

Chapter III

Experimental

Chemicals

Sodium Polystyrenesulfonate (NaPSS)

The sodium salt of polystyrenesulfonic acid (NaPSS) with a molecular weight of 70,000 and a degree of sulfonation of 1.0 (Aldrich Chemical Company) was purified by dialysis.^{1,2} The molecular weight reported by the manufacturer agreed well with that determined in the present study obtained in presence of 0.05 M sodium chloride (NaCl) at 298.15 K using the Mark-Houwink relationship,³ $[\eta] = 1.39 \times 10^{-4} M^{0.72}$, where $[\eta]$ is the intrinsic viscosity, and M is the average molecular weight. The absorption coefficient of the NaPSS solutions used at 261 nm, which is considered to be a characteristic indicator of the sample purity,² is found to be $400 \text{ dm}^3 \text{ cm}^{-1} \text{ mol}^{-1}$. Spectroscopic examination of the polyelectrolyte sample using this criterion was employed periodically to substantiate the sample purity.

Cetyltrimethylammonium Bromide (CTAB)

Cetyltrimethylammonium bromide was purchased from Aldrich Chemical Company. The surfactant was recrystallised several times until no minimum in the surface tension-concentration plot was observed and its critical micellar concentration (cmc) agreed with the literature value.⁴

Sodium Chloride (NaCl)

Sodium chloride (Fluka) was of purum grade; this was dried *in vacuo* for a prolonged period immediately before use and was used without further purification.

Solvents

Acetonitrile

Acetonitrile (E. Merck, India, 99% pure) was distilled with phosphorous pentaoxide and redistilled over calcium hydride. The purified solvent had a density of $0.76570 \text{ g cm}^{-3}$ and a coefficient of viscosity of 0.3126 mPa.s at 308.15 K ; these values are in good agreement with the literature values.⁵

Water

Triply distilled water was used for the preparation of the experimental solutions. Water was first deionized and then distilled from an all glass distilling set using alkaline KMnO_4 solution. The distilled water was then distilled twice. Precautions were taken to prevent contaminations from CO_2 and other impurities. The triply distilled water which had a specific conductance of less than $10^{-6} \text{ S.cm}^{-1}$ at 308.15 K was used for the preparation of the solutions.

Preparation of the Mixed Solvents

The acetonitrile-water mixed solvents were prepared accurately by mixing requisite amounts of acetonitrile and water by mass. The physical properties namely the densities (ρ_0), the coefficients of viscosities (η_0) and the relative permittivities (D) of these mixed solvents used 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 literature⁶ using the literature density and relative permittivity data of the pure solvents^{5,7} and the densities of the mixed solvents given in Table 1. Also included in this table are the limiting equivalent conductivities of sodium ion (Na^+) in acetonitrile-water mixtures (*cf.* Appendix).

Methods

Conductance Measurements

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 cell constant of 1.15 cm^{-1} and having an uncertainty of 0.01 percent. The cell was calibrated by the method of Lind and co-

workers⁸ using aqueous potassium chloride solution. The measurements were made in a water bath maintained within ± 0.005 K of the desired temperature. 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.

Density Measurements

The densities were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 1 mm. The pycnometer was calibrated at the experimental temperatures with deionized distilled water, methanol and acetonitrile. The precisions of the density measurements were always within $3 \times 10^{-5} \text{ g.cm}^{-3}$. The measurements were performed in a water bath which was maintained within an accuracy of 0.005 K of the desired temperature by means of an electronic relay and a contact thermometer.

Viscosity Measurements

The viscometric measurements were performed at 308.15, 313.15, and 323.15 K using a Schultz-Immergut-type viscometer⁹ with a sintered disc fitted to the widest arm to filter the solution/solvent from dust particles, if any. The measurements were made in a thermostat maintained within ± 0.005 K of the desired temperature by means of a mercury-in-glass thermoregulator, and the absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge.^{10,11} Several independent solutions were prepared, and runs were performed to ensure the reproducibility of the results. To check whether the reduced viscosities depend on the shear rate in the concentration range investigated; measurements with capillaries of different sizes were performed. This did not lead to different values of the reduced viscosity.

Surface Tension Measurements

The surface tensions of the surfactant solutions were measured at 308.15, 313.15, and 318.15 K using a Krüss (Germany) K9 tensiometer by the platinum ring detachment method. The tensiometer was connected to a water-flow cryostat to maintain the temperature equilibration. Prior to each measurement, the ring was briefly heated by holding it above a

Bunsen burner until glowing. The measurements were made in a thermostat maintained within ± 0.005 K of the desired temperature.

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.

References

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Table 1. Properties of Acetonitrile-Water Mixtures Containing 10, 20, and 40 Volume Percent of Acetonitrile at 308.15, 313.15, and 318.15 K and the Limiting Conductivity Values of Sodium Ion in the Mixed Solvent Media

T (K)	η_0 (mPa s)	ρ (g cm ⁻³)	D	λ_{Na}^0 (S cm ² mol ⁻¹)
10 percent acetonitrile				
308.15	0.8766	0.98096	72.15	58.81
313.15	0.7622	0.97893	69.89	65.15
318.15	0.6773	0.97625	68.27	70.50
20 percent acetonitrile				
308.15	0.9067	0.96485	67.94	56.21
313.15	0.7833	0.96200	66.38	62.77
318.15	0.6984	0.95912	64.84	68.03
40 percent acetonitrile				
308.15	0.8200	0.92362	60.07	51.50
313.15	0.6803	0.91730	58.87	57.84
318.15	0.5611	0.91542	57.32	65.34