

# Non-aqueous solvation behaviour of some nitrogen-containing polycationic electrolytes: 1. Partial molar volumes in propylene carbonate and sulfolane

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*(Received 31 August 1994; revised 9 January 1995)*

Studies on the solution properties of three linear crystal-violet-tagged polycationic electrolytes in dipolar aprotic solvents, viz. propylene carbonate (PC) and sulfolane, have been carried out over a small temperature range ( $298.15 \pm 5$  K for PC and  $308.15 \pm 5$  K for sulfolane). The polycations studied have *N*-alkylammonium ions, with ethylene moieties in the parent chain of the macro-ion, and *N*-alkyl- or *N*-acylammonium ions, with interspersed xylylene or 2,5-diacylthiophenylene linkages constituting a parallel track of positive nitrogen centres, in their respective molecular chain. The results of density measurements are discussed on the basis of the apparent molar volume *versus* concentration plots in terms of solvophobic and electrostrictional interactions with the media. The dominant solvophobicity in both solvents is chiefly due to the pronounced effect of electrorelaxation as opposed to the moderate electrostrictional interactions, which facilitates excessive solvent entrapment in dilute solution inside the 'pockets' provided by the parent chain carrying 'apolar residues' in cooperation with the spatial disposition of outside pendent blades of crystal violet moieties in the molecular framework. The inverse temperature effect on partial molar volumes for all systems in both solvents was explained on the basis of mobilization of the solvation layer followed by intramolecular constrictions, dense packing of solvent and/or the migration of electrostricted solvent molecules into the empty spaces within the molecule under study.

(Keywords: non-aqueous solvation; polyelectrolytes; molar volume)

## INTRODUCTION

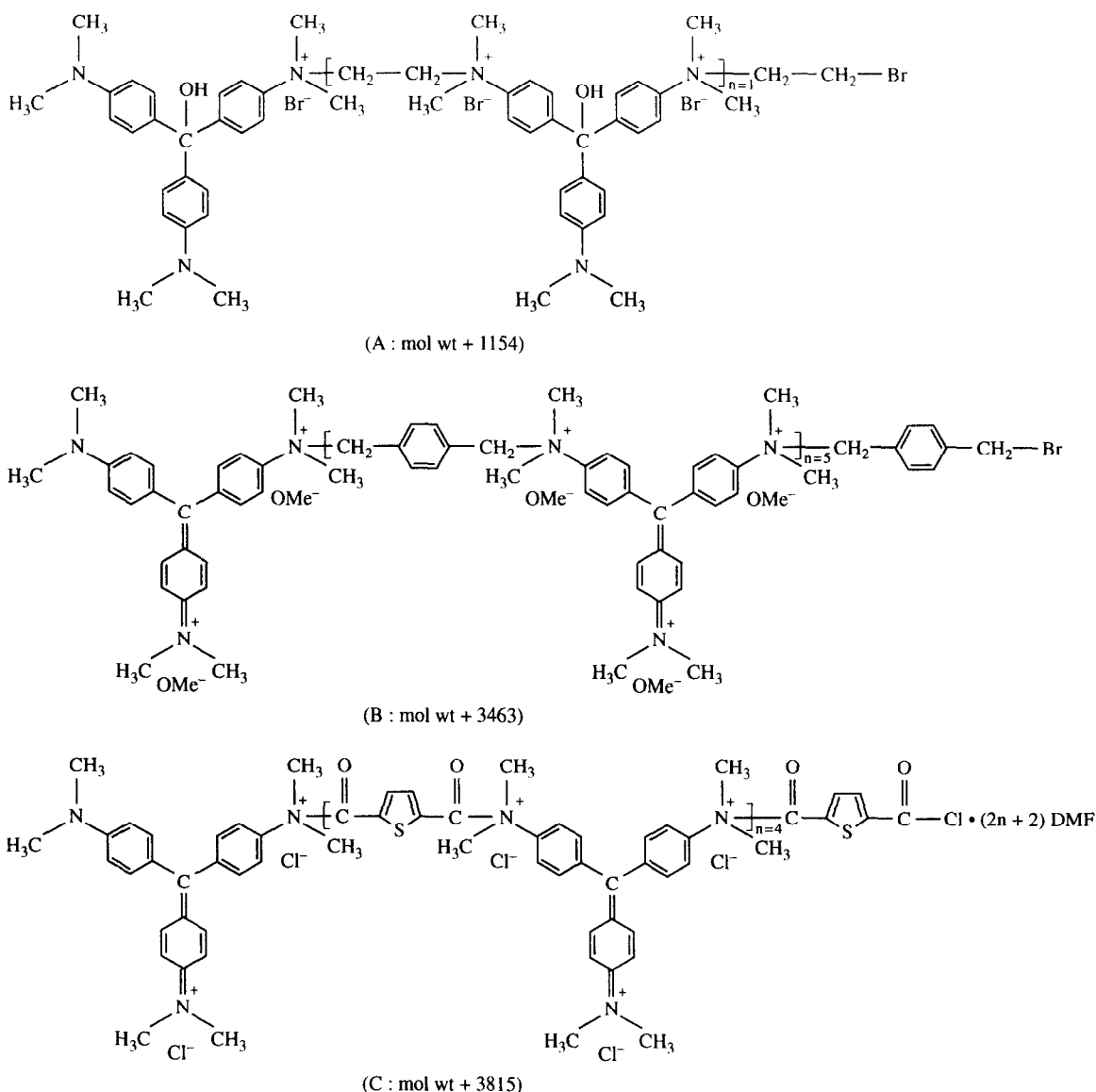
Although solvation of simple ions has been fairly extensively studied, our present state of knowledge about the solvation of polyelectrolytes is relatively limited<sup>1–4</sup>. It cannot be denied, however, that the subject is of much practical importance: the behaviour of ion-exchange resins and membranes, and of the soil conditioners and polyelectrolytes of biological importance, is largely affected by their hydration characteristics.

