Electrolytic Conductivity of Crystal Violet-Based Quaternary Ammonium Polyelectrolytes in Propylene Carbonate and Sulfolane

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The electrolytic conductivity of crystal violet-based quaternary ammonium polyelectrolytes in very dilute solutions of propylene carbonate at 25 °C and sulfolane at 30 °C has been measured. It was not possible to determine the limiting molar conductivity, Λ_0, from the nonlinear electrolyte conductivity, κ, against concentration curves for the systems studied. An empirical approach based on the Lattey equation has been used to determine limiting mobilities of polycations. A modest correlation has been made with the counterion condensation and polycation conformations in order to explain the relative magnitude of limiting molar conductivities.

Introduction

Considerable progress has been made in understanding the transport processes in polyelectrolytic solutions on the basis of the polyelectrolyte conformations, sizes, frictional coefficients, and counterion condensation theory (*1*, *2*). However, the magnitude of the electrolytic conductivity in the limit of infinite dilution in nonaqueous media has not been fully established. Unlike the situation of idealized infinitely dilute solutions of simple electrolytes which is governed by the usual Kohlraush law, the polyelectrolyte solutions lack a general dilution law owing to the diverse polyelectrolyte models involving various interionic interactions. Furthermore, in the very dilute region of a salt-free polyelectrolyte solution, one can observe a remarkable change in solvation properties depending upon the conformational alternations of the system. In the commonly accepted model for linear polyelectrolytes, the polyions are represented by charged cylinders, or line charges having a certain linear charge density. The polyions are surrounded by a counterion atmosphere, which at high charge densities may be intimately bound to (condensed on) the polyions. The aim of the present work is, therefore, to study the conductance behavior of such polyelectrolytes and to interpret the result in terms of the existing polyelectrolytic theories.

The conductance measurements were carried out with a typical class of crystal violet-tagged linear quaternary ammonium polyelectrolytes which have (i) charged nitrogen centers on the backbone of the macroions and not as side chain substituents and (ii) backbone quaternary centers constituting a parallel cationic track with quaternary nitrogens of the side groups of the molecular chain. The solvents chosen for the present studies are propylene carbonate and sulfolane (tetrahydrothiophene 1,1-dioxide) which exhibited typical ion–solvent interactions distinct from those usually observed in aqueous solutions. The moderately high dielectric constant of propylene carbonate (64.4 at 25 °C) and the intermediate dielectric constant of sulfolane (43.3 at 30 °C) together with their reasonably high dipole moments (propylene carbonate, 4.9; sulfolane, 4.7) (*3*) enable them to behave as good solvents in which ion–dipole-type solute–solvent interactions are favored. Moreover, studies in dipolar aprotic solvents may offer a reasonable estimate of high-energy electrochemical reactions (*4*) and also provide useful technological applications for chemical analysis where cations of crystal violet moieties in a polymeric network could be effective ion-exchange sites in ion sensors (*5*).

In the present investigation, the solvation characteristics of some nitrogen-based polycations in propylene carbonate at 25 °C and in sulfolane at 30 °C were studied. The treatment of the conductance results was attempted following the procedure outlined in the literature (*2*):

$$\kappa = \kappa_0 + \Lambda_0 c + c\phi(c) \qquad (1)$$

where κ and κ_0 are electrolytic conductivities of the solution and solvent, respectively, c is the molar concentration of the polyelectrolyte, and the function $\phi(c)$ denotes the effect of interionic interactions. The results of conductance measurements could also be treated according to the Lattey equation (*6*)

$$\Lambda_0 - \Lambda_c = \frac{c^{1/2}}{D + Gc^{1/2}} \qquad (2)$$

which was originally suggested for simple electrolytes and has the same form as that of the relationship proposed by Robinson and Stokes (*7*) from an extension of the Onsager theory for ions of finite sizes. However, unlike the Onsager theory, the values of D and G as obtained from the Lattey equation in the case of polyelectrolytes are unfortunately not interpretable.

