The Influence of Various Monovalent Counterions on the Thermodynamics of Proton Dissociation of Polyacrylic Acid

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Differential enthalpies of proton dissociation of polyacrylic acid have been determined calorimetrically as a function of the degree of dissociation α in the presence of K^+, Cs^+, NH_4^+ and $(CH_3)_4N^+$ at 298.15 K. The apparent dissociation constant at various α was determined from potentiometric measurements and the Gibbs free energy and the entropy changes were calculated.

Up to α about 0.4 the enthalpy and entropy changes in the presence of the four ions in this study as well as Na^+ (previously reported) are about the same and decrease in a similar manner. At higher α, ΔH_a for Na^+, K^+ and Cs^+ are close together and vary only slightly with α but showing a trend towards less negative values above $\alpha = 0.75$. The entropy changes for the alkali metal ions are the same above $\alpha = 0.5$. The enthalpy and entropy changes become significantly less negative for NH_4^+ and significantly more negative for $(CH_3)_4N^+$ compared to the alkali metal ions at higher degrees of dissociation.

A comparison of the experimental values of ΔH_a for Na^+, K^+ and Cs^+ with theoretical values derived from a solution of the Poisson-Boltzmann equation shows a qualitative agreement except at the highest α. The differences at higher α between the theoretical and experimental curves for ΔH_a may for NH_4^+ and the alkali metal ions be due to complex formation between the cations and the polyanion while the point charge approximation in the theoretical model may be the reason for the discrepancy for $(CH_3)_4N^+$.

In a previous paper the enthalpy of proton dissociation ΔH_a of polyacrylic acid in sodium

chloride solution as function of degree of dissociation α at three different temperatures was reported.[1] The experimental values were compared with a theoretical calculation of ΔH_a based on a solution of the Poisson-Boltzmann equation. The calculated ΔH_a is of the right order of magnitude and shows a correct α-dependence. The calculated decrease in ΔH_a is about -2 kJ mol^{-1} when α changes from 0 to 1. However, the observed enthalpy changes are more exothermic. The predicted temperature dependence of ΔH_a does not agree with experimental findings. Thus, although the electrostatic model provides an important insight into the behaviour of polyacrylic acid dissociation it can only partly describe interactions in the system. The size and nature of the counterions can be expected to influence the dissociation thermodynamics. Selective interaction between monovalent counterions and other polycarboxylates has been observed.[2] To study the influence of variation of counterion, ΔH_a of polyacrylic acid has been determined from calorimateric measurements at 298.15 K in the presence of K^+, Cs^+, NH_4^+ and $(CH_3)_4N^+$. Some additional experiments at higher α were made with Na^+ as counterion. Values of the apparent dissociation constant were derived from pH-measurements.

EXPERIMENTAL

Solid poly(acrylic acid) $[-CH_2CH(COOH)-]_n$ (Aldriche-Europe) with an average molecular weight of 250 000 was used without further treatment. The purity was checked by pH titration and was better than 97.0 ± 0.5 wt%. The polyacrylate + polyacrylic acid solutions (MePA + PAH, Me $= (CH_3)_4N^+$, Cs^+, K^+, Na^+ and NH_4^+) were

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Table 1. Differential enthalpies of dissociation ΔH_a of polyacrylic acid at various degrees of dissociation $\bar{\alpha}$ and total PAH concentration of 0.05 monomol kg^{-1} and Me$^+$ counterion concentration of 0.05 mol kg^{-1} (Me$^+$ = Na$^+$, K$^+$, Cs$^+$, NH$_4^+$, (CH$_3$)$_4$N$^+$) at 298.15 K.

$\bar{\alpha}$	ΔH_a/kJ mol^{-1} Na$^+$	K$^+$	Cs$^+$	NH$_4^+$	(CH$_3$)$_4$N$^+$
0.07	−0.86[a]	−1.67	−1.89	−0.92	−0.51
0.16	−2.19[a]	−2.23	−2.60	−1.92	−1.51
0.21	−	−	−2.81	−	−
0.26	−3.29[a]	−3.35	−3.48	−2.82	−2.67
0.36	−3.91[a]	−3.71	−3.96	−3.21	−3.41
0.46	−	−4.19	−4.17	−3.34	−4.03
0.56	−4.37[a]	−4.30	−4.47	−3.22	−4.71
0.66	−	−4.27	−	−2.92	−5.58
0.76	−4.64[a]	−4.15	−4.49	−2.49	−6.83
0.86	−4.36	−4.02	−	−1.51	−8.08
0.91	−4.02	−	−	−	−

