Thermochimica Acta, 142 (1989) 165–173
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMODYNAMICS OF THE PROTONATION OF SOME POLYELECTROLYTES

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(Received 14 June 1988)

ABSTRACT

Calorimetric measurements have been made at 25 °C in water to determine the heats of dilution and dissociation of some polyelectrolytes derived from natural amino acids. Similar measurements were made with their model small molecules to account for the polyelectrolyte effect. Potentiometric titrations were also carried out to determine the free enthalpy of dissociation of the polyelectrolytes as a function of the degree of dissociation. Both sets of data were used to calculate the variation of the entropy of dissociation. The experimental results are discussed in terms of the structure of the polymers and the arrangement of water around the charged groups.

INTRODUCTION

The thermodynamics of protonation (or dissociation) of natural or synthetic polyelectrolytes has been the subject of numerous works, especially for those undergoing a conformational transition such as a helix to coil transition or a compact to extended form transition [1–20]. In previous papers [18,19], we reported the synthesis and calorimetric study of a copolymer derived from a natural amino acid, alanine, namely poly(*N*-methacryloyl-L-alanine-*co*-*N*-phenylmethacrylamide). This copolymer undergoes a compact to extended form conformational transition and the free enthalpy and entropy changes of this transition were deduced from potentiometric and calorimetric measurements.

This paper reports on the study of a series of three polyacids derived from alanine, aspartic acid and glutamic acid, poly(*N*-methacryloyl-L-alanine) (PNMA), poly(*N*-methacryloyl-L-aspartic acid) (PNMAS) and poly(*N*-methacryloyl-L-glutamic acid) (PNMG) respectively (see Fig. 1: $R = CH_3$, PNMA; $R = CH_2COOH$, PNMAS; $R = CH_2$–CH_2COOH, PNMG).

These three polymers behave as normal polyelectrolytes i.e. they undergo a progressive expansion of the macromolecular chain when dissociation of the carboxyl groups occurs [21]. For the purposes of comparison, the

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Fig. 1. Formulae of the samples.

corresponding model molecules *N*-isobutyroyl-L-alanine (NIBA), *N*-isobutyroyl-L-aspartic acid, (NIBAS) and *N*-isobutyroyl-L-glutamic acid (NIBAG) were also studied. The comparison between the two series of samples allows the distinction between the ionization of isolated carboxyl groups and the effect of long range interactions between the charges in the side chains of the polymer (polyelectrolyte effect).

EXPERIMENTAL

Materials

The synthesis of the PNMA, PNMG and PNMAS polymers and of the model molecules has been described in a previous paper [22] (see Fig. 1).

Aqueous solutions were prepared by weighing and dissolving the samples in water. Their exact titre was determined by acid–base titration in order to account for the hydration water.

Methods

Potentiometric titrations

Potentiometric titrations were performed at $25 \pm 0.1^\circ$C using a fully automatic titration apparatus made up of a Radiometer pHM 65 pH meter, a Gilmont microsyringe and a Schott N 65 combined electrode. The titration was monitored by a HP 9825 computer.

Calorimetric measurements

Calorimetric measurements were made at $25 \pm 0.01^\circ$C using a Calvet-type batch differential microcalorimeter (Setaram, France). 100 ml inox cells containing a glass or Pyrex inner tube of varying volume were used. This allows the mixing of solutions having varying volume ratios. Nevertheless, in most cases, the volume ratio was 1 : 1.

Before being placed in the calorimeter, the cells were preheated to a temperature as close as possible to the inner temperature. When thermal equilibrium was attained, the calorimeter was rocked two or three times to ensure complete mixing of the solutions. The heat signal was recorded and amplified as a function of time. The heat effect (in Joules) was obtained after integration of the experimental curve.

From the experimental point of view, it is more precise to record heats of protonation than heats of dissociation to avoid the contribution from the heat of formation of water ($\Delta H = 55.815$ kJ mol^{-1}) [9] which is 10–15 times larger than the mean heat of dissociation of our samples.