Experimental Section

Solvents. Purified propylene carbonate and sulfolane (Fluka, stated purity 99 mol %; CO_2, <0.02 mol %; H_2O, <0.03 mol %; conductivities, (2–3) × 10^{-8} S cm^{-1} (25 °C) for propylene carbonate and (3–4) × 10^{-9} S cm^{-1} (30 °C) for sulfolane) were obtained according to known procedures (*3*). An automatic buret fitted in sealed containers was used as the solvent dispenser under a pressure of pure nitrogen gas to avoid contamination with CO_2 and water from the air.

Chemicals. The following four linear nitrogen-based polycationic electrolytes (abbreviated as A, B, and C) satisfy the requirements stated above, and their structures are shown in Figure 1: A, poly[*N*-ethylene monohydroxy crystal violet dibromide] (mol wt 1154); B, poly[*N*-*p*-xylene crystal

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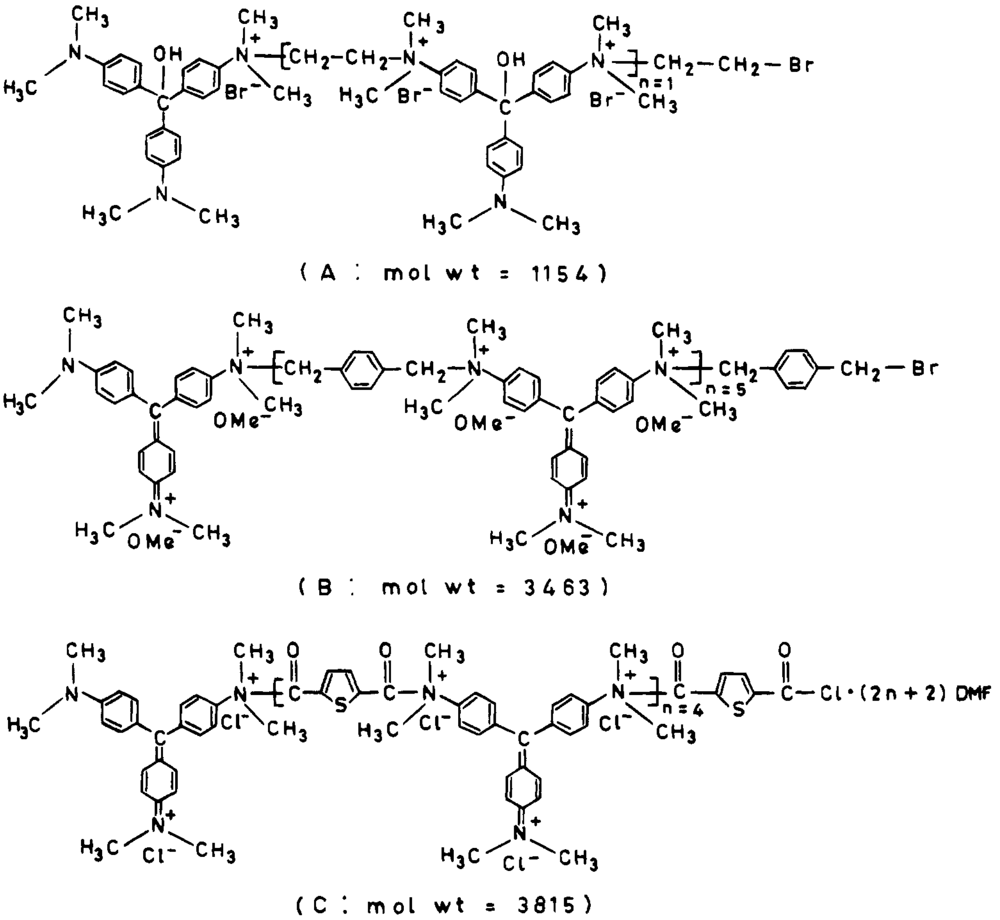

Figure 1. Structures of the polyelectrolytes: poly[*N*-ethylene monohydroxy crystal violet dibromide] (A), poly[*N*-*p*-xylene crystal violet trimethoxide] (B), and poly[*N*-2,5-diacylthiophenylene crystal violet trichloride (C).