[a] From Ref. 1.

prepared by neutralizing a stock solution of PAH with aqueous MeOH to the desired degree of neutralization α. Solid MeCl and water were then added to give solutions containing 0.05 mol kg^{-1} of Me$^+$ and 0.05 monomol kg^{-1} of (PAH + PA$^-$). The CsOH solution was freed from carbonate by running it through an ion-change column of Amberlite IRA 400. The samples of MeCl (of analytical grade) were dried before use. The molality of the HCl solution used in the calorimetric experiments was found from pH titration to be 0.5053 ± 0.0003 mol kg^{-1}.

The calorimetric measurements were made using an LKB-8721 reaction-solution calorimeter with a 100 cm^3 glass reaction vessel. The experiments were performed and evaluated as described in Ref. 3. The pH-measurements were made using a Radiometer GK 2401C combination electrode.

RESULTS

In the calorimetric measurements 0.4 × 10^{-3} mol HCl (0.8 g of a 0.5 mol kg^{-1} solution) was added to 100 cm^3 of solution containing 0.05α mol kg^{-1} MePA + 0.05(1-α) mol kg^{-1} PAH + 0.05(1-α) mol kg^{-1} MeCl. Three to four experiments were made at each α. The pH of the initial and final solutions was
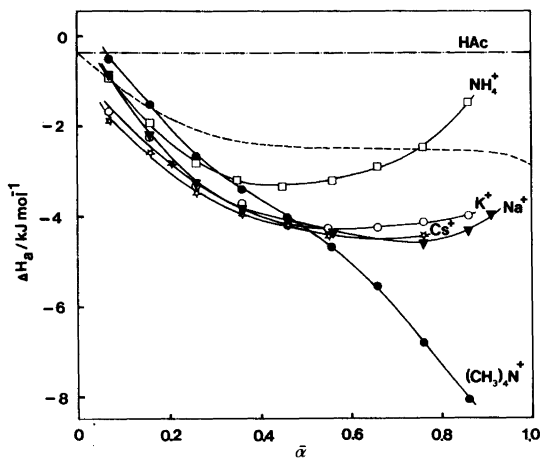

Fig. 1. ΔH_a of polyacrylic acid at various degrees of ionization α in the presence of various counterions. − − −, Theoretical curve (Ref. 1).

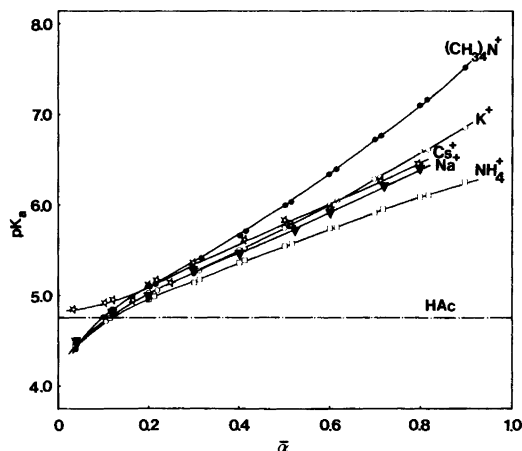*Fig. 2.* Apparent pK_a of polyacrylic acid at various α in the presence of various counterions.

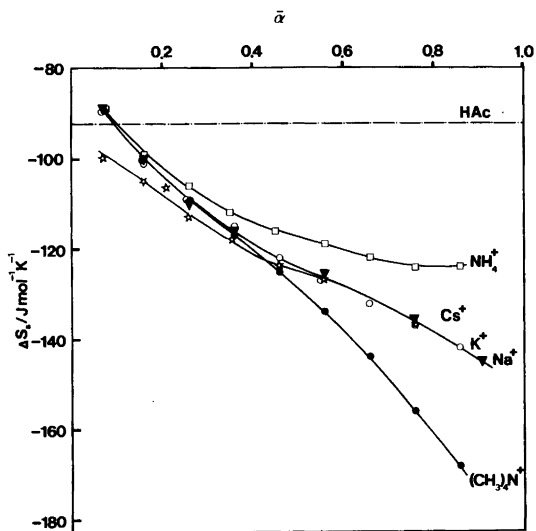*Fig. 3.* ΔS_a of polyacrylic acid at various degrees of ionization in the presence of various counterions.

