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Polymer 42 (2001) 2887–2891

polymer

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Viscometric behaviour of some hydrophobically modified cationic polyelectrolytes

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Received 14 August 2000; received in revised form 25 August 2000; accepted 11 September 2000

Abstract

Effects of the polycation structure and of the solvent nature and composition on the viscometric behaviour of some cationic polyelectrolytes with (*N*,*N*-dimethyl-2-hydroxypropyleneammonium chloride) units in the main chain and non-polar side groups (hexyloxypropyl and decyloxypropyl) were investigated. The solution viscosity of polyelectrolytes was determined over a wide concentration range, in saltless aqueous solution. The experimental data were plotted in the terms of Fuoss and Fedors equations. Viscosity of the polycation PCA_5D_1, was measured also in the mixed solvents: water/methanol and water/acetone. Polyelectrolyte behaviour was observed for PCA_5D_1 in the mixtures of water/methanol for all composition employed and in mixtures of water/acetone with the acetone content as high as 60 vol%. The intrinsic viscosity, $[\eta]$, decreased and the overlap concentration, C^*, increased with increasing organic solvent content in the mixed solvents.

Keywords: Cationic polyelectrolyte; Intrinsic viscosity; Overlap concentration

1. Introduction

Polyelectrolytes carrying a low content of hydrophobic side chains are of increasing interest for a wide variety of industrial applications such as: flocculants, thickening agents in oil recovery, latex paints, cosmetics due to the advantage both of the polyelectrolyte and the hydrophobic groups effects [1–4]. The presence of both the charged and non-polar groups in the chain also makes from this kind of polymers convenient systems to explore the role of the electrostatic and hydrophobic interactions on the solution properties of polyelectrolytes which depend strongly on the conformational behaviour of the individual chains. Viscometry is the most widely used experimental method to examine the conformational transition of polyelectrolytes in solution [5,6]. Viscosity depends very much on the chemical structure of the macroion, its size and charge density but also on the environment properties such as, the ionic strength and the solvent polarity [7–9]. Studies of the viscosity of several solution systems including polystyrene — based cationic ionomers [9], sodium polystyrenesulfonate [10], perfluorosulfonated ionomer [11], poly (methacryloyloxyethyl trimetylammoniummethylsulfate) [12], have shown that the addition of an organic solvent leads to conformational changes of polyelectrolytes, with the change in the solvent composition. Reports of the conformational transition of cationic polyelectrolytes dissolved in the mixed solvents are relatively scarce.

In the present work the intrinsic viscosity values, $[\eta]$, of some polyelectrolytes with both quaternary ammonium salt groups in the main chain and hydrophobic groups have been determined, the data being analysed to obtain information about their chain conformation in saltless aqueous solution and in various mixtures of water/methanol and water/acetone. There is no information about the behaviour of this kind of polycations neither in aqueous solution nor in the mixed solvents.

2. Experimental

2.1. Materials

Cationic polyelectrolytes were synthesised by condensation polymerisation of epichlorohydrin (ECH) with dimethylamine (DMA), *N*,*N*-dimethyl-1,3-diaminopropane (DMDAP), and primary amines with non-polar chains (hexyloxypropylamine-polymer type PCAH and decyloxypropylamine polymer type PCAD), according to the method presented in detail elsewhere [13,14]. Their general structure is presented in Scheme 1.

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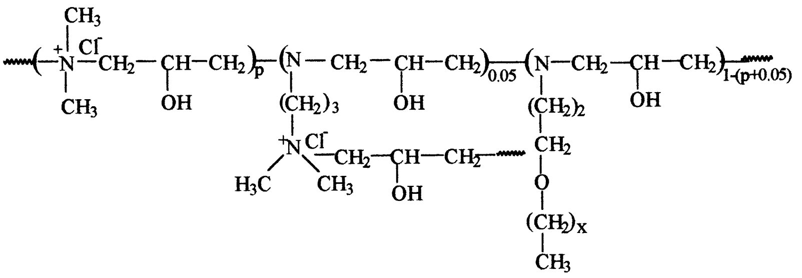
PII: S0032-3861(00)00690-X



p = 0.94, x=5, polycation PCA_5H_1; p = 0.93, x=5, polycation PCA_5H_2;

p = 0.94, x=9, polycation PCA_5D_1

Scheme 1.

