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Electrolytic Conductivity of the *N*-Chloranil- and *N*-Xylylene-Based Polyelectrolytes in Dimethylformamide and Dimethyl Sulfoxide

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Electrolytic conductivities of four typical nitrogen-based polycations, where quaternary nitrogens in the molecular chain are attached with chloranil and xylylene moieties and are interspersed with ethylene, phenothiazine, and bipyridyl (viologen), linkages, have been investigated in dimethylformamide and dimethyl sulfoxide at 25 °C. The electrolytic conductivity as a function of concentration for systems with high charge density revealed a very narrow range of linearity in the dilute region. An empirical approach based on the Lattey equation is found suitable for the determination of the limiting mobilities of the polyions.

Introduction

In polyelectrolyte solutions, which involve long-range intermolecular interactions, the pronounced changes in conformations are likely to occur in the dilute ranges of concentrations. Surprisingly, our present state of knowledge about polyelectrolyte conductivities in nonaqueous solvents is very limited.

In the continuation of our earlier work concerning polyelectrolyte solvation through density (Prasad *et al.*, 1995) and viscosity studies (Singh *et al.*, 1995), the present paper describes conductance behavior of a few typical nitrogen-based polyelectrolytes in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) having dielectric constants 36 and 45 at 25 °C, respectively. The systems studied have structural distinctions with the introduction of *N*-chloranil or *N*-xylylene free ammonium charge centers in their molecular backbone, where two proximate $\geqslant N^+-$ charge centers are either directly joined by the aliphatic chain or interceded with the polyaromatic charged heteroatom-based system. The other type of polyelectrolyte studied consists of *N*-chloranil-substituted iminium charge centers as alternating “viologen” units in the molecular chain.

Experimental Section

Solvents DMF and DMSO (99% pure, Sarabhai-Merck, stated purity 99 mol % (CO_2, <0.02 mol %; H_2O, <0.03 mol %), conductivities 1.6×10^{-8} S cm^{-1} (25 °C) (DMF) and 1.1×10^{-8} S cm^{-1} (25 °C) (DMSO)) were purified and stored as described elsewhere (Prasad *et al.*, 1995). All other chemicals either were high-purity materials or were purified before use. An automatic buret fitted into a sealed container was used as the solvent dispenser under pure nitrogen gas to avoid contamination with CO_2 and water from the air. Materials which fulfill the desired structural distinctions as stated above 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]; and **D**, poly[*N*-chloranil−viologen dichloride]. Details of the syntheses and characterizations of these polycations (structures in Figure 1) have been reported elsewhere (Prasad *et al.*, 1995).

The equipment for conductance measurements along with the methods of solution preparations and conductivity measurements have been described earlier (Srivastava *et al.*, 1988). The reported molar conductances are calculated on the basis of the number of moles of counterions available per mole of the different compounds studied.

The effect of possible adsorption in very dilute solutions of the polycations was apparently negligible, as the conductivity for a certain concentration was always found very reproducible with variation within $\pm 1 \times 10^{-7}$ S cm^{-2} after the attainment of thermal equilibrium at (25 ± 0.05) °C during the time span of (20 ± 5) h.

Theoretical Background

For simple electrolytes, molar conductivity at infinite dilution is usually obtained by extrapolating a plot of Λ_c *vs* $C^{1/2}$ to zero concentration. However, in polyelectrolyte solutions, this extrapolation is often not feasible since molar conductivities (Λ_c) are not defined when they vary upward or downward with increasing dilution. The effect has been attributed to a change in the specific conductivity (κ_o) of the solvent in the presence of the polyion (Vink *et al.*, 1981). This difficulty is, however, circumvented by using an alternative procedure for extrapolation on the basis of the following equation:

$$\kappa = \kappa_o + \Lambda_o C + C\phi(C) \tag{1}$$

where κ and κ_o are electrolytic conductivities of the solution and solvent, respectively, C is the molar concentration, and the function $\phi(C)$ denotes the effect of interionic interactions. The limiting molar conductivity (Λ_o) can be determined accurately from the slope ($d\kappa/dC$) of a plot of κ against C, provided other derivatives ($d\kappa_o/dC$ and $d[C\phi(C)]/dC$) in the differential form of eq 1

$$\frac{d\kappa}{dC} = \frac{d\kappa_o}{dC} + \Lambda_o + \frac{d}{dC}[C\phi(C)] \tag{2}$$

are neglected in comparison to Λ_o (Bizarri *et al.*, 1990).