Unfortunately, the normal thermodynamic approach to the determination of standard free energies, entropies and enthalpies of hydration of simple salts is often found to be inapplicable to polysalts. This is because the latter rarely form ions that behave reversibly in a cell and do not yield well defined crystalline solids to permit estimation of the lattice energies involved. Moreover, the application of the method based on colligative properties suffers from the disadvantage that, in the case of polysalts, such properties are largely determined by the counterions, whose activity coefficients are strongly influenced by the presence of the polyion chain, which has low osmotic activity due to high local

charge density. Since mean activity data as such do not permit individual assessment of solvophobic and electrostrictional effects, consideration of partial molar volumes, instead, has been found more useful<sup>5,6</sup>. In this sense, we have obtained partial molar volumes of three relatively large polycations, particularly nitrogen-based oligomers, in propylene carbonate (PC) and sulfolane. The investigation was exclusively directed to studies on two categories of systems: (i) those having quaternary nitrogen centres on the backbone of the macro-ion and not as side-chain substituents, and (ii) those which constitute a parallel track of positive nitrogen centres in their respective molecular chain. Materials that satisfy these requirements are specifically based on crystal violet structures with interspersed ethylene, xylylene and 2,5-diacylthiophene links in the present investigation. These systems are abbreviated hereafter as **A** for poly(*N*-ethylene monohydroxy crystal violet dibromide), **B** for poly[*N*-*p*-xylylene crystal violet trimethoxide] and **C** for poly[*N*-2,5-diacylthiophenylene crystal violet trichloride] (detailed structures are shown in *Scheme 1*).

Although the presence of the *N*-acylammonium ion in the parent chain of **C** introduces a notable distinction from compounds **A** and **B**, which possess *N*-alkylammonium ions in their structures, the three phenyl rings of crystal violet residues in oligomers **A**, **B** and **C** behave

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**Scheme 1** Detailed structures of **A**, **B** and **C** (see text for full names)

like a model of 'propeller blades' where two blades are tagged with ethylene, xylylene and 2,5-diacylthiophenylene linkages in the main chain, and the remaining blade (arm) hangs as a pendent substituent. This offers a contrasting structural distinction among the systems selected with a view to understand their solvophobic and electrostrictional solvation on the basis of individual conformations of cationic oligomers in solution.