The definitions of the acronyms of these polycations are the following: PC — polycation; A — asymmetrical amine; H and D — the hydrophobic amine; the first number means mole percent of the polyfunctional amine and the last one means mole percent of the hydrophobic amine. The hydrophobic content in the hydrophilic/hydrophobic polymers is limited by their solubility in water. It is often impossible to determine the degree of hydrophobic groups incorporation, especially for comonomers consisting of alkyl chains and consequently it was assumed that the hydrophobic amine content was the same as in the initial feed composition, as it is usually supposed for the low contents of hydrophobic component included in the hydrophilic/hydrophobic copolymers [4].

All the polycations were carefully purified by dialysis against distilled water until the absence of Cl^- ions in the external water was achieved. The diluted aqueous solutions were concentrated by gentle heating in vacuum, then the polymer was recovered by precipitation with acetone and finally purified with methanol/acetone as solvent/non-solvent. Polycations were dried in vacuum on P_2O_5 at room temperature and were characterised by the content in ionic chlorine (determined by potentiometric titration with 0.02 N aqueous $AgNO_3$ solution) (Cl_i), total chlorine (determined by the combustion method — Schöniger technique) (Cl_t) and intrinsic viscosity in 1 M NaCl solution: Cl_i 19.82, Cl_t 19.79, $[\eta]_{1\ \mathrm{M\ NaCl}} = 0.395$ dl/g for PCA_5H_1; Cl_i 20.79, Cl_t 21.36, $[\eta]_{1\ \mathrm{M\ NaCl}} = 0.465$ dl/g for PCA_5H_2; Cl_i 20.66, Cl_t 21.03, $[\eta]_{1\ \mathrm{M\ NaCl}} = 0.450$ dl/g for PCA_5D_1.

2.2. Viscosity measurements

Viscometric measurements of the polyelectrolyte solutions were carried out at 25°C with an Ubbelohde viscometer with internal dilution. All polymer solutions were made up in double-distilled water. The solution was kept about 10 min prior to the measurements for temperature equilibrium.

3. Results and discussion

Polycations used in this study differ by the charge density induced by the presence of various amounts of *N*,*N*-dimethyl-2-hydroxypropyleneammonium chloride units in the main chain and by the hydrophilic–hydrophobic properties induced by the presence of hexyloxypropyl or decyloxypropyl as substituents in their structure.

Fig. 1 presents the variation of the reduced viscosity, η_{sp}/C, versus the concentration of polymers under study, in aqueous solutions without salt. All the polymers had a typical polyelectrolyte behaviour in aqueous solutions, i.e. the η_{sp}/C values increased with decreasing the concentration of polymer solution due to the expansion of the macroion chain, which is caused by the progressively enhanced dissociation of ionisable groups and hence intensification of the intramolecular repulsive interactions between ionised groups along the chain. One can also observe the influence of the hydrophobic group content (hexyloxypropyl) by the lower expansion of the macroion in the case of PCA_5H_2 comparative with PCA_5H_1; this could indicate the decreased influence of the hydrophobic

