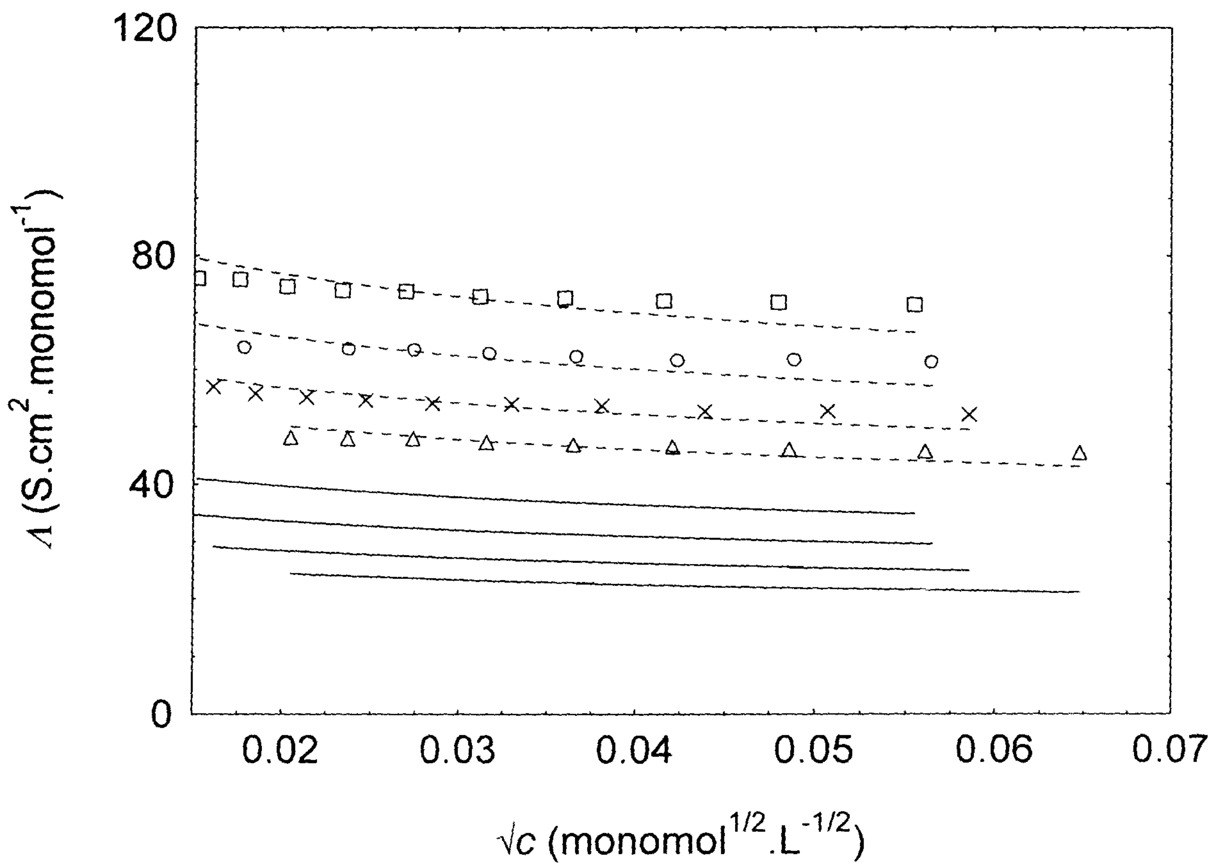

Figure 2. Comparison of the experimental values of the equivalent conductivity (Λ) of solutions of NaPSS with those predicted on the basis of the Manning counterion condensation theory and on the basis of the scaling (Colby) theory at 313.15 K. Experimental: 8 mass% methanol (*squares*), 16 mass% methanol (*circles*), 25 mass% methanol (*crosses*), 34 mass% methanol (*triangles*). Manning theory: *solid lines* for 8, 16, 25 and 34 mass% methanol respectively from top to bottom. Scaling theory: *dashed lines*.