The particular surge of interest for investigation in PC and sulfolane is mainly because of their dipolar aprotic characteristics, responsible for ion-dipole type solute-solvent interactions apparently distinct from those usually observed in aqueous solutions. Besides, the moderately high dielectric constants of PC ( $\epsilon = 64.4$  at 298 K) and sulfolane ( $\epsilon = 43.4$  at 303 K) and their high dipole moments (PC, 4.9 D, sulfolane, 4.7 D) enable them to behave as good solvents to offer a reasonable estimate of 'high-energy' electrochemical reactions<sup>7</sup>. Since solvation for polyelectrolytes has not hitherto received any attention in propylene carbonate and sulfolane, the present investigation provides significant information about the non-aqueous solution properties of polycationic solutes.

## EXPERIMENTAL

### Reagents

Purified PC and sulfolane (Fluka, stated purity 99 mol%,  $\text{CO}_2 < 0.02$  mol%,  $\text{H}_2\text{O} < 0.03$  mol%, conductivities  $< 2-3 \times 10^{-8} \Omega^{-1} \text{cm}^{-1}$ ) were obtained and stored according to the known procedure<sup>8</sup>. All other chemicals were either high-purity materials or were purified before use.

The preparation and characterization of polycationic electrolytes **A**, **B** and **C** are reported elsewhere<sup>9</sup>.

### Density measurements

The solution densities were measured using a bicapillary pycnometer of approximately  $20 \text{cm}^3$  capacity with the arms graduated in  $0.01 \text{cm}^3$  at 293.15, 298.15, 303.15 K in PC and 303.15, 308.15, 313.15 K in sulfolane. The control of temperature was performed using a cascade water bath arrangement in an air-conditioned room within a temperature range of  $\pm 0.01$  K. All solution densities were measured relative to that for pure water and buoyancy corrections were applied to all

**Table 1** Apparent molar volume equations for the crystal violet polycationic electrolytes (**A**, **B** and **C**) in propylene carbonate (PC) and sulfolane at different temperatures

System	Temperature (K)	Best equation <sup>a</sup>
<b>A/PC</b>	293.15	$\phi_v = 2591.5^* - 81499.33c^{1/2} + 859775.75c$
	298.15	$\phi_v = 2067.19^* - 55388.05c^{1/2} + 521547.95c$
	303.15	$\phi_v = 2062.85^* - 55747.44c^{1/2} + 525555.49c$
<b>B/PC</b>	293.15	$\phi_v = 1732.80^* - 26439.35c^{1/2} + 148734.83c$
	298.15	$\phi_v = 1205.50^* - 10713.64c^{1/2} + 33628.28c$
	303.15	$\phi_v = 1217.66^* - 11939.05c^{1/2} + 43235.26c$
<b>C/PC</b>	293.15	$\phi_v = 1628.24^* - 21843.27c^{1/2} + 123443.62c$
	298.15	$\phi_v = 1091.27^* + 6207.57c^{1/2} - 200855.94c$
	303.15	$\phi_v = 1078.90^* - 1074.90c^{1/2} - 84915.82c$
<b>A/Sulfolane<sup>b</sup></b>	303.15	$\phi_v = 1739.24^* - 14288.19c^{1/2} - 17627.35c$
	308.15	$\phi_v = 1450.93^* - 10028.80c^{1/2} - 19247.36c$
	313.15	$\phi_v = 1331.67^* - 3433.93c^{1/2} - 107553.62c$
<b>B/Sulfolane</b>	303.15	$\phi_v = 597.59^* - 84.77c^{1/2}$
	308.15	$\phi_v = 533.15^* + 262.08c^{1/2}$
	313.15	$\phi_v = 487.06^* + 407.64c^{1/2}$
<b>C/Sulfolane</b>	303.15	$\phi_v = 1766.73^* - 37450.85c^{1/2} + 367390.37c$
	308.15	$\phi_v = 1670.21^* - 33925.25c^{1/2} + 335370.13c$
	313.15	$\phi_v = 1657.19^* - 35775.32c^{1/2} + 351388.45c$

<sup>a</sup> Values marked by an asterisk (\*) denote limiting partial molar volumes ( $\phi_v = \bar{V}_2^0$ ) with their uncertainties not more than 1.5% (95% confidence limit)

<sup>b</sup> Equations are valid between 0 and 3.0 monomol dm<sup>-3</sup>

weights. The reproducibility of an individual density measurement was to better than  $\pm 2 \times 10^{-5}$  g cm<sup>-3</sup>, and from the entire set of five determinations, the corresponding level of certainty is computed as 95% by Student's *t* table.

