Hydrolysis of Cationic Polyacrylamides

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Synopsis

The alkaline hydrolysis of two acrylamide-based polyelectrolytes has been investigated. The experiments were carried out in buffered aqueous solutions in the pH range of 3.5–8.5 and in the temperature range of 22–50°C. ^{13}C-NMR analysis of the hydrolysis product showed that choline chloride was the substance released upon hydrolysis. The decrease in charge density of the copolymer due to the hydrolysis was studied by polyelectrolyte titration and nitrogen analysis. The results show that the rate of hydrolysis increased with increasing pH or increasing temperature. In the hydrolysis of C-PAM 1 at 22°C and pH 6, the half-life of the cationic groups was 10 days. At pH 7 the half-life was shorter, 24 h, and at pH 8.5 the reaction was very fast with a half-life of about 0.25 h. The charged groups on C-PAM 2, the polymer with the higher charge density of the two polymers studied, have somewhat longer half lives than those on C-PAM 1. This can be explained by the structure of the polymers.

INTRODUCTION

The hydrolysis of ester groups in acrylamide-based cationic copolymers, shown in Figure 1, has been described by a number of authors.[1-3] In neutral or alkaline solutions the reaction is much faster than the hydrolysis of acrylamide units to acrylic acid units. The kinetics of the latter reaction has recently been described.[4] Detailed studies of the hydrolysis of ester groups in cationic acrylamides have, however, been very limited, despite the considerable practical importance of the reaction. Therefore, the rate of hydrolysis was detected under conditions representative for some industrial applications.

In the present investigation, polyelectrolyte titration,[5] micronitrogen analysis, and ^{13}C-NMR spectroscopy have been used to study the alkaline hydrolysis of acrylamide-based polyelectrolytes. Elemental analysis and NMR has also earlier been used to characterize polyacrylamides.[6,7]

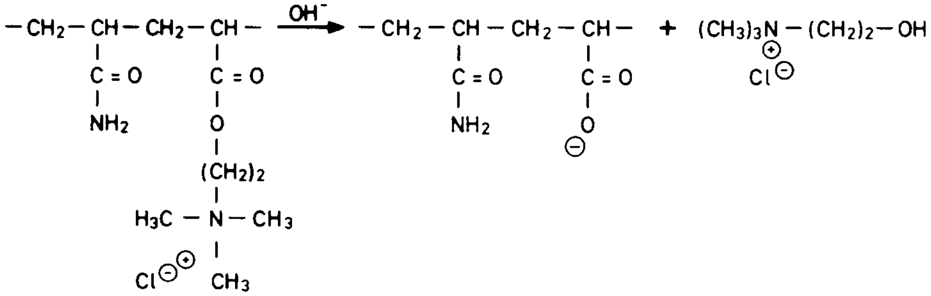

Fig. 1. The expected hydrolysis reaction of the cationic polyelectrolytes.

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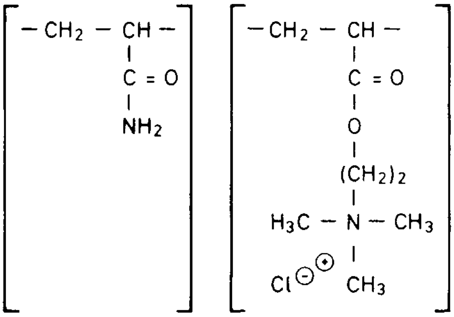

Fig. 2. The chemical structure of the monomeric units in the cationic polyacrylamides, acrylamide, and *N,N*-dimethylaminoethylacrylate quaternized with methyl chloride.

MATERIALS

The polymers used in the experiments, C-PAM 1 and C-PAM 2, were two cationic copolymers with different ratios of cationic *N,N*-dimethylaminoethylacrylate quaternized with methyl chloride to acrylamide. The structure of the monomers is given in Figure 2. The amounts of cationic groups per gram dry copolymer, further on referred to as charge densities of the copolymers, were 2.4×10^{-3} and 4.0×10^{-3} eq/g and the intrinsic viscosities were 7.6 and 5.8 dL/g, respectively. The charge densities were determined by polyelectrolyte titration. These copolymers were kindly supplied by Allied Colloids U.K. and were delivered as powders and used without further purification.

