

Effects of Concentration, Temperature and Solvent Composition on the Partial Molar Volumes of Sodium Polystyrenesulphonate in Methanol -Water Solvent Media

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Abstract

Precise measurements on the density of sodium polystyrenesulphonate solutions in methanol-water mixed solvent media containing 8, 16, and 25 weight per cent of methanol at 308.15, 318.15, and 323.15 K are reported. The degree of substitution of sodium polystyrenesulphonate used is 1, and the concentrations are varied from 1×10^{-2} to 3.8×10^{-2} monomol.l⁻¹. The results showed a slight increase on the partial molar volumes with increasing polyelectrolyte concentration. The partial molar volumes of the polyelectrolyte at infinite dilution, (\bar{V}^0) were determined. The effects of the temperature and solvent composition on the partial molar volumes are also investigated.

Keywords: *Sodium polystyrenesulphonate, polyion, partial molar volume.*

Introduction

Polyelectrolytes are polymers having ionizable groups, which in polar solvents, can dissociate into charged polymer chains (macroion) and small counterions of opposite charge.^{1,2} Solution properties of polyelectrolytes, both in the presence and in the absence of added salt, differ considerably from those of neutral macromolecular solutions or those of simple electrolytes. The origin of this specificity lies in the combination of properties derived from long-chain molecules

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with those derived from charge interactions. The high charge density on the macro ion produces a strong ionic field which attracts counter ions. This strong ionic interaction is the source of the characteristic properties of polyelectrolytes. Current interest in charged polymer solutions, in particular in high-molecular weight ionic macromolecules, is supported by the needs of biophysics since biopolymers are usually charged under physiological conditions and many of their biological functions are governed by the polyelectrolyte behavior.³ In accounting for the solution behavior of biological and synthetic polyelectrolytes, elucidation of the interactions between counter ions and charged groups on the polyion are of essential importance. Polyelectrolyte effect includes both deviations from the behavior of neutral polymers caused by the existence of charges along the polymer chain and deviations from the behavior of the electrolytes caused by the fixation of one sort of charges on the polymer chain. Therefore, in addition to the method of macromolecular characterization, electrochemical techniques have also been applied to investigate the solution behavior of polyelectrolytes.

As far as we know, there is little work in the literature dealing with the effect of the temperature on the partial molar volumes of the polyelectrolyte and no more work has been done on the effect of medium.^{4,5} In this paper, the results are reported for density measurements on sodium polystyrenesulphonate, an anionic polyelectrolyte, in methanol-water mixed solvent media with varying relative permittivity at different temperatures. A thorough knowledge of the solution behavior of polyelectrolytes deserves information on a variety of physical and chemical parameters. The partial molar volume is one of the important thermodynamic properties which may be helpful in the identification of solvent – solute as well as solute - solute interactions.⁶ Moreover, this partial molar volume is 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. Recently empirical procedures have been developed to calculate and predict the partial molar volume for non-ionic and ionic organic compounds in aqueous solutions.^{7,8} However, the evaluation of these procedures for polyelectrolyte is limited by the lack of availability of reliable experimental data of a broad variety of chemical structures and macromolecular characteristics. The effects of concentration, temperature and solvent composition on the partial molar volume have been studied for the polyelectrolyte sodium polystyrenesulphonate. Detailed definitions and explanation of the partial molar volume have been provided in several papers.⁹⁻¹¹ Hence, only basic relation pertaining to the system studied herewith will be dealt. The partial molar volume, \bar{V} , is defined by the following equation;

$$\bar{V} = (\partial V / \partial n)_{T,p} \quad (1)$$

where, ∂V represent change in total volume and n as the number of moles. The partial molar volume is often provided in units of partial molar volume

cm³/mol. If there is concentration dependence, the partial molar volumes have to be extrapolated to concentration zero using the following equation which calculate the apparent molar volume at the finite concentrations (c).⁹

$$\bar{V} = \frac{M}{\rho_0} - \frac{10^3}{c} \left(\frac{\rho}{\rho_0} - 1 \right) \quad (2)$$

where, the symbols have their usual significance and c is having the unit as equivalent concentration in monomol/L.

The aim of the present work is to analyze the influence of concentration, medium and temperature on the polyelectrolyte solution in mix solvent media by partial molar volumes. The solution densities are systematically measured for sodium polystyrenesulphonate and the partial molar volume of the polyelectrolyte is computed at the temperatures 308.15, 318.15 and 323.15 K.

