

***N*-Chloranil and *N*-Xylene Containing Polycations. Preparation and Solvation Characteristics**

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ABSTRACT: Partial molar volume studies on four new types of cationic polyelectrolytes (mol wt 1167 to 6432), where quaternized centres in oligomeric chain are essentially *N*-chloranil or *N*-xylylene ammonium/imminium moieties interspersed with ethylene, phenothiazin-5-ium and bipyridyl (viologen) links, have been undertaken in two dipolar aprotic solvents (dimethylformamide and dimethyl sulfoxide) over small temperature range ($25 \pm 5^\circ\text{C}$). A cumulative effect of competing electrostrictional and solvophobic interactions with the dipolar nonaqueous media was examined to explore the conformational alternations of these polymers at varying temperatures and concentrations.

KEY WORDS *N*-Based Polycations / Synthesis / Solvation / Molar Volume / Solvophobicity / Electrostriction /

Solvation study of polycations, where symmetry of charge potential is drastically disturbed due to intercoumbic interactions of juxtaposed charge centres, is undoubtedly an intriguing problem. Although extensive work have been reported on solvation behaviour of linear polysalts in aqueous media, the massive conjectures still remain unexplored in so far as electrostrictional and solvophobic interactions are concerned.¹ Mean activity data fail to assess these two modes of solvation in terms of conformational changes. Thus, our present state of knowledge on solution properties of polymers is rather limited and owing to the ambiguity and complications as compared to aqueous hydration, no serious attention has been paid, hitherto, over non-aqueous solvation of polyelectrolytic systems. With the advent of a series of studies on volume properties of polymers, partial molar volume data appeared an illuminating parameter to shed light on electrostrictional and solvophobic effects.²

In the continuation of our modest attempt^{3,4}

to unravel the solvation characteristic of different kind of organic polyelectrolytes in dipolar aprotic solvents, the present paper deals with the volumetric properties of polycationic electrolytes specifically of two categories: (i) having *N*-chloranil or *N*-xylylene free ammonium charge centres in their molecular backbone, where two proximate $\geq \text{N}^+$ charge centres are either directly joined by aliphatic chain or interceded with the polyaromatic charged heteroatom-based system, and (ii) those possessing *N*-chloranil imminium charge centres as a part of ring structures with alternating viologens in their repeating units. The following four linear nitrogen-based polycations (abbreviated as A, B, C, and D) which satisfy above requirements are: A, poly[*N*-chloranil-*N,N,N',N'*-tetramethylethylenediamine dichloride]; B, poly[*N*-chloranil-methylene blue dichloride]; C, poly[*N*-xylylene-methylene blue dibromide]; D, poly[chloranil viologen dichloride]. Those chemical structures are shown in Figure 1.