The buffer solutions and hence the pH levels investigated were:

pH ≈ 3.5—potassium hydrogen phthalate/hydrochloric acid

pH ≈ 5 —potassium hydrogen phthalate/sodium hydroxide

pH ≈ 6 —potassium dihydrogen phosphate/sodium hydroxide

pH ≈ 7 —potassium dihydrogen phosphate/sodium hydroxide

pH ≈ 8.5—borax/sodium hydroxide

In the polyelectrolyte titrations, an anionic polymer, potassium polyvinylsulfate (KPVS) from Wako Pure Chem. Ltd., Japan, was used and the cationic indicator used was orthotoluidine blue (OTB). Both KPVS and OTB were received as powders and used without further purification. The water used in the experiments had a conductivity of less than 1.0 μS/cm. All inorganic electrolytes used were of analytical grade.

METHODS

The experiments were performed in glass vessels which were kept in thermostated water baths at 30, 40, and 50°C and at room temperature, 22°C. The stock solutions of the copolymers had a concentration of 0.5 g/L and were kept in a refrigerator at 5°C and pH 5. To 80 mL of polymer solution a buffer was added and the total volume was adjusted to 100 mL. The total ionic strength of the solution, calculated from the addition of inorganic electrolyte, was in all cases 4×10^{-3} *M*.

In order to study the decrease in charge density of the copolymer due to the expected alkaline hydrolysis, small samples were taken from the reaction vessels and polyelectrolyte titrations were performed according to a method similar to that described by Horn.[5] Before titration HCl was added to the samples to avoid the formation of an internal salt between the quaternery amino groups and the carboxylic acid groups formed during the hydrolysis.

In order to determine the amount of choline chloride released upon hydrolysis, 500 mL of the samples were filtrated in a Amicon 8400 ultrafiltration cell (Amicon Corporation, Danvers, MA). The membrane used had a molecular mass cutoff of 30,000. No detectable amount of copolymer passed through the membrane. The nitrogen concentration in the filtrate was measured with a nitrogen analyzer from Antek Instruments, Inc. Houston, Texas (Pyroreactor 772 and Nitrogen Detector 720). Tetramethylammoniumbromide (TDBA) was used as internal standard.

In order to confirm the structure of the product of the hydrolysis, a ^{13}C-NMR measurement was performed. The filtrate, collected according to the procedure outlined earlier, was evaporated to dryness and the dry substance was dissolved in D_2O. A small amount of dioxane was added as reference.

RESULTS AND DISCUSSIONS

Products Formed during Hydrolysis

The expected product of the alkaline hydrolysis according to the reaction shown in Figure 1 is choline chloride. When the^{13}C-NMR spectrum for the hydrolysis product was compared with a reference spectrum for choline chloride,[8] good agreement was indeed found. This indicates that the reaction shown in Figure 1 is responsible for the decrease in charge density of cationic polyacrylamide upon storage. A gravimetric analysis performed after a reaction time of 24 h at pH 8.5 and 22°C showed that the yield of choline chloride was 140 mg, which is the amount expected when 250 mg of C-PAM 2 is completely hydrolyzed.

Rate of Hydrolysis

In Figure 3 the decrease in charge density and the amount of choline chloride formed are shown as a function of time. The decrease in charge density corresponds well to the increase in the amount of nitrogen in solution, which on a molar basis is equal to the amount of choline chloride released. Both polyelectrolyte titration and nitrogen analysis can obviously be used to follow the hydrolysis reaction.

