

Chapter 9

Apparent Molar Volumes of Sodium Polystyrenesulphonate in 2-Ethoxyethanol–Water Mixed Solvent Media

9.1 Introduction

A detailed understanding of the solution behaviour of polyelectrolytes requires information on a variety of physical and chemical parameters. The partial molar volume is an important thermodynamic property which may be helpful in the identification of solute-solvent and solute-solute interactions. Moreover, partial molar volumes are necessary for the application of characterization methods and physicochemical techniques including analytical and preparative ultracentrifugation, as well as small – angle X-ray and neutron scattering. Empirical procedures have been developed to calculate and predict the limiting partial molar volume for nonionic and ionic organic compounds in aqueous solutions.^{1,2} However, the evaluation by these procedures for polyelectrolyte is limited due to lack of availability of reliable experimental data for a broad variety of chemical structures and macromolecular characteristics. A molecular theory of partial molar volume of polyelectrolytes which takes into account all types of interaction in these solutions is, so far, not available.

The principal factors that govern the dissolved state of polyelectrolytes in solutions are (i) the electro-repulsive forces working between ionic sites in the polymer chain and (ii) 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 corresponds to the 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 counterion condensation on the conductivity behaviour of sodium polystyrenesulphonate in

2-ethoxyethanol–water mixtures (*cf.* Chapters 6-8). We also have investigated the influences of intrachain and interchain electrostatic interactions and the resulting coiling/expansion of the polyion chains from viscosity measurements on the viscosity behaviour of sodium polystyrenesulphonate in 2-ethoxyethanol–water mixtures (*cf.* Chapters 9 and 10). In this chapter, we report the apparent molar volumes of sodium polystyrenesulfonate in 2-ethoxyethanol–water mixtures with a view to investigate the polyion-counterion interactions as well as the solvation behaviour of the counterions.

9.2 Experimental

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 agree well with the literature values.³ Triply distilled water with a specific conductance of less than $10^{-6} \text{ S}\cdot\text{cm}^{-1}$ at 308.15 K was used for the preparation of the mixed solvents.

Sodium polystyrenesulphonate was purchased from Aldrich Chemical Company, Inc. The average molecular weight (M) of the sample was 70000 and this value agreed well with that determined in the present study (*cf.* Chapter 3 for purification and molecular weight determination).

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.⁴ Measurements were made in a water bath maintained within $\pm 0.01 \text{ K}$ of the experimental temperature. The precision of the density measurements was always within $\pm 3 \times 10^{-5} \text{ g}\cdot\text{cm}^{-3}$. Densities of 2-ethoxyethanol–water mixtures at 308.15 , 318.15 and 323.15 K are given in Table 9.1.

9.3 Results and Discussion

9.3.1 Apparent Molar Volumes

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

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

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

9.3.2 Variations of Apparent Molar Volumes with Polyelectrolyte Concentration

Figures 9.1 to 9.4 show the variations of apparent molar volumes as a function of the square root of the monomolar concentration of sodium polystyrenesulphonate in 2-ethoxyethanol–water mixtures in 25, 40, 50 and 60 mass percent of 2-ethoxyethanol in 2-ethoxyethanol–water mixtures at 308.15, 318.15, and 323.15 K. Within the concentration ranges investigated here, the ϕ_v vs. $\sqrt{c_p}$ plots are found to be linear and, moreover, as $\sqrt{c_p}$ is increased, ϕ_v increased slightly. Similar linear increases for ϕ_v with concentration have been previously reported by Conway and Desnoyers,⁵ Lawrence and Conway,⁶ Ise and Okubo⁷ and Tondre and Zana⁸ for various polyelectrolytes in aqueous solutions although the insensitivity of ϕ_v toward concentration was also reported⁴ for salts of polystyrenesulphonic 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 2-ethoxyethanol–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. $\sqrt{c_p}$ plots.

9.3.3 The Limiting Partial Molar Volumes

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

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

where S_v is the experimental slope. The values of ϕ_v^0 ($=\bar{V}_2^0$) are given Table 9.2. The correlation coefficients (r) of the regression analyses were always found to be greater than or equal to 0.990.

The limiting partial molar volumes are found to increase both (i) as the medium becomes richer in 2-ethoxyethanol at a given temperature, and (ii) as the temperature increases in a given mixed solvent medium.