Syntheses and characterizations of these new

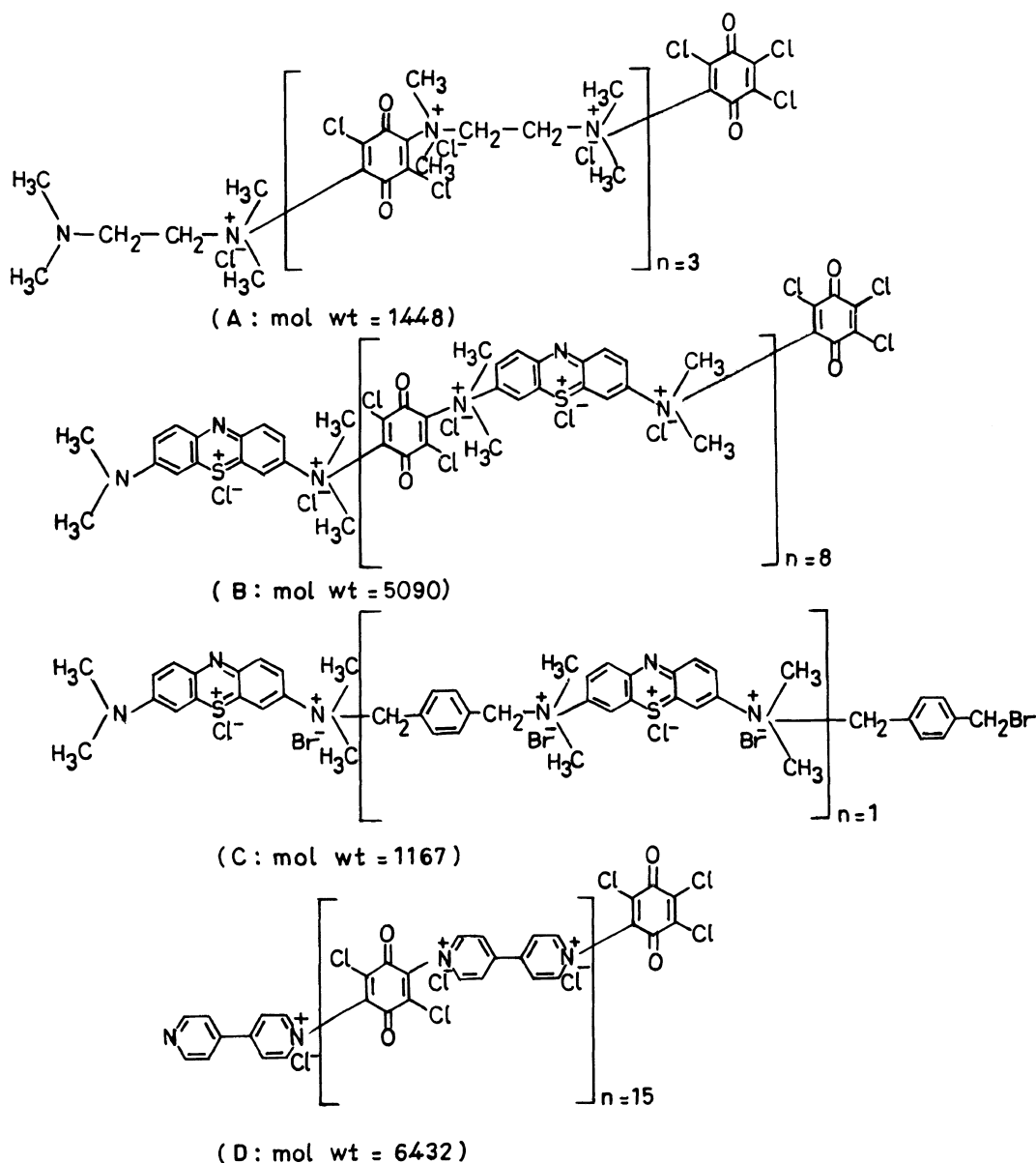


Figure 1. Chemical structures of *N*-chloranil and *N*-xylylene containing polycations.

oligomeric class of compounds are essentially an integral part of the investigation. Systems A, B, and D are prepared on the basis of Michael-type substitution-elimination reaction⁵ between tertiary amine/imine and *p*-chloranil; whereas polyelectrolyte C is made by straightforward condensation of methylene

blue and α,α' -dibromo-*p*-xylylene following Menshutkin reaction.⁶ The other part of the investigation includes density measurements of these systems in DMF and DMSO. The system D cannot be studied in DMF due to solubility restriction. The particular surge of interest for investigation in DMF and DMSO is because

of their dipolar aprotic nature which is found useful in organic and high energy reactions.⁷ Furthermore, the introduction of chloranil (an essential constituent of the commercial fungicide 'Spergon'⁸) and physiologically active phenothiazine rings⁹ in the polycationic backbone as quaternary ammonium derivatives presents interesting features to be included in the chosen set of compounds for solution studies.

EXPERIMENTAL

Materials

Solvents dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) (99% pure, Sarabhai-Merck Co.) were purified and stored as described elsewhere.⁴ All other chemicals were either high purity materials or were purified before use.

Preparation of Polyelectrolytes Studied

*A. Poly[*N*-chloranil-*N,N,N',N'*-tetramethylethylenediamine Dichloride].* Equimolar solution of *N,N,N',N'*-tetramethylethylenediamine (1.23 ml/10 ml; 0.14 M) was added to the solution of chloranil (2.0 g/50 ml, 0.14 M) in toluene. The reaction was instantly followed with a sudden change of colour into dark brown. The reaction mixture was refluxed for 4 hours and kept standing for overnight. The resulting product after several times washings with toluene, was perfectly dried in vacuum. The product was found stable upto 300°C, beyond which a distortion with sublimable white vapours was seen. *Anal.* Found: C, 39.62%; H, 4.40%; N, 7.60%. Calcd: C, 39.78%; H, 4.45%; N, 7.73%. Conductometric titration of the sample in DMF–water solvent confirms the structure (Figure 1) with 4.75 mol Cl⁻ per 1000 g of sample.