Table 1. Results of Conductance Measurements in Propylene Carbonate at 25 °C

A		B		C	
10^3c/(mol dm^{-3})	$\Lambda_c{}^a$/(S cm^2 mol^{-1})	10^3c/mol dm^{-3})	$\Lambda_c{}^a$/(S cm^2 mol^{-1})	10^3c/(mol dm^{-3})	$\Lambda_c{}^a$/(S cm^2 mol^{-1})
0.52	26.67	2.08	4.74	0.79$_5$	12.45$_5$
0.86$_5$	21.04	2.98	3.69	1.63	10.28
1.26	14.72	3.86	4.69	2.24	9.95
1.63	12.24	5.10	3.65	2.99	8.87
2.00$_5$	12.07	6.11	3.58	3.71	7.33
2.23	10.46	6.82	3.42	4.46	6.25
3.35	8.33$_5$	8.15	2.98	5.10	7.23
		9.26	2.87	6.44	6.57
		10.19	2.74	7.03	6.58
		12.13	2.42	8.53$_5$	6.06
		15.51	2.23	10.11	5.71$_5$
		19.36	2.18		

[a] Relative standard deviation or coefficient of variation ≤0.2% (in five successive measurements).

violet trimethoxide] (mol wt = 3463); C, poly[*N*-2,5-diacylthiophenylene crystal violet trichloride] (mol wt 3815). These compounds were synthesized by the straightforward condensation reaction of crystal violet and α,α′-dihalogen compounds (*viz.*, 1,2-dibromoethane, α,α′-dibromo-*p*-xylene, and thiophene-2,5-dicarboxylic acid chloride) following a known method (*8*). All the other chemicals used were of analytical grade.

Conductance Measurements. The equipment along with the methods of solution preparations and conductivity measurements were the same as described earlier (*9*). The reported molar conductances have been calculated on the basis of the moles of counterions available per mole of the different compounds used.

The effect of possible adsorption in very dilute solutions of any of the polymers is apparently negligible as the conductivity for a certain concentration was always found very reproducible with a variation within ±1 × 10^{-7} S cm^{-1} after the attainment of thermal equilibrium at 25 ± 0.05 °C during the time span of 20 ± 5 h.

Crystal violet polyelectrolytes B and C in propylene carbonate and sulfolane are found stable since both solvents are nonbasic owing to their smaller Gutmann donicities (*10*), and hence "carbocations" of crystal violet unit(s) in the molecular chain remain intact. This was supported by spectroscopic monitoring of constant λ_{max} values of their solutions for 24 h.

Results and Discussion

The results of conductance measurements of three polyelectrolytic systems (A, B, and C) in propylene carbonate at 25 °C and sulfolane at 30 °C are presented in Tables 1

Table 2. Results of Conductance Measurements in Sulfolane at 30 °C

A		B		C	
10^3c/(mol dm^{-3})	$\lambda_c{}^a$/(S cm^2 mol^{-1})	10^3c/(mol dm^{-3})	$\Lambda_c{}^a$/(S cm^2 mol^{-1})	10^3c/(mol dm^{-3})	$\Lambda_c{}^a$/(S cm^2 mol^{-1})
1.06	5.78	2.18	1.65	1.47	4.55
2.11	4.59	3.08	1.36	2.32_5	3.65
2.63	3.83_5	4.23	1.46_5	2.80	3.50
3.16_5	3.19	5.31	1.20	3.50	3.20
3.70	2.84	6.64	1.04	5.15	2.91
4.34	2.53	7.86	0.88	5.90	2.54
4.76	2.37	9.74	0.82	7.25	2.19
5.29	2.14	11.71	0.69	9.20	1.88
6.18	1.83	13.94	0.62		
		15.58	0.74		
		19.58	0.66		

[a] Relative standard deviation or coefficient of variation ≤0.3% (in five successive measurements).

