Nitrogen-based polyelectrolytes: synthesis and solvation behaviour

Bhim Bali Prasad*, Shirley Easo and Anil Kumar
Analytical Division, Chemistry Department, Banaras Hindu University, Varanasi 221 005, India

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This investigation relates to the synthesis and characterization of four linear polyelectrolytes containing crystal violet and bipyridinium moieties in the main chain, with molecular weights ranging from 1154 to 3815. Of these, two polyelectrolytes had *N*-alkylammonium ions and the other two involved typical 2,5-diacylthiophenylene linkages with *N*-acylammonium and *N*-acyliminium ions in their respective structures. The solvation characteristics of these systems are explored through density measurements in dimethylformamide and dimethylsulfoxide solvents over the small temperature range 25 ± 5°C, by analysing the concentration dependence of apparent molar volume data at various temperatures in terms of the competing solvophobic and electrostrictional interactions with the media.

(Keywords: N-based polyelectrolytes; solvation behaviour; synthesis)

INTRODUCTION

The synthesis of quaternary ammonium polyelectrolytes containing aromatic rings in the main chains has received considerable attention because of their biological importance, relatively good thermal stability and interesting solvation and ion-exchange characteristics. One of the outstanding properties of such polymers is their ability to solvate themselves. In view of its relevance to the fabrication of polymers (into fibres, films, adhesives, etc.) and the properties of ion-exchange resins and membranes (especially swelling), in addition to its implications in biological and agricultural chemistry, the subject of polyelectrolyte solvation[1-4] has drawn dramatic attention.

The purpose of the present investigation is to prepare and characterize a certain new class of structurally different nitrogen-based polycationic electrolytes with the prime aim to explore their specific solution behaviour in dipolar aprotic solvents. For this study, various forms of polycations appeared particularly interesting, such as those having: (a) quaternary nitrogen centres on the backbone of the macroion (polyions) and not as side-chain substituents; (b) backbone quaternary centres constituting a parallel cationic track with quaternized nitrogens on the side groups of the molecules; and (c) heterocyclic ring nitrogens quaternized with acyl derivatives in the repeat unit of the chain.

Compounds A, B, C and D appeared relevant in this connection. Since a large departure from simple electrolytes was not intended on account of solubility limitations, compounds B, C and D with suitable molecular weight range and size large enough for examining polyelectrolyte behaviour were chosen. Despite the fact that compound A was found to be a dimeric product, its distinct structural differences from other crystal violet oligomers led us to include it in the set of polyelectrolytes chosen for investigation.

In addition to the synthesis and characterization of crystal violet and 4,4′-bipyridinium polyelectrolytes, which formed an integral part of this work, a detailed study on the solvation behaviour of these systems through density measurements is reported in *N*,*N*-dimethylformamide (DMF) and dimethylsulfoxide (DMSO) over a small temperature range (25 ± 5°C). Owing to the solubility restriction, system A could not be studied in DMF.

Although partial molar volume results obtained from density data are quite helpful in providing a better understanding of ion–solvent interactions, particularly the identification as well as the assessment of Coulombic (i.e. electrostrictional and solvophobic) effects of solvation, non-aqueous solvation is thought to be quite different, ambiguous and more complicated than aqueous hydration. Unlike water, non-aqueous solvents do not form any solvent cage[1] around apolar residues of the solute. However, they apparently involve only 'repulsive' solute–solvent interactions by the non-polar parts, which may eventually lead the surrounding solvent molecules to get packed[1], because of the charged centre inside the void spaces formed around it. Thus, a correct description of polyelectrolyte solvation in a non-aqueous solvent should consider explicitly the electrostrictional and solvophobic interactions on the basis of the electrostatic potential and void space effect along the molecular chain. Since most polyelectrolyte studies are confined to aqueous systems only, and very little is known about their behaviour in non-aqueous solvents, the present study in aprotic media might be considered to have some special value.

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* To whom correspondence should be addressed