*B. Poly[*N*-chloranil-methylene Blue Dichloride].* The DMF solution of methylene blue (1.52 g/50 ml, 0.095 M) was added to the solution of chloranil (1.0 g/50 ml, DMF, 0.08 M). The reaction mixture was refluxed in

an oil bath (132°C) for several days. On evaporation of the solvent, a dark coloured product was obtained which was washed repeatedly from chloroform and toluene to remove unreacted materials, if any, and then dried in vacuum. mp > 330°C. *Anal.* Found: C, 46.68%; H, 3.82%; N, 8.66%. Calcd: C, 46.7%; H, 3.18%; N, 7.42%. Conductometric titration of the sample in DMF–water solvent confirms the structure (Figure 1) with 3.74 mol Cl⁻ per 1000 g of sample.

*C. Poly[*N*-xylylene-methylene Blue Dibromide].* The equimolar DMF solutions of methylene blue (1.41 g/50 ml, 0.11 M) and *p*-xylylene dibromide (1.0 g/50 ml, 0.1 M) were mixed and refluxed in oil bath (~132°C) for several days, kept standing for overnight and concentrated the solution. On evaporation of the solvent, the dark coloured product was obtained which was washed repeatedly from chloroform and toluene to remove unreacted materials, if any, and then dried in vacuum. mp > 330°C (distorted at 147°C). *Anal.* Found: C, 49.40%, H, 4.15%; N, 8.44%. Calcd: C, 49.36%; H, 4.45%; N, 7.19%. Conductometric titration of the sample in DMF–water solvent confirms the proposed structure with 4.21 mol Cl⁻ per 1000 g of sample.

*D. Poly[*N*-chloranil Viologen Dichloride].* Equimolar solution of 4,4'-bipyridine (0.64 g/40 ml, 0.1 M) was added to the solution of chloranil (1.002 g/40 ml, 0.1 M) in toluene. The reaction mixture was refluxed for 10 hours and kept standing for overnight. On evaporating the solvent, a purple-brownish product was obtained which was washed several times with toluene and then dried in vacuum. mp > 300°C (distorted). *Anal.* Found: C, 47.71%; H, 3.006%; N, 6.96%; Calcd: C, 47.70%; H, 3.004%; N, 6.95%. Conductometric titration of the sample in DMF–water solvent indicated 4.82 mol Cl⁻ per 1000 g of sample (*n* = 15), in support of the structure shown (Figure 1).

Elemental analyses (C, H, N), conductometric titrations of counterions, TLC analyses in butanol–acetic acid–water (75:15:10) mix-

ture and moreover, the end group conformations through IR spectroscopy reveal the identity of the samples prepared. The key IR bands (KBr) due to the N-CH₃ bonds of unquaternized terminals for A, B, and C are 2770–3000 cm⁻¹ (C-H stretching), 1400–1470 cm⁻¹ (C-H bending), and 1225–1280 cm⁻¹ (C-N vibration). However, for the bipyridinium polyelectrolyte D, the IR frequencies corresponded to the terminal bipyridine rings: 3090 cm⁻¹ (C-H stretching), 812 cm⁻¹ (C-H bending), 1400–1490 cm⁻¹, 906 cm⁻¹ (skeletal vibrations), and 1570 cm⁻¹ (pyridine). The 1650–1690 cm⁻¹ (>C=O) and 600–720 cm⁻¹ (C-Cl) vibrations are characteristics of chloranil moieties present in A, B, and D. The C-H stretching (2800 cm⁻¹), C-H bending (1500 cm⁻¹), and C-Br stretching (520 cm⁻¹) frequencies are characteristics of the end -CH₂Br group in system C. The vibrations 1467 cm⁻¹ (imine), 1020 cm⁻¹ (>C=S), 815–880 cm⁻¹ (C-H out of plane bending) correspond to the phenothiazine rings of compounds B and C.

All compounds are stored in vacuum desiccator to protect from moisture exposure.

Density Measurements

A pycnometer (~20 ml capacity) having bicapillary arms (scaled to 0.01 ml) was used for density measurements at 20, 25, and 30°C in the manner reported elsewhere.³ The reproducibility in density data was accurate to $\pm 1 \times 10^{-5}$ g ml⁻¹ and from the entire set of five replicate measurements for each concentration, the level of certainty was better than 98%.

