

Chapter VIII

Apparent Molar Volumes of Sodium Polystyrenesulfonate in Acetonitrile-Water Mixed Solvent Media

Introduction

The principal factors that govern the dissolved state of polyelectrolytes in solutions are firstly the electro-repulsive forces working between ionic sites in the polymer chain and secondly the interactions between the polyions and counterions surrounding the polyion chains. The first factor is related to expansibility of the polymer chains, while the second is not only reflected in counterion binding but also in the extent of solvation and the structure of the solvent in the vicinity of polyelectrolytes. Both of these factors are associated with the relative permittivity of the solvent media. Use of a series of mixed solvents gives rise to a systematic variation in the relative permittivity of the media and hence allows investigation on these interactions prevailing 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 NaPSS in acetonitrile-water mixtures (*cf.* Chapters VI and VII). In this chapter, we report the apparent molar volumes of NaPSS in acetonitrile-water mixtures with a view to investigate the polyion-counterion interactions as well as the solvation behaviour of the counterions.

Experimental

Acetonitrile (E. Merck, India, 99%) was distilled with phosphorous pentoxide and then redistilled over calcium hydride. The purified solvent had a density of $0.76570 \text{ g.cm}^{-3}$ and a co-efficient of viscosity of 0.3126 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 $10^{-6} \text{ S.cm}^{-1}$ at 308.15 K was used for the preparation of the mixed solvents.

Sodium polystyrenesulfonate employed in this investigation was purchased from Aldrich Chemical Company, Inc. The average molecular weight (M_w) of the sample was 70 kDa .

The densities were measured with an Ostwald-Sprengel 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. Measurements were made in a water bath maintained within $\pm 0.005 \text{ K}$ of the

experimental temperature. The precision of the density measurements was always within $\pm 3 \times 10^{-5} \text{ g.cm}^{-3}$. Densities of acetonitrile-water mixtures at 298.15, 308.15, and 318.15 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

$$\phi_v = \frac{M}{\rho_0} - 1000 \frac{(\rho - \rho_0)}{c\rho_0} \quad (1)$$

where c is the polyelectrolyte concentration (in monomolarity), M the molecular mass of the repeating unit of NaPSS with a degree of substitution (DS) of 1, ρ the density of the solution and ρ_0 the density of the solvent.

Variations of Apparent Molar Volumes with Polyelectrolyte Concentration

Figures 1 – 3 show the variations of apparent molar volumes as a function of the square root of the monomolar concentration of NaPSS in acetonitrile-water mixtures in 10, 20 and 40 volume percent of acetonitrile in acetonitrile-water mixtures at 298.15, 308.15, and 318.15 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 slightly. Similar linear increases for ϕ_v with concentration have been previously reported by Conway and Desnoyers,² Lawrence and Conway,³ Ise and Okubo⁴ and Tondre and Zana⁵ for various polyelectrolytes in aqueous solutions although the insensitivity of ϕ_v toward concentration was also reported⁴ for salts of polystyrenesulfonic acid and polyethylenimine in water. 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 acetonitrile-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. Moreover, at a given temperature a slight increase in the values of the slopes with increasing amount of acetonitrile in acetonitrile-water mixture was also observed. This indicates a greater polyion-counterion interaction as the solvent medium becomes richer in acetonitrile. Exactly the same conclusion regarding the counterion-binding behaviour of NaPSS in the present mixed solvent media has been drawn from our conductometric studies (*cf.* Chapter IV).

The Limiting Partial Molar Volumes

The apparent molar volumes at infinite dilution, ϕ_v^0 (equal to the limiting partial molar volumes, $V_2^{\bar{0}}$) were obtained by least-squares fitting of ϕ_v values to the equation

$$\phi_v = \phi_v^0 + S_v \sqrt{c} \quad (2)$$

where S_v is the experimental slope. The values of ϕ_v^0 ($= V_2^{\bar{0}}$) 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 0.968.

The limiting partial molar volumes are found to decrease as the medium becomes richer in acetonitrile at a given temperature, whereas in a given mixed solvent medium, $V_2^{\bar{0}}$ values are found to increase with increasing temperature.