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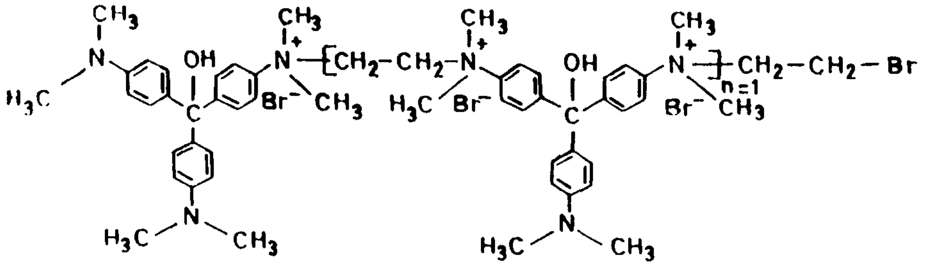
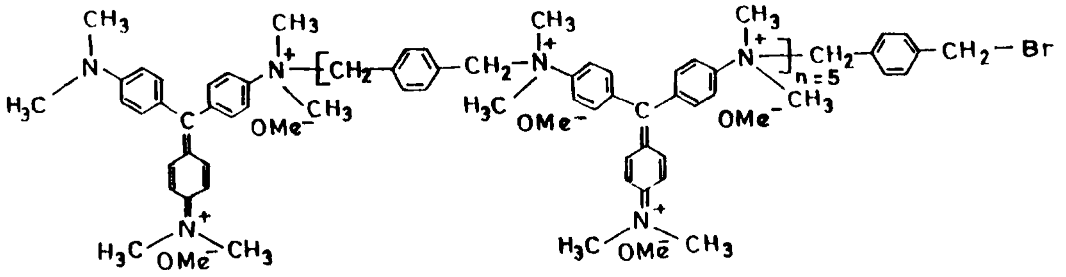
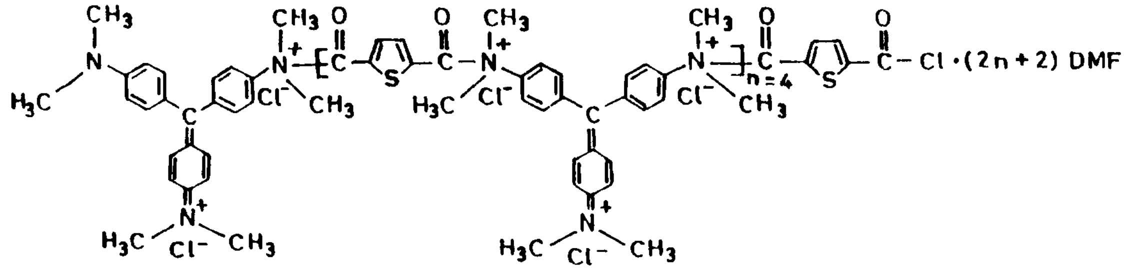


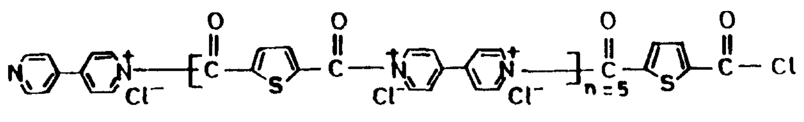
(A : mol wt = 1154)



(B : mol wt = 3463)



(C : mol wt = 3815)



(D : mol wt = 2190)

EXPERIMENTAL

Materials

The solvents, DMF and DMSO (99% pure, Sarabhai–Merck products), were distilled twice from a Pyrex glass still (specific conductivity $= (1\text{–}2) \times 10^{-8}\,\mathrm{S\,cm^{-1}}$) just prior to use and stored in an automatic dispenser, under a blanket of pure nitrogen.

The reagents, α,α′-dibromo-*p*-xylene[5], thiophene-2,5-dicarboxylic acid chloride[6] and crystal violet base[7], used in the preparation of the quaternary ammonium/iminium polyelectrolytes, were obtained following the available recipes. All other chemicals and solvents used either were high-purity materials or were purified before use.

Preparation of polyelectrolytes studied

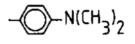
Poly(N-*ethylene monohydroxy crystal violet dibromide*) (*A*). Equimolar solutions of crystal violet base (I) and 1,2-dibromoethane (E. Merck) (II) were prepared separately by using 5.0 g of I and 1.2 ml of II in 20 ml pure ethanol in each case. The solution of I was then added to that of II, and the mixture was refluxed at 70–80°C in a water bath for 2 h. The resulting product (yield 80%) was washed several times with hot ethanol and then dried *in vacuo* at room temperature. Analysis (%): C = 56.33, H = 5.69, N = 6.83. Determination of ionic bromine by conductometric titration in DMSO–water mixture indicated 2.64 mol $\mathrm{Br^-}$ per 1000 g of sample. The indicated structure confirms the theoretical percentages (C = 56.15, H = 6.06, N = 7.27) and a total of three quaternary centres with molecular weight 1154, in agreement with the calculated non-ionic bromine (0.83 mol/1000 g) present in the system.

Poly(N-p-*xylylene crystal violet trimethoxide*) (*B*). A solution of 2.0 g (1 mol) of α,α′-dibromo-*p*-xylene in 20 ml of DMF was added to a 20 ml DMF solution of 3.15 g (1 mol) crystal violet (E. Merck) and the mixture was refluxed at ~70°C for 4 h and then kept at room temperature overnight. The reaction mixture was concentrated by evaporating the solvent at ~160°C and the residue was treated with a methanolic solution of sodium hydroxide. A blue precipitate separated, which was washed several times with water to remove sodium halides and excess alkali, if any, and finally dried *in vacuo* at ~50°C. The yield was quantitative. Analysis (%): C = 74.02, H = 7.96, N = 7.86. Determination of methoxide ions by conductometric titration of the compound in DMF–water mixture with 0.01 M ($1\,M = 1\,mol\,dm^{-3}$) hydrochloric acid indicated 4.88 mol OMe^- per 1000 g of the sample. This suggests the probable structure of the compound with a degree of polymerization $n = 5$ (molecular weight = 3463), confirming the theoretical percentages (C = 74.50, H = 8.05, N = 7.28) and a total of $3n+2$ (i.e. 17) quaternary centres in the polymeric network.