RESULTS AND DISCUSSION

Compounds A, B, and D were obtained by reacting tertiary amine/imine with chloranil following Michael-type reaction⁵ whereas C involves a typical Menshutkin reaction⁶ between tertiary amine and α,α' -dibromo-*p*-xylylene. The reaction sites in chloranil (2,3,5,6-

tetrachloro-*p*-benzoquinone) are reportedly favoured at 2,5-positions.^{8,10} These compounds in contact with water are observed to have reasonable stability without any colour change, in contrast to the earlier observation, as none of the residual tertiary amines are available as required for hydrolysis.¹⁰ In compound A, quaternary charge centres are separated by ethylene linkages, whereas in compounds B and C, these are bonded with phenothiazinium rings. The introduction of phenothiazine rings between two dimethyl substituted ammonium centres presents an interesting structural feature to explore the distinctive solvation behaviour of cations when they are either jointed by aliphatic chain or intertwined with bulkier polyaromatic = \ddot{S} -cations. The system C is deliberately included in the present set of compounds in spite of its dimeric nature in order to compare the effect of xylylene substituents, in lieu of chloranil moiety in the molecular chain of system B. The particular study to shed light over the mode of solute-solvent interactions when the polar chloranil substrate is attached with imminium charge centres, in the system D, which belongs to an important class of 'viologen' family, appears to be worthwhile. This enables us to cover a broad spectrum of solvation behaviour of diverse cationic centres interspersed in the molecular network of oligomer B and dimer C having three charge centres (two free $\geq\text{N}^+$ - and one = \ddot{S} -heteroatom), while A and D possess two free ammonium charge centres and two imminium centre, respectively, in their corresponding repeating units. Since a large departure from simple electrolytes was not primarily intended owing to solubility restrictions, all compounds in the present instance are large enough to examine the polyelectrolyte behaviour in non-aqueous solvents.

Apparent molar volumes, ϕ_v , of polyelectrolyte were calculated from the densities according to the equation²:

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

where d_0 and d represent the densities of the solvent and solutions, respectively. M_2 denotes the molecular weight of a repeating unit of polyelectrolyte, which is obtained by dividing the molecular weight of the system by the total degree of polymerization (*i.e.*, 362 for A, 565.5 for B, 583.5 for C, and 402 for D) and C is the concentration of polyelectrolyte in monomol per litre (monomol l^{-1}). Since ϕ_v values are non-linear function (except B in DMF) of the square root of concentration, the following expression (Redlich-type equation¹) for the dependence of ϕ_v with concentration:

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

where $\phi_v^0 = \bar{V}_2^\circ$ is the partial molar volume of polyelectrolyte at infinite dilution, is found best suitable for data treatment in the present work.

The theoretical slope ' S_v ', as can be derived for simple ion from the Debye-Mückel limiting law, is not possible with polymeric electrolyte solution primarily because of the asymmetry of the charged centres caused by the influence of the large electrostatic potential along the polyion chain. Another fact is the intrinsic flexibility of polyion changes in the dilute range of concentrations unlike spherical ions. Based on these considerations, all data in present study were treated by the method of curve fitting into the polynomials for polymeric systems. The resulting equations are listed in Table I. The relative standard deviation in ϕ_v is estimated to be less than 2.2% (upper confidence limit 98%, chi-test) for five replicate measurements, at each concentrations, in both solvents. The corresponding extrapolated $\phi_v^0 = \bar{V}_2^\circ$ values of different systems are portrayed in Table I at all temperatures. The estimation of cationic volumes is deliberately

Table I. Apparent molar volume equations for the *N*-chloranil and *N*-xylylene containing polycations (A, B, C, and D) in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) at different temperatures

System/Solvent	Temp/ $^\circ$ C	Best equation
A/DMF	20	$\phi_v = 700.85^* - 14518.94c^{1/2} + 87666.89c$
	25	$\phi_v = 789.38^* - 13964.38c^{1/2} + 63840.80c$
	30	$\phi_v = 835.60^* - 14543.70c^{1/2} + 67623.16c$
B/DMF	20	$\phi_v = 392.45^* - 898.38c^{1/2}$
	25	$\phi_v = 438.43^* - 1496.53c^{1/2}$
	30	$\phi_v = 667.37^* - 5957.66c^{1/2}$
C/DMF	20	$\phi_v = 1102.68^* - 41754.00c^{1/2} + 482899.03c$
	25	$\phi_v = 1064.34^* - 45294.67c^{1/2} + 542697.68c$
	30	$\phi_v = 1195.29^* - 46073.61c^{1/2} + 551275.73c$
A/DMSO	20	$\phi_v = 2327.64^* - 18762.30c^{1/2} + 437244.28c$
	25	$\phi_v = 2050.16^* - 50102.29c^{1/2} + 356283.03c$
	30	$\phi_v = 1737.15^* - 41971.96c^{1/2} + 301264.90c$
B/DMSO	20	$\phi_v = 2384.55^* - 63365.54c^{1/2} + 538803.05c$
	25	$\phi_v = 1693.46^* + 34058.51c^{1/2} + 209758.21c$
	30	$\phi_v = 1180.18^* - 92581.30c^{1/2} + 102796.25c$
C/DMSO	20	$\phi_v = 2244.60^* - 48740.91c^{1/2} + 253908.62c$
	25	$\phi_v = 2045.54^* - 43596.38c^{1/2} + 214318.89c$
	30	$\phi_v = 1702.40^* - 43390.08c^{1/2} + 313143.74c$
D/DMSO	20	$\phi_v = 1700.66^* - 34417.57c^{1/2} + 223161.26c$
	25	$\phi_v = 2192.17^* - 56324.20c^{1/2} + 428797.08c$
	30	$\phi_v = 2281.67^* - 63855.43c^{1/2} + 506299.09c$