An increase in pH or temperature leads, as expected, to an increase in the rate of the hydrolysis (Figs. 4–7). At pH 5 and a temperature of 22°C no hydrolysis can be detected during a period of 24 h, but when the polyelectrolyte solutions were stored at 22°C for a period of 13 days, a small decrease in charge density was observed as shown in Table I. At pH 3.5 the loss in

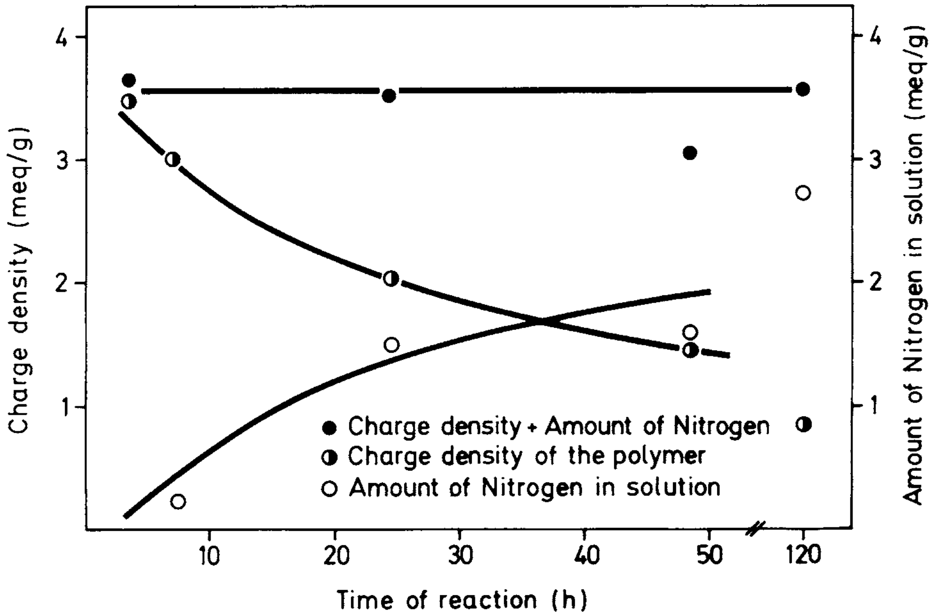

Fig. 3. The decrease in charge density as measured by polyelectrolyte titration, the amount of choline chloride formed, and the sum of these quantities after different reaction times at pH = 7.0 and temperature = 22°C for C-PAM 2: (●) charge density + amount of nitrogen; (◑) charge density of the polymer; (○) amount of nitrogen in solution.

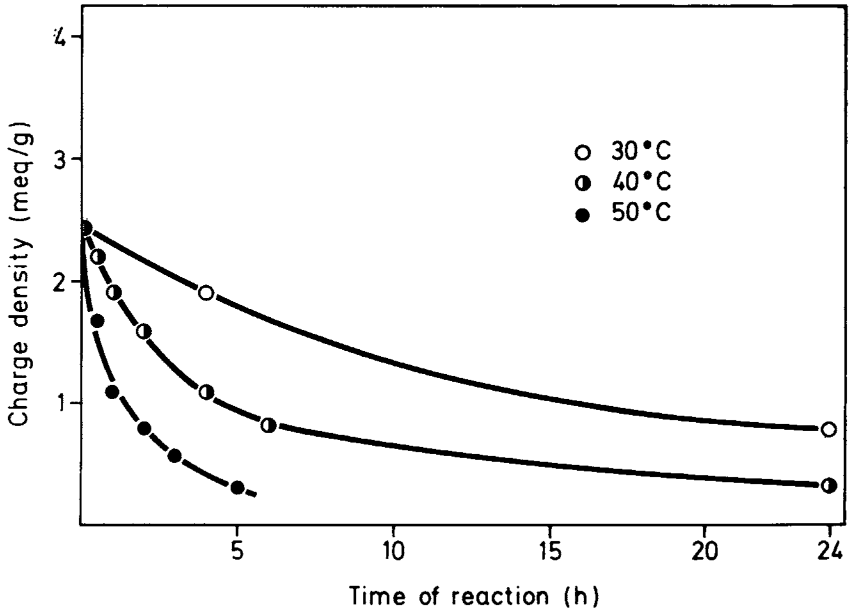

Fig. 4. The charge density as a function of time of reaction at different temperatures (°C) for C-PAM 1: (○) 30; (◑) 40; (●) 50.

