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Analysis

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4. Densitometric Titration of Poly(N-Vinylpyrrolidone-co-Maleic Acid)

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SUMMARY

Acid-base titration of poly/N-vinylpyrrolidone-co-maleic acid/ alternating copolymer was followed by densitometry in order to detect chain conformation transition found potentiometrically. Apparent molar volume (ϕ) values of the polymer were calculated for step-by-step titrated polymer samples. The effect of copolymer concentration on the conformational transition was also determined by measuring water diluted samples of each titration step. A continous increasing of ϕ was found in the case of KOH titrant, both in titration and in dilution. When NaOH was applied as a titrant, a very different ϕ profile was obtained. A minimum in ϕ vs. concentration occured in the vicinity of the half neutralization point of the dibasic polyacid.

INTRODUCTION

Since polyelectrolyte systems combine macromolecular behaviour with electrolyte properties, different types of interactions are involved in their water solutions, such as intra- and intermolecular segment-segment interactions, segment-small ion interaction, segment-solvent and small ion-solvent interactions as well as small ion-small ion ones. There are difficulties even in the pairwise determination of their parameters. It is known, that polyelectrolytes ionize considerably less than their low molecular weight analogues. The actual degree of ionization depends among others upon their concentrations. The more diluted is the solution, the more ionized is a polyelectrolyte chain, i.e. the more expanded is. Experimental evidence of this phenomenon can be drawn for instance from viscometric measurements. This polyelectrolyte behaviour can be suppressed by adding supporting electrolytes into the polymer solution. This empirical finding led to the demand for clearing up polyion-small ion interactions, which gave rise to the concept of ion-binding. A great number of methods have been used to study ion-binding (e.g.: MANNING 1969, MANNING

1972, TONDRE and ZANA 1972, SPEGT et al. 1973, ZANA and TONDRE 1974, NAGASAWA 1974, SPEGT and WEILL 1976, DAOUST and CHABOT 1980, SCHWARTZ and FRANCOIS 1981). The counter-ion effect on the behaviour of polyelectrolytes has still not been adequately cleared up.

Potentiometric titrational characteristics of poly/N-vinylpyrrolidone-co-maleic acid/ [P/NVP-co-MAc/] copolymer were discussed in the previous paper of the series (CSÁKVÁRI et al. 1984). The aim of the present work is to get more information about the pH-induced conformational transition of P/NVP-co-MAc/ by applying an independent method, densitometry, as apparent molar volume ϕ values derived from density measurements are in close correlation with conformational changes.

EXPERIMENTAL

The apparatus applied was a DMA 50 type digital precision densitometer joined with an ultrathermostate. The measurements were made at 25 ± 0.01 °C. The density values were determined from

$$d_1 - d_2 = (T_1^2 - T_2^2)A \qquad (1)$$

where d_1 is the density of the sample, d_2 is the density of water (0.99704 $g \cdot cm^{-3}$ at 25 °C) and T_1, T_2 are the detected periodic time values of the sample and of water, respectively, A is the calibration constant. Calibration was carried out with water and ethanol. The apparent molar volume ϕ of a polyelectrolyte solution of concentration c (in $mol \cdot l^{-1}$) was obtained from density values according to equation:

$$\phi = \frac{M_m}{d_o} - \frac{d - d_o}{d_o c} \cdot 10^3 \qquad (2)$$

where d and d_o are the densities of the solution and the solvent, M_m is the molecular mass of the repeating unit (-[NVP-MAc]-) of the alternating copolymer. The precision of the density measurements was $(1\text{-}2) \cdot 10^{-5}$ [$g \cdot cm^{-3}$].

The measurements were made on hydrolysed, ion-exchanged copolymer samples, $M_w = 2 \cdot 10^4$ (CSÁKVÁRI et al. 1981). 0.5 M polymer stock solution was prepared. Then different amounts of 0.1 M NaOH or KOH were added to 10 cm^3-s of the stock solution (i.e.: 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5 cm^3). These secondary stock solutions were further diluted with water. Reference solution series were made of NaOH, KOH, to provide the same concentration of the titrant as in the copolymer containing solutions.