^a Values denote limiting partial molar volumes ($\phi_v = \bar{V}_2^\circ$) with their uncertainties not more than 2.2% (98% confidence limit).

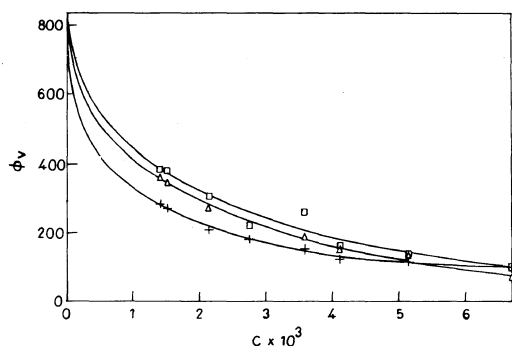


Figure 2. Concentration dependence of apparent molar volume of compound A in DMF at temperatures ($^{\circ}\text{C}$): 20 (+), 25 (Δ), and 30 (\square).

abandoned using additivity principle in the present case, since complete dissociation of counterions is impractical in low dielectric constant media even at infinite dilution. Anions are reported to be solvated negligibly in dipolar aprotic solvents and thus do not influence the ϕ_v values obtained exclusively from much favoured polycations–solvent dipole interactions.

As revealed from the Figure 2, the apparent molar volume of compound A in DMF at any temperature decreases with concentration. This exhibits a larger degree of solvophobicity in the system as a consequence of repulsive solute–solvent interactions which leads to an extensive solvent packing in the empty spaces around charged centres of the polycations.^{1,4} Notwithstanding the well established hydrophobic phenomenon in water which forms tight ice-cage (due to extensive hydrogen bonding) around apolar solutes, the orientation of aprotic solvent dipoles under the pool of charged centres of polycationic molecules facilitates ‘locking-up’ of the solvent, within the void spaces available as a result of distinctive conformational alternations in different region of solution characteristics. As is obvious in the structural figure of compound A, the quaternized nitrogen centres are in coulombic interactions with the carbonyl groups of the chloranil moieties which enforce

the positive centres to be immobilized or rigid curtailing the inter-cationic repulsion. Since charge density of cations which is shrouded by dimethyl substituents is drastically shielded by adjacent $>\text{C}=\text{O}$ groups of chloranil, the electrostrictional effect is apparently disfavoured. Furthermore, with growing population of short statured oligomer A, beyond $3 \times 10^{-3} \text{ molol}^{-1}$, the several polycations assume an entanglement structure consequently giving rise to the enhanced charge densities of the structures. This favours electrostrictional solvation just equivalent to the solvophobic interactions to level off the variation of ϕ_v with concentration in the concentrated region (solvophobic and electrostrictional solvations are completing effects). However, solvophobicity in dilute range is found to be dominant due to the apolar ethylene linkages which straighten up the conformation through massive solvation by DMF at all temperatures studied. This favours solvent packing into the space provided by the dimethyl as well as chloranil units in cooperation with the parent chain. The high value of \bar{V}_2° at all temperatures in spite of the low molecular weight clearly supports that the compound A is indeed a straightened rod even with the flexible ethylene linkages and oppose apparently any intramolecular bending in solution. The DMF thus acts as a good solvent for A.

The apparent molar volumes of B in DMF are almost insensitive towards concentration with a bit downward tendency at 20 and 25°C (Figure 3). This reflects a balancing between the two counteracting effects (*i.e.*, solvophobicity, which tends to lower the volume and electrostriction which causes a positive concentration dependence of ϕ_v) and eventually the solvophobicity is retained just an edge over the electrostrictional effect. Nevertheless, the solvophobic effect manifests itself predominating phenomenon at 30°C , throughout the concentration range studied. As the structure of B shows, the three positive centres are in a

