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PROTONATION EQUILIBRIA IN AQUEOUS SOLUTIONS OF THE HYDROLYSED COPOLYMER OF MALEIC ANHYDRIDE WITH CYCLOPENTENE

V. CRESCENZI[1], S. PAOLETTI[2] and F. DELBEN[2]
[1]Institute of Physical Chemistry, University of Rome, Rome and
[2]Institute of Chemistry, University of Trieste, 34127 Trieste, Italy

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Abstract—The thermodynamics of proton dissociation of the hydrolysed 1:1 copolymer of maleic anhydride with cyclopentene in aqueous solution has been investigated. Potentiometric, microcalorimetric and dilatometric measurements on the copolymer solutions indicate that the two acidic functions are quite strong and not very different. Relatively poor solvation of vicinal carboxyl groups could account for the behaviour of the copolymer; it could stem from steric hindrances imposed by the cyclopentene residues.

INTRODUCTION

Differences in equilibrium properties among hydrolysed 1:1 copolymers of maleic anhydride (MA) with α-olefins or with vinyl ethers in dilute aqueous solution are determined to a large extent by differences in bulkiness and hydrophobic character of substituent groups of the comonomers. For instance, on passing from MA-ethylene to MA-propene and to MA-isobutene, one finds a steadily increasing difference in acidity between the two carboxyl groups of each repeating unit [1]. This effect has been attributed, on the basis of potentiometric, calorimetric, and dilatometric data, essentially to the enthalpy of the second dissociation which becomes more unfavourable by *c.* 3.3 kcal/mol going from MA-ethylene to MA-isobutene [2]. For the latter, internal hydrogen bonds in the monodissociated state would efficiently help to resist the removal of the second proton of the repeat unit upon titration [3]. In other words, the polydicarboxylic nature of MA copolymers, already clearly developed in MA-ethylene, becomes particularly evident with increasing bulkiness of non-polar substituents along the chains. This effect is additional to possible conformational features connected with the hydrophobicity of substituents [1, 4, 5].

We report here the results of a thermodynamic characterization of a novel MA-copolymer, viz. MA-cyclopentene (MACP), in dilute aqueous solution. This copolymer has been chosen in order to investigate the influence of the structural rigidity of the comonomer on the dissociation behaviour of carboxyl groups of MA residues. Solution properties of MACP have been studied with the aid of potentiometric, calorimetric and dilatometric experiments.

EXPERIMENTAL

The sample of MACP copolymer was kindly supplied by the Snam Progetti Laboratories, San Donato Milanese, Italy, through the courtesy of Professor S. Cesca. The product was prepared in toluene with AIBN as initiator. Elemental analysis confirmed the essentially 1:1 copolymer composition. The intrinsic viscosity of the sample was 0.06 dl/g in MEK. The sample was fractionated by precipitation with petroleum ether from ethyl acetate solutions. The central fractions of the molecular weight distribution were used. Its intrinsic viscosity in acetone was 0.07 dl/g at 20°. The copolymer was hydrolysed with 0.4 M NaOH at 85° for 24 hr under N_2, then extensively dialysed, passed through a strong cation-exchange column in the acid form, and concentrated under reduced pressure at *c.* 40°. The stock solutions were titrated potentiometrically in water-dioxane mixtures (*c.* 1:1, v/v) in the presence of a large excess of simple salt (KCl or NaCl, 2 M approx.) to enhance accuracy in the detection of the equivalence points.

Tetra-*n*-butylammonium hydroxide solutions (Eastman Kodak) were purged of CO_2 by passage through an anionic exchange column in the basic form. All the other reagents were C. Erba RP products of analytical grade. Solutions were prepared using freshly doubly distilled water with a specific conductivity of *c.* 1×10^{-6} ohm^{-1} cm^{-1}.

Potentiometric, microcalorimetric, and dilatometric experiments were performed using both K^+ and tetra-*n*-butylammonium as counterion. All the data for MACP-tetra-*n*-butylammonium system (not reported here for clarity) practically coincide with those obtained with K^+ as a counterion and hereafter discussed. All the experiments were performed using procedures described in detail elsewhere [2, 4, 6].

RESULTS AND DISCUSSION

The potentiometric data for MACP in water at 25° are illustrated in Fig. 1 as a typical pH vs $\bar{\alpha}$ and pK_a ($\equiv$ pH + log(1 − α/α)) vs α plots. In these graphs, $\bar{\alpha}$ is the stoichiometric degree of neutralization ($0 \leqslant \bar{\alpha} \leqslant 1$); α is the degree of ionization of the copolymer [7]. The pK_a vs α plot is a regularly increasing curve, thus excluding the existence of a pH-induced conformational transition [4]. This conclusion is confirmed by the fact that the fluorescence emission spectrum of the cationic dye Auramine O (which has been proved to increase a hundredfold in the presence of hypercoiling polyelectrolytes) [8] does not change from that of the dye alone upon addition of MACP, even in the presence of TBA^+ as a counter-