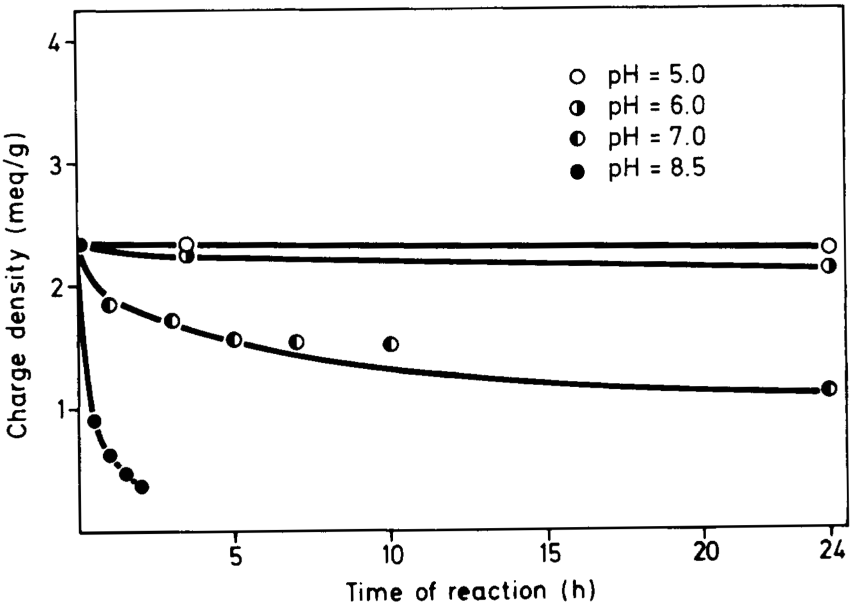

Fig. 5. The charge density as a function of time of reaction at different pH values for C-PAM 1: (○) 5.0; (◑) 6.0; (◐) 7.0; (●) 8.5.

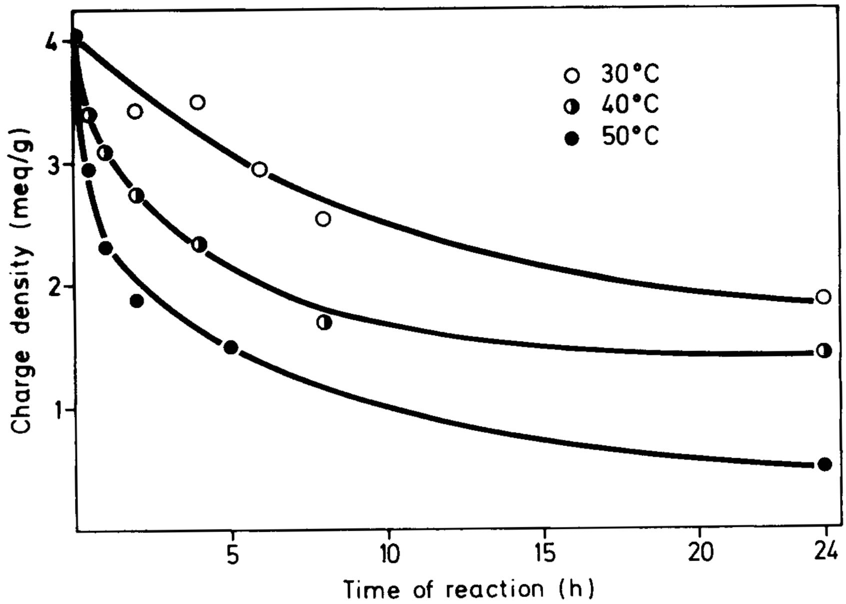

Fig. 6. The charge density as a function of time of reaction at different temperatures (°C) for C-PAM 2: (○) 30; (◑) 40; (●) 50.