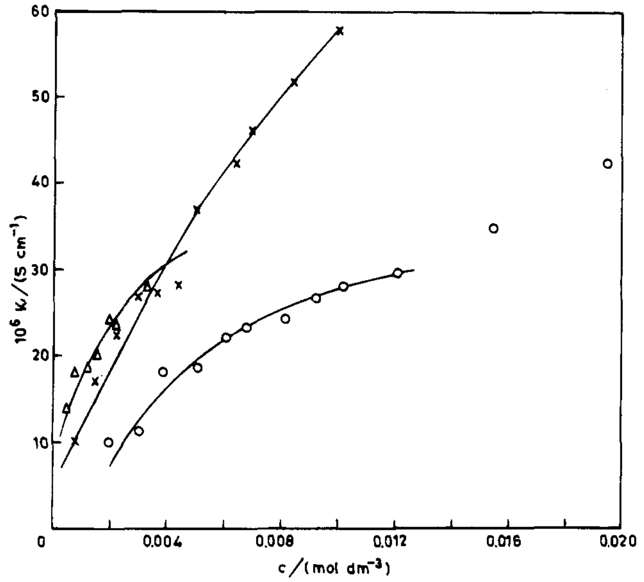

Figure 2. Concentration dependence of electrolytic conductivity in propylene carbonate: poly[*N*-ethylene monohydroxy crystal violet dibromide] (△), poly[*N*-*p*-xylene crystal violet trimethoxide] (○), and poly[*N*-2,5-diacylthiophenylene crystal violet trichloride] (×).

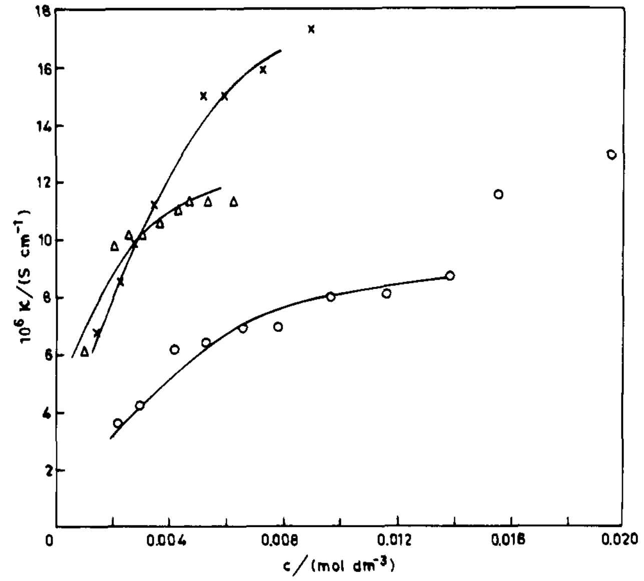

Figure 3. Concentration dependence of electrolytic conductivity in sulfolane: poly[*N*-ethylene monohydroxy crystal violet dibromide] (△), poly[*N*-*p*-xylene crystal violet trimethoxide], (○), and poly[*N*-2,5-diacylthiophenylene crystal violet trichloride] (×).

and 2. All systems demonstrate normal polyelectrolyte behavior in both solvents where molar conductivities (Λ_c) are found to increase without limit with dilution. For polyelectrolyte solutions, it is generally not possible to determine the limiting equivalent conductivity (Λ_o) by the normal procedure of extrapolation of the Λ_c–$c^{1/2}$ plot (*2*). Further, the κ vs c curves for all systems in both media are found completely nonlinear (Figures 2 and 3), and therefore extrapolation procedure based on eq 1 seems to be not applicable. One of the probable reasons for such an exceptional behavior in the present instance could be the nonlinear dependence of κ with a wide range of concentrations owing to the higher-order effects of interionic interactions included in the function $\phi(c)$. However, a representative Lattey equation plot based on the equation $c^{1/2}(\Lambda_o - \Lambda_c) = D + Gc^{1/2}$ (cf. eq 2) is shown in Figure 4, using different trial values of Λ_o for the case of compound A. 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 values of Λ_o thus obtained are 80 ± 5 (A), 25 ± 2 (B), and 50 ± 5 (C) S cm^2 mol^{-1} in propylene carbonate at 25 °C and 22 ± 4 (A), 8 ± 1 (B), and 15 ± 2 (C) S cm^2 mol^{-1} in sulfolane at 30 °C. The least-squares values of D and G obtained for the minimum Λ_o line in both solvents are given in Table 3.