Density values were determined in each titration step for the polymer and for the corresponding alkali metal ion containing solutions.

RESULTS AND DISCUSSION

As to the first, on the basis of the measurements and calculations it should be pointed out, that for partly or entirely titrated P/NVP-co-MAc/ the additivity of the molar volume values of the ionic components, found for simple electrolytes is not valid for all the data sets determined.

On the other hand, ϕ values of the copolymer, obtained with the same amounts of the two titrants are not equal. Molar volume values of six differently diluted polyacid samples, titrated to 100 % are collected in Tab.I.

Table I

Polyacid concentration	Titrant	
	NaOH	KOH
$10^2 \cdot mol \cdot l^{-1}$	ϕ $cm^3 \cdot mol^{-1}$	ϕ $cm^3 \cdot mol^{-1}$
3.45	165	190
2.30	160	192
1.72	160	194
1.15	165	197
0.86	151	200
0.69	148	204

As it can be seen, dimensional differences of the polymer chains using different titrants are significant.

Detailed analysis of the calculated ϕ values can be got applying ϕ vs. c plots (Fig.1, Fig.2).

It is shown in Figure 1, that a continous increase in apparent molar volume occurs in the case of KOH titrant by increasing the degree of titration as well as by further dilution of the step-by-step titrated polymer samples.

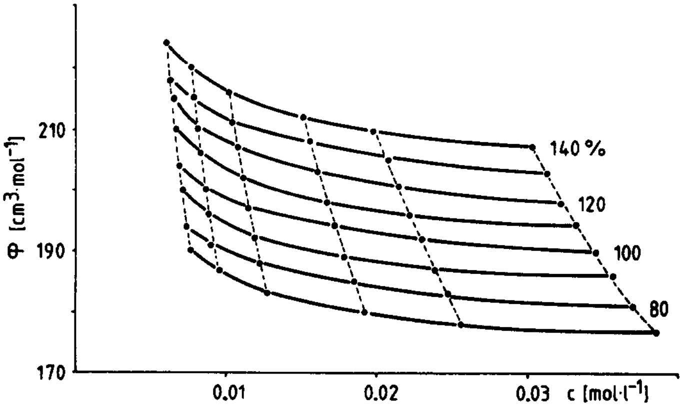

Figure 1. Densitometric titration profile of P/NVP-co-MAc/ using KOH titrant.

Very different titrational profile was obtained applying NaOH as a titrant. Two titrational curves are shown in Figure 2. The minimum on the curve of titration by NaOH corresponds to the half neutralization point of the dibasic polyacid (100 % titrated monoanion). Furthermore, the depth of the minimum is concentration dependent. These findings are in accordance with the potentiometric titrational characteristics of the polymer studied (CSÁKVÁRI et al. 1984).

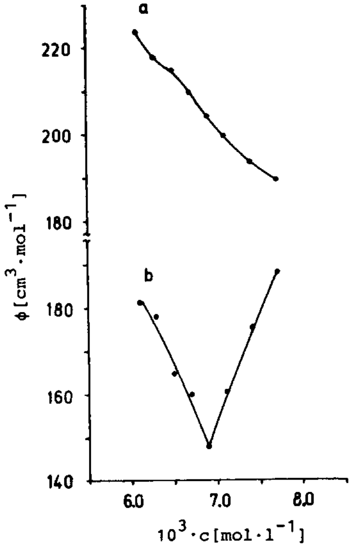

Figure 2: ϕ values of step-by-step titrated P/NVP-co-MAc/ in the highest dilution applied; titrant: KOH (a), NaOH (b).

It can be concluded, that during titration a part of the counter ions present in the solution is retained by the polyacid even at high dilution. Continous pH-induced conformational transition occurs during titration. Different cations are bound in different extent and probably in different manner to the polyanion. Thus the dimensions of P/NVP-co-MAc/ chains are altered by the cations taking part in ion-binding. Densitometric titration proved to be a proper tool for the determination of the conformational changes occuring during titration. The advantage of NaOH over KOH in the determination of the chemical composition of P/NVP-co-MAc/ reported earlier (CSÁKVÁRI et al. 1984) is confirmed by densitometric measurements.

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