

Chapter 3

Experimental

Chemicals

Sodium Carboxymethylcellulose

Three sodium carboxymethylcellulose samples with average molecular weights (M_w) of 90,000 [degree of substitution (DS) = 0.7], 250,000 [DS = 0.9], and 700,000 [DS = 0.9] were purchased from Aldrich Chemical Company. The average molecular weights of these

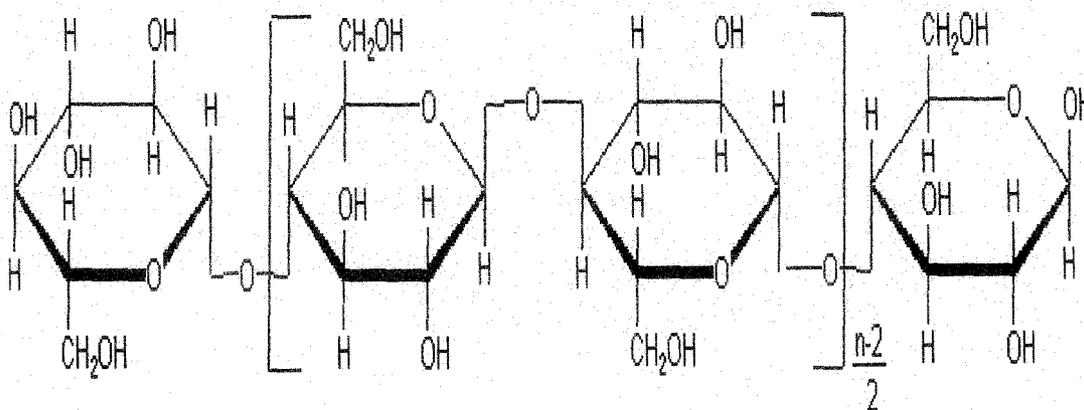


Fig. 1. Diagrammatic representation of a cellulose molecule.

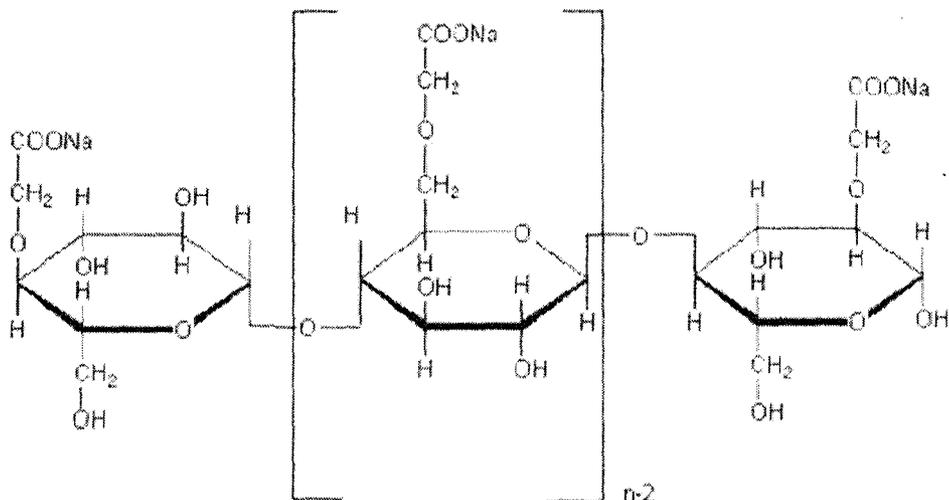


Fig. 2. Sodium carboxymethylcellulose with a degree of substitution of 1.

samples agree well with their viscosity average molecular weights obtained in presence of 0.1 N NaCl using the Mark-Houwink constants from the literature.¹ The degrees of substitution of these samples obtained using a conductometric procedure as described by Eyley *et al.*² are also found to be in good agreement with those declared by the manufacturer. The representative Figure 1 displays the Fourier Transform Infrared (FTIR) spectrum of one of the sodium carboxymethylcellulose samples used ($M_w = 90,000$) in the present study and Table 1 gives the assignments of the important peaks observed.³

Salts

Sodium chloride, sodium bromide, potassium chloride, and barium chloride were of Fluka purum or puriss grade; these were dried *in vacuo* for a prolonged period immediately before use and were used without further purification.

Methanol

Methanol (Acros Organics, 99% pure) was distilled twice. The middle fraction was collected and redistilled. The purified solvent had a density of $0.77728 \text{ g.cm}^{-3}$ and a co-

efficient of viscosity of 0.4747 mPa.s at 308.15 K; these values are in good agreement with the literature values.

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} S.cm^{-1} at 308.15 K was used for the preparation of the solutions.

Preparation of the Mixed Solvents

The methanol-water mixed solvents were prepared accurately by mixing requisite amounts of methanol 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 298.15, 308.15, 318.15, and 328.15 K are reported in Table 1. The relative permittivities of methanol-water mixtures at the experimental temperatures were obtained with the equations as described in the literature⁴ using the literature density and relative permittivity data of the pure solvents^{5,6} and the densities of the mixed solvents given in Table 1.

Methods

Fourier Transform Infrared (FTIR) Spectral Measurements

The spectrum of sodium carboxymethylcellulose was recorded in the 4000-400 cm^{-1} range at a resolution of 1 cm^{-1} with a Shimadzu 8300 FTIR spectrophotometer using the potassium bromide disk sampling technique.

The characteristic peaks are given in Table 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 1.14 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 $\pm 0.01 \text{ K}$ 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 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 $3 \times 10^{-5} \text{ g}\cdot\text{cm}^{-3}$. 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.