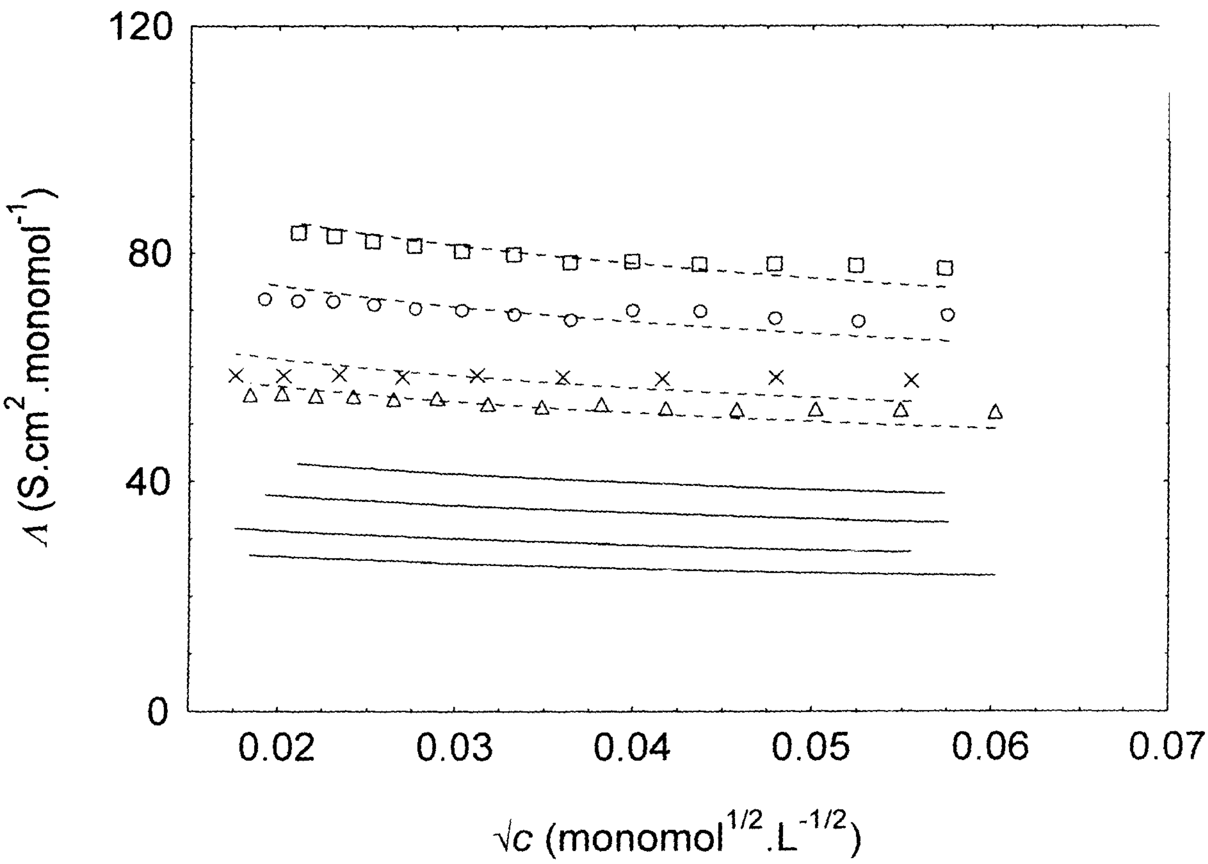

Figure 3. Comparison of the experimental values of the equivalent conductivity (Λ) of solutions of NaPSS with those predicted on the basis of the Manning counterion condensation theory and on the basis of the scaling (Colby) theory at 318.15 K. Experimental: 8 mass% methanol (*squares*), 16 mass% methanol (*circles*), 25 mass% methanol (*crosses*), 34 mass% methanol (*triangles*). Manning theory: *solid lines* for 8, 16, 25 and 34 mass% methanol respectively from top to bottom. Scaling theory: *dashed lines*.