## RESULTS AND DISCUSSION

Apparent molar volumes  $\phi_v$  of a repeat unit of polyelectrolyte were calculated from the densities according to the equation<sup>6</sup>:

$$\phi_v = \frac{M_2}{d} + \frac{1000d - M_2C}{C} \left( \frac{1}{d} - \frac{1}{d_0} \right) \quad (1)$$

where  $d_0$  and  $d$  represent the densities of the solvent and solutions, respectively,  $M_2$  denotes the molecular weight of the polyelectrolyte divided by the degree of polymerization, i.e. the molecular weight of the repeat unit (577 for **A**, 577 for **B**, 763 for **C**), and  $C$  measures the polyelectrolyte concentration in monomol dm<sup>-3</sup>. We found that  $\phi_v$  values are not a linear function of the square root of concentration and can be expressed in terms of  $C$  using a Redlich-type equation<sup>2</sup>:

$$\phi_v = \phi_v^0 + S_v C^{1/2} + b_v C \quad (2)$$

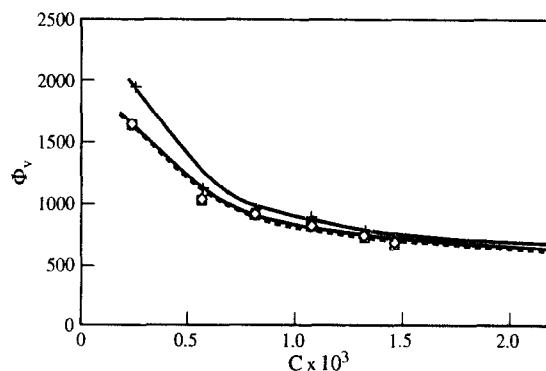
where  $\phi_v^0 \equiv \bar{V}_2^0$  is the partial molar volume of polyelectrolyte at infinite dilution. Unfortunately, the theoretical slope  $S_v$  cannot be calculated for polymeric electrolytes employing the Debye-Hückel limiting law in any solvents, whether aqueous or non-aqueous. This is because of the fact that the spherical symmetry of the charged centres is drastically affected and there is a large electrostatic potential along the polyion chain, whose intrinsic flexibility also alters in the dilute range of concentrations. Thus, the data were least-squares fitted to polynomials through a computer program, and the resulting equations are listed in Table 1. The relative standard deviation in  $\phi_v$  is estimated to be less than

$\sim 1.5\%$  (confidence limit 95%) for five replicate measurements in both solvents. The corresponding limiting parameters  $\phi_v^0 \equiv \bar{V}_2^0$  of different systems are computed from best-fit equations (Table 1) at different temperatures. The estimation of cationic volumes is equivocal by using the additivity principle in the present case since anions are least solvated in dipolar aprotic solvents and some association of counterions cannot be ruled out even at infinite dilution<sup>10</sup>. This was evident by the application of Manning's counterion condensation theory, which defines a dimensionless charge density parameter ( $\xi$ ) of a linear polymer as:

$$\xi = \frac{l_B}{b} = \frac{e^2}{\epsilon k_B T b} \quad (3)$$

where  $l_B = e^2/\epsilon k_B T$  is the Bjerrum length (0.97 nm for PC at 298.15 K and 1.42 nm for sulfolane at 303.15 K) and  $b$  is the average charge spacing along the fully extended axis of the real polyion chain (9.5 Å for **A**, 8.0 Å for **B** and 10.0 Å for **C**). For univalent counterions, the value  $\xi = 1$  is critical. This treatment resulted in  $\xi$  values exceeding the critical value of unity for all systems studied in both solvents. A fraction  $(1 - \xi^{-1})$  of the total polyion charge was thus neutralized by condensation of counterions to lower the net effective polyion charge density to the critical value ( $\xi = 1$ ). Accordingly, the fractions of associated ('condensed') counterions per polymer fixed charge are found to be 0.01, 0.17 and 0.03 in PC at 298.15 K and 0.33, 0.44 and 0.29 in sulfolane at 303.15 K for polyelectrolytes **A**, **B** and **C**, respectively. The extent of counterion condensation is apparently larger in sulfolane ( $\epsilon = 43.3$ ) as compared to that in PC ( $\epsilon = 64.4$ ).