Another empirical approach for evaluation of polyion conductivities from the conductance data is the application of the Lattey equation (Lattey, 1927), namely,

$$\Lambda_o - \Lambda_c = \frac{C^{1/2}}{D + GC^{1/2}} \tag{3}$$

which was originally suggested for simple electrolytes and has the same form as that of the relationship proposed by Robinson and Stokes (1954) from an extension of the Onsager theory for ions of finite sizes. However, unlike the Onsager theory, the values of D and G in the case of polyelectrolytes are unfortunately not interpretable.

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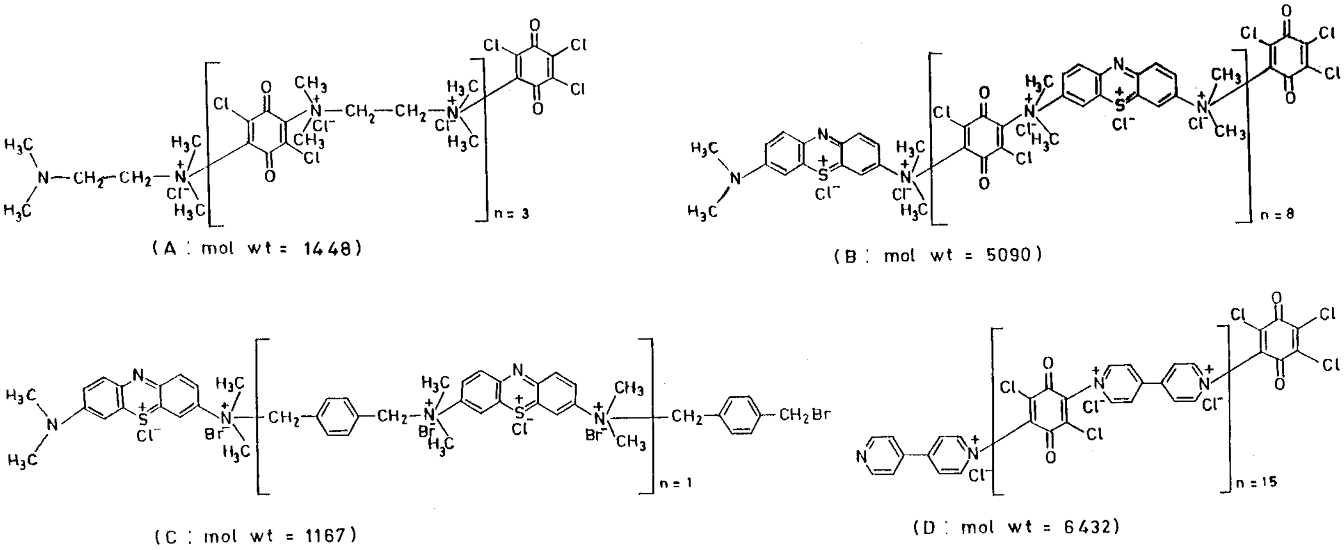

(A : mol wt = 1448)
(B : mol wt = 5090)
(C : mol wt = 1167)
(D : mol wt = 6432)

Figure 1. Structures of the polyelectrolytes.

Expressing Λ_o in terms of the limiting molar conductivities of the individual ions, one obtains the equation

$$\Lambda_o = \Lambda_{o_{ip}} = f(\lambda_{o_i} + \lambda_{o_p}) \tag{4}$$

where $f \leq 1$ is an interaction parameter denoting the apparent degree of ionization and the fraction of free counterions (Schmitt *et al.*, 1973). (The subscripts i and p denote the counterion and polyion, respectively.) The parameter f is expressed by

