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 polyelecrolyte 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 sals 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).

Debapratim Ghosh
(Debapratim Ghosh)

Bijan Das
(Bijan Das)
Supervisor

PROFESSOR OF CHEMISTRY
University of North Bengal

Place: North Bengal University
Date: March 23, 2012