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Potentiometric and viscometric study of the alkalization of latex dispersions of ethyl acrylate – methacrylic acid copolymers in the presence of salt

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Abstract: The behavior of latices of ethyl acrylate – methacrylic acid copolymers during alkalization was investigated using potentiometric titration and viscometry. In the presence of NaCl in dispersion medium pH and viscosity were lower compared to salt-free dispersions. Due to strong electrostatic interactions at low salt concentration the apparent dissociation constant of the carboxylic groups is small and the polymer segments bearing these groups are in extended conformations. The screening effect at higher salt concentration increases the apparent dissociation constant and decreases the extension of the polymer segments. The pH and viscosity of latex dispersions alkalized in the presence of salt are thus smaller.

Key words: Latex dispersions – ethyl acrylate – methacrylic acid copolymers – alkalization – dissociation constant – viscosity

1. Introduction

The alkalization of dispersions of latices consisting of statistical copolymers of ethyl acrylate – methacrylic acid can produce structural changes of the latex particles [1, 2]. At low acid content, the latex particles only swell; at acid contents greater than ca 40 wt.% the particles dissolve [3]. Due to these structural changes a typical plateau or even a maximum on the titration curves as well as an anomalous increase in the apparent dissociation constant over a certain range of dissociation degrees were observed. The structural changes also increased the viscosity of the latex dispersion and decreased the optical turbidity (clarification of dispersions) [3, 4].

As the behavior of these systems is generally determined by electrostatic interactions, structural changes of the latex particles during alkalization should depend on the ionic strength of the dispersion medium. This work concerns a detailed investigation of the alkalization of the latices at various salt concentrations. In contrast to earlier works [3, 4] carried out with the as-received latices (containing various amounts of low-molecular-weight electrolytes alkalized with ammonium hydroxide which does not guarantee complete dissociation of the neutralized carboxylic groups) we used dialyzed latices and sodium hydroxide. Parallel to potentiometric titration, the viscosity of the dispersions was measured.

2. Materials and methods

2.1. Dispersions

The latices of ethyl acrylate – methacrylic acid copolymers used included three characteristic types, whose particles swell during alkalization (15.0 wt.% of methacrylic acid in copolymer, denoted EM 15), partly dissolve to supermolecular aggregates (49.0 wt.% of the acid, EM 50) or undergo molecular dissolution (69.1 wt.% of the acid, EM 70) [3]. The latices were prepared at the Research Institute for Synthetic Resins and Lacquers, Pardubice (Czech Republic) by semi-continuous emulsion polymerization with a monomer emulsion feed, as described in earlier works [3, 4]. This procedure ensured relatively homogeneous latex particles of statistical copolymers. Dispersions containing 25 wt.% of copolymer after polymerization of 1–2 pH were diluted with distilled water to a concentration of ca 15 wt.% of copolymer and dialyzed (Dialysierschlauch Kalle Aktiengesellschaft, Wiesbaden, FRG), first against distilled water and then against twice distilled water (specific conductivity 2–3 μS cm^{-1}) until the conductivity was constant. The total content of acidic groups in the copolymer was determined by conductometric titration with NaOH (OK 104 conductoscope, Radelkis, Hungary). The diameter of the latex particles, determined by photon correlation spectroscopy (Coulter Nano Sizer, Coulter Electronics Ltd., England), was 330 nm (EM 15), 137 nm (EM 50) and 285 nm (EM 70).

2.2. Measurement of pH and viscosity

Dispersions containing 0.2 wt.% of solids were prepared by the dilution of the dialyzed latex with twice distilled water and addition of a certain amount of standard NaCl and NaOH solutions necessary to achieve the required salt concentration and extent of alkalization. A part of the dispersion was used for viscosity measurement and the rest for pH determination. The relative viscosity $\eta_r = \eta/\eta_0$ was calculated from latex viscosity η and the viscosity of dispersion medium η_0 measured in Ostwald-type viscometers at 25 ± 0.02 °C. pH was measured in a nitrogen atmosphere at 25 °C (digital PHM 64 pH-meter, with a G 2321 combined electrode, Radiometer, Copenhagen). The measurement was always carried out ca 24 h after sample preparation. Under these conditions, hydrolysis of the ethyl acrylate was negligible.