$$f = 1 - [0.55\xi^2/(\pi + \xi)] \qquad \xi \leq 1 \tag{5a}$$

$$f = 0.866\xi^{-1} \qquad \xi \geq 1 \tag{5b}$$

The charge density parameter ξ is given by the expression

$$\xi = \frac{l_B}{b} = \frac{e^2}{\epsilon k_B T b} \tag{6}$$

where l_B is the Bjerrum length at which two electronic charges (e) in a solvent of permittivity ϵ interact with an energy of k_BT and b is the charge spacing along the polyion contour as derived from respective plane projections [b = 3.95 (**A**), 4.51 (**B**), 6.56 (**C**), and 6.72 cm (**D**)]. For dilute solutions of polyions, Manning's theory (Manning, 1969) states that the effective spacing of the charged groups on the polyion cannot be less than a critical value corresponding to $\xi = 1$ in the case of monovalent charged groups and monovalent counterions. Therefore, for $\xi > 1$, the fraction $1 - \xi^{-1}$ of counterions will condense on the polyion to lower the effective value of ξ and the dissociated counterions behave in accordance with the Debye–Hückel approximation.

The limiting molar conductivity of the polyion (λ_{o_p}) also depends directly on α, the degree of ionization, according to the relation

$$\lambda_{o_p} = \frac{F^2\alpha|Z_p|}{f_{pw}} \tag{7}$$

where F is the Faraday constant, $|Z_p|$ is the stoichiometric charge number of the polyion, and f_{pw} is its hydrodynamic friction coefficient, which is the interaction resulting from the viscous drag exerted by the polyion on the electroneutral solvent. For $\xi < 1$, α becomes unity, whereas for $\xi > 1$, α approximates the reciprocal of the charge density. The parameter f_{pw} could be related to the respective diffusion coefficient (D) on the basis of the Einstein relation (Vink *et al.*, 1981), i.e.,

$$D = RT/f_{pw} \tag{8}$$

Table 1. Conductance of Various Polyelectrolytes in Dimethylformamide at 25 °C[a]

A		B		C	
10^3C/(mol dm^{-3})	$10^5\kappa$/(S cm^{-1})	10^3C/(mol dm^{-3})	$10^5\kappa$/(S cm^{-1})	10^3C/(mol dm^{-3})	$10^5\kappa$/(S cm^{-1})
1.06	11.35	1.75	20.9	1.20	16.3
2.40	11.9	2.40	15.8	1.33	17.4
2.60	12.2	2.90	16.8	2.00	23.7
3.70	14.0	4.20	17.4	2.70	19.1
6.60	14.0	4.66	19.3	4.30	24.8
7.10	14.4	5.10	26.0	5.00	22.6
8.90	15.3	5.50	26.0	6.40	23.6
11.50	15.8	5.90	32.1	7.80	38.8
		6.70	38.8	9.50	39.4
		7.30	41.7	10.70	37.8

[a] Relative standard deviation (or coefficient of variation) in κ, ≤2.4%; relative standard deviation (or coefficient of variation) in C, ≤0.16%.

Results and Discussion

The results of conductance measurements of polyelectrolytic systems **A**, **B**, **C**, and **D** in DMF and DMSO at 25 °C are presented in Tables 1 and 2 (the system **D** could not be studied in DMF because of the solubility restriction). All systems demonstrate normal polyelectrolyte behavior in both solvents where molar conductivities (Λ_c) are found to concomitantly increase without limit upon dilution. The κ *vs* C curves for systems **B** and **C** in DMF and for **C** in DMSO are found to be completely nonlinear (Figures 2 and 3), and therefore, the extrapolation procedure based on the conductivity equation (3) for obtaining Λ_o seems to be no longer feasible in these cases.