Ionic Limiting Partial Molar Volumes

In order to investigate the specific behaviour of the polyion and the counterion comprising the polyelectrolyte, it is necessary to split the $V_2^{\bar{0}}$ values into their ionic components. Now, the limiting partial molar volumes of sodium ion could be obtained from the literature $V_2^{\bar{0}}$ values of NaCl, sodium tetraphenylborate (NaBPh₄), and tetraphenylphosphonium chloride (Ph₄PCl) in acetonitrile-water mixtures at 298.15 K⁶ by employing the tetraphenylphosphonium tetraphenylborate (TPTB) assumption.⁷ We, therefore, have separated the limiting partial molar volumes of NaPSS in acetonitrile-water mixtures at that particular temperature. The limiting partial molar volumes of sodium ion are, however, not available at the relevant compositions of the acetonitrile-water mixtures at which our measurements have been carried out. The available values of the limiting partial molar volumes of NaCl, NaBPh₄, and Ph₄PCl in acetonitrile-water mixtures at 298.15 K were, therefore, plotted against the volume per cent of acetonitrile in acetonitrile-water

mixtures and the $V_2^{\bar{0}}$ values of these electrolytes at the desired compositions have been generated from the smooth master curves. These were then employed to obtain the limiting partial molar volume of sodium ion *via* the TPTB assumption.

Various Contributing Factors to the Ionic Limiting Partial Molar Volumes

Following Millero,^{8,9} the ionic limiting partial molar volume, $V_{\text{ion}}^{\bar{0}}$, can be attributed to the following components

$$V_{\text{ion}}^{\bar{0}} = V_{\text{intr}}^{\bar{0}} + V_{\text{elec}}^{\bar{0}} + V_{\text{str}}^{\bar{0}} + V_{\text{cage}}^{\bar{0}} \quad (3)$$

where $V_{\text{intr}}^{\bar{0}}$ is the intrinsic partial molar volume (the positive increment in the $V_{\text{ion}}^{\bar{0}}$ value due to intrinsic volume of the ion; as a rule an intrinsic ionic volume in a solution is considered to be equal to its crystallographic volume¹⁰), $V_{\text{elec}}^{\bar{0}}$ is the electrostriction partial molar volume (the negative increment equal to the decrease in molar solute volume due to ion-solvent electrostrictive interaction), $V_{\text{str}}^{\bar{0}}$ is the disordered or void-space partial molar volume (the increment due to the destruction of solvent structure in the region of the ionic co-sphere) and $V_{\text{cage}}^{\bar{0}}$ is the caged partial molar volume (the negative increment characteristic of solvophobic “structure-making” parts of the ions in solution, due to the filling of the intermolecular cavities of the solvent structure).

It may be pointed out that the electric forces due to the negative charges on the structural units of NaPSS affect strongly the surrounding solvent molecules and hence for the carboxymethylcellulose polyion, $V_{\text{elec}}^{\bar{0}}$ will contribute significantly to its limiting partial molar volume. Because of the polar nature of acetonitrile-water mixtures, the apolar part will also contribute to the polyion limiting partial molar volume through the term $V_{\text{cage}}^{\bar{0}}$. Sodium ion, on the other hand, has nothing to do with caged partial molar volume.

Effect of Medium and Temperature on the Limiting Partial Molar Volumes

Table 3 shows that the limiting partial molar volume of the polyion decreases with increasing amount of acetonitrile in the acetonitrile-water mixtures. This indicates that the total contribution of the terms $V_{\text{elec}}^{\bar{0}}$ and $V_{\text{cage}}^{\bar{0}}$ becomes more important over that of the term $V_{\text{str}}^{\bar{0}}$ as the solvent medium becomes richer in acetonitrile. This is a manifestation of the

predominance of the combined influence of the polyion-solvent electrostrictive interaction and the solvophobic filling of the intermolecular cavities of the solvent structure by the apolar parts of the polyion with increasing acetonitrile content in the medium. For sodium ion, on the other hand, the disordered partial molar volume plays the leading role. In case of the polyelectrolyte as a whole, however, the polyion is governing the solution behaviour. Here also the limiting partial molar volume of NaPSS decreases with increasing amount of acetonitrile in the acetonitrile-water mixtures (Table 2) like the polyion. An increase in the temperature increases the limiting partial molar volume of NaPSS in a given mixed solvent medium as can be seen from Table 2. This might be ascribed to the growing importance of the disordered partial molar volume due to a temperature-induced desolvation of the counterion leading to more counterion binding at higher temperatures as observed earlier from conductivity measurements (Chapter IV).