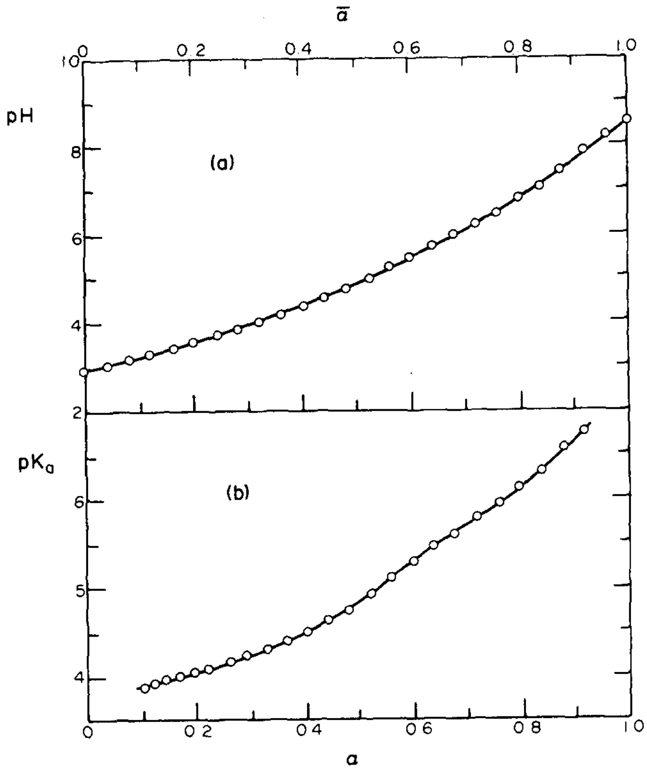

Fig. 1. (a) Potentiometric titration of MACP in water, at 25° with KOH; polymer concentration 10^{-2} equiv/l. (b) Apparent pK_a dependence on α for MACP aqueous solution titrated with KOH at 25°; polymer concentration 10^{-2} equiv/l.

ion, which is known to enhance the hypercoiling tendency of polymers bearing hydrophobic substituents [4, 9, 10]. It is evident that MACP behaves in water, as far as the free energy of ionization is concerned, as a monomeric bicarboxylic acid with very similar first and second ionization pK_a values [9]. More revealing are the calorimetric data of Fig. 2 in which the enthalpy of dissociation, $\overline{\Delta H}_{diss}$ (kcal/mol H^+) of MACP in water at 25° is plotted as a function of α. Here in fact the dissociation of *two* (first neighbour-

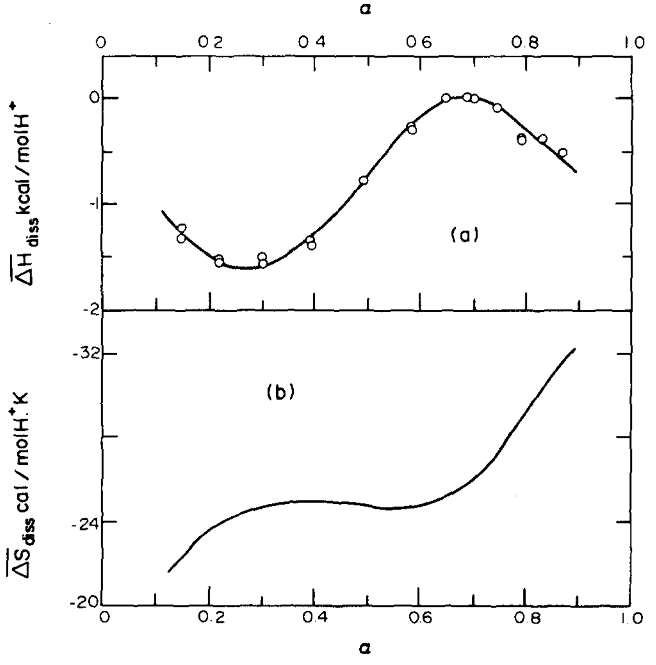

Fig. 2. Enthalpy change (a, kcal/mol H^+) and entropy change (b, cal/mol H^+ K) on proton dissociation of MACP, partially neutralized with KOH in water at 25°; polymer concentration 10^{-2} equiv/l.