The degree of alkalization expressed as $\alpha' = [\mathrm{Na}^+]/c_{\mathrm{MAA}}$ was, for $0 < \alpha' < 1$, practically equal to the degree of dissociation α of carboxylic groups, defined by the relationship:

$$\alpha = ([\mathrm{Na}^+] + [\mathrm{H}^+])/c_{\mathrm{MAA}} , \tag{1}$$

where [Na$^+$] corresponds to the molar concentration of NaOH consumed, [H$^+$] is the molar concentration of hydrogen ions calculated from the pH assuming activity coefficient equal to unity, and c_{MAA} is the molar concentration of monomeric units of methacrylic acid. The apparent dissociation constant K_{app} of the carboxylic groups was calculated from the relationship:

$$pK_{\mathrm{app}} = \mathrm{pH} + \log[(1 - \alpha)/\alpha] . \tag{2}$$

3. Results and discussion

3.1. Alkalization of the latices without salt addition

The pH of all the latices used and also their relative viscosity (further, viscosity) varied in a similar manner during alkalization (Fig. 1). After an initial rapid increase, the pH exhibited a plateau or even a slight maximum followed by a shallow minimum. The latex clarified near to the minimum. While this shape of titration curves has already been described for the

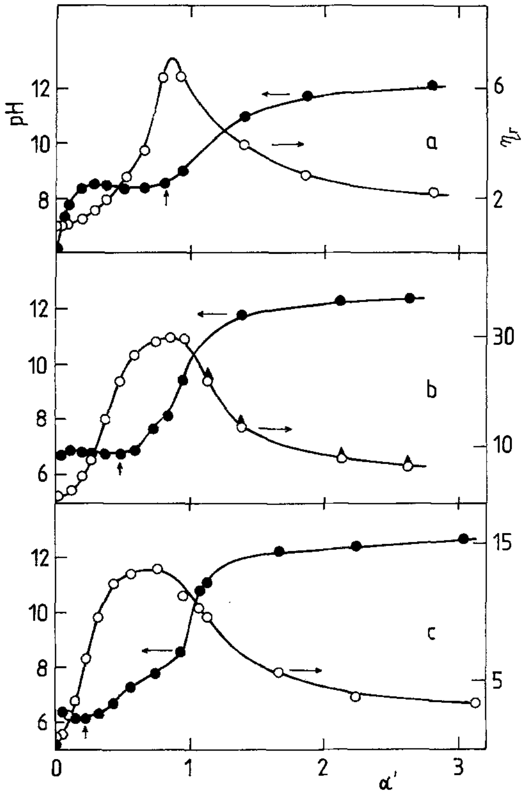

Fig. 1. Changes of pH (●) and relative viscosity η_r (○) of latex dispersions with the degree of alkalization, α', no NaCl added. η_r (▲) after addition of NaCl at $\alpha' = 0.94$. Latices: a) EM 15; b) EM 50; c) EM 70. The vertical arrows indicate point of clarification of the latex dispersion

alkalization of undialyzed latices with ammonium hydroxide [4], the viscosity changed in a different manner when compared to undialyzed latices having a similar copolymer composition and concentration. In contrast to the slow increase of viscosity to the limiting value [3], the viscosity of the dialyzed latices increased to a sharp maximum at $\alpha' = 0.70$–0.85 and then decreased to a final value approximately 20–25% of the maximum value.

As the acid content in the copolymer increased, the plateau on the titration curve shortened, the maximum shifted to lower pH and the point of clarification occurred at lower degrees of alkalization (Fig. 1). Simultaneously, the viscosity increased at lower degrees of alkalization and the maximum was broadened. Because of the approximately identical ionic strength and similar degree of polymerization of the copolymers [5], the higher viscosity of latex EM 50 is obviously related to the presence of the molecular aggregates.

The change in the structure of the latex particles during alkalization is better reflected by the apparent dissociation constant K_{app} (Fig. 2). It is obvious that the rapid increase in both K_{app} and the viscosity occurred approximately at the same degree of dissociation which corresponded to the pH maximum on the titration curve. The increase in K_{app} with the degree of dissociation may reflect the rise of the local dielectric constant in the environment of carboxylic groups [4]. Hence, the increase K_{app} reflects increased accessibility of the groups inside the latex particles to the dispersion medium due to the gradual disintegration of the particles. This effect predominates over accompanying increase of the electrostatic interactions which make dissociation more difficult and causes K_{app} to decrease. The rapid increase in the viscosity of the alkalized latex of low concentration corresponding primarily to an increase in the hydrodynamic volume of the latex particles, confirms significant changes of their structure.

The further increase in K_{app} and viscosity (Fig. 2) with alkalization is caused by extensive changes of the structure of the particles. The clarification of the latices occurred just before reaching the maximum of K_{app} and indicated a complete swelling or even dissolution of the particles. At these degrees of dissociation most of the carboxylic groups are accessible to dispersion medium, electrostatic interactions predominate and K_{app} decreases. Further changes of the structure of particles are not possible, which is reflected in the decreasing slope of the viscosity curve with the increasing degree of dissociation. Proceeding alkalization causes an increase in expansion of the swollen particles of latex EM 15, while, in latices EM 50 and EM 70, it corresponds to expansion and disintegration of the aggregates or to dissolution of macromolecules. In analogy with polyelectrolyte solutions, the maximum viscosity corresponds to the greatest expansion of these units.