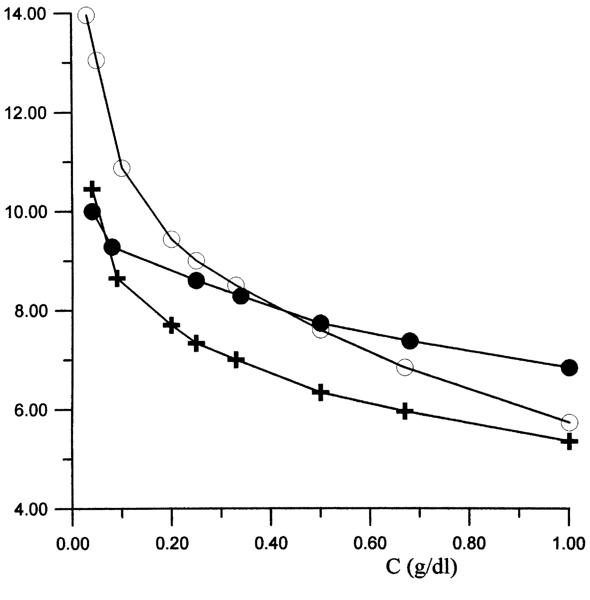


Fig. 1. Variation of the reduced viscosity (η_{sp}/C) versus the concentration (C) of cationic polyelectrolyte with non-polar side groups, in H_2O at 25°C: (×) PCA_5H_1; (●) PCA_5H_2; (○) PCA_5D_1.

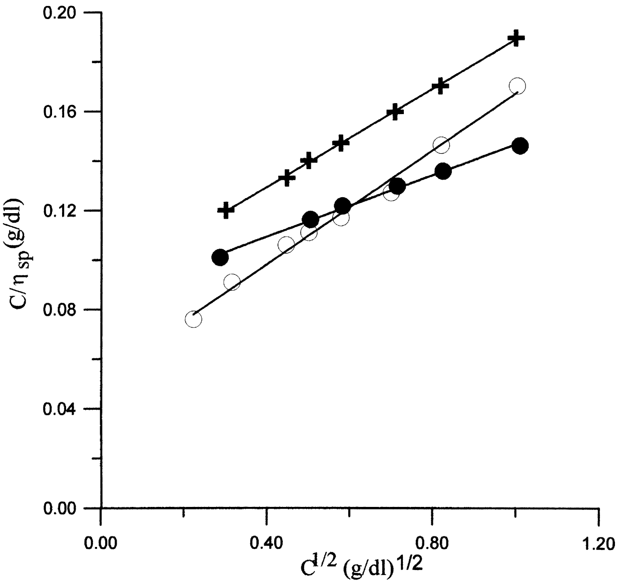


Fig. 2. Representation of the Fuoss equation for: (×) PCA_5H_1; (●) PCA_5H_2; (○) PCA_5D_1.

attractions on the chain conformation in the case of these polymers.

The curves shown in Fig. 1 can be linearised applying the Fuoss [15] (1) and Fedors [16–18] (2) equations:

$$\eta_{sp}/C = A/(1 + BC^{1/2}) \tag{1}$$

where A = the intrinsic viscosity; B = constant

$$1/[2(\eta_r^{1/2} - 1)] = 1/[\eta]C - 1[\eta]Cm; \tag{2}$$

where Cm = a polymer concentration parameter.

The curves obtained by calculating the viscometric data for the ionic polymers in terms of the Fuoss and Fedors equations are presented in Figs. 2 and 3.

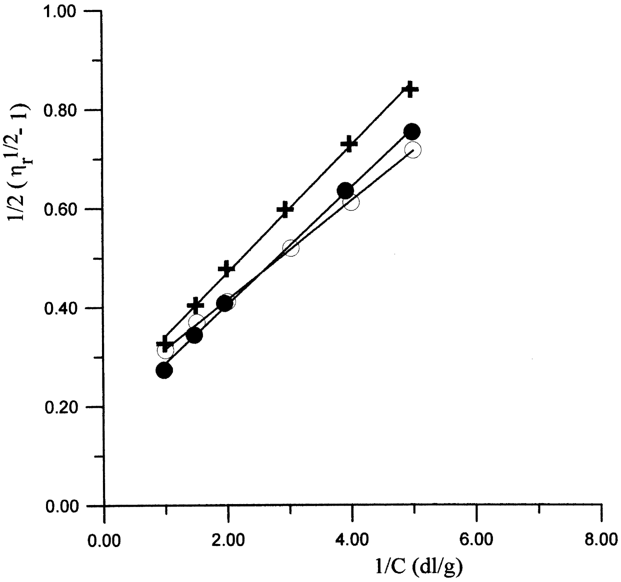


Fig. 3. Representation of the Fedors equation for: (×) PCA_5H_1; (●) PCA_5H_2; (○) PCA_5D_1.