*Poly(*N*-2,5-diacylthiophenylene crystal violet trichloride) (C).* Compound C is a condensation product of thiophene-2,5-dicarboxylic acid chloride (I) and crystal violet (II). Equimolecular solutions of I (2.56 g/100 ml) and II (5 g/100 ml) were prepared separately in DMF by slight heating. The solution of I was then added to that of II and the mixture was refluxed at ~70°C for about 5 h with continuous stirring. After concentrating the reaction mixture by evaporating the solvent, it was stirred intermittently until a sticky solid separated. The product was recrystallized from a concentrated solution of acetonitrile and dried *in vacuo* at ~90°C to obtain a crystalline hygroscopic product in 60% yield. The sample was stored in a vacuum desiccator to exclude moisture. Analysis (%): C = 57.99, H = 5.92, N = 9.77. Ionic chlorine determination by conductometric titration in DMF indicated 3.68 mol Cl^- per 1000 g of the sample, which apparently suggests 14 quaternary nitrogens in the structure. The theoretical percentages (C = 58.18, H = 6.02, N = 9.12) of elements are calculated on the consideration that $2n+2$ (i.e. 10) molecules of DMF are tightly held as solvent of crystallization with the polymer lattice. The results are consistent with a calculated non-ionic chlorine of 0.24 mol/1000 g.

*Poly(*N*-2,5-diacylthiophenylene 4,4′-bipyridinium dichloride) (D).* To a solution of thiophene-2,5-dicarboxylic acid chloride (1.28 g/50 ml dry acetonitrile, 1 mol), a solution of 4,4′-bipyridine (Köch-light) (0.95 g/50 ml dry acetonitrile, 1 mol) was added dropwise with constant stirring. The mixture was kept at room temperature. Immediately a white-coloured precipitate was separated out. The mixture was digested for half an hour. It was filtered, washed several times with hot acetonitrile, and then vacuum desiccated at 60°C for about 5 h. Analysis (%): C = 51.82, H = 2.86, N = 7.19. Determination of ionic chlorine by conductometric titration indicated 5.01 mol Cl^- per 1000 g of the sample. The proposed structure with $n = 5$ (molecular weight = 2190) seems to be consistent with the analysis of ionic chlorine and the calculated value of 0.47 mol/1000 g for the non-ionic chlorine. Thus the theoretical percentages of elements are: C = 52.6, H = 2.73, N = 7.66.

Compounds A, B, C and D were found to be unfusible up to 200°C, as revealed by t.g.a. Elemental analyses (C, H, N), conductometric titrations of counterions, t.l.c. analyses in butanol–acetic acid–water (80:15:5) mixture and, moreover, the end-group conformations through i.r. spectroscopy reveal the identity of the samples prepared. The principal i.r. bands due to the N–CH_3 bonds of unquaternized terminals



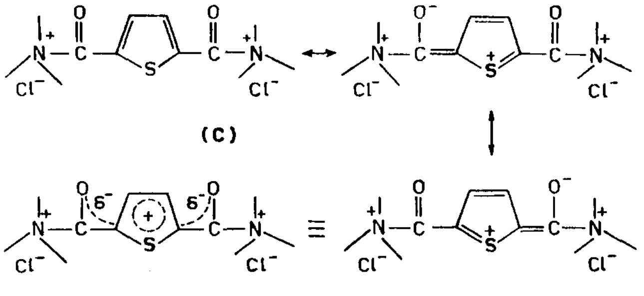
for all crystal violet systems were virtually identical as follows: 2800 cm^{-1} (C–H stretching), 1440–1480 cm^{-1} (C–H bending) and 1350 cm^{-1} (C–N vibration). However, for the 4,4′-bipyridinium polyelectrolyte D, the i.r. frequencies (KBr) corresponded to the terminal bipyridine rings: 3060 cm^{-1} (C–H stretching), 790 cm^{-1} (C–H bending), 1480, 1530 (C=C stretching) and 1640 cm^{-1} (>C=N–C substituted imine vibration). The C–H stretching (2800–2900 cm^{-1}), C–H bending (~1520 cm^{-1}) and C–Br stretching (570 cm^{-1}) frequencies are characteristic of the end –CH_2Br group in systems A and B, while the stretching vibrations at 1680–1780 cm^{-1} (>C=O) and 530–560 cm^{-1} (C–Cl) provide strong evidence for end acyl chloride (–COCl) groups in compounds C and D.

