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Carriers

Physico-Chemical Studies of Polymeric Carriers
5. Salt Effect on Conformational Transition

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SUMMARY

Densitometric conformational studies were made on poly(1-vinyl-2-pyrrolidone-*co*-maleic acid) in the presence of LiCl, NaCl, KCl, $CaCl_2$, and $MgCl_2$ in order to control ion-binding of the polyanion in dilute aqueous solution. Experimental verification of principal role of deprotonation in the conformational transition of the polyacid chains during titration is given. Correlation was found between the apparent molar volume of the copolymer and the ionic radius of the bound cation.

INTRODUCTION

As it was reported in the previous papers of this series, alkaline counter ions are retained by the polyacid, poly(N-vinylpyrrolidone-*co*-maleic acid) P(NVP-*co*-MAc), and the titrational process involves conformational transition of the polymer chains. Both deprotonation and ion-binding may induce conformational changes. As to the former, an increase in chain dimensions can be expected owing to the repulsion of negatively charged sites of the chain. The effect of ion-binding is supposed to be more complex (e.g.: FELBER et al. 1968, BEGALA and STRAUSS 1972, TONDRE and ZANA 1972, MANNING 1979, STRAUSS et al. 1979, MANNING 1981). For theoretical as well as for practical reasons it appeared important to learn more about these two expectedly distinguishable steps. The aim of our present work is to study conformational changes of P(NVP-*co*-MAc) in the presence of various cations added as chloride salts to the polymer solution in order to clear up the role of the cation in the process.

EXPERIMENTAL

Apparent molar volume (ϕ) values of the polymer were determined according to the densitometric method described earlier (CSÁKVÁRI et al. 1984a). The measurements were carried out on hydrolysed, ion-exchanged copolymer samples, prepared according to PATÓ et al. 1982, with $\overline{M}_w = 2 \cdot 10^4$ determined viscometrically and calculated by equation $[\eta] = 3.25 \cdot 10^{-4}\ \overline{M}^{\ 0.62}$ (CSÁKVÁRI et al. 1981). 0.05 M polyacid stock solution was prepared, then different amounts of 0.1 M LiCl, NaCl, KCl, $MgCl_2$ or $CaCl_2$ were added to 10 - 10 cm^3 of the stock solution. These solutions were further diluted with water. Density values were determined for the samples and for the corresponding reference solutions. Reference solutions were made of LiCl, NaCl, KCl, $MgCl_2$ and $CaCl_2$, providing the same concentrations of them as in the copolymer solutions. Precision of the density measurements was $(1 - 2) \cdot 10^{-5}$ $[g \cdot cm^{-3}]$. Calibration was carried out with water and ethanol and checked before and after each series of experiments. Duplication of experiments resulted in accuracy of ϕ values with ± 1 %.

RESULTS AND DISCUSSION

Comparing ϕ values of P(NVP-*co*-MAc) obtained in the presence of NaOH and those of NaCl containing solutions, it has been found, that in the first case ϕ alters between 150 - 189 $cm^3 \cdot mol^{-1}$, while in the latter case ϕ values are somewhat lower: 130 - 160 $cm^3 \cdot mol^{-1}$. The same tendency is valid for KOH/KCl containing polyacid solutions, i.e. 177-224 $cm^3 \cdot mol^{-1}$ and 130 - 154 $cm^3 \cdot mol^{-1}$, respectively. This indicates, that ion-binding of alkaline ions is affected by coions too. That is, the same amount of cation present in the solution apparently behaves differently if it is introduced as basis or as salt. It is especially striking when comparing the ϕ *vs.* concentration functions of the system containing KOH and KCl. The continous increase of ϕ observed during titration of the polyacid with KOH (CSÁKVÁRI et al. 1984b, 1985) can not be found applying the chloride salt of the cation. These findings have led to the assumption, that proton dissociation is the first step in the process, for which OH^- groups are responsible. Hydroxyl ions introduced are consumed in the deprotonation step by water formation, and the polyacid chains are expanded due to the intramolecular electrostatic repulsion. Nearby cations embedded by electrostatically polarized water molecules are trapped by the negatively charged sites of the polyacid chains. It is not the case if chloride salt is added, i.e. solvated chloride ions have smaller effect on chain conformation. As a consequence P(NVP-*co*-MAc) chains are less expanded in dilute alkaline solution if cation introduced is the same, but co-ions are Cl^- instead of OH^-.

