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3. Potentiometric Titrational Behavior of Poly(N-Vinyl-Pyrrolidone-Co-Maleic Acid)

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SUMMARY

Aqueous acid-base titration measurements were made on alternating poly/N-vinylpyrrolidone-co-maleic acid/ copolymer. It was found, that P/NVP-co-MAc/ behaves as a monobasic polyacid in potentiometric titration. Furthermore it was concluded, that definite dissociation constant can not be determined in the usual way, as the actual value of K depends on the nature of the titrant as well as on the concentration of the polyacid solution. Continous pH-induced conformational transition of polymer chains occured during titration. Stabilizing effect of sodium ion on the ring structure of monoanion units is supposed.

INTRODUCTION

On purpose to determine the monomer ratio dependence of the chemical composition an independent controlling method is required because of uncertainty in elemental analysis. Therefore the aim of our present work is to examine titrational properties of P/NVP-co-MAc/.

The potentiometric titrational curves of polyelectrolytes have generally rather indefinite appearance. Titrational behaviour of copolymers of maleic acid have been studied by several groups of investigators. It was found, that the correlation between the apparent dissociation constant and the degree of dissociation of the primary carboxyl groups is not as simple as it was indicated earlier (FERRY et al. 1951). pH-induced conformational transition of maleic acid-styrene copolymer was reported earlier (SAKURADA et al. 1970, OHNO et al. ref. 6 in OHNO et al. 1973). They supposed a transition from a tightly coiled uncharged form to a highly charged expanded one, similarly to that of poly/methacrylic acid/.

According to several authors unusual potentiometric behaviour of MAc polymers can be attributed to a strong local interaction between two carboxyl groups of MAc in the polymer. These effects are usually treated as nearest neighbour interactions. For example Lifson derived an equation for the potentiometric titration of a polyacid in terms of the nearest neighbour interaction between ionized sites (LIFSON 1957). A modification of Lifson's theory was applied for a poly/diprotic acid/ (SCHULZ and STRAUSS 1972). Recently a novel approach was suggested (MINAKATA et al. 1981), where both the neighbour and the long-range interactions were taken into account. The authors concluded that for low degree of ionization an all- trans chain seemed to be the most stable form, while for higher degree of ionization a G'TTTGTTT chain conformation would be more acceptable.

On the other hand, the formation of a monoanion ring was supposed for MAc copolymers (e.g. MUTO et al. 1973, FELBER and PURDIE 1971, BEGALA and STRAUSS 1972) on the analogy of the ring structure found in hydrogen maleate anion (CARDWELL et al. 1953, NAGAKURA 1964, CHRISTENSEN et al. 1967).

EXPERIMENTAL

Alternating copolymer of NVP and MAc studied (M_W = 20 000) was prepared and characterized in our previous communications (CSÁKVÁRI et al. 1981a, PATÓ et al. 1982). Polyacid solutions contained 0.1135 g hydrolyzed, ion-exchanged polymer diluted with 10; 15; 20; 30; 60 cm^3 water. Titration was carried out with 0.1 M titrants (NaOH and KOH). Aqueous solutions were prepared using double distilled carbonate-free water.

pH measurements were performed at 25 °C with a RADELKISZ OP-208 type Precision Digital pH meter and RADELKISZ OP-08083 type combined glass electrode. The pH meter was calibrated with RADELKISZ K-21 (pH = 2.16 ± 0.03 at 25 °C) and K-71 (pH = 7.10 ± 0.03 at 25 °C) buffer solutions and checked with K-91 (pH = 9.21 ± 0.03 at 25 °C) buffer solution.

RESULTS AND DISCUSSION

Titrational profile of P/NVP-co-MAc/ alternating copolymer is rather "smeared out" as it is found in general for polyacids. Therefore $\Delta pH/\Delta V$ and $\Delta^2 pH/\Delta V^2$ *vs*. titrant volume (*V*) curves give more information on titrational behaviour of the copolymer. Potentiometric titration of P/NVP-co-MAc/ with NaOH shows only one inflection in the vicinity of the half neutralization point, i.e. half of the actual carboxyl group content is titrated (as an example see Fig.1). Also one inflection was found for some other MAc polymers (RESTRAINO et al. 1956, DEMCHENKO et al. 1971, GAYLORD 1975, MINAKATA et al. 1981).

The oscillation shown in the derivative curves in Fig.2. corresponds probably to the conformational transition of the chain, while the peak in the vicinity of the half neutralization point is presumably in correlation with the monoanion ring formation. If it is so, then these phenomena can be explained by the following:

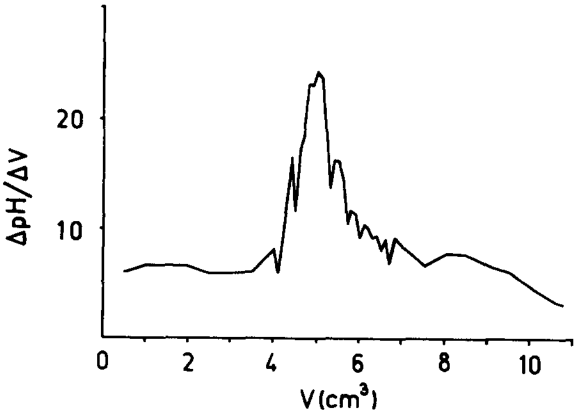

Figure 1: P/NVP-co-MAc/ titrated with 0.1 M NaOH, sample concentration: 0.025 mole·l^{-1}