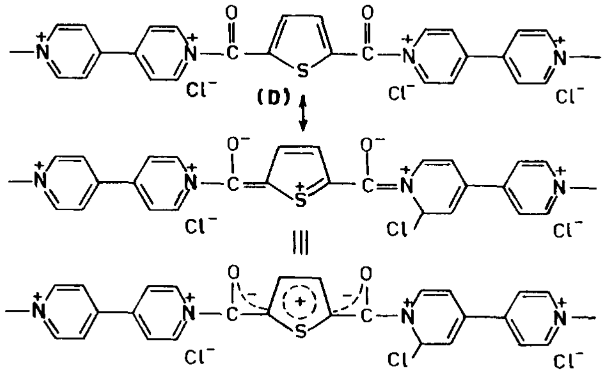
Density measurements

The solution densities (reproducibility better than $2 \times 10^{-5}\,g\,ml^{-1}$) were determined by means of a bicapillary pycnometer of approximately 20 ml capacity with arms graduated to 0.01 ml in the manner already reported elsewhere[4].

RESULTS AND DISCUSSION

The terminal dimethyl nitrogens of crystal violet readily undergo normal Menschutkin reactions[8] with α,ω-dihalo compounds, viz. 1,2-dibromoethane, α,α′-dibromo-*p*-xylene and thiophene-2,5-dicarboxylic acid chloride, giving rise to stable quaternary ammonium polysalts (the halide counterions in compound B were instantaneously exchanged with methoxide ions to yield a relatively stable and non-hygroscopic solid). The pendent moieties carrying basic dimethylamine groups in crystal violet residues of compound A are essentially uncharged, whereas in compounds B and C, they carry positive charges as 2,5-cyclohexadiene-1-ylidine-*N*-methylmethanaminium ions, constituting a parallel track of several positive charges in cooperation with the quaternary nitrogens of the parent chain. Polycondensation of thiophene-2,5-dicarboxylic acid with crystal violet or 4,4′-bipyridine resulted in typical polysalts C and D possessing *N*-acylammonium and *N*-acyliminium bonds, respectively. The markedly stable and solid nature of these *N*-acyl derivatives might be attributed to the presence especially of 2,5-thiophenylene linkages, which impart stability to these compounds through resonance-stabilized intramolecular electrostatic binding[9,10]:


(C)



The above resonance stabilization confers an increased conjugation with partial double-bond character of the substituents in the 2,5-positions and hence the rigidity of thiophene linkages. The additional forces that stabilize these structures are an electrostatic (or salt) bond formed between the oppositely charged groups on the surface of the molecule.

From density measurements of the above oligomeric cationic compounds, the apparent molar volumes (ϕ_v) for a repeat unit of the system were calculated using the relation[2,4]:

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

where d and d_0 represent the density of the solution and solvent, respectively; M_2 denotes the molecular weight of the polyelectrolyte divided by the total degree of polymerization (i.e. 577 for A, 577 for B, 763 for C and 365 for D; the molecular weight of a repeat unit); and C measures the polyelectrolyte concentration in millimoles per litre (monomol l^{-1}). Values of the partial molar volume ($\bar{V}_2^\circ$) were obtained by extrapolating the ϕ_v–concentration plots to zero concentration. A decrease in ϕ_v with concentration was considered to be indicative of a solvophobic effect, whereas an increase of ϕ_v was related to the manifestation of the electrostrictional interaction with the solvent[1,2].

Although the uncertainty in ϕ_v is estimated to be ~1%, larger uncertainties (~3–30%) could be involved in the graphical extrapolation of the linear portion of ϕ_v–C plots in obtaining $\bar{V}_2^\circ$ in the present study. An accurate estimate of polyionic volume could be available using the additive principle as in the case of simple electrolytes. However, one could contend that this should not be applicable for polycationic electrolytes in a medium of lower permittivity, in which some of the counterions must remain bound to the polyion even at infinite dilution. It should be noted further that the contribution of counterions in determining ϕ_v and $\bar{V}_2^\circ$ is insignificant in dipolar aprotic solvents, where anions are least solvated and ion–dipole type solute–solvent interactions with polycations are largely favoured.

Analysis of the apparent molar volume data for compounds B, C and D at 20, 25 and 30°C (*Figures 1–3*) in DMF reveals a sharp increase of ϕ_v with concentration, indicating a tendency to level off beyond $\sim 2\times10^{-3}$ monomol l^{-1}. This may suggest that, overall, the system is experiencing a larger degree of electrostrictional effect in comparison with the competing solvophobic effect. For a given concentration the actual value of ϕ_v apparently represents the net result of two opposing effects[2]. The extrapolated values of apparent molar volumes for all the systems are presented in *Table 1*.

