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THE APPARENT AND PARTIAL MOLAR VOLUMES OF SODIUM CARBOXYMETHYLCELLULOSE IN ACETONITRILE-WATER MIXED SOLVENT MEDIA

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ABSTRACT

The volumetric properties of Sodium Carboxymethylcellulose (NaCMC) in acetonitrile-water mixed solvent media containing (0.10, 0.20, and 0.40) volume fractions of acetonitrile were studied by measuring the density of solutions at temperatures (298.15, 308.15, 313.15, and 318.15) K. Besides studying the solvation behavior of the counterions, the study was focused on investigating the interactions between the counterion and the polyion. In the specified temperature range, a linear increase for apparent molar volume (ϕ_v) with increasing polyelectrolyte concentration was observed in a medium with fixed volume fractions of acetonitrile. However, at a given temperature as the medium became richer in acetonitrile the limiting partial molar volumes ($\bar{V}_2^0$) registered a decrease. But, when a polyelectrolyte solution in a fixed medium underwent a step-wise increase in temperature then $\bar{V}_2^0$ values increased thereby leading to the inference that a temperature-induced desolvation of the counterions results in more counterion binding at higher temperatures.

Keywords: Sodium Carboxymethylcellulose, Mixed Solvent Media, Partial Molar Volume, Counterion Binding, Ion-Solvent Interactions

INTRODUCTION

Polyelectrolytes have numerous techno-industrial usages and they motor the molecules which are necessary for the survival of living organisms.[1-5] As such they have attracted the attention of many researchers. However, the properties of polyelectrolyte solutions deviate considerably from those of neutral polymeric solutions and those of simple electrolytic solutions. And the chief factors responsible for determining the properties of polyelectrolyte solutions are (i) the electro-repulsive forces that operate in between the ions of a polymer chain and (ii) the two-ways exchanges that take place in between the polyions and counterions. Of these, the first factor causes the polymer chain to expand. But the second factor not only operates in the binding of counterion, but it also has its role in determining the degree of solvation besides influencing the structure of the solvent lying near the polyelectrolytes. Finally, each of these factors in isolation affects the relative permittivity of the solvent media. When a number of mixed solvents are taken then one can observe systematic variation in the relative permittivity of the media. Using this variation one can investigate the interactions that go on in the polyelectrolyte solutions.[6-9]

Since the thermodynamic properties of polyelectrolyte solutions are useful in illuminating the ongoing structural interactions in solutions, they have been made use in the present investigation. Examples would make the matter clear. If the study of partial molar volumes[10-14] of solutes under infinite dilution facilitates the understanding of solute-solvent and solvent-solvent interactions, then the solute-solute interactions can be studied using concentration dependence of apparent molar volume[14-17] of solute. The present investigation is geared towards the understanding of polyion-counterion interactions as well as the solvation behavior of the counterions using the apparent and partial molar volumes of Sodium Carboxymethylcellulose (NaCMC) in acetonitrile-water mixtures. To do so, the solution densities of

NaCMC were measured and the apparent molar volumes of polyelectrolyte solutions were calculated at experimental temperatures.

EXPERIMENTAL

Acetonitrile (purchased from E. Merck, India with a purity >99%) was fractionally distilled with phosphorous pentoxide. The middle fraction was collected and redistilled with calcium hydride. The density and viscosity co-efficient of the distilled acetonitrile at 308.15 K were 0.76570 ± 0.00003 g.cm^{-3} and 0.31260 ± 0.00004 mPa.s respectively, values which conformed with the physical properties of the distilled acetonitrile as reported by the literature.[18] The mixed solvents were prepared with triple-distilled water with specific conductance value ~10^{-6} S.cm^{-}1. The measured values of density and viscosity of the mixed solvents at (298.15, 308.15, 313.15, and 318.15) K are shown in Table-1. With the help of density and relative permittivity values of the pure solvents[18,19] at experimental temperatures and following the method of literature,[20] the relative permittivities of the solvent mixtures were evaluated and are also incorporated in Table-1.

Table-1: Physical Properties of Acetonitrile-Water Mixtures Containing (0.10, 0.20, And 0.40) Volume Fraction of Acetonitrile at (298.15, 308.15, 313.15, And 318.15) K
^{a} Evaluated following the method as represented in ref 20.

