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ORIGINAL CONTRIBUTION

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# Behaviour of cationic polyelectrolytes upon binding of electrolytes: effects of polycation structure, counterions and nature of the solvent

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**Abstract** The effects of polycation structure, counterions and the nature of the solvent on the interaction between low-molecular-weight salts with some cationic polyelectrolytes in water and methanol were investigated. The polyelectrolytes used in this study were cationic polymers with quaternary nitrogen atoms in the backbone with or without a nonpolar side chain (polymer type $PCA_5H_1$, $PCA_5D_1$ and $PCA_5$) or tertiary amine nitrogen atoms in the main chain (polymer type PEGA). LiCl, NaCl, KCl, NaBr, NaI and $Na_2SO_4$ were used as low-molecular-weight salts. The interaction between polycations and salts was followed by viscometric and conductometric measurements. The study of the interaction of monovalent counterions with cationic polyelectrolytes emphasized an increase in the interaction with the decrease in the radius of the hydrated counterion, both for strong polycations and for weak polycations, suggesting that counterion binding is nonspecific. In the case of $SO_4^{2-}$ anions, the $\Lambda_m$–$c^{1/2}$ curve passes through a minimum at $c_p$ values between $1 \times 10^{-3}$ and $3 \times 10^{-3}$ unit mol/l; this phenomenon can be explained by the maximum counterion interaction owing to the capacity of the polyvalent counterion to bind two charged groups by intra- or interchain bridges. The investigation of the influence of the polycation structure on the counterion binding indicated an increase in charged group–counterion interactions with a decrease in the nonpolar chain length and an increase in the quaternary ammonium salt group content (charge density) in the chain. The polyelectrolyte with tertiary amine groups in the chain, PEGA, showed, on one hand, a cation adsorption order as $K^+ > Na^+ > Li^+$ and, on the other hand, a stronger association between ions and PEGA chains in methanol than in water owing to the poorer solvating effect of methanol on the cations.

**Keywords** Cationic polyelectrolyte · Counterion binding · Viscosity · Conductivity · Neutral salts

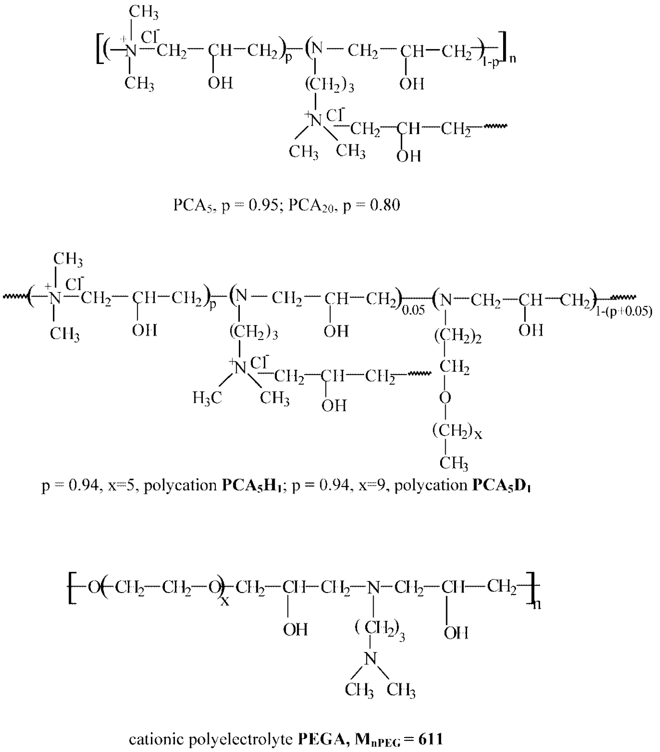
## Introduction

The study of polyelectrolyte solutions has attracted great attention, the increasing effort in theoretical explanations and experiments resulting in a deeper understanding of the polyelectrolyte behaviour in solution. Knowledge of the polyelectrolyte solution properties is very important because these properties determine the use of polymers in certain industrial and environmental applications, such as paper processing, membranes, flocculants, etc. [1–5]. The properties of the polyelectrolyte solutions are strongly influenced by the interactions in the polyion–counterion system depending on a great number of parameters, such as the chemical structure of the macroion, its size and charge density, the type of charges [6–9], the counterion size, its polarizability and valence, the water structure around the counterion [8, 10–13], the ionic strength, pH and the solvent polarity [14–18].

In this study the effects of polyion structure, counterions and the nature of the solvent on some cationic polyelectrolyte–counterion interactions in aqueous solution and in methanol were examined. The polyelectrolytes used in this work were polycations with *N*,*N*-dimethyl-2-hydroxypropyleneammonium chloride units or tertiary amine nitrogen atoms in the main chain.