Table 1
Intrinsic viscosity values obtained by the Fuoss and Fedors methods

Sample	$[\eta]_{Fuoss}$ (dl/g)	$[\eta]_{Fedors}$ (dl/g)
PCA_5H_1	11.16	7.87
PCA_5H_2	11.90	8.20
PCA_5D_1	19.23	9.19

As can be observed straight lines are obtained for all the samples over a wide range of concentration allowing to calculate the intrinsic viscosity values. The results obtained by fitting the Fuoss and Fedors equations to the viscometric data of the cationic polyelectrolytes are listed in Table 1.

The analysis of these data shows that the intrinsic viscosity values obtained by the Fedors equation are lower than those obtained by the Fuoss equation.

The concentration range employed for this study may be considered to include the overlap concentration, C^*, at which polymer coils begin to overlap each other (separating the semidilute/dilute regime) as is usually known for polyelectrolyte solutions [19]. We determine C^* values both experimentally as the concentration at which the viscosity is twice the solvent viscosity [20] and by means of the following equation [21], Table 2:

$$C^* = 1/[\eta] \tag{3}$$

where $[\eta]$ = intrinsic viscosity.

The results obtained for C^* by means of the above mentioned methods are listed in Table 2.

The $[\eta]$ values calculated by the Fedors equation led to the C^* values closer to C^* values experimentally determined, than those calculated in accordance with the Fuoss equation.

As it was already mentioned in Section 1 the viscosity of a polyelectrolyte solution also depends on the environment, i.e. the solution ionic strength, the solvent polarity which affects the electrostatic interactions between the charged groups of the polyion. Viscosity of the PCA_5D_1 polycation in the mixtures of water/methanol and water/acetone was investigated to observe the conformation changes of the macroion chain with decreasing the solvent polarity.

The reduced viscosity of PCA_5D_1 in the mixed solvent water/methanol of various compositions as a function of the polymer concentration is shown in Fig. 4. It is observed that the reduced viscosity values increase with decreasing

Table 2
Overlap concentration, C^*, for some hydrophobically cationic polyelectrolytes

Sample	C^*_{exp} (g/dl)	$C^* = [\eta]^{-1}_{Fedors}$ (g/dl)	$C^* = [\eta]^{-1}_{Focuss}$ (g/dl)
PCA_5H_1	0.112	0.127	0.089
PCA_5H_2	0.156	0.166	0.084
$PCA_5\ D_1$	0.100	0.108	0.052

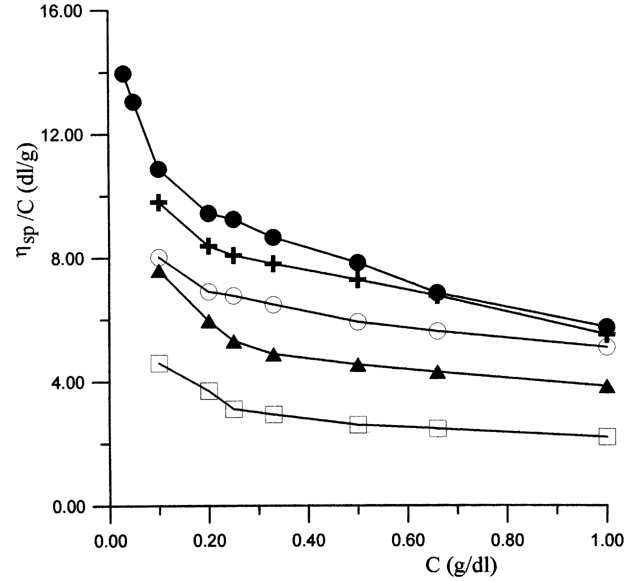


Fig. 4. Variation of the reduced viscosity (η_{sp}/C) versus the concentration (C) of PCA_5D_1 in water /methanol mixture: (●) H_2O; (×) 75/25; (○) 50/50; (▲) 25/75; (□) methanol.

polymer concentration for all employed compositions of the mixed solvent.