T / K	ρ_0 / g.cm^{-3}	η_0 / mPa.s	D^a
$\phi_1 = 0.10$			
298.15	0.98307	1.0642	75.62
308.15	0.98096	0.8766	72.15
313.15	0.97893	0.7622	69.89
318.15	0.97625	0.6733	68.27
$\phi_1 = 0.20$			
298.15	0.97046	1.1003	72.19
308.15	0.96485	0.9067	67.94
313.15	0.96200	0.7833	66.38
318.15	0.95912	0.6984	64.84
$\phi_1 = 0.40$			
298.15	0.93800	1.0398	63.48
308.15	0.92362	0.8200	60.07
313.15	0.91730	0.6803	58.87
318.15	0.91542	0.5611	57.32

NaCMC (purchased from Sigma-Aldrich, USA) had an average molecular weight (M_w) ~90,000 and 0.70 carboxymethyl groups per anhydroglucose unit. Fresh stocks solutions were used for each measurement in order to avoid problems associated with aging and contamination of the solutions from a microorganism, since such observations do occur in the dilute polyelectrolyte solutions.[21]

For all density measurements, an Ostwald-Sprengel type pycknometer (bulb volume of 25 cm^3 and capillary diameter 1 mm) was used. The pycknometer was standardized at the experimental temperatures with distilled water, methanol, and acetonitrile. Densities of the solutions were measured in a thermostatic water bath having an accuracy of ± 0.005 K. The precision of the density measurements was always within ± 3 x 10^{-5} g.cm^{-3}.

RESULTS AND DISCUSSION

Thermodynamic quantities like partial or apparent molar volumes of the solute[10] are often used to study the structural interactions of polyions in solutions. In general, the partial molar volume ($\bar{V}_2^0$) of the solute in a solution is the change in volume per mole of solute added to the mixture at constant temperature, pressure, and composition, i.e., $\bar{V}_2^0 = \left(\partial V / \partial n_2\right)_{T,P,n_1}$. On the other hand, the formal contribution of the solute to the total volume of the solute-solvent system is defined as the apparent molar volumes (ϕ_v). The apparent molar volume of the polyelectrolyte in solution is amenable to calculation using the following equation:

$$\phi_\mathrm{v} = \frac{M}{\rho_0} - 1000\frac{(\rho - \rho_0)}{c_\mathrm{p}\rho_0} \qquad (1)$$

Where, c_p is the polyelectrolyte concentration (in monomolarity), *M* the molar mass of the repeating unit of NaCMC with 0.70 carboxymethyl groups per anhydroglucose unit, ρ and ρ_0 are the density of the solution and solvent respectively. Table-2 shows the apparent molar volume of the NaCMC in different acetonitrile-water mixed solvents at various temperatures.

Table-2: Concentration, Density, and Apparent Molar Volume of NaCMC in Acetonitrile-Water Mixtures Containing (0.10, 0.20, And 0.40) Volume Fraction of Acetonitrile at (298.15, 308.15, 313.15, And 318.15) K

T / K	*c* / monomol.l^{-1}	ρ / g.cm^{-3}	ϕ_v / cm^3.mol^{-1}
	$\phi_1 = 0.10$		
298.15	0.00168	0.98322	131.31
	0.00224	0.98327	131.30
	0.00325	0.98336	131.35
	0.00684	0.98368	131.39
	0.01122	0.98407	131.45
308.15	0.00232	0.98116	134.72
	0.00453	0.98135	134.83
	0.00581	0.98146	134.87
	0.00686	0.98155	134.92
	0.01106	0.98191	135.03
313.15	0.00176	0.97908	135.97
	0.00341	0.97922	136.18
	0.00518	0.97937	136.28
	0.00719	0.97954	136.38
	0.00944	0.97973	136.48
318.15	0.00142	0.97637	137.11
	0.00237	0.97645	137.21
	0.00368	0.97656	137.37
	0.00595	0.97675	137.58
	0.01003	0.97709	137.87
	$\phi_1 = 0.20$		
298.15	0.00248	0.97069	129.43
	0.00410	0.97084	129.50
	0.00648	0.97106	129.59
	0.00767	0.97117	129.61