9.3.4 Ionic Limiting Partial Molar Volumes

To investigate the specific behaviour of the polyion and the counterion comprising the polyelectrolyte, it is necessary to split the \bar{V}_2^0 values into their ionic components. Now in order to evaluate the limiting partial molar volume of polystyrenesulphonate ion, that of the sodium ion needs to be ascertained. As a representative case, we have executed the separation of the limiting partial molar volumes at 318.15 K. For this purpose, we have obtained the limiting partial molar volumes (\bar{V}_2^0) of sodium bromide (NaBr), sodium tetraphenylborate (NaBPh₄), and tetrabutylammonium bromide (Bu₄NBr) in 2-ethoxyethanol–water mixtures at 318.15 K from the measurement of their densities as a function of concentration. From these limiting partial molar volumes, the ionic limiting partial molar volumes of the sodium ion were obtained by the “reference electrolyte” method as suggested by Millero.⁹ We have used here tetrabutylammonium tetraphenylborate (Bu₄NBPh₄) as the reference electrolyte. The ionic limiting partial molar volumes of the sodium ion thus obtained were then subtracted from the limiting partial molar volumes of the polyelectrolyte as whole to obtain the respective contributions of the polyion. The ionic limiting partial molar volumes of the sodium and the polystyrenesulphonate ion in 2-ethoxyethanol–water mixtures at 318.15 K are listed in Table 9.3.

9.3.5 Various Contributing Factors to the Ionic Limiting Partial Molar Volumes

Following Millero,^{9,10} the ionic limiting partial molar volume, \bar{V}_{ion}^0 , can be attributed to the following components

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

where \bar{V}_{intr}^0 is the intrinsic partial molar volume (the positive increment in the \bar{V}_{ion}^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), \bar{V}_{elec}^0 is the electrostriction partial molar volume (the negative increment equal to the decrease in molar solute volume due to ion-solvent electrostrictive interaction), \bar{V}_{str}^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 \bar{V}_{cage}^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 sodium polystyrenesulphonate affect strongly the surrounding solvent molecules and hence for the polystyrenesulphonate polyion, \bar{V}_{elec}^0 will contribute significantly to its limiting partial molar volume. Because of the polar nature of 2-ethoxyethanol–water mixtures, the apolar part will also contribute to the polyion limiting partial molar volume through the term \bar{V}_{cage}^0 . Sodium ion, on the other hand, has nothing to do with caged partial molar volume.

9.3.6 Effect of Medium and Temperature on the Limiting Partial Molar Volumes

Table 9.3 shows that the limiting partial molar volume of the polyion increases initially with increasing amount of 2-ethoxyethanol in the 2-ethoxyethanol–water mixtures, reaches a maximum at around 50 mass percent of 2-ethoxyethanol and decreases thereafter. This indicates that the contribution of the term \bar{V}_{str}^0 overrides the sum of the contributions of the terms \bar{V}_{elec}^0 and \bar{V}_{cage}^0 below 50 mass percent of 2-ethoxyethanol in the mixed solvent media, whereas above 50 mass percent of 2-ethoxyethanol, the total contribution of the later two terms predominates over the contribution of the term \bar{V}_{str}^0 . The increment of the volume due to the destruction of solvent structure in the region of the ionic co-sphere is thus playing the major role in determining the limiting partial molar volume of the polyion when the mixed solvent media contain less than 50 mass percent of 2-ethoxyethanol. There is, however, a 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 beyond 50 mass

percent of the cosolvent in the medium. The influence of temperature on the limiting partial molar volume of sodium polystyrenesulphonate is very small. An increase in the temperature increases the limiting partial molar volume of sodium polystyrenesulphonate in a given mixed solvent medium as can be seen from Table 9.2. This might be ascribed to a slight growth 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 4).

9.4 Conclusions

The present investigation indicates that in 2-ethoxyethanol–water mixed solvent media counterion binding would become quite appreciable as the concentration of sodium polystyrenesulphonate is increased, thereby weakening the ion-solvent interactions. A delicate balance of the influences of the volumetric terms \bar{V}_{str}^0 , \bar{V}_{elec}^0 and \bar{V}_{cage}^0 is found to control the volumetric behaviour of this polyelectrolyte in 2-ethoxyethanol-water mixed solvent media. A temperature-induced desolvation of the counterions leading to more counterion binding at higher temperatures was also inferred from this study.