In the experiments on the heat of protonation, 1 volume of the sample solution at a concentration of 2–3% by weight at a degree of neutralization α, (adjusted with NaOH) and 1 volume of an HCl solution were placed in the two compartments of the mixing cell. The amount of HCl was adjusted so that the change of the degree of neutralization α_1 to α_2 ($\Delta\alpha$) was no larger than 0.06 in each experiment. This procedure is essential because the heat of protonation (or dissociation) of a polyacid depends on its degree of dissociation. In addition, overall heats of protonation (from $\alpha = 1$ to $\alpha = 0$) were also recorded for the small model molecules.

Separate dilution experiments were also carried out on the same sample solutions, replacing HCl solutions by water (1 : 1 dilutions). The results were used to correct the heat of protonation data for sample dilution effects. In the same way, the small corrections for the heats of dilution of HCl were also obtained, in good agreement with calculations based on the values of the National Bureau of Standards [23].

In the following, the results are presented as $\Delta H_{\text{diss}} = f(\alpha)$ where $\alpha = (\alpha_1 + \alpha_2)/2$ and ΔH_{diss} is the enthalpy of dissociation at a given α value, calculated as

$$\Delta H_{\text{diss}} = -(Q - Q_{\text{d}_1} - Q_{\text{d}_2})/m \tag{1}$$

where Q is the recorded heat effect obtained by adding m mol of HCl to a solution of the partially neutralized sample, Q_{d_1} is the heat of dilution of the sample and Q_{d_2} is the heat of dilution of HCl.

The calorimeter was calibrated for the Joule effect and tested by measuring the heat of dilution of NaCl solutions [24].

RESULTS AND DISCUSSION

Heats of dilution

Figures 1 and 2 show the variation of the heat of 1 : 1 dilution versus α for the model molecules NIBA, NIBAS and NIBAG, and the polymers PNMA, PNMAS and PNMG respectively.

For NIBA (Fig. 2), the value of ΔH_{d} is independent of α within experimental error. The mean value is -290 ± 30 J mol^{-1}. For NIBAS and NIBAG, the heat of dilution decreases at values of α greater than 0.4–0.5 i.e. the process becomes more exothermic. At low α values, hydrogen bonds

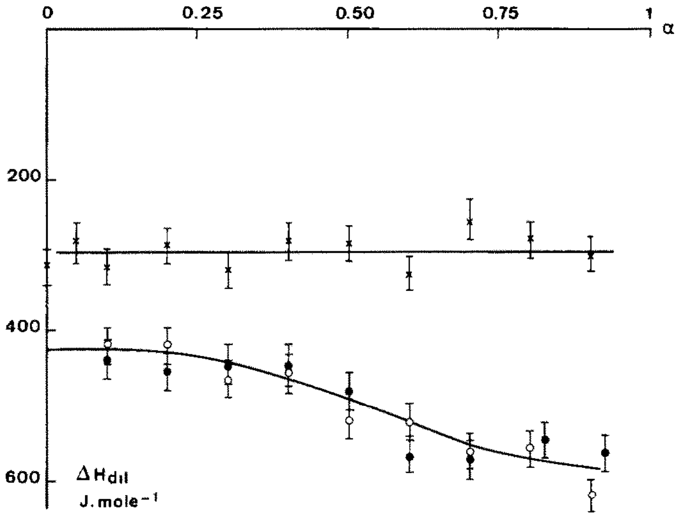

Fig. 2. Variation of the heat of dilution versus α for the model molecules: ×, NIBA; ○, NIBAG; ●, NIBAS.

exist between the two carboxyl groups in NIBAS or NIBAG. The dilution probably induces the breaking of these hydrogen bonds which is an endothermic process. At $\alpha \sim 0.4$, the second carboxyl group begins to ionize and hydrogen bonds are already broken, which explains why the dilution is more exothermic beyond this value.