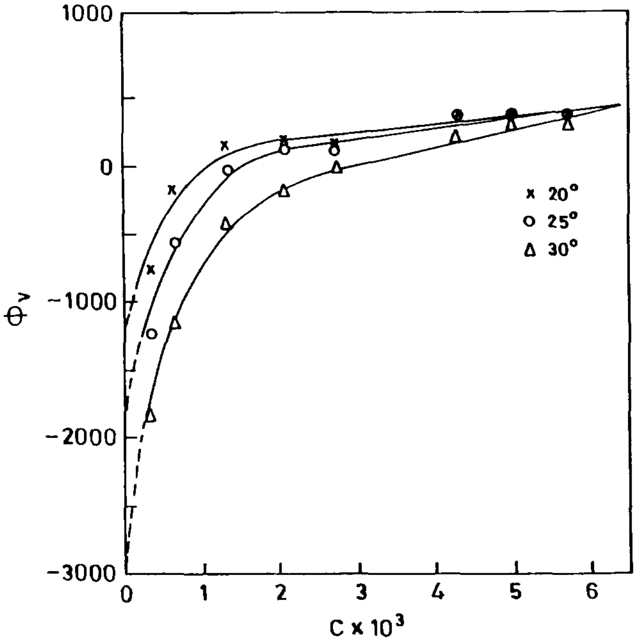


Figure 1 Concentration dependence of apparent molar volume of compound B in DMF

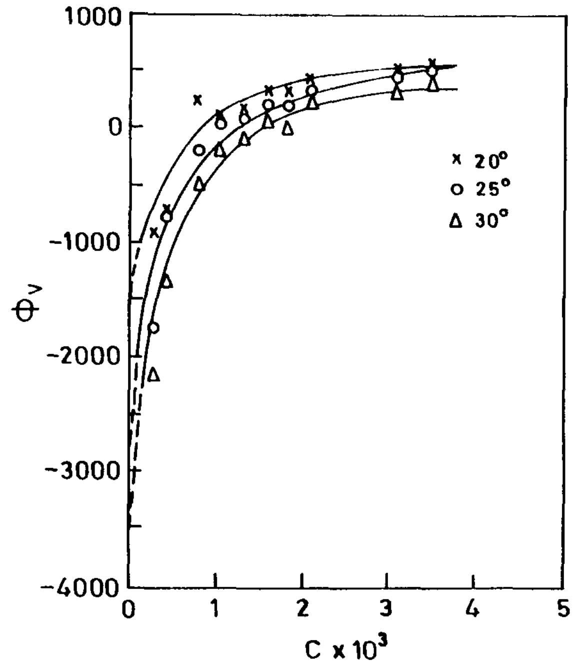
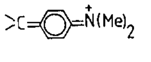


Figure 2 Concentration dependence of apparent molar volume of compound C in DMF

As is evident from the structure of a monomeric unit of the system B, the two quaternary nitrogens in proximity with electron-rich xylylene moieties possess lower charge density as compared to the pendent quaternary centre



of the crystal violet and, therefore, at infinite dilution, the two methoxide counterions in the main backbone are

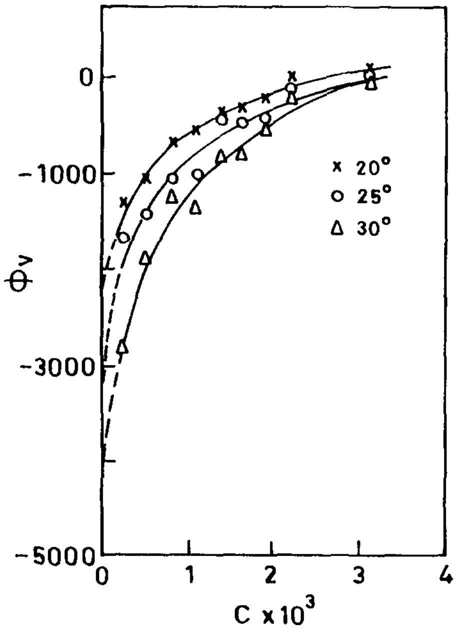


Figure 3 Concentration dependence of apparent molar volume of compound D in DMF

Table 1 Values of $\bar{V}_2^\circ$ for the crystal violet and 4,4'-bipyridinium polyelectrolytes (A, B, C and D) in DMF and DMSO

	Partial molar volume^a (ml monomol^{-1})					
	DMF			DMSO		
System	20°C	25°C	30°C	20°C	25°C	30°C
A	–	–	–	408	365	340
B	−1200	−1800	−2900	1800	1400	1550
C	−1500	−2800	−3500	3500	2800	1900
D	−2200	−3100	−4000	3000	2500	1600