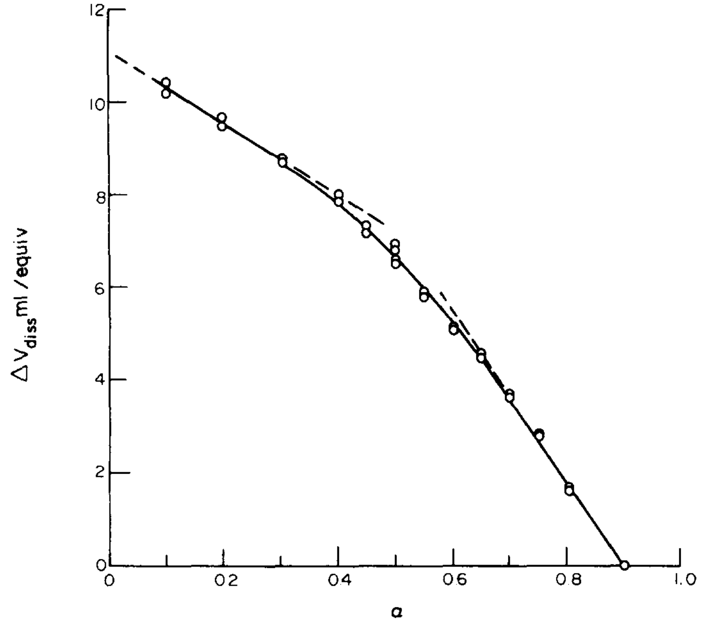

Fig. 3. Volume change in ml/equiv. on proton addition to the K^+ salt form of MACP in water at 25°; polymer concentration 10^{-2} equiv/l. The abscissae are to be read to the left.

ing) —COOH groups is discernible, although largely overlapping, and may be characterized by different enthalpic values. As a first approximation, we can assume for MACP an enthalpy of "first ionization" of at least -1.6 kcal/equiv, while the "second ionization" would have $\overline{\Delta H}_{diss} = 0$ approx. (see Fig. 2).

As a consequence, noting the potentiometric results of Fig. 1, one may immediately derive the dependence of the entropy of ionization ($\overline{\Delta S}_{diss}$) upon α for MACP in water ($\overline{\Delta S}_{diss} = \overline{\Delta H}_{diss}/T + 2.303\, R \cdot pK_a$; see Fig. 2).

The entropy causes, quite naturally, a decreasing function of MACP charge density, mainly because the number of water molecules engaged in the solvation of the ionized groups along the chains and the stiffness of the chains both increase with α. Charge dependent solvation effects for MACP are clearly shown by the dilatometric data of Fig. 3. In agreement with the trend exhibited by the $\overline{\Delta H}_{diss}$ (and $\overline{\Delta S}_{diss}$) values, we can distinguish three regions in the volume of protonation against α plot of Fig. 3. Up to $\alpha \simeq 0.3$, the differential volume of dissociation, $\overline{\Delta V}_{diss}$ (i.e. the slope of the initial linear portion of the plot), amounts to -9.3 ml/mol H^+ while, for $\alpha > \sim 0.7$, $\overline{\Delta V}_{diss}$ is -18.5 ml/mol H^+. These two values evidently represent the characteristic volume changes associated with the creation of one fixed charge and two neighbouring fixed charges, respectively, onto MACP chains. The linearity of the plot of Fig. 3 in the two extreme regions indicates that with MACP there are only small, if any, cooperative effects throughout the ionization process. This is of course quite different from the effect found with a variety of charged vinyl polymers in water, such as poly(acrylic acid), PAA [10], and with the copolymer of maleic acid with ethylene, MAE [10, 11]. The difference between the $\overline{\Delta V}_{diss}$ values for $\alpha \rightarrow 1$ and for $\alpha \rightarrow 0$ [$\Delta(\overline{\Delta V}_{diss})$] can also be revealing. In fact, for poly(carboxylic acids) and their low molecular weight analogues, $\Delta(\overline{\Delta V}_{diss})$ is known to increase with increasing extent of hydrogen bond formation between nearest neighbour carboxyl groups [9, 12].

Considering PAA and MAE as two examples for which such H-bond formation is very low and extensive respectively, we have: $\Delta(\overline{\Delta V}_{diss}) = -3$ ml/mol H^+ (PAA), and -14 ml/mol H^+ (MAE) in water at 25°. For MACP we find $\Delta(\overline{\Delta V}_{diss}) = -9$ ml/mol H^+, under similar experimental conditions. From the previous discussion, this would then indicate that carboxyl groups of MA residues in MACP are internally H-bonded only to a limited extent. Moreover, for MACP the integral volume change of dissociation, i.e. the total volume change associated with the increase in overall solvation brought about by charging the polymer molecule, becomes closer to that found with PAA than with MA.

In conclusion, our data show that MACP is built up by the enchainment of nearly independent pairs of carboxyl groups. The first ionization is favoured energetically with respect to the second ionization: the entropy loss in the latter process is, however, insufficient to make the difference between the associated free energies large enough as to render vicinal —COOH groups potentiometrically distinguishable.

The relatively poor solvation of vicinal carboxyl groups, which can explain such small entropy loss, may result from steric hindrances imposed by the cyclopentene residues. The latter could favour, probably for all α values, local conformations with *trans* vicinal ionizable groups and, at the same time, they could shield intrachain electrostatic interactions.

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