For PNMA, PNMG and PNMAS, the ΔH_d values are always less negative than for the model molecules (the dilution of the polymer is less exothermic) (Fig. 3). This may be explained by a chain effect associated with a change in the structure of the solvent: the dissolution of the polymer chain in water requires the breaking of some water clusters, which is an endothermic process. Similar results were obtained with poly(acrylic acid), the dilution of which is less exothermic than that of its model molecule, propionic acid [25].

For all the polymers, the heat of dilution suddenly decreases between $\alpha = 0.3$ and $\alpha = 0.5$. Previous works have shown that no conformational change occurs for these samples and that they only undergo a progressive expansion of the polymer chain upon charging of the carboxyl groups [21]. One explanation is that strong intramolecular hydrogen bonds are formed between the carboxyl groups of the side chains, especially when the polymers are un-ionized. Upon dilution, some hydrogen bonds are broken and this endothermic process could explain the rather low heats of dilution at $\alpha < 0.3$. The dilution of poly(sodium acrylate) is also more exothermic than the dilution of poly(acrylic acid) [25]. Another explanation is based on Manning's theory, which predicts that the critical charge density at which the ion condensation behaviour appears is $\alpha = 0.3$. In this case, the variation

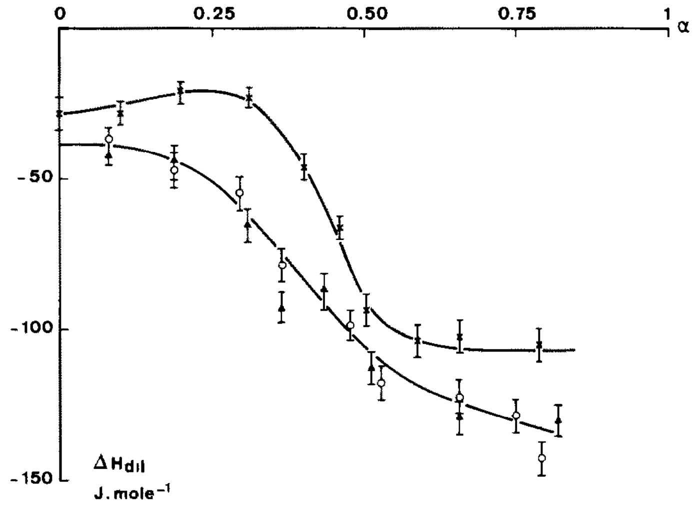

Fig. 3. Variation of the heat of dilution versus α for the polymers: ×, PNMA; ▲, PNMAS; ○, PNMG.

in ΔH_d would be due to a change in the arrangement of the water molecules around the ions and polyions [26].

Heats of dissociation

As expected for a small molecule containing only one ionizable group, the heat of dissociation of NIBA is independent of the average degree of dissociation as shown in Fig. 4. Partial protonation experiments ($\Delta\alpha < 0.06$) give $\Delta H_{\mathrm{diss}} = -1160 \pm 230$ J mol^{-1} whereas overall protonation experiments ($\Delta\alpha \sim 0.95$) give $\Delta H_{\mathrm{diss}} = -1310 \pm 20$ J mol^{-1}.

For NIBAS and NIBAG which are dicarboxylic acids, the heat of dissociation of the second carboxyl group, beyond $\alpha = 0.5$, is more negative than that of the first one (Fig. 4), as is generally observed for this class of compounds [27,28].

The heat of dissociation of the polymers depends on the degree of dissociation (Fig. 5). The difference between ΔH_{diss} and ΔH^0, (the extrapolated value at $\alpha = 0$) becomes more negative with increasing dissociation. For the three polymers, the ΔH^0 value is close to the value obtained for the corresponding model molecule. This behaviour is very similar to that of poly(acrylic acid) (PAA) and other poly(carboxylic acids) [8,13].