[a] Estimated errors: ~10–30% (DMF) and ~3–15% (DMSO)

expected to be dissociable whereas the other in the pendent group apparently remains undissociated in a low-dielectric-constant medium (DMF). Under such conditions, these two quaternaries, without counterions in the parent chain, presumably compete to share the undissociated methoxide ion of the side chain. As a consequence, the propeller blades of crystal violet residues in the oligomer might exert intramolecular bendings with constriction in the void spaces available between their blades. Thus it becomes difficult for the larger DMF molecules to pack into the narrowed void spaces provided by the xylylene groups on the backbone of the polyions in cooperation with the spatial disposition of the propeller blades of crystal violet moieties. This causes a diminished solvophobic effect in competition with the predominating electrostrictional solvation[1], despite the reduced charge density of the quaternary nitrogens present in the individual molecules. The marked electrostrictional interactions in this case could be rationalized if one considered a large electrostatic potential along the polycation conformation, assuming a 'stacked' molecular ordering of compact molecules due to the long-range intermolecular charged interactions even in dilute solutions analogous to aqueous systems[11]. However, at higher concentration beyond $\sim 2 \times 10^{-3}$ monomol l^{-1}, the increased population of polyions may lead to an overall increase of intermolecular spacings (free volume) through an aggregate feasible under the pool of counterions. This facilitated an easier mode of incorporation of the solvent into the free volume, enhancing the solvophobic character just sufficiently to overcome the electrostatic contribution of solvation, and thereby a levelling tendency at higher concentration was observed in the ϕ_v–C profile at all the temperatures studied.

The general nature and interpretations of the ϕ_v–C plots for compounds C (*Figure 2*) and D (*Figure 3*) resemble those of system B (*Figure 1*) in DMF, at all temperatures. The larger negative value of $\bar{V}_2^\circ$ of compound C than that of system B revealed a higher degree of contraction in its total polymeric structure; the contraction in molecule B is chiefly due to crystal violet shrinkage, whereas the major constriction in compound C involved intramolecular Coulombic interactions in crystal violet and 2,5-diacylthiophenylene moieties as well. The extremely high negative value of ϕ_v in the dilute range for system D reflects some sort of major contraction in spite of its smaller molecular weight. This may be supported by the fact that the system may orient presumably in a curled shape under the force of interactions of common associated counterions with the bare quaternary nitrogens including, to some extent, the intramolecular Coulombic attractions in diacylthiophenylene residues of the polycation. The magnitude of such coiling or curling seems to be relatively small in the crystal violet oligomers as compared to D, obviously because of the stereochemical hindrance caused by the bulky side-group substituents in the system concerned.

The decreasing trends of $\bar{V}_2^\circ$ with increasing temperature in all three compounds may be associated with the mobilization of the compact electrostricted DMF molecules in dilute solution, which paves the way for easier contraction of the molecule under the force of various interactions, as the temperature is raised. In system B this type of contraction goes along *N*-xylylene bonds by intramolecular attraction between the electron-rich xylylene moiety and positively charged pendent substituents. In compound C, it is due to the loosening of the electrostatically bound layer of solvent molecules, which conceivably enjoy greater freedom to move from the vicinity of acylthiophenylene polar residues towards the crystal violet pockets at higher temperature, leaving them relatively free to have an intramolecular Coulombic contraction. Finally, in compound D, it is attributed to the migration of electrostricted DMF either into the puckered rings of 4,4'-bipyridine[4] or towards the bulk of the medium, facilitating relatively great ease in curling tendency at 30°C along *N*-acyliminium bonds as compared to other lower temperatures. The high negative values of $\bar{V}_2^\circ$ could be attributed, in all cases, to the overwhelming magnitude of the ion–solvent attraction, causing a significant contraction of the solvated cells around the system, exclusively under the influence of electrostatic bonding force of the DMF molecules (Gutmann donicity = 26.6)[12] with the positively charged nitrogen centres of the polyion concerned. Furthermore, in the absence of any accommodation of DMF molecules in the void spaces of the present systems at infinite dilution, the overall contraction is favoured so much that it completely overrides the already shrinking intrinsic volume component of the molecule, contributing high negative magnitude of net partial molar volume[13,14].

As DMSO has relatively higher dielectric constant ($\varepsilon = 45.0$ at 25°C) than DMF[12] ($\varepsilon = 36.1$ at 25°C) and the values of ϕ_v are increased upon dilution in the case of the systems B, C and D (*Figures 4–7*), it is reasonable to assume that most of the counterions of the polyelectrolytes are apparently being dissociated, leading to the major expansion of the available void spaces as a result of intramolecular repulsion between the positive centres of the system. The observed solvophobicity in these systems is chiefly due to the 'locking up'[1] of the solvent molecules in the 'pockets' provided by the parent chain carrying apolar (solvophobic) residues, namely xylylene and phenylene rings in cooperation with the pendent substituents. Despite the assumption that there may be some intermolecular arrangement of DMSO molecules involving some weak hydrogen bonds between the O atoms and the methyl hydrogens, the remarkable solvophobicity of this solvent towards apolar residues of solutes in the very dilute region cannot be assumed to be equivalent to the hydrophobic effect in water, because the magnitude of the structural effect of DMSO is reported to be insignificant in comparison to the effect observed in water[15]. The O atom is at the negative end of the S=O dipole of DMSO and can be approached unhindered by positively charged ions under the force of electrostatic interactions; whereas the solvophobic residues will simultaneously exert a push to the surrounding solvents towards the repulsive region of the solute–solvent interaction potential surface[15] and lead to the packing of solvent into the available empty spaces.