Conclusions

The present investigation indicates that in acetonitrile-water mixed solvent media counterion binding would become quite appreciable as the concentration of the sodium polystyrene sulfonate is increased, thereby weakening the ion-solvent interactions. Moreover, the polyion is found to govern the volumetric behaviour of the polyelectrolyte as a whole in these solutions. The predominance of the combined influence of the polyion-solvent electrostrictive interactions and the solvophobic filling of the intermolecular cavities of the solvent structure by the apolar parts of the polyion with increasing acetonitrile content in the medium was observed. A temperature-induced desolvation of the counterions leading to more counterion binding at higher temperatures was also inferred from this study.

References

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Table 1. Densities, ρ (g cm^{-3}) of Acetonitrile-Water Mixed Solved Media at 298.15, 308.15, and 318.15 K

<i>T</i> (K)	ρ (g cm^{-3})		
	Vol Percent of Acetonitrile		
	10	20	40
298.15	0.98307	0.97046	0.93800
308.15	0.98096	0.96485	0.92362
318.15	0.97625	0.95912	0.91542

Table 2. Limiting Partial Molar Volumes, V_2^0 ($\text{cm}^3 \text{ monomol}^{-1}$) of NaPSS in Acetonitrile-Water Mixed Solved Media at 298.15, 308.15, and 318.15 K

T (K)	V_2^0 ($\text{cm}^3 \text{ monomol}^{-1}$)		
	Vol Percent of Acetonitrile		
	10	20	40
298.15	107.10 ± 0.04	105.58 ± 0.04	102.73 ± 0.05
308.15	108.72 ± 0.09	107.04 ± 0.03	105.07 ± 0.05
318.15	109.64 ± 0.07	108.41 ± 0.07	106.41 ± 0.04

Table 3. Limiting Partial Molar Volumes, $V_2^{\bar{0}}$ [(cm³ mol⁻¹) or (cm³ monomol⁻¹)] of Sodium Ion (Na⁺) and Polystyrenesulfonate Ion (PSS⁻) in Acetonitrile-Water Mixed Solved Media at 298.15 K

Ion/Polyion	$V_2^{\bar{0}}$ [(cm ³ mol ⁻¹) or (cm ³ monomol ⁻¹)]		
	Vol Percent of Acetonitrile		
	10	20	40
Na ⁺	-9.12	-7.14	-3.35
PSS ⁻	116.22	112.72	106.08