Limiting molar conductivities derived from both treatments based on both eqs 2 and 3 are given in Table 3. A representative Lattey equation plot (compound **A** in DMF) based on eq 3 is shown in Figure 4, using different trial values of Λ_o. In any instance, the minimum value of Λ_o which yielded a linear plot was chosen as the limiting molar conductance of the system concerned. The least squares values of D and G obtained for the minimum Λ_o line in both solvents are given in Table 4. The Λ_o values derived

Table 2. Conductance of Various Polyelectrolytes in Dimethyl Sulfoxide at 25 °C[a]

A		B		C		D	
10^3C/ (mol dm^{-3})	$10^5\kappa$/ (S cm^{-1})	10^3C/ (mol dm^{-3})	$10^5\kappa$/ (S cm^{-1})	10^3C/ (mol dm^{-3})	$10^5\kappa$/ (S cm^{-1})	10^3C/ (mol dm^{-3})	$10^5\kappa$/ (S cm^{-1})
0.95	5.9	0.75	7.8	1.35	8.4	1.17	6.5
1.66	8.6	1.41	10.2	1.92	11.2	2.09	7.20
1.90	10.2	2.39	14.0	2.82	13.1	3.25	8.9
2.63	12.3	2.80	15.7	3.38	12.7	3.95	9.1
2.86	12.7	3.05	15.1	5.05	17.6	5.22	11.9
3.72	15.1	3.53	16.9	6.23	20.0	5.92	11.2
4.78	15.7	4.07	20.1	7.05	15.7	7.34	12.3
6.59	20.91	4.59	20.1			8.14	12.3
8.32	20.01	5.83	24.3			8.41	13.5
8.78	23.6	7.63	24.3			9.89	13.6
11.63	23.3						

[a] Relative standard deviation (or coefficient of variation) in κ, ≤2.4%; relative standard deviation (or coefficient of variation) in C, ≤0.16%.

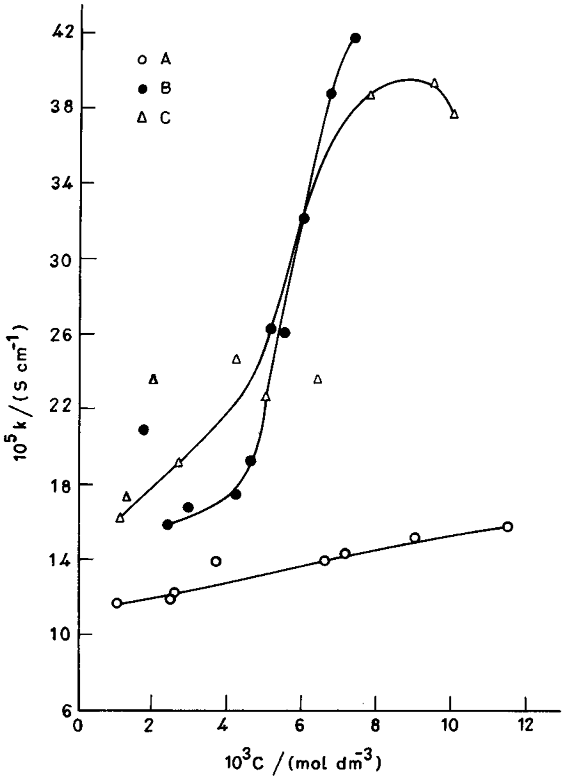

Figure 2. Concentration dependence of electrolytic conductivity in dimethylformamide: **A** (○); **B** (●); **C** (△).

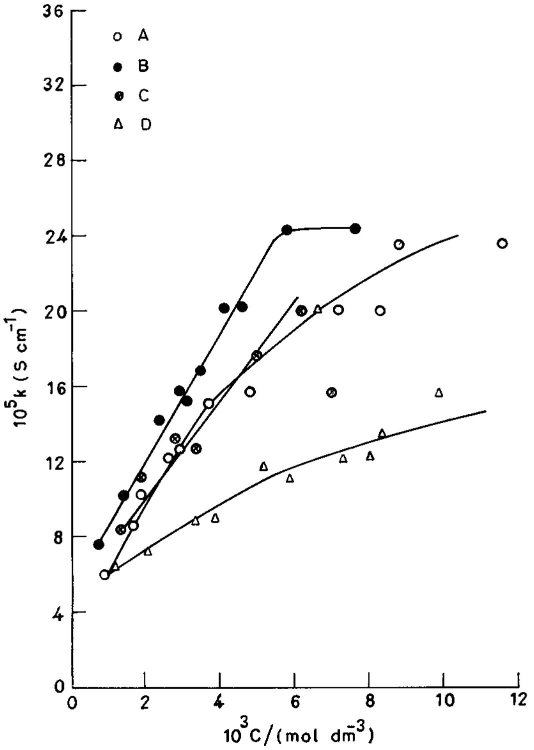

Figure 3. Concentration dependence of electrolytic conductivity in dimethyl sulfoxide: **A** (○); **B** (●); **C** (⊗); **D** (△).

from κ *vs* C plots and those from the Lattey equation are not identical with each other. The κ *vs* C curves show a very restricted range of linearity, indicating the presence of polyion–polyion interactions beyond this region. Any measurement in this region would be questionable for the determination of Λ_0.