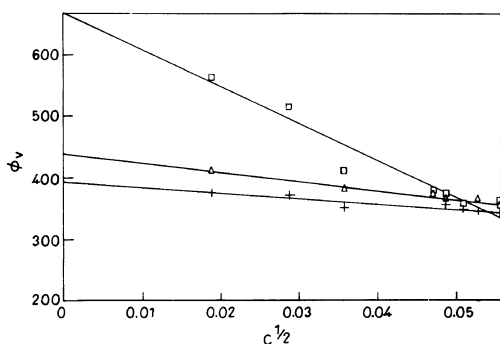


Figure 3. Concentration dependence of apparent molar volume of compound B in DMF at temperatures ($^{\circ}\text{C}$): 20 (+), 25 (Δ), and 30 (\square).

chain, of which the $=\overset{+}{\text{S}}$ - of the phenothiazin-5-ium ring is fixed as heteroatom while other two $\geq\overset{+}{\text{N}}$ -centres are absolutely free for orientation in solution. The electrostatic repulsions between these $\geq\overset{+}{\text{N}}$ -centres with interceding $=\overset{+}{\text{S}}$ -keep charges apart and involved with the polar attraction from the neighbouring carbonyl groups of chloranil. Although solvophobic solvation is being facilitated in various void spaces available between the 'puckered' structure¹¹ of phenothiazinium residue with $\overset{+}{\text{N}}$ -arms at 3,7-positions as well as between the rings of methylene blue and chloranil, the electrostrictional solvation in this case is being completely disfavoured due to the shielding of polycationic charge density by the neighbouring $>\text{C}=\text{O}$ groups of chloranil moieties, particularly at 30 $^{\circ}\text{C}$. However, the proposed shielding effect is apparently insufficient at 20 and 25 $^{\circ}\text{C}$, resulting in an enhanced electrostatic contribution which counterbalances the solvophobicity considerably.

It may be pointed out that the best fit equation for B in DMF is based on the linear function of the square root of C with negative slope.¹ This is considered as an approximation of symmetrical single ion behaviour in DMF. The lower values of \bar{V}_2° obtained at all temperatures, despite the longer chain of the system, reflect that DMF acts as a bad solvent for B, in contrary to A, causing curling in the

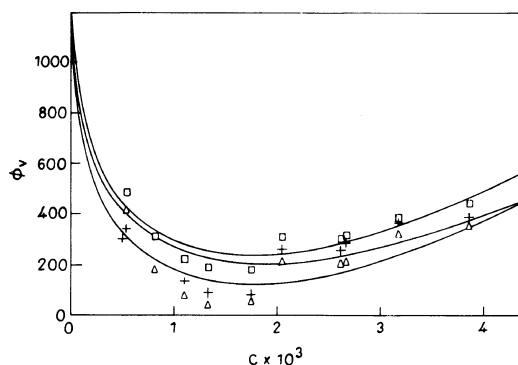


Figure 4. Concentration dependence of apparent molar volume of compound C in DMF at temperatures ($^{\circ}\text{C}$): 20 (+), 25 (Δ), and 30 (\square).

molecular chain.

Compound C in DMF exhibits a valley-shaped curve (Figure 4) initially showing solvophobic behaviour and subsequently displaying the electrostrictional effect as predominating mode of solvation. Of the three positive centres in the chain, the two $\geq\overset{+}{\text{N}}$ - are free to demonstrate orientation in absence of any polar moieties in proximity, contrary to the case of B. The reason for dominant solvophobicity is same as depicted in the case of B. However, the sudden increase in ϕ_v vs. C plot beyond 2×10^{-3} mol l^{-1} at all temperatures, recorded an overwhelming magnitude of electrostrictional solvation. The rationale of such observations can be focussed on the basis of the fact that being a relatively short chain as compared to B, the dimeric molecules of C, have tendency to stack one over the other, with the pool of counterions available in the media of lower permittivity, and thereby enhancing the net charge density of the stacked molecules considerable enough to demonstrate electrostrictional solvation. It is to be noted that such stacking tendency in the case of B is restricted either due to the obstructions created by the 'protruded' configuration of chloranil moiety or due to the larger chain length of polymer. In spite of the lower molecular weight of compound C as compared to B, the higher value of \bar{V}_2° indicates that the

system C has greater freedom to expand, in absence of the polar chloranil substituents by the phenomenon of 'electrorelaxation' as opposed to the electrostriction^{12,13} in the dilute region. However, the system B cannot enjoy such electrorelaxation due simply to the presence of chloranil in the longer chain which, instead, brings upon a major constriction in the chain molecule at all temperatures studied. The slightly small apparent molar volumes at 25°C as compared to that at 20°C in concentrated region beyond 1×10^{-3} monomol l⁻¹ are due to interpenetration (destabilisation) in the domains of molecular chains of C resulting in the migration of electrostricted solvent into the empty spaces so produced in the new geometry. However, such destabilisation of the solvation layer of aggregates are surprisingly either non-existing or ineffective at 30°C.