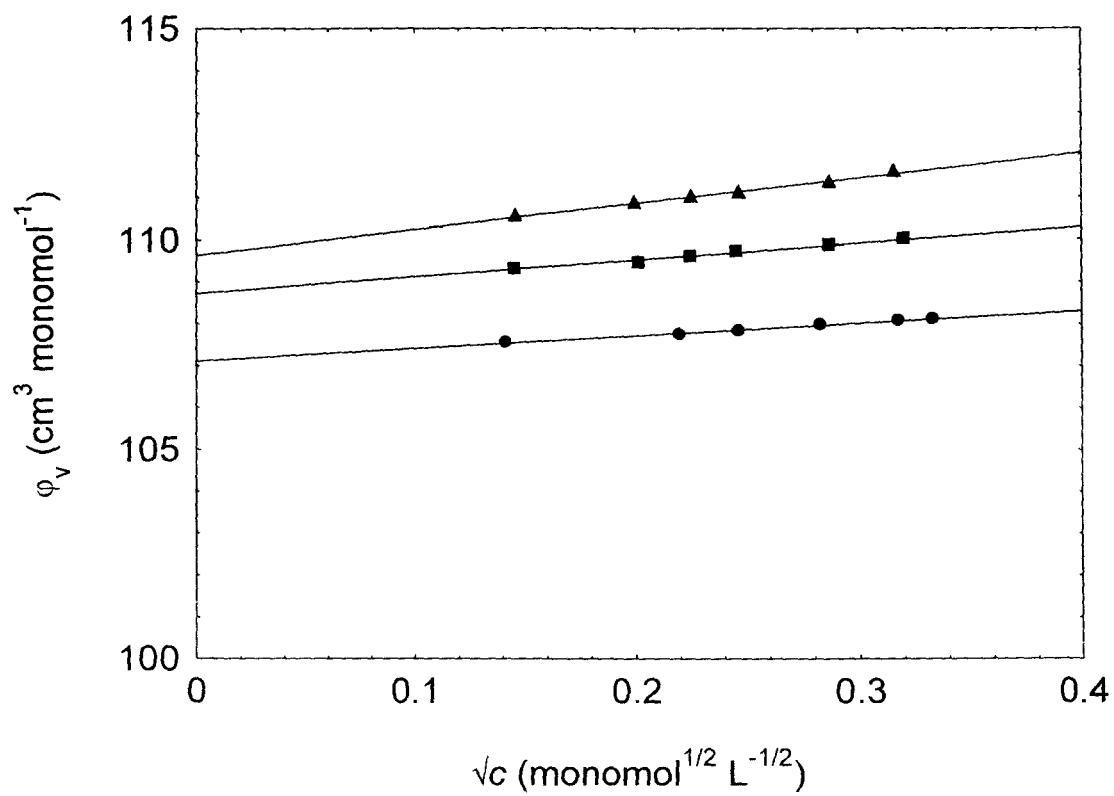


Figure 1. Apparent molar volumes of NaPSS in 10 vol percent of acetonitrile in acetonitrile-water mixed solvent medium at 298.15 K (●), 308.15 K (■), and 318.15 K (▲).