Apparent molar volumes of compounds **A**, **B** and **C** at 293.15, 298.15 and 303.15 K in PC are portrayed as graphs of  $\phi_v$  vs.  $C$  in Figures 1–3. As is shown in Figure 1, the apparent molar volume of compound **A** at any temperature decreases with increases in concentration, exhibiting a tendency to level off beyond  $\sim 0.002$  monomol dm<sup>-3</sup>. This suggests that, on the whole, the system is experiencing a larger degree of solvophobicity. Solvophobicity in non-aqueous solvents is somewhat different from hydrophobicity in water, as the former do not form any tight solvent cage around apolar solutes. However, they involve 'repulsive' solute-solvent interactions<sup>11</sup>, giving rise to solvent packing under the pool of adjacent positive centres. In the present instance, the



**Figure 1** Concentration dependence of apparent molar volume of compound **A** and PC at various temperatures (K): 293.15 (+), 298.15 ( $\diamond$ ) and 303.15 ( $\square$ )

'locking up'<sup>2</sup> of solvent molecules occurs in void spaces provided by the parent chain consisting of ethylene linkages in cooperation with the spatial disposition of the outside pendent blades of crystal violet moieties in the molecular framework. The larger values of  $\phi_v$  and  $\bar{V}_2^0$  at all temperatures reveal that the system **A** experiences a reasonably good magnitude of ion-solvent interactions in PC in spite of its lower molecular weight. The solvent PC acts as a good solvent, which inhibits the polymer-polymer contacts<sup>12</sup> and consequently restricts intramolecular bending or folding of blades of crystal violet residues, under any interactions. In spite of intramolecular interactions to some extent between positive centres and the lone pairs of electrons of unquaternized nitrogens of the pendent structures, the void spaces (provided between the main backbone and pendent side groups, including those between the propeller blades of crystal violet moieties in disposition with the hydroxyl bonds from their central carbon atoms) still appear to be wide enough for the packing of solvent molecules. This causes a predominant solvophobic effect in competition with electrostatic solvation<sup>2</sup> at all temperatures studied. The large expansion of molecular volume towards the infinitely dilute region is attributed to the combined effect of inter-coulombic repulsions between the positive nitrogen centres of the main backbone as well as electrostatic repulsions between dimethylamino groups carrying lone pairs of electrons in the pendent substituents of crystal violet residues of the molecule. The quaternary nitrogens of the parent chain experience a moderate shielding effect from the basic nitrogens of the pendent groups owing to the obstruction created by the enormous packing between empty spaces furnished by the parent skeleton in cooperation with the spatial disposition of the outside pendent groups. However, these positive centres exert a relatively low degree of electrostrictional solvation primarily because of the effective blocking caused by the attached bulkier phenylene and dimethyl units in close proximity with each other. At higher concentrations, the 'stacking tendency'<sup>13</sup> of the short, rigid and dye-tagged molecules of **A**, one above the other, enhances the total positive charge density of the system. This apparently facilitates a considerable magnitude of electrostrictional solvation, which turns out to be just enough to overcome the effect of solvophobicity, and thereby yields linearity in the latter part of the  $\phi_v$  vs.  $C$  profiles, at all temperatures, in the present instance.

The striking decrease<sup>4</sup> of  $\phi_v$  and  $\bar{V}_2^0$  values from 293.15 to 298.15 K in this case is associated with the perturbation of immobilized PC molecules into the void spaces. This paves the way for easier contraction of the system in the dilute region owing to the intramolecular coulombic interactions between the positively charged main backbone and electron-rich pendent side groups, which results in a consequent squeezing of solvent molecules packed therein, as the temperature is raised. Interestingly, the confidence limits on  $\bar{V}_2^0$  at 298.15 and 303.15 K for all systems in PC overlap (Table 1); the said perturbation of PC molecules no longer remains active to cause further constriction of polycation **A** at 303.15 K.