This typical polyelectrolyte behaviour, which is usually observed in saltless aqueous solution, occurs because the ionisable groups along the chain can ionise in this polar solvent. One can also note that the reduced viscosity values, at constant polymer concentration, decreases as the methanol content in the mixed solvent increases. The addition of a less polar solvent, CH_3OH with dielectric constant $\epsilon = 32.7$ at 25°C, into water, $\epsilon = 78.39$, decreases the medium polarity which brings about the weakening of the dissociation along the polyion backbone; consequently, the Coulomb repulsive interactions between the ionised groups decrease allowing the chain to coil more tightly.

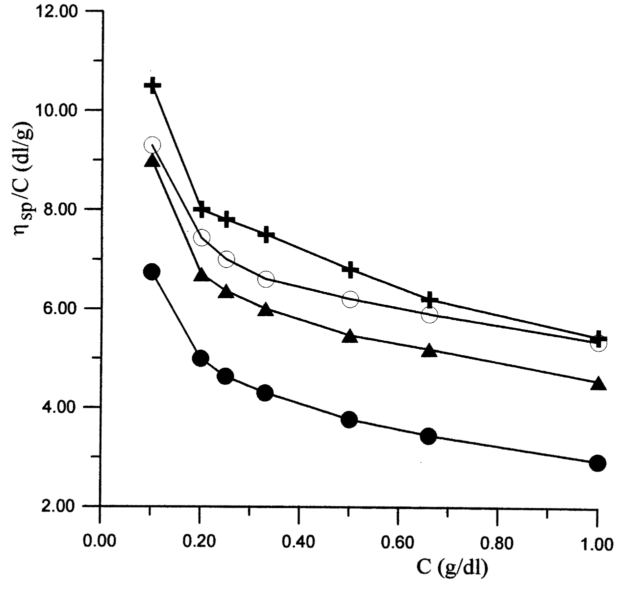


Fig. 5. Variation of the reduced viscosity (η_{sp}/C) versus the concentration (C) of PCA_5D_1 in water/acetone mixture: (×) 75/25; (○) 60/40; (▲) 50/50; (●) 40/60.

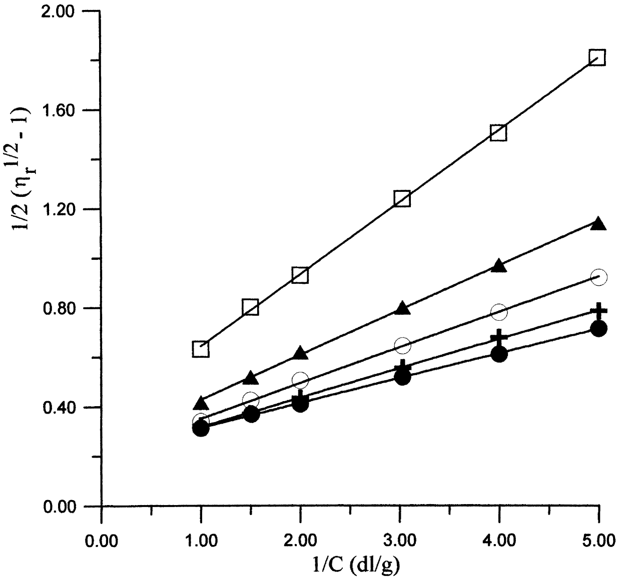


Fig. 6. Representation of the Fedors equation for PCA_5D_1 in water/methanol mixture: (●) H_2O; (×) 75/25; (○) 50/50; (▲) 25/75; (□) methanol.

Similar η_{sp}/C–C profiles have been observed for PCA_5D_1 in mixtures of water/acetone (Fig. 5). Acetone being a nonsolvent for this polymer, the measurements were performed to determine the acetone content in the mixture where the precipitation of the polyelectrolyte takes place.