9.5 References

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Table 9.1 Densities (ρ_0) of 2-Ethoxyethanol–Water Mixed Solvent Media at 308.15, 318.15 and 323.15 K

T (K)	ρ_0 (g·cm ⁻³)			
	Mass % of 2-Ethoxyethanol			
	25	40	50	60
308.15	0.99758	0.99747	0.99361	0.98680
318.15	0.98807	0.98696	0.98004	0.96832
323.15	0.98394	0.98378	0.97610	0.96253

Table 9.2 Limiting Partial Molar Volumes (\bar{V}_2^0) of Sodium Polystyrenesulphonate in 2-Ethoxyethanol–Water Mixed Solved Media at 308.15, 318.15 and 323.15 K

<i>T</i> (K)	\bar{V}_2^0 (cm ³ ·monomol ⁻¹)			
	Mass % of 2-Ethoxyethanol			
	25	40	50	60
308.15	108.01 ± 0.02	109.03 ± 0.02	109.33 ± 0.01	110.65 ± 0.01
318.15	108.20 ± 0.01	109.11 ± 0.02	110.04 ± 0.02	110.84 ± 0.02
323.15	108.28 ± 0.03	109.22 ± 0.01	110.16 ± 0.02	110.93 ± 0.01

Table 9.3 Limiting Partial Molar Volumes, \bar{V}_{ion}^0 of Sodium Ion (Na^+) and Polystyrenesulphonate Polyion (PSS^-) in 2-Ethoxyethanol–Water Mixed Solved Media at 318.15 K

Ion / Polyion	\bar{V}_{ion}^0 ($\text{cm}^3 \cdot \text{monomol}^{-1}$)			
	Mass % of 2-Ethoxyethanol			
	25	40	50	60
Na^+	7.44	-0.60	0.14	2.27
PSS^-	100.76	109.71	109.90	108.57

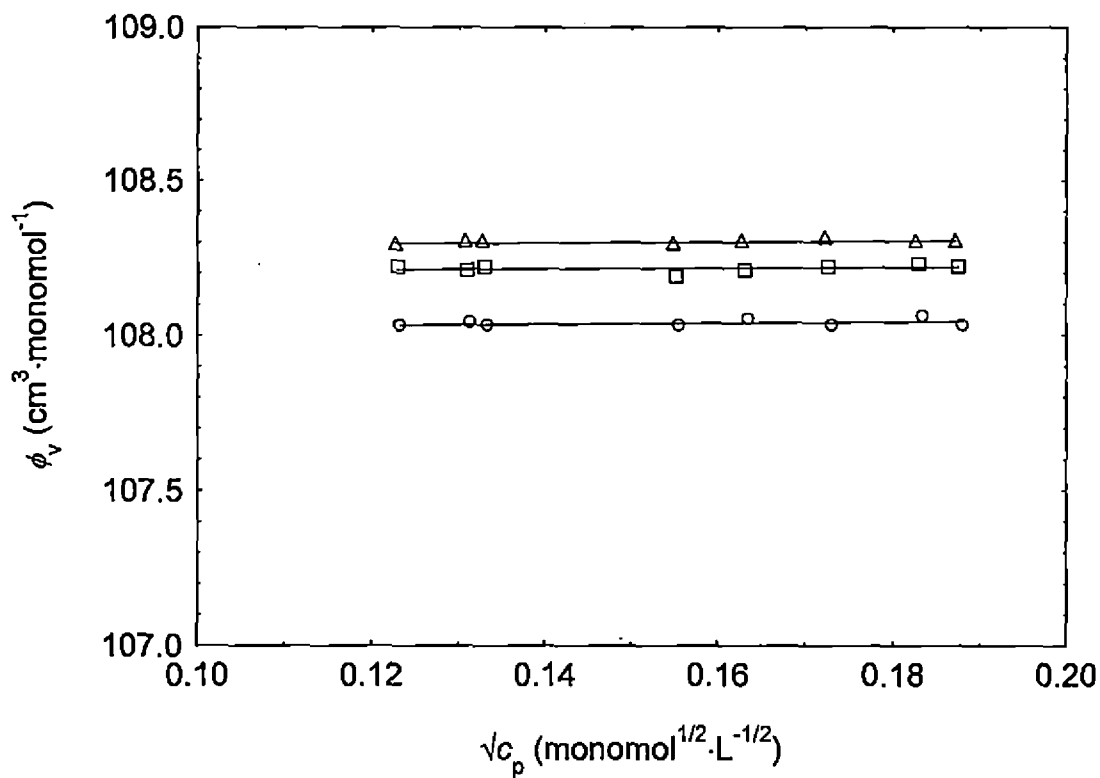


Figure 9.1 Polyelectrolyte concentration dependence of the apparent molar volumes of sodium polystyrenesulphonate in 25 mass percent 2-ethoxyethanol–water mixed solvent medium at 308.15 K (○); 318.15 K (◻); 323.15 K (Δ).