For PNMA, ΔH_{diss} rapidly decreases between $\alpha = 0$ and $\alpha = 0.3$ then remains nearly constant up to $\alpha = 0.8$. The break at $\alpha = 0.3$ was also observed for PAA [8,13] and has been theoretically predicted and attributed to ion condensation [8,13,26]. For PAA, the excess enthalpy of dissociation at high α values is about -4.6 kJ mol^{-1} (5, 8, 13), against -1.88 kJ mol^{-1} for PNMA. This is explained by the longer side chains of PNMA, which

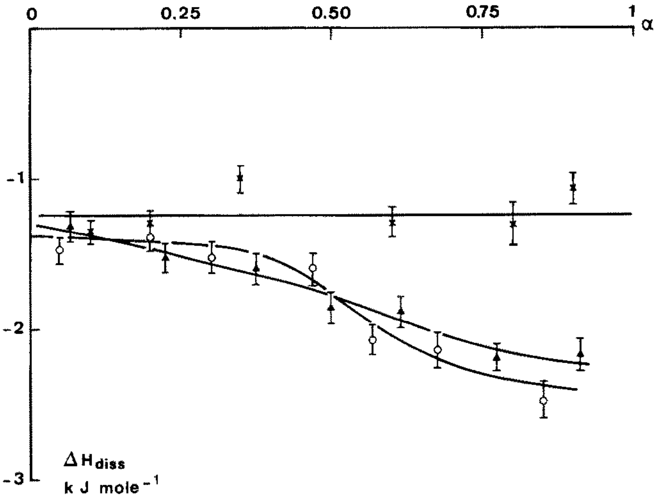

Fig. 4. Variation of the heat of dissociation versus α for the model molecules: ×, NIBA; ○, NIBAG; ▲, NIBAS.

increases the average distance between the carboxylate groups and thus decreases the electrostatic interactions. In other words, ion condensation on the polymer is less important with PNMA than with PAA. With PNMAS and PNMG in contrast, the excess enthalpy of dissociation is close to that of PAA because the distance between the two carboxylate groups in the side

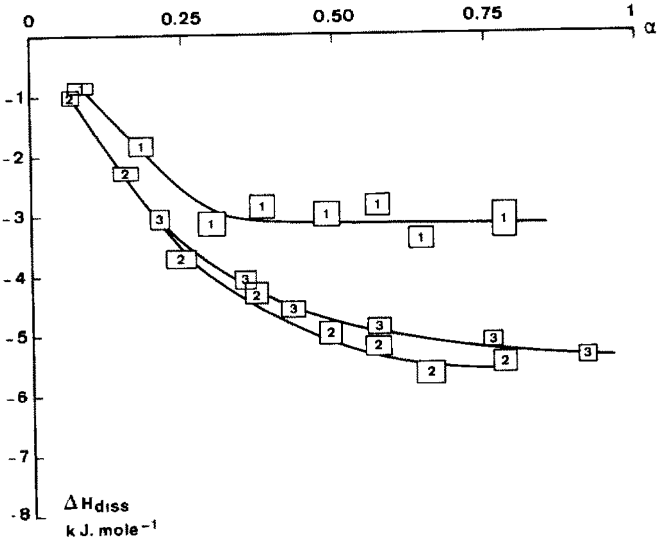

Fig. 5. Variation of the heat of dissociation versus α for the polymers: 1, PNMA; 2, PNMAS; 3, PNMG. Error area takes into account the error in ΔH_{diss} and the change in the degree of dissociation.