The general nature and interpretations of  $\phi_v$  vs.  $C$  plots for compound **B** (Figure 2) resemble those of **A** (Figure 1) in PC, at all temperatures studied. Expansion of available void spaces in this instance occurs as a result

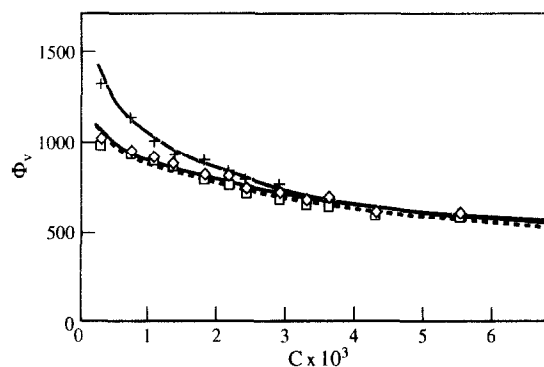


Figure 2 Concentration dependence of apparent molar volume of compound **B** in PC at various temperatures (K): 293.15 (+), 298.15 ( $\diamond$ ) and 303.15 ( $\square$ )

of intramolecular mutual repulsions between the parallel track of positive nitrogens of the system, which facilitates easier entrapment of the solvent molecules in these void spaces, showing a major solvophobic effect. However, the marginal solvation under electrostrictional mode in this case could be chiefly due to: (i) the presence of *p*-xylylene moiety in between the two quaternary centres of a repeat unit of the molecular chain, which drastically reduces the charge density of the polycation; (ii) the blocking effect by the methyl as well as other bulky phenylene groups shrouding  $N^+$  centres of the polymeric backbone; and (iii) the blocking of pendent  $N^+$  centres by the attached bulkier cyclohexadiene substituents in cooperation with dimethyl groups. The decrease of  $\bar{V}_2^0$  values particularly from 293.15 to 298.15 K (Table 1) is associated with the dense packing of the surrounding PC molecules into relatively enlarged openings between the cationic track of individual polymeric molecules of **B**, at infinite dilution, with net reduction in the total volume, as the temperature is raised. The almost equal  $\bar{V}_2^0$  at 298.15 and 303.15 K is, however, indicative of optimization of the effect involving solvent packing in void spaces.

The extent of solvophobic solvations in **C** (Figure 3) appears to be interestingly limited in the present system as compared to **B**. This is because of the possibility of hindrance created against the solvent packing by dimethylformamide (DMF) molecules, which are loosely bound as the solvent of crystallization probably to the carbonyl groups of 2,5-diacylthiophenylene moieties of

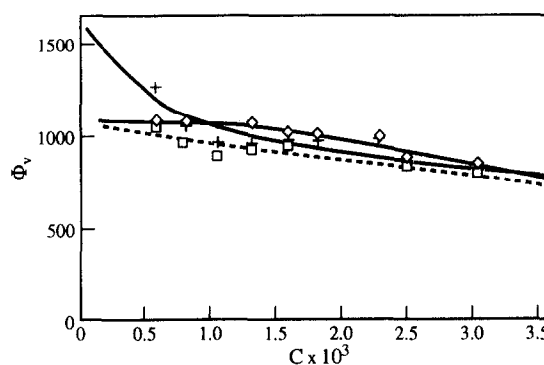
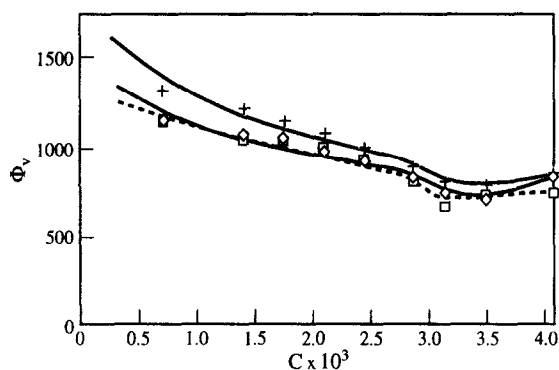
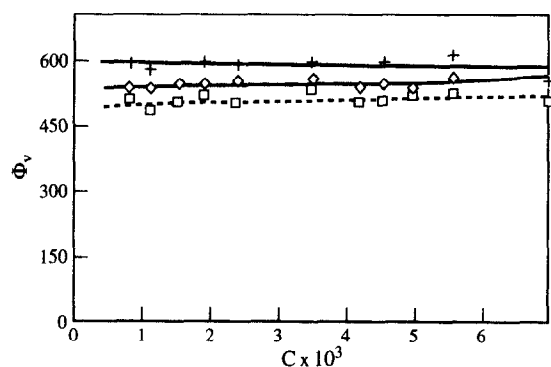


