Chapter 8

Apparent Molar Volumes of Sodium Carboxymethylcellulose in Methanol-Water Mixed Solvent Media

Introduction

The principal factors that govern the dissolved state of polyelectrolytes in solutions are (i) the electrostatic repulsions between the ionic sites in the polyion chain and (ii) the interactions between the polyions and neighbouring counterions. The first factor is related to expansibility of the polyion chains, whereas the second is not only manifested in counterion condensation but also in the degree of solvation and the structure of the solvent in the vicinity of polyelectrolytes. Both of these factors are influenced by the relative permittivity of the solvent media. Use of a series of mixed solvents allows a systematic variation in the relative permittivity of the media, and hence enables investigation on these interactions operative in polyelectrolyte solutions. We have already investigated the influence of intramacromolecular electrostatic repulsions and the resulting coiling/expansion of the polyion chains from viscosity measurements on sodium carboxymethylcellulose in methanol-water mixtures. In this chapter, we report the apparent molar volumes of sodium carboxymethylcellulose in methanol-water mixtures with a view to investigate the polyion-counterion interactions as well as the solvation behaviour of the counterions.

Experimental

Methanol (Acros Organics, 99% pure) was distilled with phosphorous pentoxide and then redistilled over calcium hydride. The purified solvent had a density of 0.77728 $g.cm^{-3}$ 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.[1] Triply distilled water with a specific conductance of less than 10^{-6} $S.cm^{-1}$ at 308.15 K was used for the preparation of the mixed solvents.

Sodium carboxymethylcellulose was purchased from Aldrich Chemical Company, Inc. 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 those obtained from physiochemical characterization in the present study.

Density measurements were carried out on an Anton Paar DMA-4500M digital precision densimeter. The precision of the density measurements was $3 \cdot 10^{-5}$ g.cm^{-3} Calibration of the densimeter was done at each temperature using dry air under ambient pressure, and deionized triply distilled water. Densities of methanol-water mixtures at 298.15, 303.15, 308.15 and 313.15 K are given in Table 1.

Results and Discussion

Apparent Molar Volumes

The apparent molar volumes (ϕ_v) of the polyelectrolyte in solution can be calculated using the conventional equation

$$\phi_v = \frac{M}{\rho_0} - 1000\frac{(\rho - \rho_0)}{c_p \rho_0} \qquad (1)$$

where c_p is the polyelectrolyte concentration (in monomolarity), *M* the molecular mass of the repeating unit of sodium carboxymethylcellulose with a degree of substitution (*DS*) of 0.7, ρ the density of the solution and ρ_0 the density of the solvent.

Variations of Apparent Molar Volumes with Polyelectrolyte Concentration

Figs. 1 – 3 show the variations of apparent molar volumes as a function of the square root of the monomolar concentration of sodium carboxymethylcellulose in methanol-water mixtures containing 10, 20 and 30 volume percent of methanol at 298.15, 303.15, 308.15, and 313.15 K. Within the concentration ranges investigated here, the ϕ_v *vs.* $\sqrt{c}$ plots are found to be linear and, moreover, as $\sqrt{c}$ is increased, ϕ_v increased marginally. Similar linear increases for ϕ_v with concentration have been previously reported by Conway and Desnoyers,[2] Lawrence and Conway,[3] Ise and Okubo[4] and Tondre and Zana[5] for various polyelectrolytes in aqueous solutions although the insensitivity of ϕ_v toward concentration was also reported[4] for salts of polystyrenesulfonic acid polyethylenimine. It should be pointed out that the concentration dependences observed in the present study are small compared to those for most simple electrolytes. The possible explanation for the positive slopes in methanol-water mixed solvent media might be that counterion binding would become quite appreciable as the concentration of the polyelectrolyte is increased, thereby weakening the ion-solvent interactions. As a consequence, contraction of the solvent medium would be lowered with increasing concentration of the polyelectrolyte, resulting in a net positive volume change per monomole of the added polyelectrolyte, and, therefore, in a positive slope of the ϕ_v vs. $\sqrt{c}$ plots.