This work was stimulated, on one hand, by the fact that most of the studies of counterion-polyelectrolyte interactions were carried out in systems containing anionic polyelectrolytes and counterions; by comparison, studies on cationic polyelectrolytes are relatively rare [8, 11–13]. On the other hand, these polyelectrolytes have proved efficiency in fields such as water purification, formation of bi- and tricomponent complexes (polycation/polyanion, polycation/dye, polycation/dye/polyanion) [19–21] and surface modification. Since in these application areas low-molecular-weight salts can appear and taking into account that there is no information about the behaviour of these kinds of polyelectrolytes in the presence of salts, it was of interest to study this problem.

Polyelectrolyte–counterion interactions were followed by viscometric and conductometric methods.



PCA$_5$, p = 0.95; PCA$_{20}$, p = 0.80

p = 0.94, x=5, polycation **PCA$_5$H$_1$**; p = 0.94, x=9, polycation **PCA$_5$D$_1$**

cationic polyelectrolyte **PEGA, M$_{nPEG}$ = 611**

**Scheme 1**

## Experimental

### Materials

Cationic polyelectrolyte PCA$_5$ was synthesized by condensation polymerization of epichlorohydrin with dimethylamine, *N*,*N*-dimethyl-1,3-diaminopropane [22]; the primary amines, hexyloxypropylamine (polymer type PCA$_5$H$_1$) and decyloxypropylamine (polymer type PCA$_5$D$_1$) were used to obtain polycations with nonpolar side chains [23]. PEGA polycation was obtained by polyaddition of poly(ethylene glycol) (PEG) diglycidylethers with *N*,*N*-dimethyl-1,3-diaminopropane [24]. Their general structure is presented in Scheme 1. The definitions of the acronyms of these polycations are the followings: PC – polycation, A – asymmetrical diamine; 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.

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 heating them in a vacuum, then the polymer was recovered by precipitation with acetone and finally purified with methanol/acetone as solvent/nonsolvent. The polycations were dried in a vacuum on P$_2$O$_5$ at room temperature and were characterized by the content of 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 aqueous solution: Cl$_i$ 23.22, Cl$_t$ 23.58, $[\eta]_{1M\ NaCl} = 0.680$ dl/g for PCA$_5$; Cl$_i$ 19.82, Cl$_t$ 19.79, $[\eta]_{1M\ NaCl} = 0.395$ dl/g for PCA$_5$H$_1$; Cl$_i$ 20.66, Cl$_t$ 21.03, $[\eta]_{1M\ NaCl} = 0.450$ dL/g for PCA$_5$D$_1$.

The charge density of PEGA obtained by conductometric titration with 0.1 N HCl was 1.53 mEq/g. The salts used (LiCl, NaCl, KCl, NaBr, NaI·2H$_2$O, Na$_2$SO$_4$) were analytical grade products and were used without further purification.

### Methods

Viscometric measurements of the polyelectrolyte solutions were performed with an Ubbelohde viscometer with internal dilution at 25 °C. Conductometric measurements were carried out with a Radiometer Copenhagen model CFM 2d, using a CDC 114 conductivity cell. The bidistilled water used as a solvent had a specific conductivity of 1.6–2.4 $\mu$S.

## Results and discussion

### Viscometric study of the polymer solutions

In salt-free aqueous solution, the polymers studied exhibited peculiar behaviour of the polyelectrolytes [22– 24].

The interaction of low-molecular-weight salts with polyelectrolyte in aqueous solution represented by changes in the reduced viscosity as a function of the nature of the salt and concentration, for PCA$_5$D$_1$, is illustrated in Fig. 1. The polymer concentration ($c_p$) was kept constant 1.0 g/dl. One may observe that by the introduction of various amounts of salt into the polyelectrolyte solution the reduced viscosity values