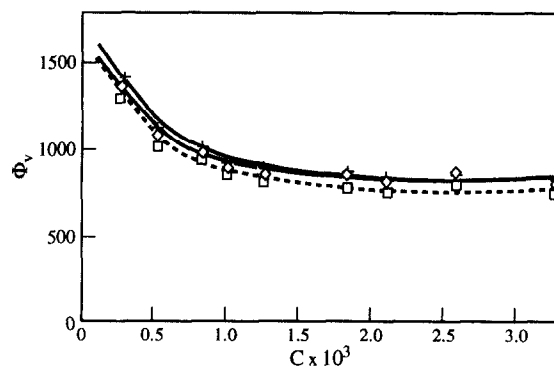
Figure 3 Concentration dependence of apparent molar volume of compound **C** in PC at various temperatures (K): 293.15 (+), 298.15 ( $\diamond$ ) and 303.15 ( $\square$ )



**Figure 4** Plots of apparent molar volume vs. concentration for compound **A** in sulfolane at various temperatures (K): 303.15 (+), 308.15 ( $\diamond$ ) and 313.15 ( $\square$ )



**Figure 5** Plots of apparent molar volume vs. concentration for compound **B** in sulfolane at various temperatures (K): 303.15 (+), 308.15 ( $\diamond$ ) and 313.15 ( $\square$ )



**Figure 6** Plots of apparent molar volume vs. concentration for compound **C** in sulfolane at various temperatures (K): 303.15 (+), 308.15 ( $\diamond$ ) and 313.15 ( $\square$ )

the system. The moderation of  $\phi_v$  vs.  $C$  behaviour, which demonstrates a small variation with concentration showing a slightly decreasing trend at any temperature studied, is due to an appreciable amount of culmination in solvophobic behaviour with increasing population of polycations, in competition with the involved electrostrictional effect, as a result of somewhat restricted mode of accommodation of large PC molecules into the limited void spaces of the molecular aggregates. Such constrictions are largely favoured due to the inter- and intramolecular induced coulombic interactions between the  $\pi$ -excessive 2,5-diacylthiophenylene linkages and  $\pi$ -deficient

pendent substituents consisting of cyclohexadiene dimethyliminium groups and due to the restricted charge repulsion by the presence of polar diacyl moieties as well. The rather large apparent molar volumes at 298.15 K as compared to other temperatures in the concentrated region are primarily due to interpenetration of the domains of molecular chains of **C** resulting in the overlapping of available electrostricted solvents. Such interpenetration and overlapping of the solvation layers of the aggregates are surprisingly either non-existent or ineffective at 303.15 K. The decrease of  $\bar{V}_2^0$  values also indicates an overall constriction in the polyion chain at infinite dilution, which is exclusively being facilitated by the mobilization of solvation layers with the initial increase of the temperature which later gets optimized at 303.15 K like **B**.

The variations of  $\phi_v$  with concentration in sulfolane at 303.15, 308.15 and 313.15 K are illustrated in *Figures 4–6*. The general solvation behaviour of the system **A** in sulfolane is similar to that in PC. However, the upward tendency of  $\phi_v$  vs.  $C$  plots (*Figure 4*) is associated with the stacking nature of the dye-tagged<sup>13</sup> molecules of **A** at higher concentrations. There is a possible stricture in the stacked aggregations as a result of counterion condensations ( $1 - \xi^{-1} = 0.33$ ), which imposes restrictions on the packing of the solvent. Furthermore, with the larger positive charge density of stacked polymeric molecules, the electrostrictional effect manifests itself as the predominant phenomenon, which apparently overrides the contributions due to solvophobicity, in the present instance.