measured and the amount of HCl not reacting with the polyacrylate ion was estimated. The change in the degree of dissociation was 0.08 except at $\alpha = 0.10$ where it was 0.06. The observed enthalpy changes ΔH_{obs} are the sum of the enthalpy of protonation of polyacrylate ion and the enthalpy of dilution of HCl. The enthalpy of proton dissociation ΔH_a was calculated from

$$\Delta H_a = -\Delta H_{obs} + \Delta H_{diln}(HCl)$$

where $\Delta H_{diln}(HCl)$ denotes the enthalpy change for the infinite dilution of 0.51 mol kg^{-1} HCl. At 298.15 K, $\Delta H_{diln}(HCl)$ is -1.176 kJ mol^{-1}.[4] A more detailed description of the evaluation of ΔH_a is given in Ref. 1. Values of ΔH_a found in the present study are given in Table 1. Previously reported values in the presence of Na$^+$ are included. The mean degree of dissociation $\bar{\alpha}$ is shown in the first column and the found values of ΔH_a in the presence of the indicated cation are shown in the following columns. The estimated uncertainty expressed as twice the overall standard deviation of the mean is 0.10 kJ mol^{-1}. To illustrate the α-dependence for the various counterions, values of ΔH_a are plotted against $\bar{\alpha}$ in Fig. 1. Included in the figure is a curve representing the theoretical values of ΔH_a for polyacrylic acid as function of α calculated from a solution of the Poisson-Boltzmann equation.[1] The enthalpy of

dissociation of acetic acid is assumed to equal the enthalpy of proton dissociation of an isolated carboxyl group.

Values of the apparent dissociation constant were calculated from the results of the pH measurements: $pK_a = pH + {}^{10}\log(1-\alpha)/\alpha$. The found values are summarized in Fig. 2. Estimates of the entropy change ΔS were calculated from

$$\Delta S_a = \Delta H_a/T - R \ln 10 pK_a$$

Fig. 3. shows a plot of ΔS_a as function of $\bar{\alpha}$ for the various counterions, ΔS_a for acetic acid is included in the figure.

DISCUSSION

The entropy changes ΔS_a are strongly negative and dominate the proton dissociation equilibrium of polyacrylic acid. Although the enthalpy changes ΔH_a become more exothermic with increasing α, ΔS_a decreases more rapidly leading to increasing values of pK_a. Up to α of 0.4 there are only minor differences in ΔH_a and ΔS_a between the various counterions. There is, however, a small but significant spread at the lowest α which may indicate specific interaction between Cs$^+$ and the undissociated polyacid. At the higher α the curves representing ΔH_a and ΔS_a continue to lie close together for the three alkali metal ions. There is a qualitative agreement between the theoretical curve calculated for ΔH_a and the experimental curves except at the highest α where the experimental curves indicate a trend towards less exothermic values. The differences between the Na$^+$, K$^+$ and Cs$^+$ ions are apparently too small to have any significant influence on the measured properties of the ionization of polyacrylic acid.

It sppears that the NH$_4^+$ is more effective and the large (CH$_3$)$_4$N$^+$ less efficient than the alkali metal ions in screening the carboxylate groups and thus reducing the effective charge density of the polyion. In the theoretical calculation of ΔH_a the counterions are treated as point charges. This approximation can be expected to give significant errors for systems with large ions and this is probably the main reason for the divergence of the experimental curve for (CH$_3$)$_4$N$^+$ from the calculated curve in Fig. 1. A plot of ΔH_a against ΔS_a gives for (CH$_3$)$_4$N$^+$ an approximately straight line over the whole α-range with a slope of about -100 K. The curves for the

smaller ions are linear and parallel to the line for $(CH_3)_4N^+$ up to α about 0.5. At higher α the curve for NH_4^+ turns sharply upwards while the curves for the alkali metal ions bend away from the $(CH_3)_4N^+$ line to become almost parallel to the ΔS_a-axis. Alkali metal ions are known to form complexes with ions of di- and tricarboxylic acids [5,6] and it seems likely that complex formation will also occur in polyacrylate solutions. The NH_4^+ ion has the possibility to form hydrogen bonds which could lead to more extensive complex formation and accordingly more effective screening than the alkali metal ions. The tendency for $(CH_3)_4N^+$ to interact specifically with the polyacrylate ion should be small and non-specific interactions can be expected to dominate. The differences between the theoretical and experimental curves for ΔH_a (Fig. 1) may therefore for the smaller ions be due to specific interactions between the cations and the polyanion while for $(CH_3)_4N^+$ it may be due to the point charge approximation in the theoretical model.

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