

Chapter 3

Experimental

3.1 Chemicals

3.1.1 Sodium Polystyrenesulphonate

The anionic polyelectrolyte sodium polystyrenesulphonate with a molecular weight of 70000 and a degree of sulfonation of 1.0 was purchased from Aldrich Chemical Company, Inc., and 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 sodium polystyrenesulphonate 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.

3.1.2 Sodium Chloride

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

3.2 Solvents

3.2.1 2-Ethoxyethanol

2-Ethoxyethanol (G.R.E. Merck) was distilled with phosphorous pentoxide and then redistilled over calcium hydride. The purified solvent had a density of $0.92497 \text{ g}\cdot\text{cm}^{-3}$ and a coefficient of viscosity of $1.8277 \text{ mPa}\cdot\text{s}$ at 298.15 K; these values are in good agreement with the literature values.⁴

3.2.2 Water

Triply distilled water was used for the preparation of the experimental solutions. Water was first deionized and then distilled in an all glass distilling apparatus using alkaline KMnO_4 solution. The distilled water was then redistilled twice. Precautions were taken to

prevent contaminations from CO₂ and other impurities. The triply distilled water had a specific conductance of less than $10^{-6} \text{ S}\cdot\text{cm}^{-1}$ at 308.15 K.

3.3 Preparation of the Mixed Solvents

2-Ethoxyethanol–water mixed solvents were prepared by mixing requisite amounts of 2-ethoxyethanol 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, 318.15 and 323.15 K are reported in Table 3.1. The relative permittivities of 2-ethoxyethanol–water mixtures at the experimental temperatures were obtained with the equations as described in the literature⁵ using the literature density and relative permittivity data of the pure solvents^{4,6} and the densities of the mixed solvents given in Table 3.1.

3.4 Methods

3.4.1 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 %. The cell was calibrated by the method of Lind and co-workers⁷ using aqueous potassium chloride solution. The measurements were made in a water bath maintained within $\pm 0.005 \text{ K}$ 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.

3.4.2 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 using their literature values.^{6,8} The precisions of the density measurements were always within $3 \times 10^{-5} \text{ g}\cdot\text{cm}^{-3}$. The measurements were performed in a water bath which was maintained within an accuracy of 0.01 K of the desired temperature by means of an electronic relay and a contact thermometer.

3.4.3 Viscosity Measurements

The viscometric measurements were performed at 308.15, 313.15, 318.15 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 ± 0.01 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. The reduced viscosity (η_{sp}/c_p ; η_{sp} = specific viscosity and c_p = polyelectrolyte concentration) is obtained from

$$\frac{\eta_{sp}}{c_p} = \frac{t - t_0}{t_0} \frac{1}{c_p} \quad (1)$$

where t and t_0 are the measured flow times of the polyelectrolyte solution and of the pure solvent, respectively.

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.

3.5 References

1. P. Chu and J. A. Marinsky, *J. Phys. Chem.*, **71**, 4352 (1967).
2. M. Reddy and J. A. Marinsky, *J. Phys. Chem.*, **74**, 3884 (1970).
3. A. Takahashi, T. Kato and M. Nagasawa, *J. Phys. Chem.*, **71**, 2001 (1967).
4. G. Douheret and A. Pal, *J. Chem. Eng. Data*, **33**, 40 (1988).
5. M. Pal and S. Bagchi, *J. Chem. Soc., Faraday Trans. I*, **81**, 961 (1985).
6. R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, 2nd ed., Butterworths, London (1959).
7. Jr. J. E. Lind, J. J. Zwolenik and R. M. Fuoss, *J. Am. Chem. Soc.*, **81**, 1557 (1959).
8. N. Saha, B. Das and D. K. Hazra, *J. Chem. Eng. Data*, **40**, 1264 (1995).
9. J. Schulz and E. H. Immergut, *J. Polym. Sci.*, **9**, 279 (1952).
10. B. Das and D. K. Hazra, *Bull. Chem. Soc. Jpn.*, **65**, 3470 (1992).
11. B. Das and D. K. Hazra, *J. Phys. Chem.*, **99**, 269 (1995).

Table 3.1 Densities (ρ_0), Coefficients of Viscosities (η_0) and Relative Permittivities (D) of 2-Ethoxyethanol–Water Mixtures Containing 10, 25, 40 and 50 Mass % of 2-Ethoxyethanol at 308.15, 313.15, 318.15 and 323.15 K

T (K)	ρ_0 (g·cm ⁻³)	η_0 (mPa·s)	D
10 mass % 2-ethoxyethanol			
308.15	0.98926	1.3099	69.87
313.15	0.99287	1.1017	68.13
318.15	0.99019	0.8961	66.55
323.15	0.99536	0.8943	65.08
25 mass % 2-ethoxyethanol			
308.15	0.99758	1.8430	60.13
313.15	0.99245	1.5293	58.70
318.15	0.98807	1.2738	57.37
323.15	0.98394	1.0923	56.11
40 mass % 2-ethoxyethanol			
308.15	0.99747	1.9545	50.54
313.15	0.99101	1.7015	49.28
318.15	0.98696	1.4274	48.14
323.15	0.98378	1.2317	47.10
50 mass % 2-ethoxyethanol			
308.15	0.99361	1.9234	44.30
313.15	0.98514	1.7195	43.03
318.15	0.98004	1.4552	41.95
323.15	0.97610	1.2762	40.96