

Chapter III

Experimental

Chemicals

Sodium Carboxymethylcellulose (NaCMC)

NaCMC was purchased from Aldrich Chemical Company. The average molecular weight (M_w) of the sample was 90,000 with a degree of substitution (DS) of 0.70, and these values agree well with the viscosity average molecular weight of the sample obtained in presence of 0.1 N NaCl using the Mark-Houwink constants from the literature¹ and the degree of substitution obtained from a conductometric procedure as described by Eyer *et. al.*² Figure 1 displays the Fourier Transform Infrared (FTIR) spectrum of NaCMC used in the present study and Table 1 gives the assignments of the important peaks observed.³ A very good agreement with the literature values³ was observed.

Alkali-metal Salts

The alkali-metal salts (Fluka) were of purum or puriss grade; these were dried *in vacuo* for a prolonged period immediately before use and were used without further purification.

Solvents

Acetonitrile

Acetonitrile (E. Merck, India, 99% pure) was distilled with phosphorous pentoxide and then redistilled over calcium hydride. The purified solvent had a density of $0.76570 \text{ gm.cm}^{-3}$ and a coefficient of viscosity of 0.3126 mPa.s at 308.15 K ; these values are in good agreement with the literature values.⁴

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 had a specific conductance of less than $10^{-6} \text{ S.cm}^{-1}$ at 308.15 K.

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 2. The relative permittivities of acetonitrile-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 2.

Methods

Fourier Transform Infrared (FTIR) Spectral Measurements

The spectrum of NaCMC was recorded in the $4000\text{-}400 \text{ cm}^{-1}$ range at a resolution of 1 cm^{-1} with a Shimadzu 8300 FTIR spectrophotometer using the potassium bromide (KBr) disk sampling technique.

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-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.

Density Measurements

The densities were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm³ 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 x 10⁻⁵ gm.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.

Viscosity Measurements

The viscometric measurements were performed at 308.15, 313.15 and 323.15 K using a Schultz-Immergut-type viscometer⁸ 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.^{9,10} 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.

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. FTIR Peak Assignments for NaCMC

Peak position (cm⁻¹)	Assignment
3436.50	O-H stretch
2925.93	CH ₂ stretch (asymmetric)
1602.08	COO ⁻ (asymmetric)
1420.37	COO ⁻ (symmetric)
1060.70	C-O stretch (RCH ₂ OH)

Table 2. Densities, ρ (g.cm⁻³), Coefficients of Viscosities, η_0 (mPa.s) and Relative Permittivities (D) of Acetonitrile-Water Mixtures Containing 10, 20 and 40 Volume Percent of Acetonitrile at 308.15, 313.15, and 318.15 K

<i>T</i> (K)	ρ (g.cm ⁻³)	η_0 (mPa.s)	<i>D</i>
10 Vol% Acetonitrile			
308.15	0.98096	0.8766	72.15
313.15	0.97893	0.7622	69.89
318.15	0.97625	0.6733	68.27
20 Vol% Acetonitrile			
308.15	0.96485	0.9067	67.94
313.15	0.96200	0.7833	66.38
318.15	0.95912	0.6984	64.84
40 Vol% Acetonitrile			
308.15	0.92362	0.8200	60.07
313.15	0.91730	0.6803	58.87
318.15	0.91542	0.5611	57.32

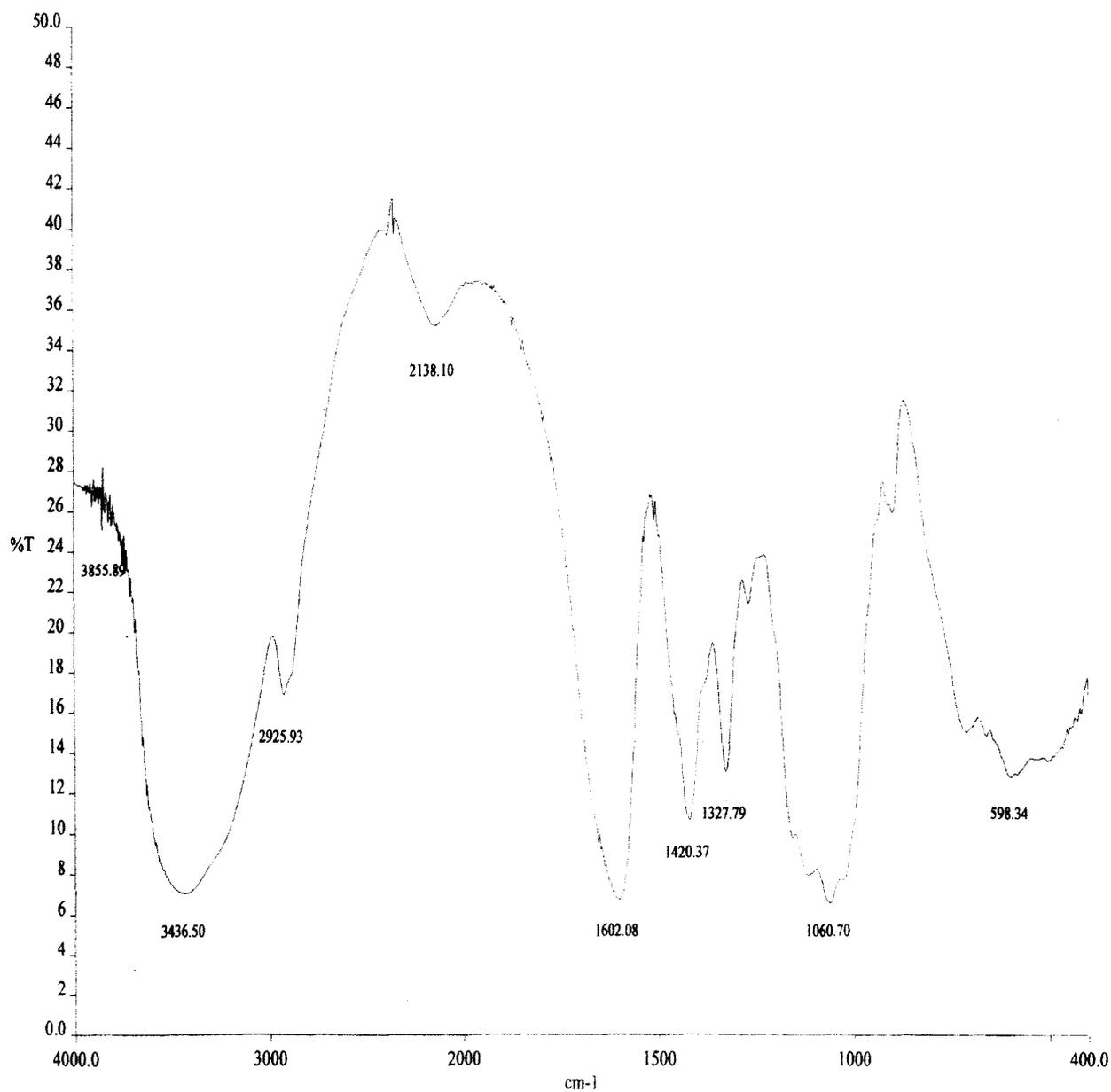


Figure 1. FTIR spectrum of NaCMC