The polycationic limiting mobilities (λ_{0_p}) derived from eq 4 are shown in Table 5. These are observed abnormally higher as compared with the limiting molar conductance of simple ions. This indicates that the resistance to movement of the polyion is less than the sum of the resistances of the individual monomeric ions forming its structure (Rios *et al.*, 1990). The other possibility for larger λ_{0_p} for polycations is due to their larger solvophobicity which augments the respective mobilities in the dipolar aprotic media.

The Λ_0 values derived in DMF follow the sequence **B** (MW 5090) > **A** (MW 1448) > **C** (MW 1167), whereas the same in DMSO follow the sequence **B** (MW 5090) > **D** (MW 6432) > **C** (MW 1167) > **A** (MW 1448).

Table 3. Limiting Molar Conductances of Polyelectrolytes at 25 °C (Λ_0/(S cm^2 mol^{-1}))[a]

	A	B	C	D
	Dimethylformamide			
Lattey equation plot	760	1190	700	–
κ *vs* $C^{1/2}$ plot	433	–	–	–
	Dimethyl Sulfoxide			
Lattey equation plot	330	450	380	400
κ *vs* $C^{1/2}$ plot	357	340	–	116

[a] Dashes indicate nonfeasibility of the treatment.

System **A** possesses lower mobility in DMF as compared to **B**, in spite of its smaller size (n = 3) (Table 3). This behavior could be explained on the basis of the structural background of the system, where quaternized nitrogen centers exert Coulombic interactions from both sides with carbonyl groups of chloranil moieties and immobilize themselves to curtail intercationic repulsions amidst massive solvation by DMF as reported earlier (Prasad *et al.*, 1995). The high charge density of **A** in DMF and higher counterion condensation attenuate the movement of poly-