The effect of different cations on chain conformation was examined applying different chloride salt solutions. A marked dependence of ϕ on the nature of the cations is observed. Correlation is found between chain dimensions and ionic radius of the cation retained by the polyacid (cf. Fig.1) interesting to note, that monovalent Na^+ ions result in similar values to those, obtained with divalent Ca^{2+} ions. The same is true for Li^+ and Mg^{2+} ions. It is in accordance with the well-known cell membrane permeability studies (e.g.: CHOCK and TITUS 1973). Invers proportionality of ϕ and ionic radius of the cation can be explained with hydration, i.e. the smaller is the ionic radius of the ion, the greater

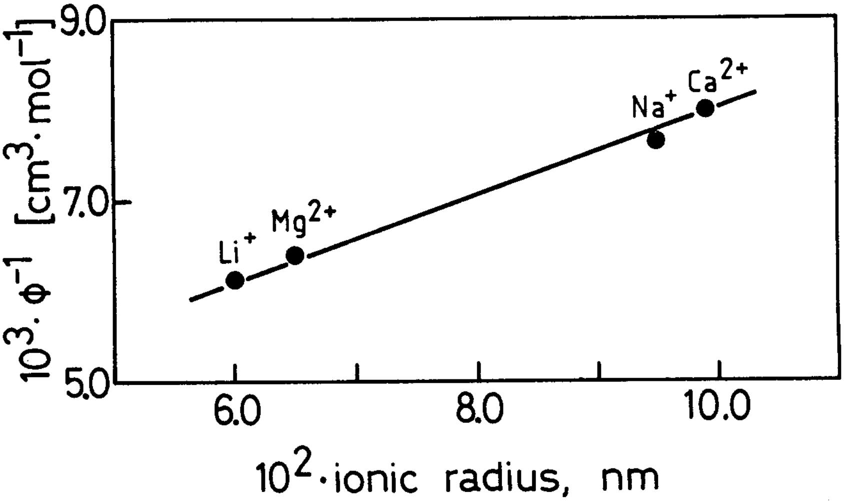

Fig.1. Variation of apparent molar volume of P(NVP-co-MAc) as a function of ionic radius of the bound cation. Polymer concentration: 6.9·10^{-3} mol·dm^{-3}, mole ratio of polyacid and added salt is 1.

is its hydration sphere. Thus, intramolecular segmental interactions result in conformational changes with larger dimensional change for the polyacid with the more hydrated cation.

The effect of added salt on ϕ values of the polyanion is shown in Tab.1. It can be seen, that in the case of NaCl and $CaCl_2$, similarly to the densitometric titrational results (CSÁKVÁRI et al. 1984b), ϕ values are the smallest if added salt and monoanion units are in equivalent amounts. LiCl and $MgCl_2$ have an opposite effect on chain conformation under the same conditions,

Table 1. Apparent molar volume of P(NVP-co-MAc) depending on the amount of added salt. Polyacid concentration: 6.9·10^{-3} mol·dm^{-3}.

Mole ratio of salt and monoanion unit	Apparent molar volume (in $cm^3 \cdot mol^{-1}$)				
	Li^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
0.60	148	148	142	152	142
1.00	165	131	140	156	125
1.20	156	157	140	152	170

while in the case of KCl practically no detectable alteration of ϕ was found. (Reproducibility of ϕ determination is $\pm$ 1 $cm^3 \cdot mol^{-1}$.)

The effect of dilution on the conformation of P(NVP-*co*-MAc) in the presence of added salt is shown in Tab. 2. Slight decrease of apparent molar volume occurs applying NaCl and $CaCl_2$. In the presence of LiCl ϕ is constant in the range of polymer concentration: 1.15 - $3.45 \cdot 10^{-2}$ $mol \cdot dm^{-3}$, below this range ϕ increases. In the case of KCl and $MgCl_2$ no characteristic alteration is found. On the basis of the above data it can be concluded, that in the concentration range studied, which is suitable for potentiometric titration of the polyacid, chain dimensions of P(NVP-*co*-MAc) depends on the ionic radius of the retained cation rather than on the ionic strength of the solution.

Table 2. The effect of dilution on the apparent molar volume of P(NVP-co-MAc) if mole ratio of salt and monoanion unit of the polymer is 1.

Polymer concentration	Apparent molar volume (in $cm^3 \cdot mol^{-1}$)				
$10^2 \cdot mol \cdot dm^{-3}$	Li^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
3.45	152	155	149	153	137
2.30	150	155	141	156	132
1.72	149	152	141	155	136
1.15	150	141	140	153	136
0.86	154	142	130	149	129
0.69	169	131	140	156	125

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