The increase of \bar{V}_2° , in all compounds, with temperature confirms the general volume expansion theory. The increase in \bar{V}_2° is apparently the result of mobilization (perturbation) of the DMF solvation layer with rise in temperature. However, the migration of electrostricted solvent^{3,4} into the empty spaces or bulk of solution, which causes volume diminution, is lacking in the present study. This is attributed to the fact that the electrostricted solvents around free $\geq N^+$ are blocked by dimethyl substituents and are firmly held up with the polar substituents ($>N$ -chloranil or $>N$ -xylylene) of polycations, at all temperatures.

As DMSO has relatively higher dielectric constant ($\epsilon=45.0$ at 25°C) than DMF¹⁴ ($\epsilon=36.1$ at 25°C) and the values of ϕ_v are increased upon dilution in the systems A, B, and C, 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' of the solvent molecules in

the pockets provided by the parent chain carrying apolar (solvophobic) residues, which enforce the DMSO dipole to remain in the repulsive region with somewhat structured fashion in the packed state.⁴

The sharp decrease in ϕ_v with C for all compounds demonstrate larger degree of solvophobicity in DMSO. However, the higher volumes occupied in DMSO as compared to DMF show greater electrorelaxation owing to the higher permittivity of solvent which favours largely the interionic repulsion. This broadens the cavities or entrenches provided by the parent chain carrying apolar residues of phenothiazinium (B, C), bipyridyl (D), *N*-ethylene (A) or *N*-xylylene (C) linkages, where the negative end of S=O dipole of DMSO molecule 'locks-up' in the repulsive region of dipole interaction potential.¹⁵

Compound A showed linearly in ϕ_v vs. C profile (Figure 5) at all temperatures beyond 3×10^{-3} monomol l⁻¹ in DMSO, similar to DMF, displaying a little electrostrictional contribution as a resultant effect.

The higher partial molar volume of B in DMSO as a result of unhindered electrostriction ridicules the possibility of intramolecular interactions in contrast to the system B in DMF; its larger molecules are, however, not fully expanded at par with other low molecular weight systems. The solvent DMSO acts as a

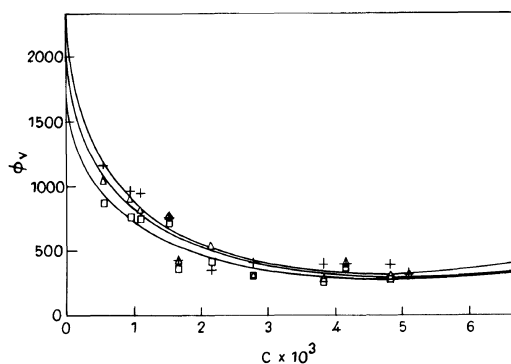


Figure 5. Concentration dependence of apparent molar volume of compound A in DMSO at temperatures (°C): 20 (+), 25 (Δ), and 30 (□).

good solvent for B. The observed levelling tendency at all temperatures beyond 1.5×10^{-3} monomol l^{-1} (Figure 6) reflects the significant electrostrictional contribution to counterbalance the effect of solvophobicity.

The stacking nature of C is diminished in DMSO as proposed in DMF. In DMF, the puckered phenothiazinium rings¹¹ sit one above the other within their foldings; whereas, the DMSO molecules accommodate themselves within these foldings of phenothiazine rings which consequently restrict stacking and thereby the electrostrictional solvation, at higher concentrations (Figure 7). Furthermore, the magnitude of \bar{V}_2° is comparable to B at 20°C in spite of its lower molecular weight. This is attributed to the easier interionic

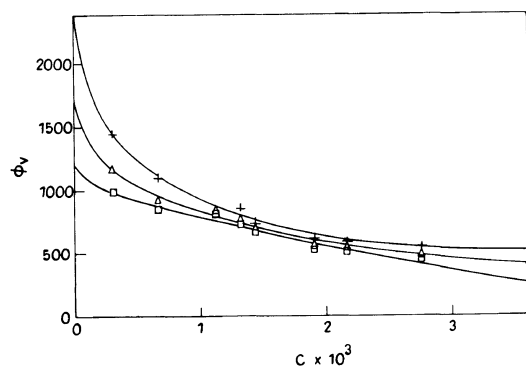


Figure 6. Concentration dependence of apparent molar volume of compound B in DMSO at temperatures (°C): 20 (+), 25 (Δ), and 30 (\square).