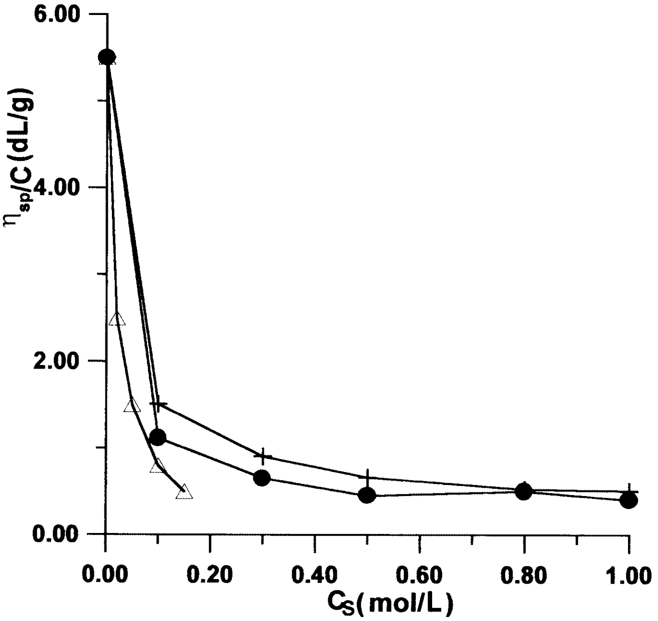


**Fig. 1** Variation of reduced viscosity ($\eta_{sp}/c$) of PCA$_5$D$_1$ with salt concentration ($c_s$): NaCl (*crosses*), NaBr (*circles*), NaI (*triangles*), $c_p = 10$ g/l

drop with the increase in the salt concentration ($c_s$); the decreasing viscosity with increasing salt concentration is attributed to shrinkage of the macroion chain owing to the screening of the charged groups of the chain by the counterions in excess. At the same salt concentration, the reduced viscosity values decrease in the following sequence $Cl^- > Br^- > I^-$; counterion binding decreases in the reverse order.

The increase in polyion–counterion interactions from $Cl^-$ to $I^-$, i.e. with the decrease in the radius of the hydrated counterion, indicates the counterion binding is not accompanied by appreciable dehydration and suggests, as assumed by other authors [25], that the counterion binding in the halide series is nonspecific. The counterion condensation phenomenon is specific for polyelectrolytes and depends on their charge density and persists in the presence of low-molecular-weight salts even at salt concentration up to 1 M [26]. It is also known that the presence of a low-molecular-weight electrolyte in an aqueous solution of polyelectrolyte decreases the solubility of the latter more, the more strongly the ions are bound to the ionized groups. In the case of $I^-$ anion, PCA$_5$D$_1$ becomes insoluble at salt concentration greater than $1.5 \times 10^{-1}$ M.

## Conductometric study of the polymer solutions

It is known that the electrical transport properties of the polyelectrolyte solution in the presence of low-molecular-weight salts vary with the counterion type, suggesting the difference in the strength of the interactions of these polymers with counterions. The theory [27] predicts that the counterions associated with the polyion do not contribute to the conductivity, whereas the free counterions behave as in a simple salt solution. In this study we pursued the variation of the molar conductivity of polyelectrolyte ($\Lambda_m$) in an aqueous salt solution versus polyelectrolyte concentration. $\Lambda_m$ in a salt solution may be expressed by [28]

$$\Lambda_m = 10^3(k - k_0)/c \ , \qquad (1)$$

where $k$ and $k_0$ are the specific conductivities of the salt solution with and without added polyelectrolyte and $c$ is the polyelectrolyte concentration, expressed in moles per litre.

As can be seen in Fig. 2, the molar conductivity of the PCA$_5$D$_1$ solution in the presence of uni-univalent low-molecular-weight salts increases with decreasing $c_p$. In the case of the $SO_4^{2-}$ counterion, the $\Lambda_m$–$c^{1/2}$ curve exhibits a minimum between $1 \times 10^{-3}$ and $3.10^{-3}$ unit mol/L; the minimum can be explained by the increase in the counterion–polyion interactions owing to the capacity of the polyvalent counterion to bind two cationic groups by intra- or interchain bridges. One may also observe that at the same polymer concentration, $\Lambda_m$ decreases in the following sequence: $Cl^- > Br^- > I^- > SO_4^{2-}$, i.e. the counterion binding increases in the same order; these results are in agreement with those obtained by viscometric measurements.

To gain information about the influence of the polycation structure on the counterion binding, the

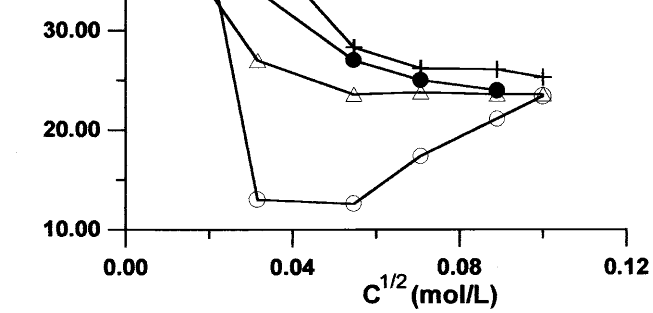


**Fig. 2** Variation of molar conductivity ($\Lambda_m$) of PCA$_5$D$_1$ with polyelectrolyte concentration ($c_p$) in aqueous salt solution: NaCl (*crosses*), NaBr (*filled circles*), Na I (*triangles*), Na$_2$SO$_4$ (*open circles*) $c_s = 1 \times 10^{-3}$ M