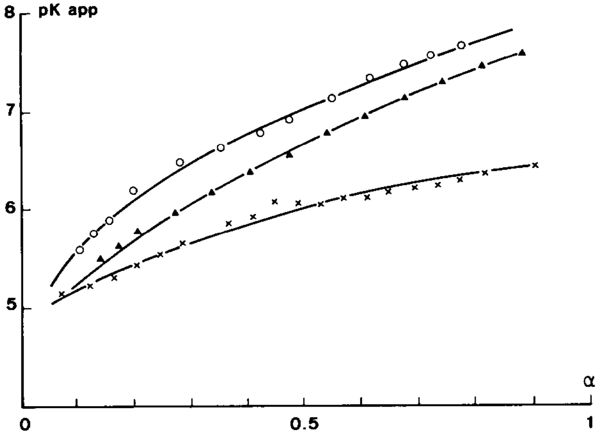

Fig. 6. Variation of the apparent ionization constant pK_{app} versus α for the polymers: ×, PNMA; ▲, PNMAS; ○, PNMG.

chain is nearly the same though they are far from the main chain of the polymer (the two carboxyl groups are separated by 2 carbon atoms in PAA and PNMAS, and by 3 carbon atoms in PNMG).

From the potentiometric titration data, the apparent ionization constant pK_{app} may be calculated by

$$pK_{app} = pH - \log(\alpha/(1-\alpha)) \tag{2}$$

Figure 6 shows the variation of pK_{app} versus α for the three polymers. In all cases, pK_{app} increases smoothly with α, reflecting the increasing electrostatic interactions between the carboxylate groups when the degree of dissociation increases.

At high α values, the pK_{app} is much higher for PNMAS and PNMG because of the presence of two carboxyl groups.

For each α value, the free enthalpy of dissociation ΔG_{diss} may be calculated according to

$$\Delta G_{diss} = 2.303RT(pK_{app}) \tag{3}$$

and then the value of the entropy of dissociation ΔS is obtained by

$$\Delta S_{diss} = (\Delta H_{diss} - \Delta G_{diss})/T \tag{4}$$

Figure 7 shows the variation of ΔS_{diss} versus α for the three polymers together with that relative to PAA [8]. In all cases, the entropy of dissociation is more and more negative with the charging of the carboxyl groups. This may be attributed to the immobilization of the water molecules which organize around the charged groups with a loss of entropy.

The entropy change is always lower for PNMA than for PAA, indicating a weaker water immobilization. This is related to a lower charge density due to longer side chains.

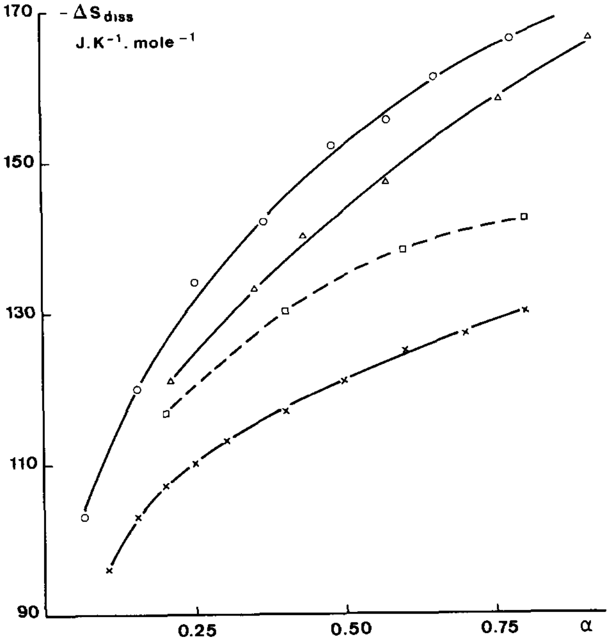

Fig. 7. Variation of the entropy change of dissociation versus α for the polymers: ×, PNMA; △, PNMAS; ○, PNMG; □, PAA.

In contrast, the presence of two carboxyl groups in PNMAS and PNMG creates a high local electrostatic field which strongly retains the water molecules.

These results emphasize the role played by the structure of the polymers with direct effect on the entropy and enthalpy of ionization and, thus, on the free energy which is frequently used to represent the ionization behaviour of a polyelectrolyte.

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