The Λ_o's derived in both solvents follow the sequence A (mol wt 1154) > C (mol wt 3815) > B (mol wt 3463). The drastic reduction in the magnitude of limiting conductivities in sulfolane as compared to those in propylene carbonate for all systems may apparently be due to the highly viscous nature of sulfolane. The observed Λ_o sequence in propylene carbonate seems to agree with the increasing trend of maximum cross dimensions ($\bar{S}$) [23.6 (Å) (A) < 25.1 Å (C) < 56.7 Å (B) at 25 °C] obtained in viscosity measurements of these polyelectrolytes in propylene carbonate (*11*). [The maximum cross dimension ($\bar{S}$) is a measure of the volume occupied by the polymer in solution and could be estimated by the relation $\bar{S} = 0.7\langle R_g{}^2\rangle^{1/2}$, where $\langle R_g{}^2\rangle$ is the mean square end-to-end length of the polymer in the Flory and Fox equation (*12*).] On the other hand, the Λ_o values found in the case of sulfolane do not agree with the $\bar{S}$ value trend [31.6 Å (A) < 69.96 Å (B) < 91.6 Å (C) at 30 °C].

System A possesses higher mobility, whereas B shows the lowest conductivity in propylene carbonate and sulfolane. From the structure of compound A, the pendant substituents of crystal violet residues carry no charge centers in contrast to B or C. Further, since propylene carbonate and sulfolane act as good solvents which considerably restricts any type of interactions such as polymer–polymer contacts and/or intramolecular bending due to Coulombic interactions between quaternized centers (without counterions) and lone pairs of electrons of unquaternized nitrogens in the pendant chain, the system A might assume a short-rigid structure with high local positive charge density along the polyion chain, resulting in larger

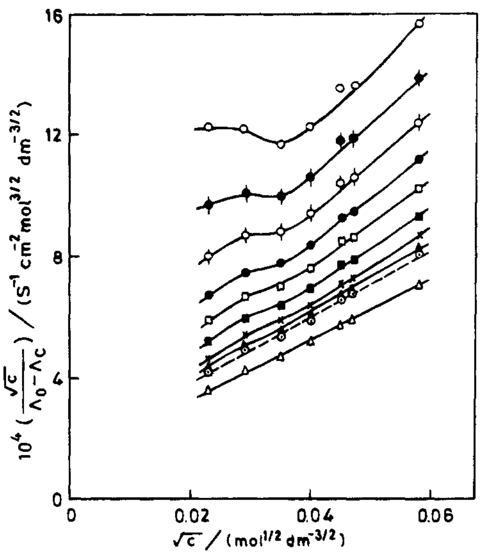

Figure 4. Lattey equation for poly[*N*-ethylene monohydroxy crystal violet dibromide] (A) in propylene carbonate using different values of Λ_o: 45 (○); 50 (●); 55 (○); 60 (●); 65 (□); 70 (■); 75 (×); 78 (▲); 80 (⊙); 90 (△). The plot shown for Λ_o = 80 (⊙) represents the least-squares line.