Density measurements were also carried out on an Anton Paar DMA-4500M digital precision densimeter. The precision of the density measurements was $3 \cdot 10^{-5} \text{ g}\cdot\text{cm}^{-3}$. Calibration of the densimeter was done at each temperature using dry air under ambient pressure, and deionized triply distilled water.

Viscosity Measurements

The viscometric measurements were performed at 308.15 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 $\pm 0.01 \text{ K}$ 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 Sodium Carboxymethylcellulose

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_2OH)

Table 2. Densities, ρ (g.cm^{-3}), Coefficients of Viscosities, η_0 (mPa.s) and Relative Permittivities (D) of Methanol-Water Mixtures Containing 10, 20 and 30 Volume Percent of Methanol at Different Temperatures

T (K)	ρ (g.cm^{-3})	η_0 (mPa.s)	D
10 Vol% Methanol			
298.15	0.98297	1.0844	75.09
308.15	0.97973	0.8665	71.57
318.15	0.97604	0.7020	68.18
20 Vol% Methanol			
298.15	0.96963	1.3106	71.61
308.15	0.96632	1.0217	68.14
318.15	0.96162	0.8075	64.80
328.15	0.95841	0.5306	61.43
30 Vol% Methanol			
298.15	0.95620	1.4712	67.65
308.15	0.95160	1.1418	64.25
318.15	0.94626	0.8957	60.99
Methanol			
298.15	0.78659	0.5446	32.66
308.15	0.77728	0.4747	30.74
318.15	0.76774	0.4185	29.92

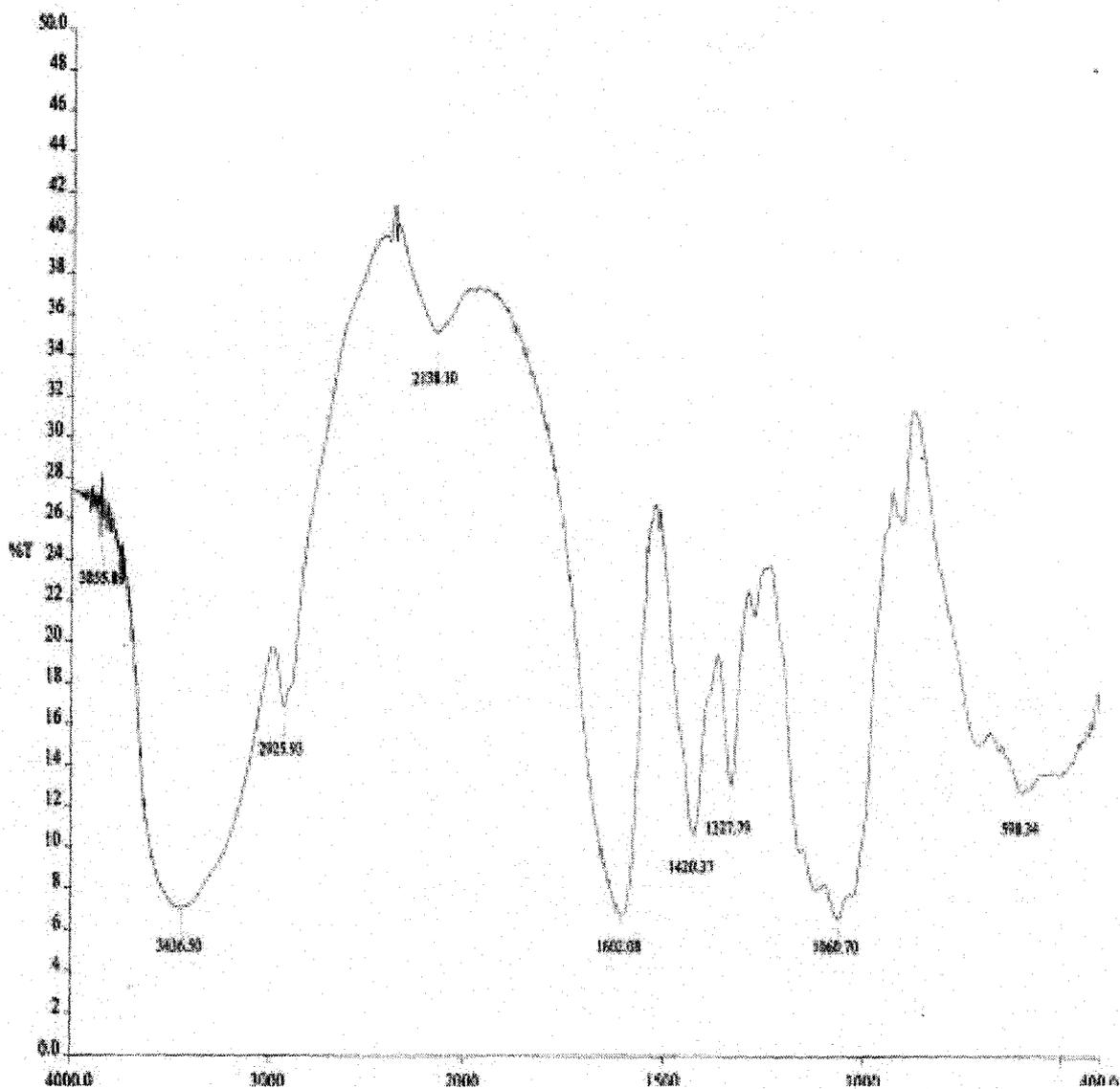


Fig. 1. FTIR spectrum of sodium carboxymethylcellulose.