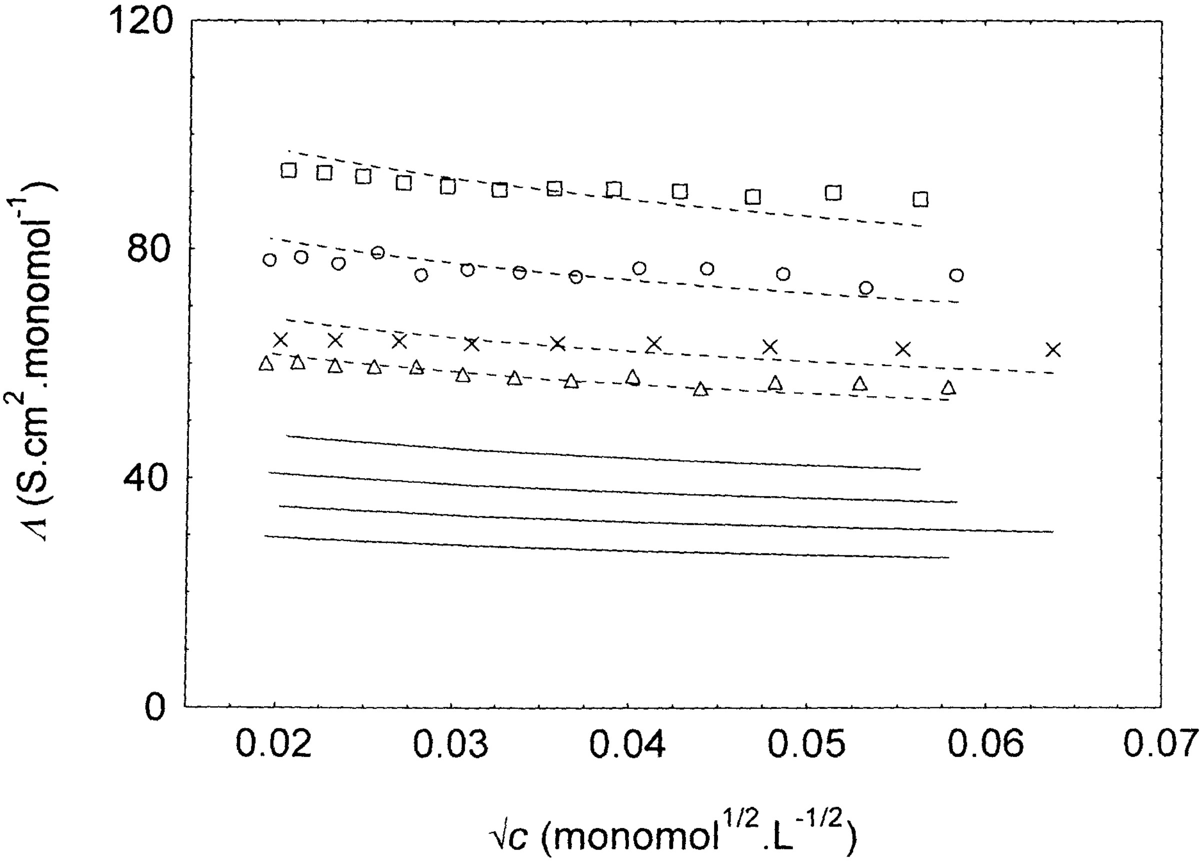

Figure 4. Comparison of the experimental values of the equivalent conductivity (Λ) of solutions of NaPSS with those predicted on the basis of the Manning counterion condensation theory and on the basis of the scaling (Colby) theory at 323.15 K. Experimental: 8 mass% methanol (*squares*), 16 mass% methanol (*circles*), 25 mass% methanol (*crosses*), 34 mass% methanol (*triangles*). Manning theory: *solid lines* for 8, 16, 25 and 34 mass% methanol respectively from top to bottom. Scaling theory: *dashed lines*.

Table 1. The Surface Tensions and the Specific Conductances of Methanol-Water Mixed Solvent Media

T(K)	Property	8 mass% methanol	16 mass% methanol
308.15	γ_0 (dyn.cm^{-1})	56.9	49.1
	κ_0 (μS.cm^{-1})	0.73	0.59
318.15	γ_0 (dyn.cm^{-1})	55.6	47.3
	κ_0 (μS.cm^{-1})	0.85	0.72
323.15	γ_0 (dyn.cm^{-1})	54.8	46.4
	κ_0 (μS.cm^{-1})	0.90	0.77

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