	0.01081	0.97146	129.67
308.15	0.00155	0.96499	132.68
	0.00366	0.96518	132.86
	0.00611	0.96540	133.01
	0.00834	0.96560	133.10
	0.01035	0.96578	133.17
313.15	0.00235	0.96221	134.09
	0.00426	0.96238	134.25
	0.00640	0.96257	134.40
	0.00798	0.96271	134.49
	0.01058	0.96294	134.62
318.15	0.00214	0.95931	135.08
	0.00520	0.95958	135.42
	0.00645	0.95969	135.52
	0.00850	0.95987	135.66
	0.01041	0.96004	135.78
$\phi_1 = 0.40$			
298.15	0.00150	0.93815	126.20
	0.00441	0.93844	126.41
	0.00662	0.93866	126.52
	0.00773	0.93877	126.59
	0.00914	0.93891	126.64
308.15	0.00162	0.92378	129.45
	0.00355	0.92397	129.66
	0.00528	0.92414	129.78
	0.00793	0.92440	129.91
	0.00987	0.92459	130.00
313.15	0.00131	0.91743	130.67
	0.00438	0.91773	131.01
	0.00663	0.91795	131.16
	0.00786	0.91807	131.23
	0.01022	0.91830	131.37
318.15	0.00297	0.91571	131.87
	0.00544	0.91595	132.10
	0.00678	0.91608	132.18
	0.00802	0.91620	132.28
	0.00957	0.91635	132.37

Representative plot (Fig.-1) records the changes in apparent molar volumes of the polyelectrolyte solutions as a function of the square root of the monomer concentration of NaCMC. Within the concentration range 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. In the past, Conway and Desnoyers,[22] Lawrence and Conway, [23] Ise and Okubo[24] and Tondre and Zana[12] have reported similar linear increases for ϕ_v concentration for various polyelectrolytes in aqueous solutions. However, the insensitivity of ϕ_v toward concentration has also been reported[24] for salts of polystyrene sulfonic 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 positive slopes in acetonitrile-water mixed solvent media were probably due to the weakening of the ion-solvent interactions, which, in turn, was possibly due to appreciable counterion binding brought about by the increase in the polyelectrolyte concentration. This increase in the concentration of polyelectrolyte solutions must have led to the lowering of the contraction of the solvent medium resulting in a net positive volume change per monomole of the polyelectrolyte added, hence the positive slope of the ϕ_v vs. $\sqrt{c_p}$ plots.