Experimental Methods

Methanol (E. Merck, India, 99% pure) was distilled with phosphorous pentoxide and then redistilled over calcium hydride. The purified solvent had a density of 0.7772 g.cm⁻³ and a co-efficient of viscosity of 0.4742 mPa.s at 308.15 K; these values are in good agreement with the literature values.¹² Triply distilled water with a specific conductance less than 10⁻⁶ S.cm⁻¹ at 308.15 K was used for the preparation of the mixed solvents. The physical properties of methanol-water mixed solvents used in this study at 308.15, 318.15, and 323.15 K are reported in Table 1. The relative permittivity of methanol-water mixtures at the experimental temperatures were obtained by regressing the relative permittivity data as function of solvent composition from the literature¹³ and are included in Table 1.

Table 1: Properties of methanol-water mixtures containing 8, 16, and 25 weight % of methanol at 308.15, 318.15, and 323.15 K.

T/K	ρ_0 /g.cm ⁻³	η_0 / mPa.s	D
8 per cent methanol			
308.15	0.9797	0.8665	71.57
318.15	0.9760	0.7017	68.18
323.15	0.9741	0.6375	66.45
16 per cent methanol			
308.15	0.9663	1.0217	68.14
318.15	0.9616	0.8075	64.80
323.15	0.9588	0.7300	63.15
25 per cent methanol			
308.15	0.9516	1.1418	64.25
318.15	0.9463	0.8957	60.99
323.15	0.9433	0.8052	59.41

Sodium polystyrenesulphonate (NaPSS) employed in these investigations was purchased from Aldrich Chemical Company, Inc. The average molecular weight (M_w) of the sample was *ca.* 70,000. To measure density the pycnometric method was used. The stock solutions were freshly prepared for each concentration series to avoid problems of aging and microorganism contamination, which was found to occur with diluted polyelectrolyte solutions.¹⁴

The densities of solutions were determined by the use of Ostwald-Sprengel type pycnometer of about 10 cm³ capacity. The sample solution was transfused into the pycnometer by using a medical syringe. The pycnometer was then tightly fixed in a thermostat at the experimental temperatures within ± 0.005 K. After thermal equilibrium was attained, the mass of the pycnometer was measured with electronic balance and the density was calculated. Density measurements are believed to be precise within ± 0.00005 , which is satisfactory for our purpose. 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.

Results and Discussion

The partial molar volumes for the sodium polystyrenesulphonate in three different methanol-water mixtures (containing 8, 16, and 25 weight per cent of methanol) at 308.15, 318.15 and 323.15 K are depicted in Figs 1, 2 and 3 which show the variation of partial molar volumes of the investigated solutions as a function of the polymer concentration. From these figures, it is evident that the partial molar volumes exhibit a slight increase with increasing concentration within the concentration range investigated here. Obviously, the concentration dependence of partial molar volumes follows one and the same pattern at all the temperatures and solvent composition investigated. In fact, the variations of \bar{V} with polymer concentrations are always found to be linear. We, therefore, determined the limiting partial molar volumes (\bar{V}^0) by extrapolating the \bar{V} values to zero polymer concentration.

The slopes of \bar{V} vs polymer concentration graph are always found to be positive in methanol-water mixtures, indicating strong ion-ion interactions in these media. The strong ion-ion interactions lead to sufficient counterion binding onto the polyion chain and this also been established from our earlier conductivity study.¹⁵ The possible explanation for the positive slopes in the present mixed solvent media may be that the counter ion binding would become quite appreciable in these media as the concentration of the polymer is increased, thereby weaker ion-solvent interactions. As a consequence, contraction of the solvent would be gradually lowered with increasing concentration of the polyelectrolyte, resulting in a net

positive volume change per monomol of the added polyelectrolyte. Moreover, the slopes are found to increase in the mixed solvent media become richer in methanol, irrespective of temperature indicating greater counter ion binding with increasing amount of methanol in the solvent mixtures.

The effects of temperature and relative permittivity on the partial molar volume values are directly evident from figures 1, 2 and 3. At each temperature, the partial molar volume values are found to decrease with decreasing relative permittivity in going from 8 per cent to 25 weight per cent methanol-water mixtures over the entire concentration range investigated. An increase in temperature, on the other hand, is found to increase the partial molar volume in a given solvent medium as manifested in these figures. Evaluation of the limiting partial molar volumes (\bar{V}^0) leads to important insight as to the solution behavior of sodium polystyrene-sulfonate. The \bar{V}^0 values thus obtained along with the slopes and the correlation coefficients of fits, (as r^2) are listed in Table 2. It is apparent that the slopes pass through a minimum at 318.15 K in 8 weight per cent system.