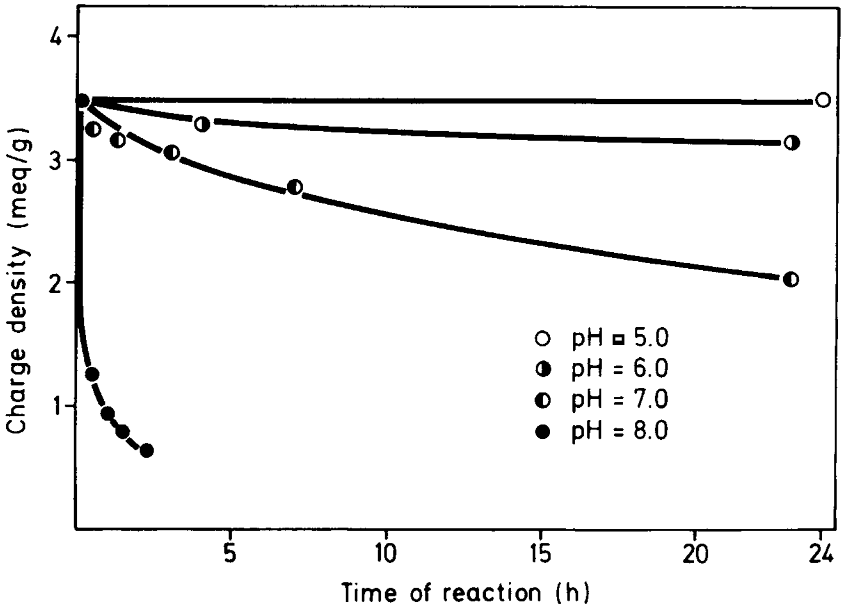

Fig. 7. The charge density as a function of time of reaction at different pH values for C-PAM 2: (○) 5.0; (◑) 6.0; (◐) 7.0; (●) 8.0.

charge density is also very small during a reaction time of 24 hours, as shown in Table II.

The half-lives of the cationic groups on the copolymers are compared in Table III. It is seen that the cationic groups have a somewhat longer half-life on C-PAM 2 than on C-PAM 1 at pH values of 6 and 7. An explanation could be that the carboxylic groups formed during the reaction reduce the local concentration of hydroxide ions in the vicinity of the copolymer chains and that the reaction is consequently[9-11] inhibited. Since C-PAM 2 has a higher initial charge density, the inhibition effect will be more pronounced for this polymer.

TABLE I

Charge Density of the Polyelectrolyte Solutions When Stored at 22°C and pH = 5.0 ± 0.2

	Time of reaction (days)					
	0	1	4	6	12	13
Charge density (meq/g) C-PAM 1	2.5	2.4				2.0
Charge density (meq/g) C-PAM 2	3.5	3.6	3.4	3.4	3.2	3.1

TABLE II

Charge Density of the Polyelectrolyte Solution C-PAM 2 When Stored at 22°C and pH = 3.5 ± 0.2

	Time of reaction (hours)	
	0	23
Charge density (meq/g)	4.0	3.9

TABLE III
Half-Lives of the Cationic Groups on C-PAM 1 and C-PAM 2 at 22°C and Different pH Values

pH	C-PAM 1	C-PAM 2
6	10 days	14 days
7	24 h	62 h
8.5	≈ 0.25 h	≈ 0.25 h

At pH = 8.5 the reaction is so fast that no significant difference between the two copolymers can be detected.

A further mathematical treatment of the data according to standard kinetic theories gave an ambiguous result. This may be due to the change in the structure of the polymer during the hydrolysis reaction.

The anionic acrylate groups formed during the hydrolysis can form an internal salt with the cationic trimethylaminoethyl groups. This formation of an internal salt is a possible explanation of a noticeable increase in the turbidity of the solution which occurs when the polyelectrolyte has lost more than approximately 80% of its initial charge. At this point the charge density can no longer be detected by polyelectrolyte titration as the end point is not sufficiently sharp.

SUMMARY

When aqueous solutions of cationic polycarylamid-based copolymers are hydrolyzed, choline chloride is released, as shown by ^{13}C-NMR spectroscopy, and the cationic groups are converted to acrylate groups. The decrease in charge density due to the hydrolysis can be followed by polyelectrolyte titration and nitrogen analysis. The results show that at pH values above 6 the hydrolysis is fast and cannot be neglected when experiments are performed under such conditions.

As expected, the rate of hydrolysis is increased when the pH or the temperature is increased. The half-lives of the cationic groups seem to be dependent on the initial charge densities. It seems that if the charged groups are closer to each other, the hydrolysis reaction will be slightly inhibited.

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