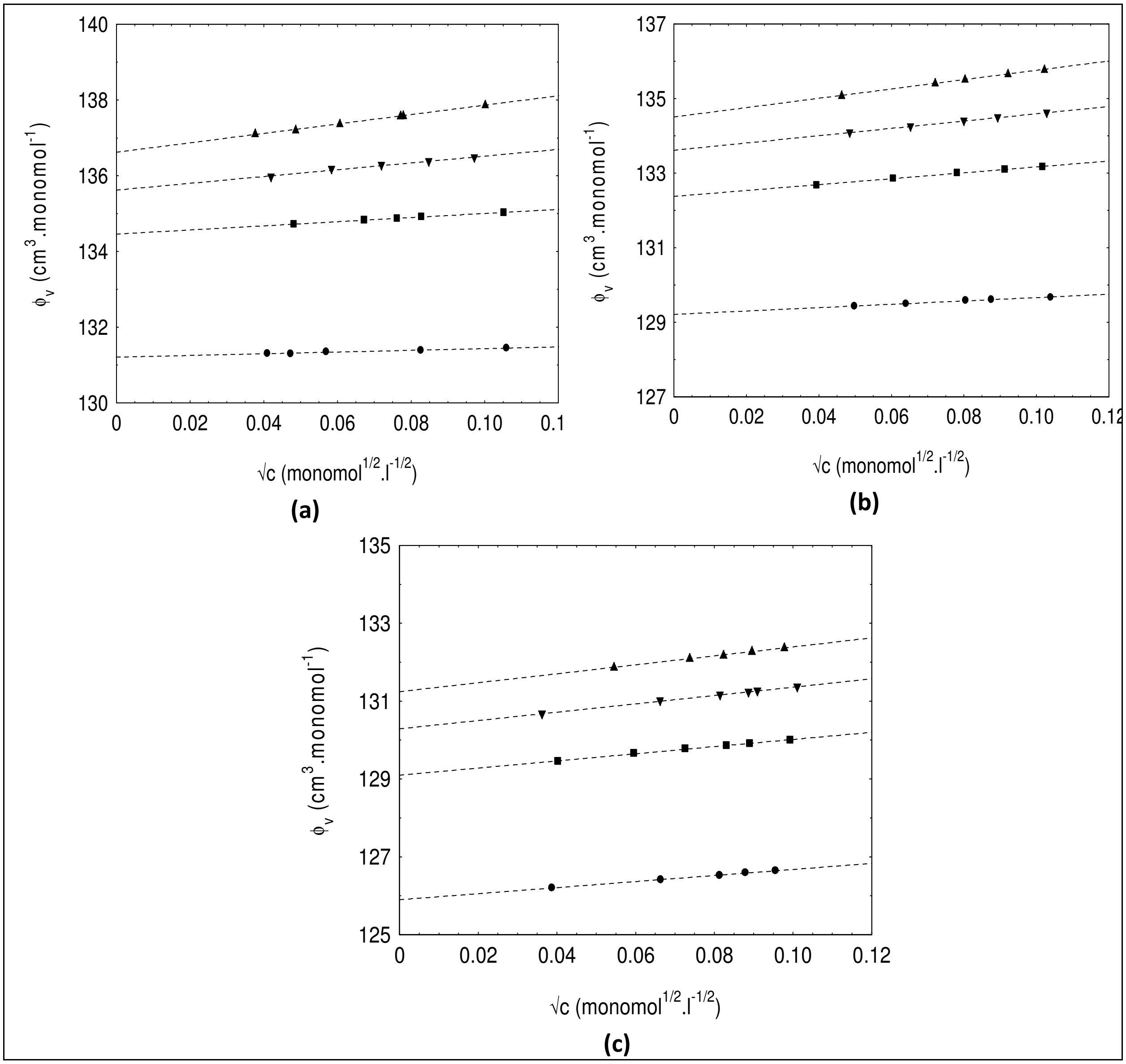

Fig.-1: Apparent Molar Volumes of NaCMC with **(a)** 0.10 **(b)** 0.20 and **(c)** 0.40 Volume Fraction of Acetonitrile in Acetonitrile-Water mixed Solvent Medium at 298.15 K (●), 308.15 K (■), 313.15 K (▼), and 318.15 K (▲).

Masson[25] equation was made use of to obtain the apparent molar volumes at infinite dilution, ϕ_{v}^{0} (=$\bar{V}_2^0$) by the least-squares fitting of ϕ_{v} values.

$$\phi_{\mathrm{v}} = \phi_{\mathrm{v}}{}^{0} + S_{\mathrm{v}}\sqrt{c_{\mathrm{p}}} \qquad (2)$$

Where S_{v} is the experimental slope. Table-3 shows the apparent molar volumes at infinite dilution, ϕ_{v}^{0} (=$\bar{V}_2^0$) at different temperatures. Regression analysis of the data gives a correlation coefficient (*r*) of ≥ 0.985. At a given temperature, when the medium is enriched with acetonitrile there is a decrease in the limiting partial molar volumes. But, as the temperature increases in a given mixed solvent $\bar{V}_2^0$ increases.

Table-3: Limiting Partial Molar Volumes, $\bar{V}_2^0$ /Cm^3.Mol^{-1} of NaCMC in Acetonitrile-Water Mixed Solved Media At (298.15, 308.15, 313.15, And 318.15) K

	$\bar{V}_2^0$ / cm^3.mol^{-1}		
T/K	$\phi_1 = 0.10$	$\phi_1 = 0.20$	$\phi_1 = 0.40$
298.15	131.21 ± 0.02	129.21 ± 0.02	125.90 ± 0.01
308.15	134.46 ± 0.01	132.38 ± 0.02	129.10 ± 0.02
313.15	135.62 ± 0.05	133.62 ± 0.01	130.29 ± 0.01
318.15	136.62 ± 0.02	134.51 ± 0.02	131.24 ± 0.02

To investigate the specific behavior 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, the limiting partial molar volumes of sodium ion could be obtained from the literature values of $\bar{V}_2^0$ of NaCl, sodium tetraphenylborate ($NaBPh_4$), and tetraphenylphosphoniun chloride (Ph_4PCl) in acetonitrile-water mixtures at 298.15 K[26] by employing the tetraphenylphosphoniun tetraphenylborate (TPTB) assumption.[27] We, therefore, have separated the limiting partial molar volumes of NaCMC in acetonitrile-water mixtures in the given condition. The limiting partial molar volumes of sodium ion are, however, not available at the relevant experimental compositions of the acetonitrile-water mixtures. The already known values of the limiting partial molar volumes of NaCl, $NaBPh_4$, and Ph_4PCl in acetonitrile-water mixtures at 298.15 K were plotted vis-à-vis the volume fraction of acetonitrile in acetonitrile-water mixtures. Then the $\bar{V}_2^0$ values of these electrolytes were extrapolated in the context of the present investigation. The result was then used to get the limiting partial molar volume of sodium ion *via* the TPTB assumption.