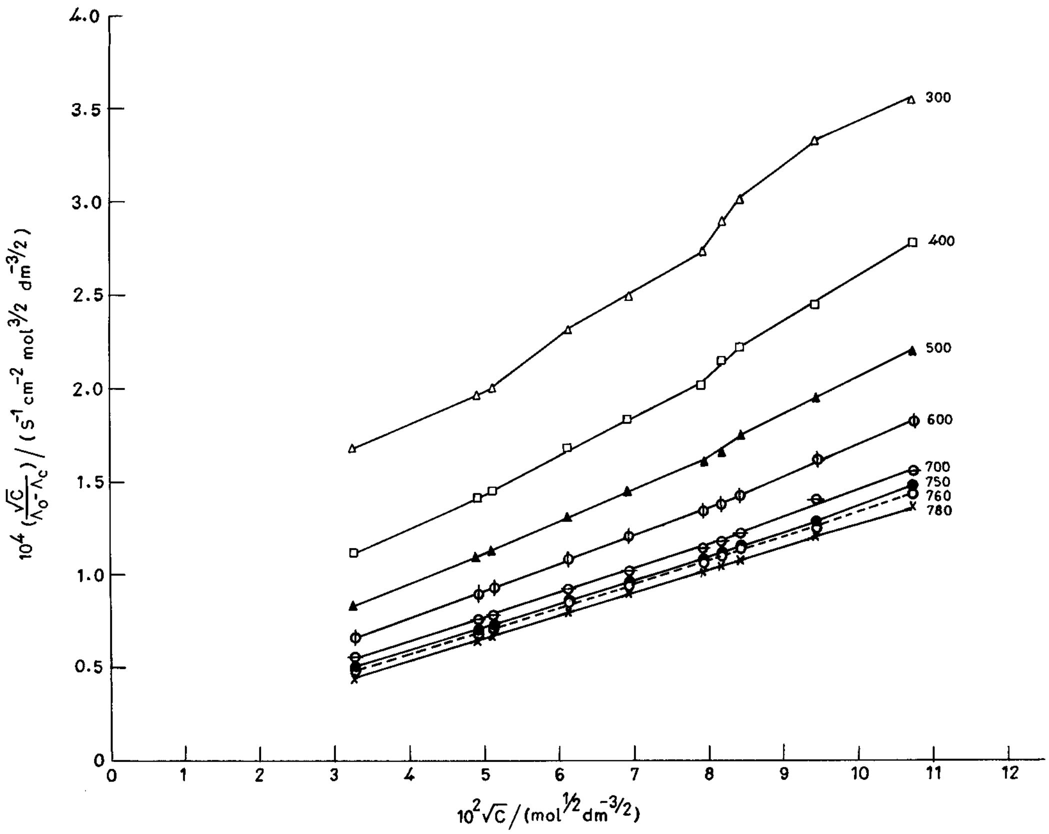

Figure 4. Lattey equation plots for **A** in dimethylformamide using different values of Λ_o: 300 (△); 400 (□); 500 (▲); 600 (circle with vertical line); 700 (circle with horizontal line); 750 (●); 760 (○); 780 (×). The plot shown for Λ_o = 760 (○) represents the least squares line.

Table 4. Parameters *D* and *G* Derived from the Lattey Equation[a]

	A	B	C	D
Dimethylformamide				
$10^6 D/(S^{-1} cm^{-2} mol^{3/2} dm^{-3/2})$	88.8	1.0	13.3	–
$10^6 G/(S^{-1} cm^{-2} mol)$	109.8	1.6	136.9	–
Dimethyl Sulfoxide				
$10^6 D/(S^{-1} cm^{-2} mol^{3/2} dm^{-3/2})$	55.5	*b*	5.4	*b*
$10^6 G/(S^{-1} cm^{-2} mol)$	0.3	6.2	24.9	0.3

[a] $C^{1/2}/(\Lambda_o - \Lambda_c) = D + GC^{1/2}$. [b] Negligible.

Table 5. Parameters Derived on the Basis of Counterion Condensation on Polycations at 25 °C

system	ξ	f	α	$f_{pw} \times 10^{-6}$/ (kg s^{-1} mol^{-1})	$D \times 10^5$/ (cm^2 s^{-1})	λ_{o_p}/ (S cm^2 mol^{-1})
A/DMF	4.37	0.19	0.23	4.55	54.40	3763.9
B/DMF	3.83	0.23	0.26	12.60	19.63	5187.2
C/DMF	2.63	0.33	0.38	31.12	7.95	682.3
A/DMSO	3.51	0.25	0.28	15.96	15.50	1306.5
B/DMSO	3.07	0.28	0.32	51.45	4.80	1563.8
C/DMSO	2.11	0.41	0.47	29.24	8.45	897.9
D/DMSO	2.06	0.42	0.48	156.40	1.58	923.7

ions despite the fact that the viscous drag ($f_{pw} = 4.55 \times 10^6$ kg s^{-1} mol^{-1}, Table 5) experienced by the polyion **A** is quite less in DMF.

System **B** shows the highest mobility in DMF despite being made up of a long chain (n = 8) (Table 3). This is attributed to the cumulative effects of two factors: (i) the lower charge density per unit cation reduces the magnitude of counterion condensation and thereby augments the mobility of the polyionic chain and (ii) the structural conformation allows a typical curling of the relatively large polycationic chain along the $\geq N^+$–chloranil polar linkages, giving rise to an approximation of a "pearl necklace" model which offers permeability toward the solvent transport as suggested elsewhere (Singh *et al.*, 1995).

System **C** shows the lowest mobility which seems incompatible insofar as its short dimeric stature is concerned. This is attributed to an oblong type conformation of the system which forms counterion bridges between the two rigid chains of dimers as revealed from the viscosity study (Singh *et al.*, 1995). The system thus acts as an "impermeable" coil toward the solvent transport. Notwithstanding the fact that the polycation **C** experiences the larger extent of counterion dissociation, its transportation is largely restricted by the proposed geometry of the system ($f_{pw} = 31.12 \times 10^6$ kg s^{-1} mol^{-1}, Table 5).