The Limiting Partial Molar Volumes

The apparent molar volumes at infinite dilution, ϕ_v^0 (= limiting partial molar volumes, $\bar{V}_2^0$) were obtained by least-squares fitting of ϕ_v values to the equation

$$\phi_v = \phi_v^0 + S_v\sqrt{c} \tag{2}$$

where S_v is the experimental slope. The values of ϕ_v^0 (= $\bar{V}_2^0$) and S_v are given Table 2. The correlation coefficients (r) of the regression analyses were always found to be greater than or equal to 0.9723.

The limiting partial molar volumes are found to decrease as the medium becomes richer in methanol at a given temperature, whereas in a given mixed solvent medium, $\bar{V}_2^0$ values are found to increase with increasing temperature.

Effect of Medium and Temperature on the Limiting Partial Molar Volumes

The limiting partial molar volume of sodium carboxymethylcellulose decreases with increasing amount of methanol in the methanol-water mixtures at any given temperature (Table 2), and this might be due to more efficient polyion-coiling driven by greater counterion condensation as the medium becomes richer in methanol. An increase in the temperature, on the other hand, increases the limiting partial molar volume of sodium carboxymethylcellulose in a given mixed solvent medium as can be seen from Table 2. This might be ascribed to the growing importance of the contribution to the partial molar volume due to a temperature-induced desolvation of the counterions leading to more counterion binding at higher temperatures as observed earlier from conductivity measurements (Chapter 4).

Conclusions

The present investigation indicates that in methanol-water mixed solvent media counterion binding would become quite appreciable as the concentration of the polyelectrolyte is increased, thereby weakening the ion-solvent interactions. Influences of the medium and the temperature on the limiting partial molar volumes have also been discussed.

References

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Table 1. Densities (ρ) of Methanol-Water Mixed Solved Media at 298.15, 303.15, 308.15, and 313.15 K

T (K)	ρ (g.cm^{-3})		
	Vol.% of Methanol		
	10	20	30
298.15	0.98297	0.96963	0.95620
303.15	0.98138	0.97688	0.95393
308.15	0.97973	0.96632	0.95160
313.15	0.97791	0.96407	0.94893

Table 2. Limiting Partial Molar Volumes ($\bar{V}_2^0$) of Sodium Carboxymethylcellulose in Methanol-Water Mixed Solved Media at 298.15, 303.15, 308.15, and 313.15 K

T(K)	V_2^0 (cm^3.mol^{-1})		
	Vol.% of Methanol		
	10	20	40
298.15	181.60	178.75	175.93
303.15	183.45	180.84	177.44
308.15	184.86	181.93	178.91
313.15	186.53	183.50	180.15