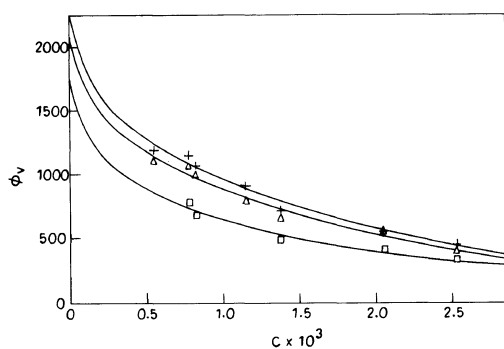


Figure 7. Concentration dependence of apparent molar volume of compound C in DMSO at temperatures (°C): 20 (+), 25 (Δ), and 30 (\square).

repulsions in C with dilution. Such repulsion is hindered owing to the chloranil substituent in the molecular chain of compound B.

The observed decrease of \bar{V}_2° with temperature in cases of A, B, and C could be attributed to the fact that the coulombic interactions between $\geq N^+$ - and $>C=O$ of chloranil or xylene become activated with the mobilization of DMSO structures packed in the pockets of molecular chains and force to squeeze out of them toward bulk, and thus reduce the net volume occupied by the system concerned. The decrease in ϕ_v with temperature may also be accorded with the perturbation of electrostricted solvents and subsequently migration into the enlarged openings of puckered rings of phenothiazin-5-ium moiety.

The electrostrictional solvation in dilute region in the case of D in DMSO is disfavoured due to diminished charge density caused by delocalisation of charges in the ring structures of bipyridyl moiety which experiences, although feeble, an electrostatic attraction with the carbonyl group of chloranil substituents. The drastic decrease in \bar{V}_2° as compared to other chloranil-based systems reflects some sort of curling in the larger chain of D. This provides enormous empty spaces for solvent packing to demonstrate solvophobicity in dilute solution. The levelling off in the latter part of ϕ_v - C curve at all temperatures (Figure 8) as is observed in

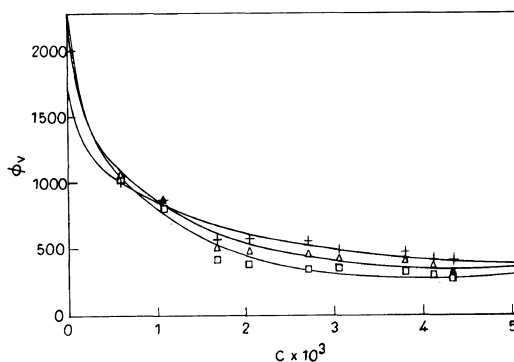


Figure 8. Concentration dependence of apparent molar volume of compound D in DMSO at temperatures (°C): 20 (+), 25 (Δ), and 30 (\square).

A, also suggest the redressal of solvophobic behaviour of the polycation by the increased contribution due to the electrostrictional effect with growing population of the system in the shape of some form of molecular aggregations. One most interesting observation with this system is noticed, when the temperature is increased, that is, the same system which followed general expansion theory in the dilute range, subsequently resumed the inverse temperature-effect on volume in concentrated region. This clearly indicates that the solvent dipoles in the solvation layer, whether may it be in 'solvophobic' packed form or in electrostrictional modes, are firmly rearranged along *N*-chloranil dipole, in somewhat structured fashion, approximating a solvent envelope (*cf.*, hydrogen bonded water cluster). Such structures are likely to be swollen as temperature is raised and then get disturbed in the process of agglomeration at high concentration shrouding themselves in the pockets of polycationic aggregates so produced. Under such circumstances, the curling behaviour subsequently gets intensified under the pool of counterions making the molecule relatively compact. This compactness apparently enhances the charge density of aggregates which facilitates the electrostrictional mode of solvation to counter-balance the effect of solvophobicity; and thereby, levelling the ϕ_v -*C* profile in concentrated region, at all temperatures.

It might be noted that the squeezing of the entrapped solvent by enhanced openings of *N*-chloranil with increasing temperature, like systems A and B in dilute solution is not feasible with the system D because heteroatom ring imminium charge centre do not involve so strong interaction with $>C=O$ of chloranil as free ammonium charges do in A and B. On the other hand, the intense electrostrictional solvation layer in concentrated region is

perturbed (mobilized) and migrates to the proximate cavities available in the bipyridyl moiety, resulting in a decrease in apparent molar volume with the increase of temperature. The magnitude of such volume reduction in DMSO, thus depends on the rate of migration of electrostricted solvent molecules and the extent of void spaces available.

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