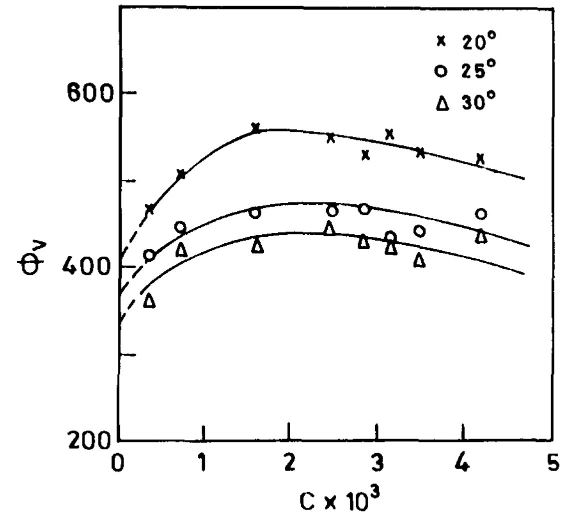


Figure 4 Plots of apparent molar volume vs. concentration for compound A in DMSO

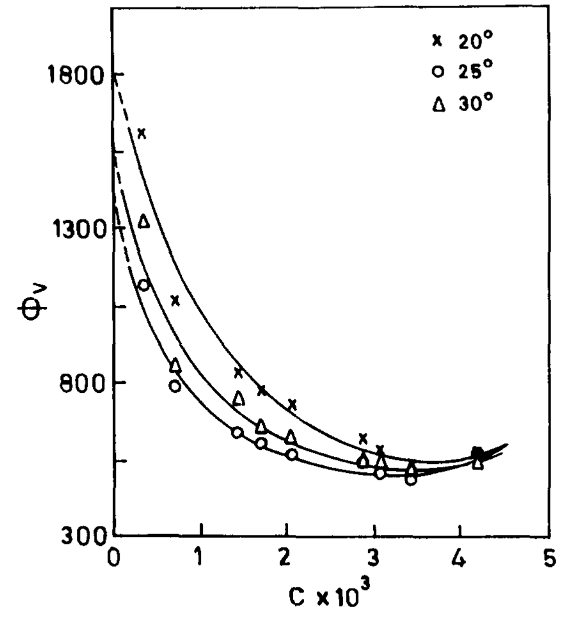


Figure 5 Plots of apparent molar volume vs. concentration for compound B in DMSO

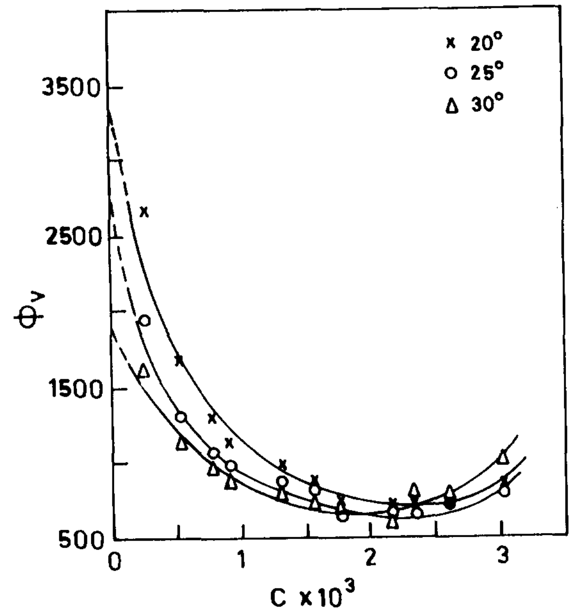


Figure 6 Plots of apparent molar volume vs. concentration for compound C in DMSO

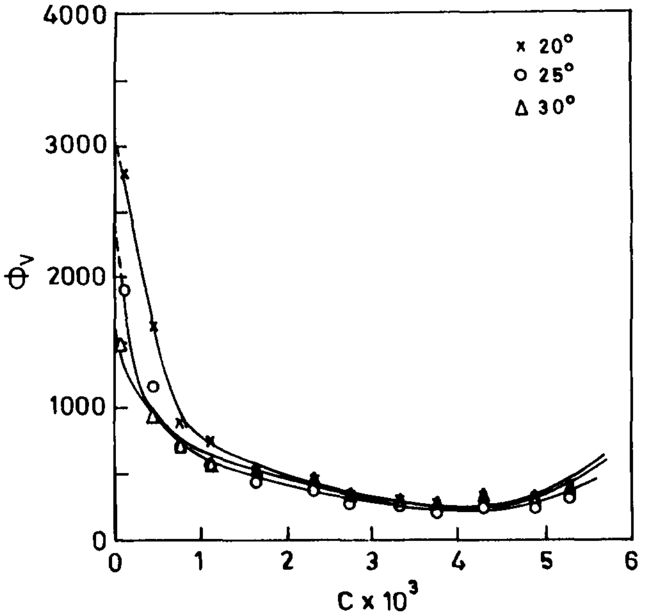


Figure 7 Plots of apparent molar volume vs. concentration for compound D in DMSO

In spite of the lower molecular weight of compound D as compared to B, the higher positive value of $\bar{V}_2^\circ$ of this compound in DMSO indicates a linear conformation with relatively high degree of expansion. Owing to the presence of polar resonating structures of marginal dipole moment in compounds C and D, as shown earlier, these systems would enjoy relatively great freedom to expand, giving much higher values of $\bar{V}_2^\circ$ by the phenomenon of 'electrorelaxation' as opposed to electrostriction[13].