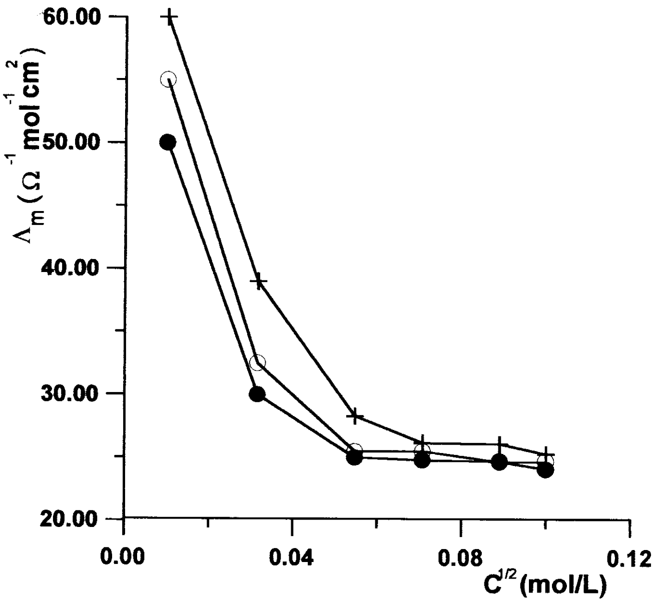


**Fig. 3** Variation of $\Lambda_m$ with $c_p$ in 1 × $10^{-3}$ M NaCl aqueous solution: $PCA_5D_1$ (*crosses*), $PCA_5H_1$ (*open circles*), $PCA_5$ (*filled circles*)

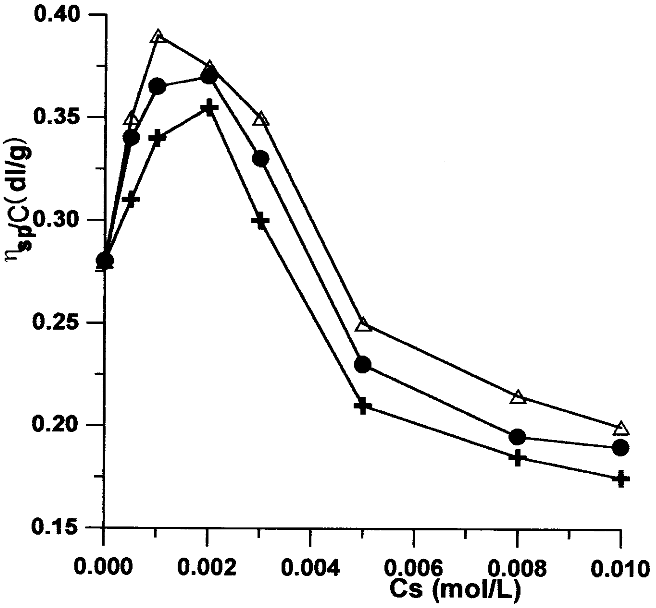


**Fig. 4** Reduced viscosity of PEGA versus $c_s$ in methanol solution: LiCl (*crosses*), NaCl (*circles*), KCl (*triangles*), $c_p = 10$ g/L

interaction between the same salt (NaCl) and cationic polyelectrolytes differing both in their number of *N*,*N*-dimethyl-2-hydroxypropyleneammonium chloride units in the main chain and in the length of the nonpolar side chain was followed (Fig. 3).

For the same polyelectrolyte concentration, the $\Lambda_m$ values decrease in the order $PCA_5D_1 > PCA_5H_1 > PCA_5$, i.e. with the decrease in the length of the nonpolar chain and the increase in the number of quaternary ammonium salt groups (charge density). This might be taken as an indication that the presence of a nonpolar chain in the polyelectrolyte structure brought about the decrease in the polyion–counterion interactions; thus, the electrostatic interactions appear as a dominant factor influencing the counterion binding process in the case of these cationic polymers.

As mentioned in the Introduction another type of polyelectrolyte studied in this work was a polyelectrolyte with tertiary amine nitrogen groups in the main chain (PEGA). This kind of polymer can bind both cations and anions owing to the presence of the PEG chains in the backbone. Previously, we reported data for the interaction of PEGA with salts containing an alkali-metal cation (Na) and a series of different anions in aqueous solution [13]. In the present study, the interest focused on the interaction between PEGA and inorganic salts containing different cations ($Li^+$, $Na^+$ and $K^+$) in methanol. The ability of PEGA to donate electron pairs to stabilize the cation is enhanced compared to PEG owing to the presence of two types of heteroatoms, N and O, in the chain.