Table 3. Parameters *D* and *G* of the Lattey Equation[a]

	A	B	C
	Propylene Carbonate		
D	0.000 25	0.000 42	0.000 17
G	0.011 56	0.040 69	0.020 88
	Sulfolane		
D	0.000 75	0.000 16	0.001 22
G	0.039 90	0.012 36	0.064 11

[a] $c^{1/2}(\Lambda_o - \Lambda_c) = D + Gc^{1/2}$, poly[*N*-ethylene monohydroxyl crystal violet dibromide] (A), poly[*N*-*p*-xylene crystal violet trimethoxide] (B), and poly[*N*-2,5-diacylthiophenylene crystal violet trichloride] (C). Units: *D*, $s^{-1}\,cm^{-2}\,mol^{3/2}\,dm^{-3/2}$; *G*, $s^{-1}\,cm^{-2}$ mol. Error limit 4%.

mobilities in these solvents. The decrease in limiting conductivities of B in propylene carbonate and sulfolane is due to the possible screening of the effective charge of the polyion by π-excessive adjacent xylene moieties and also with a subsequent decrease in the number of "free" counterions as a consequence of the higher tendency of counterion binding of the basic methoxide ion, even at infinite dilution. The drastic decrease, however, in limiting conductivity of B in sulfolane may be taken as indicative of the larger extent of counterion condensation presumably in the form of "ion-pairing", in the poor medium of intermediate dielectric constant. System C has higher conductivity as compared to B in propylene carbonate and sulfolane in spite of their somewhat comparable molecular weights. This may be because of the curling nature of C which assumes an impermeable "globular"-type conformation in propylene carbonate. However, the free-draining behavior of C in sulfolane, as found in viscosity studies (*11*), is quite puzzling and incompatible to render a high mobility which, in all expectations, might offer a larger friction coefficient toward solvent transport as compared with B. This indicates that the mobility of polycation C is not accountable in terms of its size and conformation, but seems to be dependent solely on its higher charge density in the absence of any association of chloride ion with polycation in contrast to the methoxide counterion binding with polymer B in extremely dilute solutions. The presence of π-excessive (*13*) thiophenylene units in the polymeric network of C has a negligible shielding effect on the positive charge density of the polycation because of the better solvation in sulfolane. On the other hand, this may facilitate counterion dissociation to a large extent. The counterion condensation in sulfolane for B may thus be considered as a specific factor to determine its position in the Λ_o sequence despite its lower hydrodynamic volume ($\bar{S}$ = 69.96 Å) as compared to that ($\bar{S}$ = 91.6 Å) of C. The ratio of limiting conductivities of B and C is close to that of the reciprocals of maximum cross dimensions ($\bar{S}$) of molecules concerned in propylene carbonate. Such a relationship is not practicable in sulfolane where mobilities are not accountable on the basis of size estimates.

Excluding the case of B for which the extent of counterion association, *i.e.*, methoxide ion binding appears to be somewhat exceptionally large in both solvents, the following polycationic limiting mobilities (λ_o^+) for A and C can be derived on subtraction of $\lambda_{o\mathrm{Br}^-}$ (18.7 S cm^2 mol^{-1} in propylene carbonate at 25 °C and 8.9 S cm^2 mol^{-1} in sulfolane at 30 °C) and $\lambda_{o\mathrm{Cl}^-}$ (15.9 S cm^2 mol^{-1} in propylene carbonate at 25 °C and 9.3 S cm^2 mol^{-1} in sulfolane at 30 °C) values (*14, 15*) as the case may be, from their respective limiting molar conductivities: 61.3 ± 5 (A), 34.0 ± 5 (C) S cm^2 mol^{-1} in propylene carbonate at 25 °C and 13.1 ± 4 (A), 5.7 ± 2 (C) S cm^2 mol^{-1} in sulfolane at 30 °C. As is evident, it is difficult to obtain any direct correlation among these limiting cation mobilities, which are obtained from the Lattey equation when assuming the simple additivity rule. Furthermore, it appears implausible to modify these values with the lack of the estimates of corrections based on Manning's self-diffusion coefficient ratio (*1, 16*) of the counterions or Eisenberg's ϕ (*2, 17*). Although both propylene carbonate and sulfolane have somewhat similar solvation characteristics, the relatively intermediate dielectric constant [64.4 (propylene carbonate), 43.3 (sulfolane)] of the latter still warrants the detailed exploration of counterion condensation theory (*1*) in the present investigation.

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