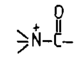
Although DMSO enjoys greater nucleophilic character (Gutmann donicity = 29.8)[12], the quaternary nitrogen centres (without counterions at infinite dilution) of polyelectrolytes are primarily engaged in interionic Coulombic repulsions and obviously are not free for long-range coordination interactions (electrostatic bonding) under the force of nucleophilic action of DMSO, in contrast to the DMF medium. It may be further noted that the 'carbonium' sites of crystal violet oligomers B and C remain unattacked by the coordination interactions[16] of aprotic solvents. This was evident from the fact that no colour fading was observed in these solutions, where nucleophilic action is possibly either geometrically hindered or energetically not favoured.

The observed lowering of $\bar{V}_2^\circ$ with temperature (*Table 1*) reflects an extensive packing of somewhat structured[15] DMSO molecules in relatively enlarged openings of individual polymeric molecules, at infinite dilution with net reduction in the total volume. However, a moderation of behaviour is observed at 30°C in the case of compound B with ϕ_v and $\bar{V}_2^\circ$ assuming intermediate values. This appears to be due to the reduced solvophobicity in competition with the electrostrictional effect as a result of the somewhat restricted mode of accommodation of DMSO molecules into the contracted void spaces, seemingly produced due to the action of the induced π-electron interaction of xylyl moiety with naked positiveley charged nitrogen of the pendent group at elevated temperature.

The pattern of concentration dependence of the ϕ_v (*Figure 4*) of A in DMSO is quite interesting. The nature of the ϕ_v–C curves at all temperatures indicated a net electrostrictional effect at lower concentrations, attainment of a maximum (at $\sim 1.6 \times 10^{-3}$ monomol l^{-1}) and then a decrease in ϕ_v reflecting solvophobicity. As could be seen from the structure of compound A, the positive charges, interspersed with ethylene linkages in the main chain, are most likely free from counterion association at infinite dilution, and as such they experience intramolecular bending under interaction with the lone pair of electrons of the unquaternized nitrogen in the pendent structure. This results in net constriction of the empty spaces between the crystal violet blades and exposition with the hydroxyl bond towards its central carbon atom. Furthermore, the absence of any electron-rich xylylene moieties (unlike compound B) in the backbone would enable the quaternized centres in the relatively small system to exert high positive local charge density, and to be more accessible to the solvent molecule for electrostrictional interactions. However, at higher concentrations ($> 1.6 \times 10^{-3}$ monomol l^{-1}) beyond the maximum, the possible formation of geometrical structures consisting of short and rigid polycations, held together in the pool of common counterions[4], might favour solvent entrapment within the empty spaces of the arrangement so produced. The reduction in the partial molar volumes at higher temperatures (*Table 1*) may be explained on the basis of the fact that the electrostricted DMSO molecules may be mobilized to migrate into any of the empty spaces provided by the backbone of the dimeric cation, giving rise to a net decrease in volume with increase of temperature. The actual volume of ϕ_v at any temperature would be determined by the volume of the available void spaces and the degree of freedom of the electrostricted solvents to migrate into it.

CONCLUSIONS

Synthesis of nitrogen-based polyelectrolytes containing crystal violet and 4,4′-bipyridine moieties with interspersed ethylene, xylylene and 2,5-thiophenylene links appeared feasible through condensation polymerization involving Menschutkin reactions. The marked stability beyond room temperature and, moreover, the solid nature of *N*-acylammonium and *N*-acyliminium oligomers due to the resonance-stabilized 2,5-thiophenylene linkages present in their molecular structures appear to be very promising since the


$$>\overset{+}{N}-\overset{\overset{O}{\|}}{C}-$$

bond is known to be extremely unstable.

Correlation of the solvation characteristics of these polycations in the solvents DMF and DMSO of intermediate permittivity could be made on the basis of the spatial disposition of the substituents as a result of intramolecular constriction and/or expansion in the system.

Although partial molar volumes as obtained by freehand extrapolation involve large errors, the systematic order in which the $\bar{V}_2^\circ$ values appear to depend on temperature in the individual cases is considered interesting and meaningful. The reduction in partial molar volume for all systems in both solvents with increase of temperature is explained on the basis of increased perturbation (mobilization) of immobilized solvation layers followed by intramolecular constriction of the system, as well as the dense packing of solvent and/or the migration of electrostricted solvent molecules into the empty spaces available within the molecule under study.

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