The extent of competition for solvophobic interaction in **C** is seemingly higher in sulfolane than PC (*Figure 6*), in the dilute region, which suggests that sulfolane is a reasonably better solvent than PC in this case. Therefore, any type of intramolecular constriction, unlike the case of solutions in PC, is inhibited in sulfolane, which consequently promotes enough solvent packing in the empty spaces so produced in the molecule. Furthermore, the viscous nature of sulfolane also mitigates the hindrance caused by the several DMF molecules ( $2n + 2$ ) adhered to the sample **C**. This would lead to an overall extensive packing in the void spaces available in the system. The balancing effect in the present instance can be explained on the basis of optimization of the compact and stacked network of aggregations with increasing population of the polyions **C**, where further solvent incorporations (solvophobic interactions) are disfavoured. Consequently, solvophobicity is preponderant to an extent just enough to counterbalance the enhanced solvation under electrostrictional mode, at all temperatures studied. Although the reduction in partial molar volumes observed from 303.15 K ( $1767 \text{ cm}^3 \text{ monomol}^{-1}$ ) to 308.15 K ( $1670 \text{ cm}^3 \text{ monomol}^{-1}$ ) is remarkable, the negligible decrease of  $\bar{V}_2^0$  at 313.15 K ( $1657 \text{ cm}^3 \text{ monomol}^{-1}$ ) is indicative of the restriction in further packing of the solvent molecules similar to PC, in the insufficient openings at elevated temperatures. The lower sensitivity of  $\bar{V}_2^0$  with temperature points to the more rigid conformation of **C** in sulfolane as compared to that in PC.

The most interesting behaviour is noted for compound **B** in sulfolane: unlike **A** and **C**, the system **B** demonstrated practically a negligible change in  $\phi_v$  at any temperature (*Figure 5*). This represents a net balance

between the two competing and opposing effects of solvophobic and electrostrictional interactions throughout the concentration range studied. It appears that both effects are curtailed here to an equal extent: where solvophobic solvation is restricted due to limited space owing to intramolecular electrostatic contacts between xylylene and  $\pi$ -deficient pendent arms of crystal violet unit, the electrostrictional interactions are lessened as a net result of the fraction ( $1 - \xi^{-1} = 0.44$ ) of methoxide counterions condensed to the polycationic chain to counterbalance both effects.

The reduction in partial molar volume of **B** at higher temperature (Table 1) can be explained on the basis of increased perturbation (mobilization) of immobilized solvent molecules as has been suggested for **A** in PC. The actual value of  $\phi_v$  in these cases at any temperature could be determined by the volume of available void spaces and the degree of freedom of the electrostricted solvents to migrate into them and the extent of mobilization of packed molecules of solvent present in cavities of the polycation.

The lower  $\bar{V}_2^0$  in sulfolane for **A** and **B** (Table 1) confirms the viscous property of sulfolane, which restricts to some extent the phenomenon of 'electrorelaxation'<sup>14,15</sup> in the solution phase. However, despite the lower molecular weight of compound **A** compared to the other systems, the higher value of  $\bar{V}_2$  indicates a relatively high degree of expansion and linear conformation in both solvents under study. Further, in compound **C**, the polar resonant structures along 2,5-diacylthiophenylene linkages apparently contribute a very marginal dipole moment and compact conformations of polycation in PC and sulfolane. Under such circumstances, system **C** enjoys greater freedom to expand, giving a considerably higher value of  $\bar{V}_2^0$  by 'electrorelaxation' as opposed to electrostriction. Although the viscous nature of sulfolane tends to restrict the expansion to some extent by electrorelaxation, the higher value of  $\bar{V}_2^0$  for **C** in sulfolane as compared to PC is due to the relatively difficult molecular constriction in sulfolane. The strikingly small

$\bar{V}_2^0$  values for **B** as compared to **C** in sulfolane, despite their comparable magnitude of molecular weight, are interesting. This indicates a lesser degree of expansion between the proximate ionic centres apparently due to the lower permittivity of the medium, where the binding capacity of methoxide ions is even more pronounced.

Although the solvents PC and sulfolane are basically non-nucleophilic in character towards 'carbonium' centres of crystal violet residues<sup>16</sup>, a 'weak' long-range solute-solvent coordination (donor-acceptor) interaction in both PC ( $DN_{SbCl_5} = 15.1 \text{ kcal mol}^{-1}$ ) and sulfolane ( $DN_{SbCl_5} = 14.9 \text{ kcal mol}^{-1}$ ) along  $N^+$  ions is also feasible apart from their normal solvation<sup>17</sup>.

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