The viscometric behaviour of PEGA in methanol in the presence of LiCl, NaCl and KCl is presented in Fig. 4. One may observe the same behaviour for all the salts, i.e. the reduced viscosity values increase and pass through a maximum at a salt concentration of about $10^{-3}$ M for KCl and $2 \times 10^{-3}$ M for LiCl and NaCl; one may assume the increase in the salt concentration, at fixed polymer concentration, leads, firstly, to an increase in the number of adsorbed cations on the chain, the polymer chain becomes charged and similar charges repel each other, leading to the expansion of the macroion. A further increase in the salt concentration brought about a decrease in the reduced viscosity values. Probably, at higher salt concentration the charges on the chain are screened by salt and consequently a reduction of the hydrodynamic dimension of the coil takes place.

One can also note over the entire concentration range considered the reduced viscosity values decrease in the order $K^+ > Na^+ > Li^+$, that is, the affinity of PEGA for counterions decreases in the same order, i.e. the rule of the ionic atmosphere binding is obeyed. Similar behaviour is observed in the case of poly(ethylene oxide) macromolecules – alkali series interactions [29].

## Conductometric measurements

To obtain information about the influence of the nature of the solvent on the PEGA–alkali-metal ions interactions the measurements were carried out both in water and in methanol.

At a given concentration of added salt, an increase in the $\Lambda_m$ values is observed when the PEGA concentration

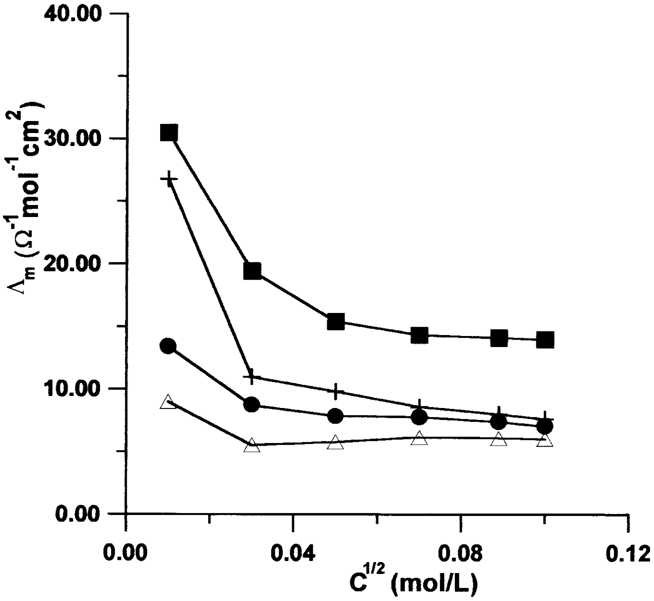


**Fig. 5** Variation of $\Lambda_m$ of PEGA with $c_p$: NaCl in $H_2O$ (*squares*), LiCl in $CH_3OH$ (*crosses*), NaCl in $CH_3OH$ (*circles*), KCl in $CH_3OH$ (*triangles*), $c_s = 1 \times 10^{-3}$ M

increases (Fig. 5); the increase in $\Lambda_m$ on dilution is attributed to a lower association of macromolecules with cations. One can also see at the same polyion concentration the molar conductivity values decrease in the same order as that observed by viscosity measurements, i.e. $K^+ > Na^+ > Li^+$.

On the other hand, one may observe that for the same salt, NaCl, at fixed PEGA concentration, the $\Lambda_m$ value is lower in $CH_3OH$ than that observed in $H_2O$, indicating a stronger salt polymer association in the case of the former solvent owing to the poorer solvating effect of methanol on the cations.

## Conclusions

1. Interactions between monovalent counterions and cationic polyelectrolytes increase with a decrease in the radius of the hydrated counterion, both for strong polycations and for weak polycations; we suggest the counterion binding in the halide series is an ionic atmospheric binding.
2. $SO_4^{2-}$ anions are preferentially bound to the ionic groups compared to monovalent ones owing to the capacity of the polyvalent counterion to bind two groups by inter- or intrachain bridges.
3. The presence of nonpolar side chains in the polyelectrolyte structure brought about a decrease in the polyion–counterion interactions; thus, the electrostatic interactions appear as the dominant factor influencing the counterion binding process in the case of these cationic polymers.
4. The affinity of PEGA chains for cations decreases in the following order: $K^+ > N^+ > Li^+$; the association between $Na^+$ and PEGA chains was stronger in methanol than in water.

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