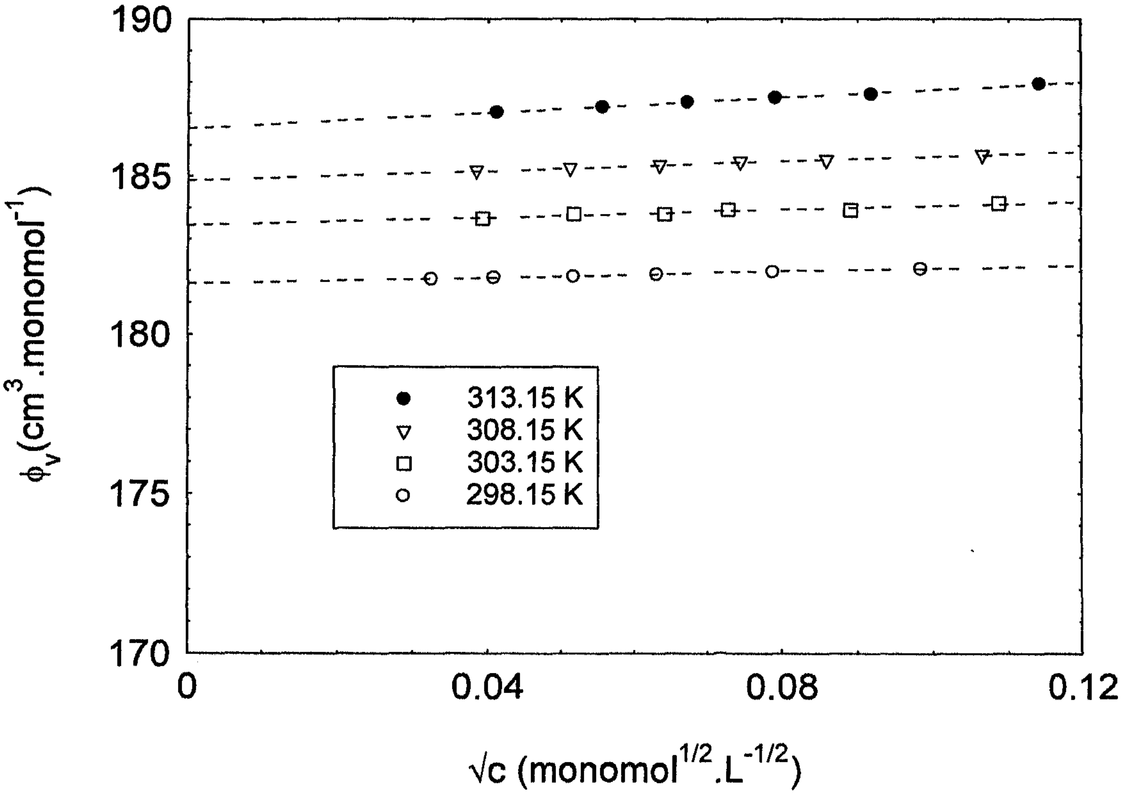

Fig. 1. Apparent molar volumes of sodium carboxymethylcellulose in methanol-water mixed solvent medium containing 10 vol. % of methanol at different temperatures.