In DMSO, the relatively low conductivities are solely due to the higher volumes occupied as compared to those in DMF (Prasad *et al.*, 1995). This is because of the greater electrorelaxation effect owing to the higher permittivity of DMSO which contributes interionic repulsions to a larger extent. This broadens the cavities or trenches provided by the parent chain carrying apolar residues of *N*-ethylene (**A**), phenothiazinium (**B**, **C**), *N*-xylylene (**C**), and bipyridyl (**D**) linkages where the DMSO molecules "lock-up" under a solvophobic mode of interactions and therefore efficiently curtail the conductance of the polycations.

The polyion **A** has the highest charge density in DMSO, giving rise to a higher degree of counterion condensation. In addition to the "noncurling rigid" structural conformation of **A** (Singh *et al.*, 1995), the observed counterion binding drastically reduced the polyionic mobility.

The charge density of polyion **B** in DMSO is decreased as compared to that in DMF, and thus, the counterion binding is more restricted. Surprisingly, the decrease in polyionic mobility in DMSO is incompatible when there is an enhanced degree of ionization. This, however, is explained on the basis of electrorelaxation which curtails the extent of curling along the $\geq N^+$−chloranil linkages to render a retardation in polycationic transport.

The position of **C** in DMSO in the conductivity sequence could be justified on the basis of its structural considerations. Being a short statured polycation, the transport of a dimeric polycation was facilitated as any molecular association of oblong nature is not feasible due to the extensive solvophobic packing of DMSO clusters within the foldings of phenothiazinium moieties (Prasad *et al.*, 1995).

The system **D** has the least charge density and thus experiences the minimum counterion condensation. Accordingly, the conductivity of the polyion is more favored and becomes further augmented through the structural alternation into a "permeable coil" (Singh *et al.*, 1995). This facilitates an easier flow of polyions in the DMSO medium.

On circumspection of the results listed in Table 5, it is observed that the hydrodynamic frictional coefficient (f_{pw}) decreased steadily with increasing charge density of the polyelectrolytes studied. This is because of the fact that the extent of counterion condensation is reasonably enhanced with the increase of charge density which alters particularly the respective conformation of larger polyions (**B** and **D**) to adopt the chain coiling in solution. It should be borne in mind that deviation from Manning's condensation theory, when the polymer configuration is different from the rodlike structure, is quite likely because larger polycations (**B** and **D**) assume a higher degree of coiling. In such a case, no tangible conclusion could be drawn in the absence of a study on the variation of counterions in the polyelectrolyte concerned. Furthermore, there are virtually no compliances of conductivities with any of the parameters such as maximum cross-dimensions ($\bar{S}$) [63.3 Å (**A**), 94.01 Å (**B**), and 47.2 Å (**C**) in DMF and 42.35 Å (**A**), 87.35 Å (**B**), 78.12 Å (**C**), and 116.13 Å (**D**) in DMSO at 25 °C], mean square end-to-end lengths ($\langle Rg^2 \rangle^{1/2}$) [90.42 Å (**A**), 126.41 Å (**B**), and 67.5 Å (**C**) in DMF and 60.5 Å (**A**), 124.8 Å (**B**), 111.6 Å (**C**), and 165.9 Å (**D**) in DMSO at 25 °C], and the respective plane projection distances (P) [23.7 Å (**A**), 108.3 Å (**B**), 19.7 Å (**C**), and 201.7 Å (**D**)] of the polymers studied. This warranted the conformational alterations of polycations to be invoked in our discussions as the key factor to justify the observed conductivity sequences in both solvents.

In conclusion, the behavior of flexible polyelectrolytes is considerably difficult to rationalize by current polyeletrolyte theories based on simple electrostatic models because an isolated molecule of a high molecular weight polyelectrolyte cannot maintain a rodlike conformation in very dilute solutions. Thus, a proper scrutiny of the solvation effect is imperative to explain the polyelectrolyte limiting conductivity in such instances.

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