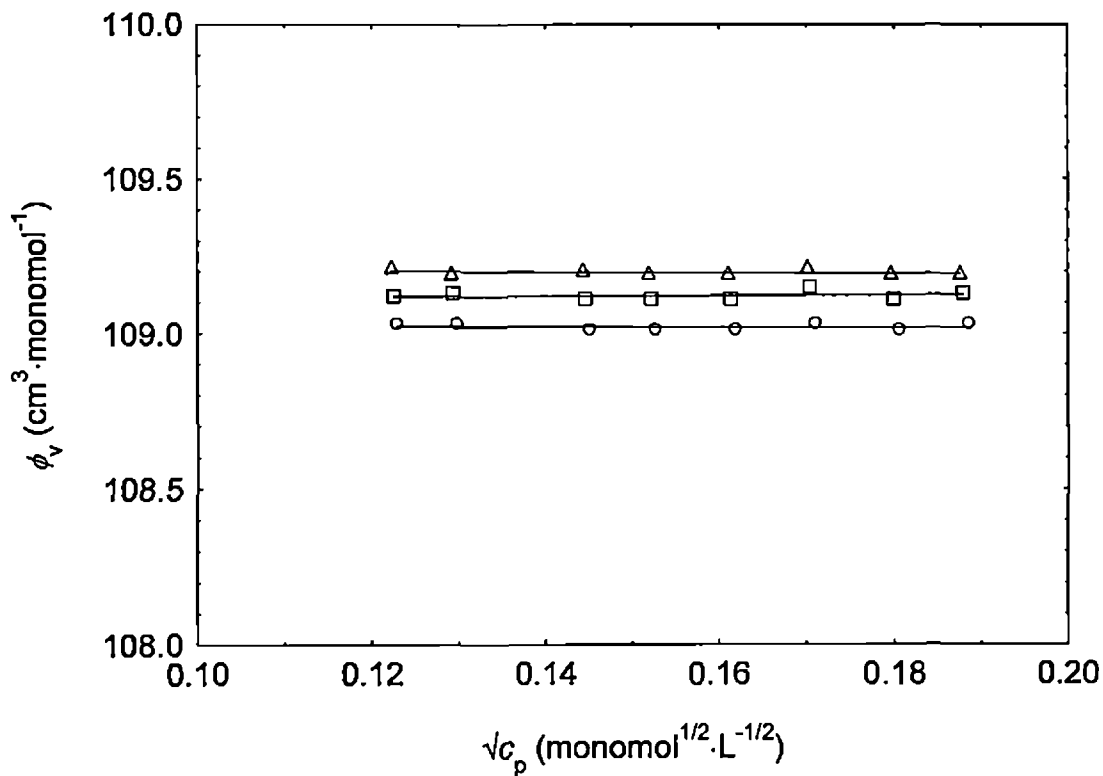


Figure 9.2 Polyelectrolyte concentration dependence of the apparent molar volumes of sodium polystyrenesulphonate in 40 mass percent 2-ethoxyethanol–water mixed solvent medium at 308.15 K (\circ); 318.15 K (\square); 323.15 K (Δ).