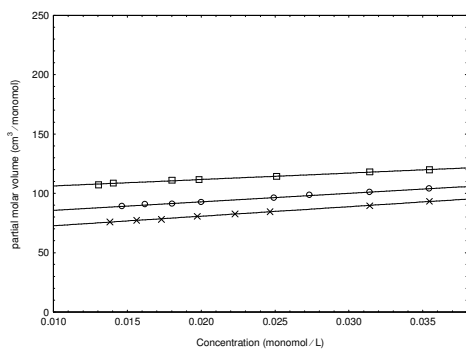


Figure 1: Concentration dependence of partial molar volume for sodium polystyrenesulphonate at 308.15K, in different methanol-water mixtures (squares, 8 per cent methanol; circles, 16 per cent methanol; crosses, 25 per cent methanol).

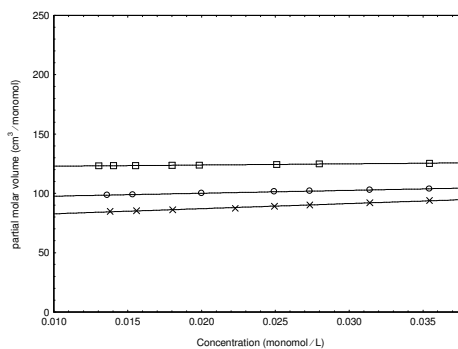


Figure 2: Concentration dependence of partial molar volume for sodium polystyrenesulphonate at 318.15K, in different methanol-water mixtures (squares, 8 per cent methanol; circles, 16 per cent methanol; crosses, 25 per cent methanol).

Furthermore, slopes are found to increase whereas the limiting partial molar volumes values are found to decrease as the solvent medium gets richer in methanol at a given temperature. On the other hand, limiting partial molar volumes in all compositions are found to increase with temperature (Table 2). The relative permittivity of the medium decreased at a given temperature with increasing in the methanol content. Lower relative permittivity promotes greater counterion-binding, and hence a lower amount of uncondensed counter ions in going from 8 to 25 weight per cent of methanol in the mixed solvent media over the entire range of temperatures investigated.

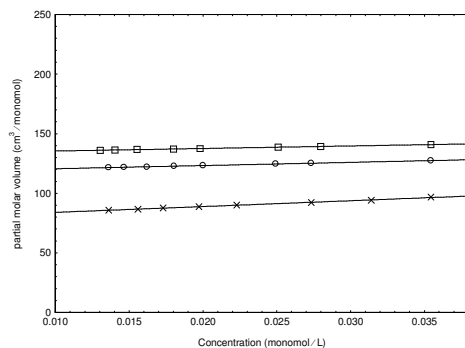


Figure 3: Concentration dependence of partial molar volume for sodium polystyrenesulphonate at 323.15K, in different methanol-water mixtures (squares, 8 per cent methanol; circles, 16 per cent methanol; crosses, 25 per cent methanol).

Table 2: Limiting partial molar volumes (\bar{V}^0), experimental slopes and the correlation coefficients of fits (as r^2) of sodium polystyrenesulphonate from figures 1, 2 and 3 in Methanol-Water mixtures at 308.15, 318.15 and 323.15 K.

wt % of methanol	T = 308.15 K			T = 318.15 K			T = 323.15 K		
	slope	\bar{V}^0	r^2	slope	\bar{V}^0	r^2	slope	\bar{V}^0	r^2
8	544	101	0.993	101	122	0.990	211	133	0.996
16	716	78.5	0.996	244	95.2	0.996	269	118	0.998
25	803	64.7	0.998	430	78.4	0.991	488	79.1	0.997

Conclusions

Experimental results for the partial molar volumes of salt-free solution of a polyelectrolyte sodium polystyrenesulphonate in methanol-water mixed solvent media have been presented as a function of polymer concentration and temperature. The partial molar volumes are found to increase with increasing temperature over the entire concentration range investigated in a given mixed solvent medium whereas these values are found to decrease as the relative permittivity of the medium decreases. Estimation of the slopes and limiting partial molar volumes provide

important insight regarding the solution behavior of this polyelectrolyte in methanol-water mixtures.

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