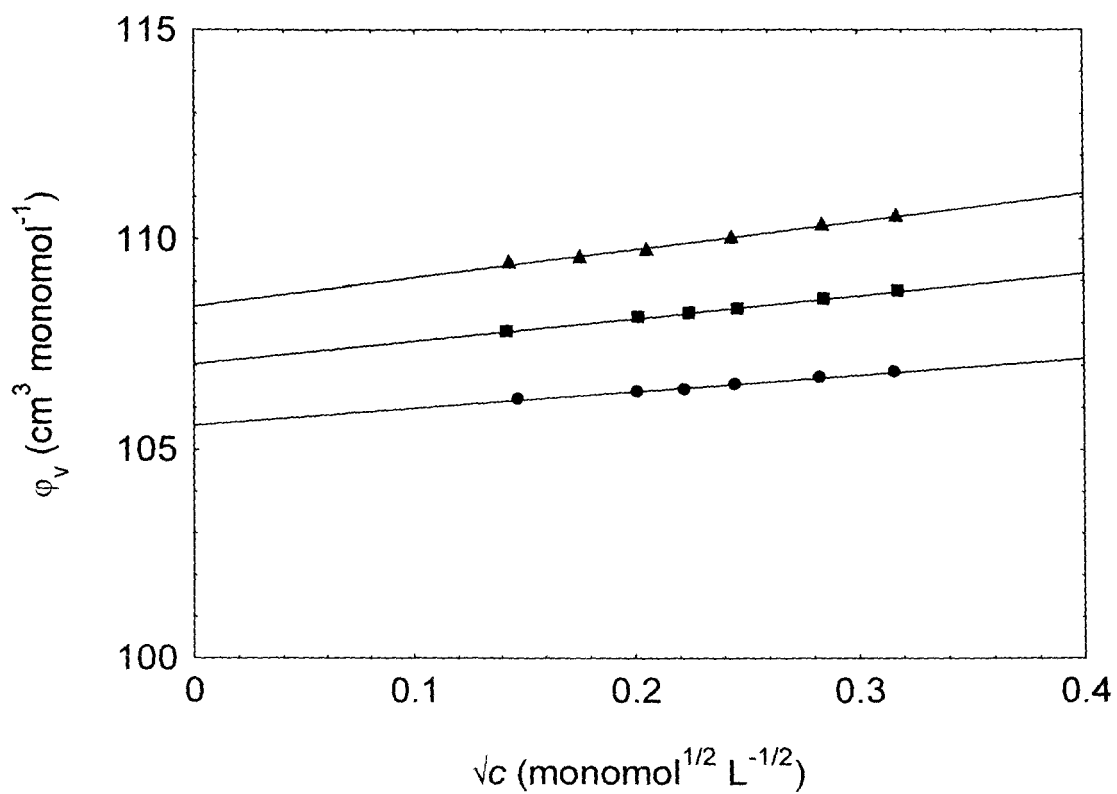


Figure 2. Apparent molar volumes of NaPSS in 20 vol percent of acetonitrile in acetonitrile-water mixed solvent medium at 298.15 K (●), 308.15 K (■), and 318.15 K (▲).

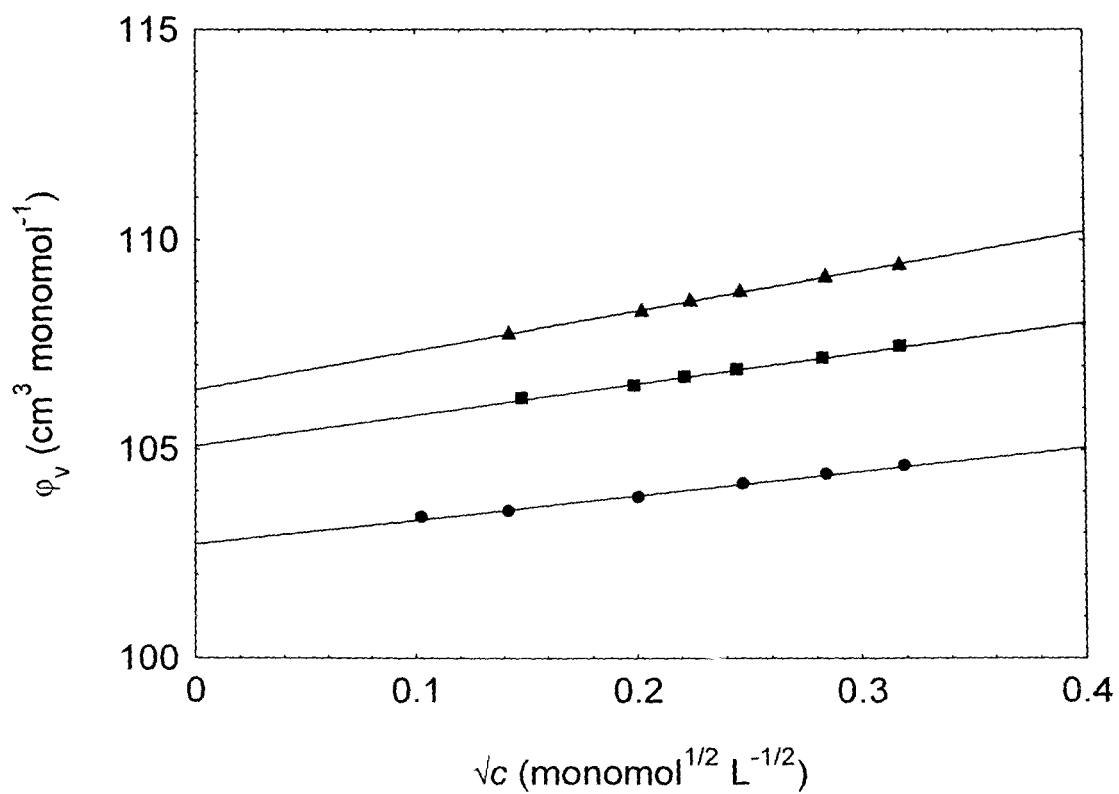


Figure 3. Apparent molar volumes of NaPSS in 40 vol percent of acetonitrile in acetonitrile-water mixed solvent medium at 298.15 K (●), 308.15 K (■), and 318.15 K (▲).