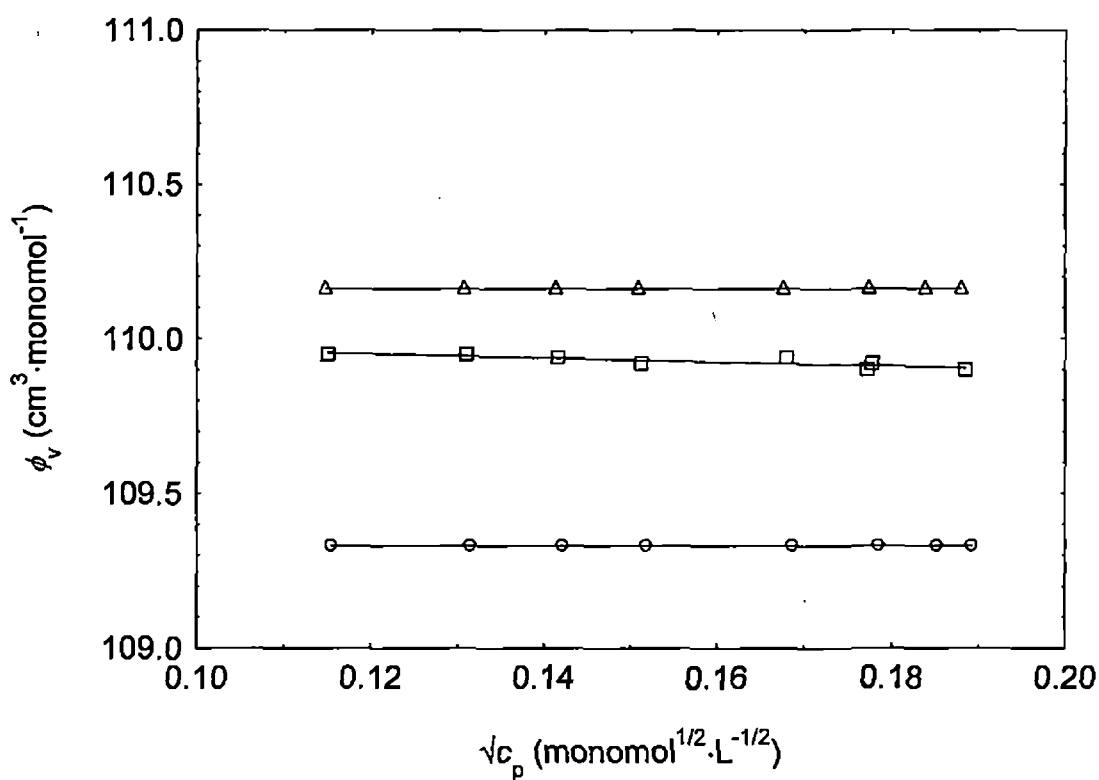


Figure 9.3 Polyelectrolyte concentration dependence of the apparent molar volumes of sodium polystyrenesulphonate in 50 mass percent 2-ethoxyethanol–water mixed solvent medium at 308.15 K (o); 318.15 K (□); 323.15 K (Δ).

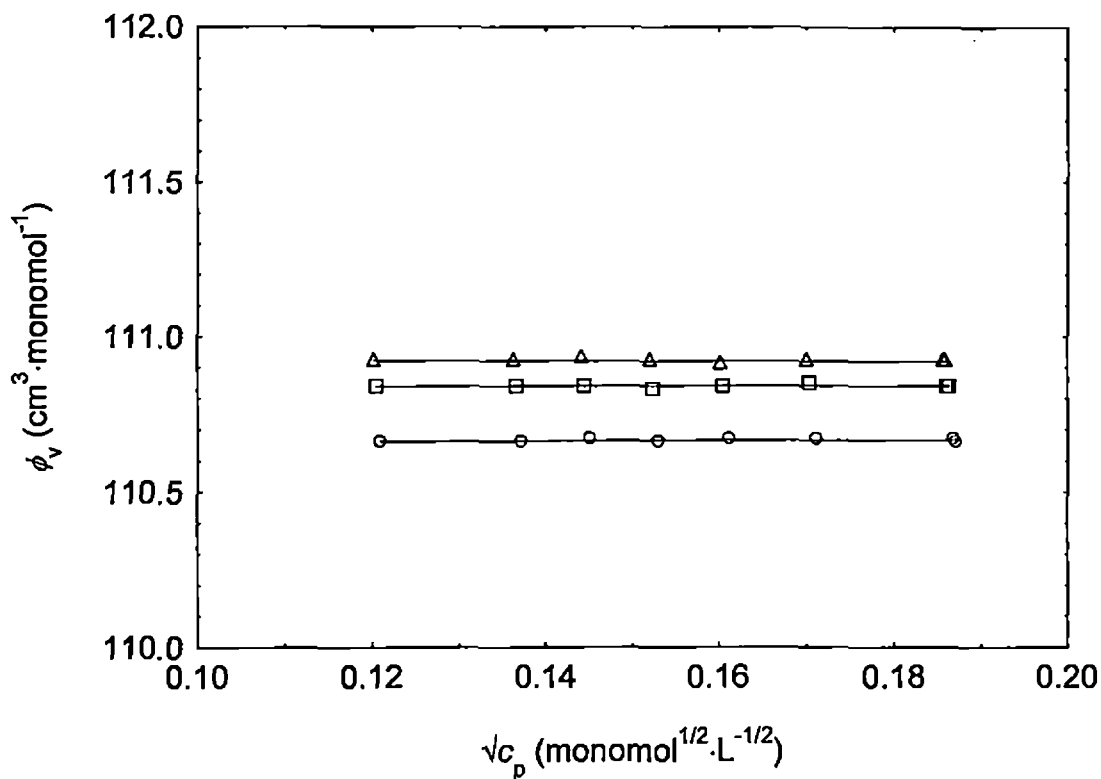


Figure 9.4 Polyelectrolyte concentration dependence of the apparent molar volumes of sodium polystyrenesulphonate in 60 mass percent 2-ethoxyethanol–water mixed solvent medium at 308.15 K (o); 318.15 K (□); 323.15 K (Δ).