One can see the polyelectrolyte behaviour of PCA_5D_1 in the water/acetone solvent with the acetone content as high as 60 vol%. The precipitation of PCA_5D_1 was observed

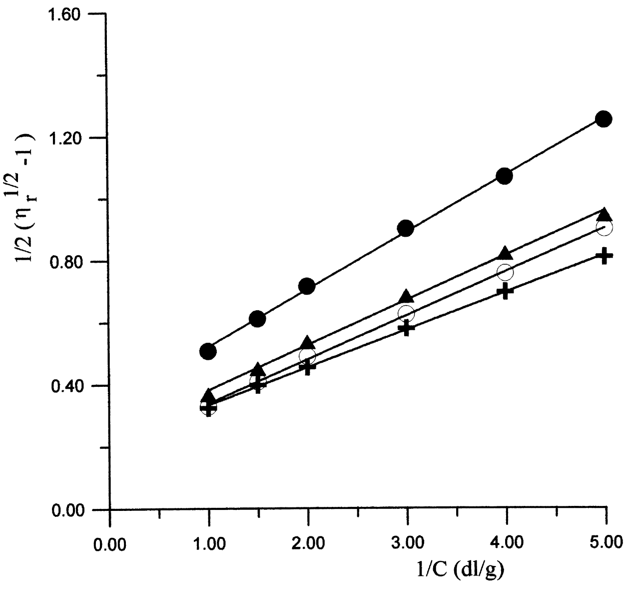


Fig. 7. Representation of the Fedors equation for PCA_5D_1 in water/acetone mixture: (×) 75/25; (○) 60/40; (▲) 50/50; (●) 40/60.

Table 3
Intrinsic viscosity and overlap concentration for PCA_5D_1 in the water/organic solvent mixtures

Organic solvent (vol%)	Methanol			Acetone		
	$[\eta]_{\text{Fedors}}$ (dl/g)	$C^* = 1/[\eta]_{\text{Fedors}}$ (g/dl)	C^*_{exp} (g/dl)	$[\eta]_{\text{Fedors}}$ (dl/g)	$C^* = 1/[\eta]_{\text{Fedors}}$ (g/dl)	C^*_{exp} (g/dl)
25	7.81	0.128	0.131	7.75	0.129	0.120
40	–	–	–	6.57	0.152	0.160
50	6.40	0.156	0.154	6.02	0.167	0.170
60	–	–	–	5.07	0.197	0.200
75	5.73	0.174	0.182	–	–	–
100	3.18	0.314	0.330	–	–	–

when acetone content in the water/acetone mixture was raised beyond 60 vol%; the ion pair attraction between the charged groups and counterions, which competes with the electrostatic repulsion between the charged groups resulted in the intermolecular aggregation which led to the phase separation of the PCA_5D_1 polycation.

The viscometric behaviour of PCA_5D_1 in the mixed solvents water/methanol and water/acetone is shown to fit well with the Fedors equation (Figs. 6 and 7).

Table 3 presents the intrinsic viscosity and the overlap concentration, C^*, values for PCA_5D_1 in various mixtures of water/methanol and water/acetone.

The decrease of the $[\eta]$ values and the anticipated increase of C^* values confirm the reduction of the hydrodynamic dimension of the macromolecular coils as the content of the organic solvent in the mixture increases. It is also important to note the agreement between the C^* values obtained according to Refs. [20,21].

4. Conclusions

The viscosity of some cationic polyelectrolytes carrying non-polar side groups, over a wide concentration range, in salt-free aqueous solution, was determined. All the aqueous solutions of polymers showed a typical polyelectrolyte behaviour in the absence of added salt, i.e. the η_{sp}/C values increased with decreasing the concentration of polymer solution due to the expansion of the macroion chain. The experimental data were plotted in terms both of Fuoss and Fedors equations. The $[\eta]$ values calculated by the Fedors equation led to the C^* values closer to C^* values experimentally determined, than those calculated in accordance with the Fuoss equation.

Polyelectrolyte behaviour was observed for PCA_5D_1 also in the mixtures of water/methanol for all the composition employed and in the mixtures of water/acetone with the acetone content as high as 60 vol%. When the acetone content was raised beyond 60 vol% the phase separation was observed in the solution of PCA_5D_1. The intrinsic viscosity, $[\eta]$, decreased and the overlap concentration, C^*, increased with increasing organic solvent content in the mixed solvents which indicates the reduction of the macromolecular coil size.

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