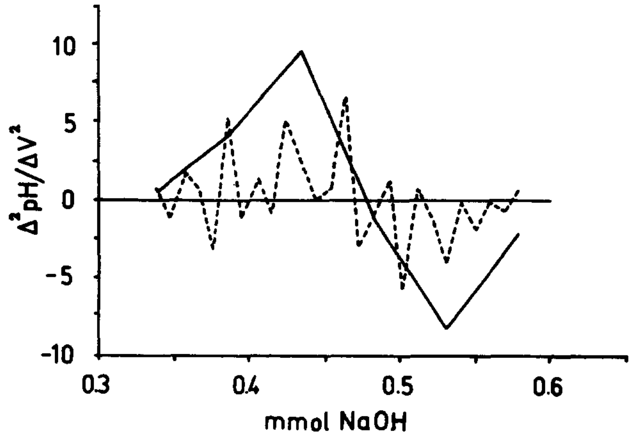

Figure 2: Second derivative of the titration curve of P/NVP-co-MAc/, c = 8·10^{-3} mole·l^{-1}, titrant: 0.1 M NaOH; solid line titration steps by 0.5 cm^3-s, dotted line titration by 0.1 cm^3-s.

each step of titration involves proton dissociation and as a consequence, the local charge density increases along the chain, therefore a conformational change is generated. Very likely ring formation occurs from mono-anion, and a fraction of cations retained by the polymer chain is able to stabilize the rings formed, thus local charge density is lowered.

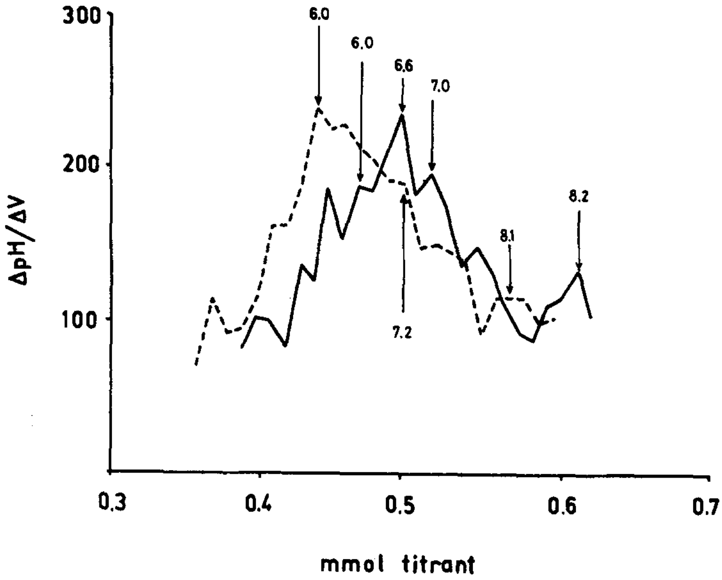

Figure 3: Titration of P/NVP-co-MAc/ with 0.1 M NaOH (solid line) and 0.1 M KOH (dotted line), $c = 0.03$ $mole \cdot l^{-1}$. Curves are labelled with some informative pH values.

As it is demonstrated in Fig.3 and in Fig.4., definite dissociation constant can not be determined for poly/N-vinylpyrrolidone-co-maleic acid/, since it depends on the nature of the cation as well as on the concentration of the system, but as a rule, the value of the half neutralization point of P/NVP-co-MAc/ is between pH 6 - 7.2.

As it is demonstrated in the figures, titration with NaOH can be applied for the determination of the chemical composition of the copolymer studied, as in this case titration results in one inflection or peak in the vicinity of the half neutralization point. Contrary, with KOH an uncertain inflection appears at smaller volume of the titrant. We wish to note that the statement in our previous work (CSÁKVÁRI et al. 1981b), i.e. "the composition of copolymers can not be determined by the MAc titration" is to be referred to the so called acid number determination method.

Because of the uncertainty of the classical "acid number" determination arising from the endpoint character of the method, we propose to take the whole titration profile of each sample and determine the maximum or inflection from the first or the second derivatives of pH. In this way we get the half neutralization point.

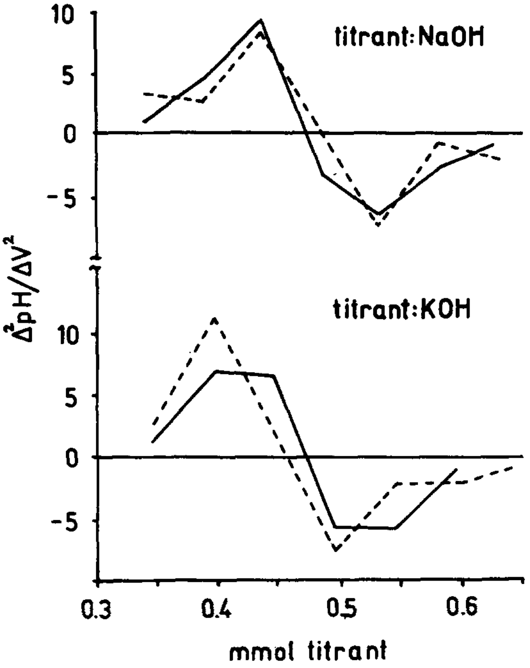

Figure 4: Titrational behaviour of P/NVP-co-MAc/ with different titrants. Solid lines $c = 1.7 \cdot 10^{-2}$ mole$\cdot l^{-1}$, dotted lines $c = 3.3 \cdot 10^{-2}$ mole$\cdot l^{-1}$.

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