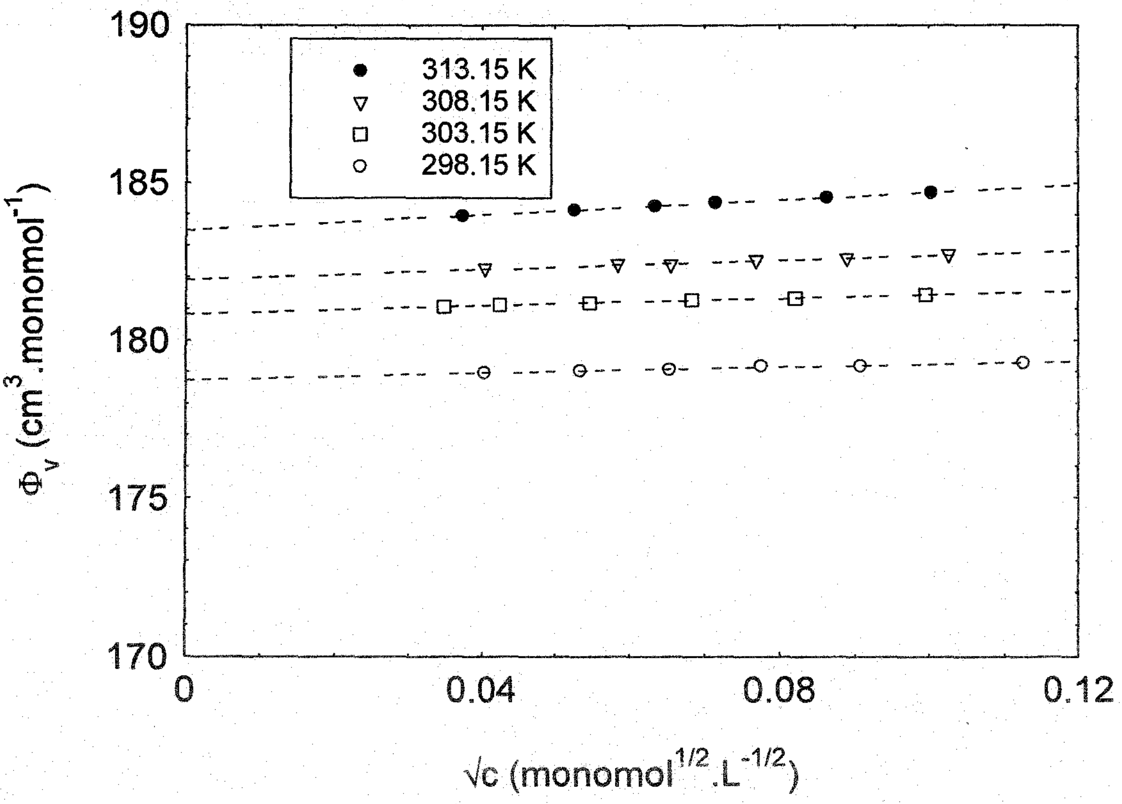

Fig. 2. Apparent molar volumes of sodium carboxymethylcellulose in methanol-water mixed solvent medium containing 20 vol. % of methanol at different temperatures.

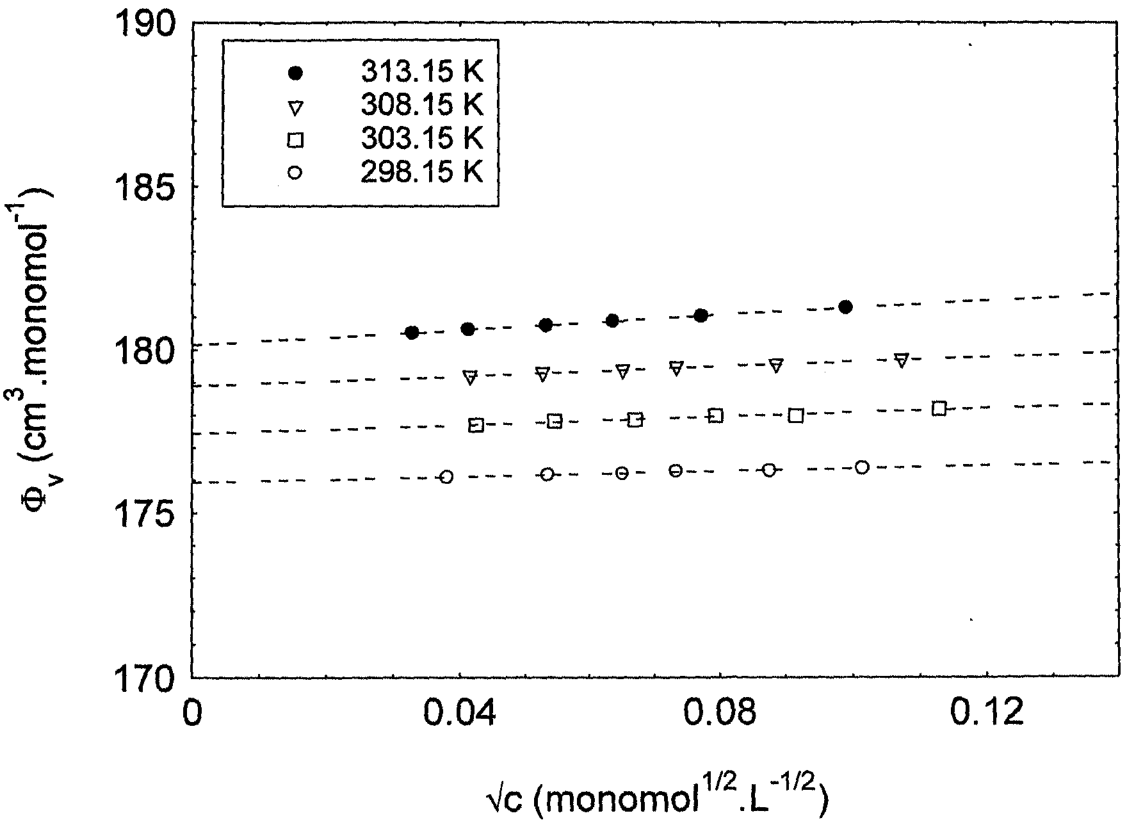

Fig. 3. Apparent molar volumes of sodium carboxymethylcellulose in methanol-water mixed solvent medium containing 30 vol. % of methanol at different temperatures.