In Millero's,[28,29] work the ionic limiting partial molar volume, $\bar{V}_{ion}^0$, was considered as the combination of the following components:

$$\bar{V}_{ion}^0 = \bar{V}_{\mathrm{int}\,r}^0 + \bar{V}_{elec}^0 + \bar{V}_{str}^0 + \bar{V}_{cage}^0 \qquad (3)$$

Where, $\bar{V}_{\mathrm{int}\,r}^0$, the intrinsic partial molar volume, is the minute positive change in the $\bar{V}_{ion}^0$ caused by the intrinsic volume of the ion is as per the rule intrinsic ionic volume in a solution is equal to its crystallographic volume.[30] $\bar{V}_{elec}^0$, the electrostriction partial molar volume, is the minute negative change which is equal to the decrease in molar solute volume caused by ion-solvent electrostrictive interaction. $\bar{V}_{str}^0$ is the void-space partial molar volume which is illumined by minute change caused by the destruction of solvent structure in the region of the ionic co-sphere. $\bar{V}_{cage}^0$ is the caged partial molar volume. This refers to the minute negative change which is characteristic of solvophobic "structure-making" parts of the ions in solution. This, in turn, is caused by 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 NaCMC affect strongly the surrounding solvent molecules and hence for the carboxymethylcellulose polyion, $\bar{V}_{elec}^{0}$ 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 $\bar{V}_{cage}^{0}$. Sodium-ion, on the other hand, has nothing to do with caged partial molar volume.

Table-4 indicates that as the acetonitrile-water mixtures are enriched with acetonitrile, the limiting partial molar volume of the polyion decreases. This indicates that the total contribution of the terms $\bar{V}_{elec}^{0}$ and $\bar{V}_{cage}^{0}$ becomes more important over that of the term $\bar{V}_{str}^{0}$ as the solvent medium is enriched 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 a leading role. In the case of the polyelectrolyte as a whole, however, the polyion is governing the solution behavior. Here also the limiting partial molar volume of NaCMC decreases with augmentation of acetonitrile in the acetonitrile-water mixtures (Table-3) like the polyion. An increase in the temperature increases the limiting partial molar volume of NaCMC in a given mixed solvent medium as can be seen from Table-3. This might be ascribed to the growing importance of the disordered partial molar volume owing to a temperature-induced desolvation of the counterion leading to more counterion binding at higher temperatures as observed earlier from conductivity measurements.[31]

Table-4: Limiting Partial Molar Volumes, $\bar{V}_2^{0}$ ($Cm^3.Mol^{-1}$) of Sodium Ion (Na^+) And Carboxymethylcellulose Polyion (CMC^-) In Acetonitrile-Water Mixed Solvent Media At 298.15 K

Ion / Polyion	$\bar{V}_2^{0}$ / $cm^3.mol^{-1}$		
	$\phi_1 = 0.10$	$\phi_1 = 0.20$	$\phi_1 = 0.40$
Na^+	-9.12	-7.14	-3.35
CMC^-	140.33	136.35	129.25

CONCLUSION

The present investigation indicates that in acetonitrile-water mixed solvent media as we increase the concentration of the polyelectrolyte, the counterion binding increases noticeably and thereby weakens the ion-solvent interactions. Moreover, the polyion is found to govern the volumetric behavior of the polyelectrolyte as a whole in these solutions. Besides, there is a predominant influence of both the polyion-solvent electrostrictive interactions and the solvophobic filling of the intermolecular cavities of the solvent structure which are seen to be caused by the apolar parts of the polyion when the medium was enriched by acetonitrile. A temperature-induced desolvation of the counterions leading to more counterion binding at higher temperatures was also inferred from this study.

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