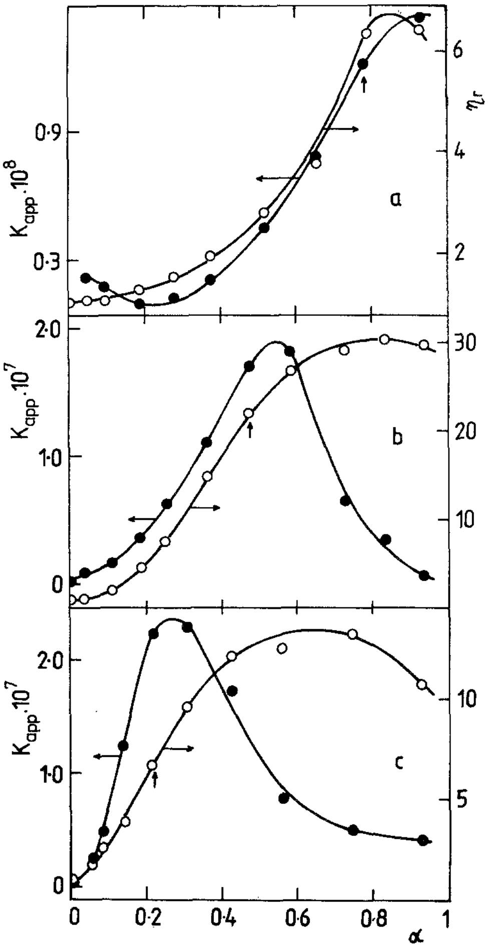

Fig. 2. K_{app} (●) and relative viscosity η_r (○) of latex dispersion as a function of the degree of dissociation, α, no NaCl added. Latices: a) EM 15; b) EM 50; c) EM 70. The vertical arrows indicate point of clarification of the latex dispersion

The viscosity decrease at higher degrees of alkalization was obviously caused by the strong screening effect of Na^+ and OH^- ions. This assumption was proved by the addition of NaCl instead of NaOH to the latex EM 50 alkalized to $\alpha' = 0.94$; practically the same viscosity decrease was found (Fig. 1b).

3.2. Alkalization of latices in the presence of salt

Addition of NaCl decreased pH and changed the shape of the titration curves mentioned above which, at the highest salt concentration, approached the shape found for soluble polyelectrolytes (Fig. 3). The presence of the salt also affected the flow behavior of the alkalized latices (Fig. 4). With increasing salt concentration, the viscosity was reduced and began to increase at higher degrees of alkalization. The relative height of the viscosity maximum decreased and, at the highest salt concentration, viscosity increased to a limiting value only.

The screening effect of low-molecular-weight electrolytes decreases the electrostatic interaction between ionized carboxylic groups on the polymer chains, which increases the acidity of the polyacids and decreases their viscosity. The decreasing pH and viscosities of the alkalized latex dispersions with increasing NaCl concentration indicate this effect to be operative during structural changes of the latex particles. One may expect that a decrease in the repulsions between the charges reduces the structural changes of particles. Consequently, the changes would occur at higher degrees of dissociation in the presence of salt. The clarification of the latex and a maximum of K_{app} which indicates complete swelling of the latex particles were found at the same degree of dissociation (latex EM 50 for example, Fig. 5) within experimental error. It thus follows that, for a given degree of dissociation, the presence of the salt affects primarily the dissociation constant of the carboxylic groups accessible to the dispersion medium and the conformation of the polymer segments bearing these groups. At low salt concentrations, the screening effect of the NaCl is small, K_{app} is also small and the pH is relatively high. If the structural changes make dissociation easier, pH after an initial increase can decrease with further alkalization. Then a maximum pH occurs on the titration curves. The polymer segments bearing ionized carboxylic groups are

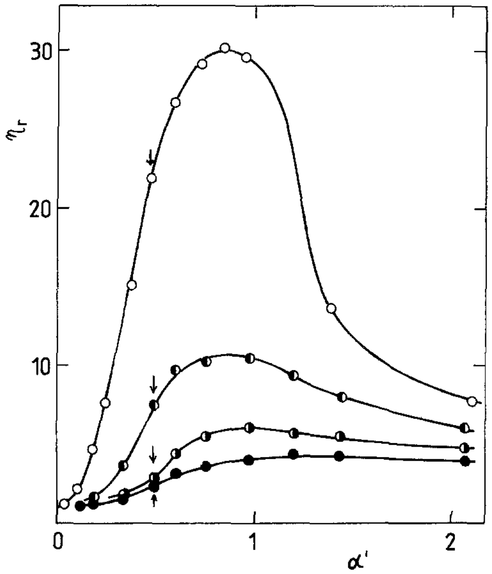

Fig. 4. Changes of relative viscosity η_r of latex EM 50 with the degree of alkalization, α', at various NaCl concentrations. Symbols are the same as in Fig. 3

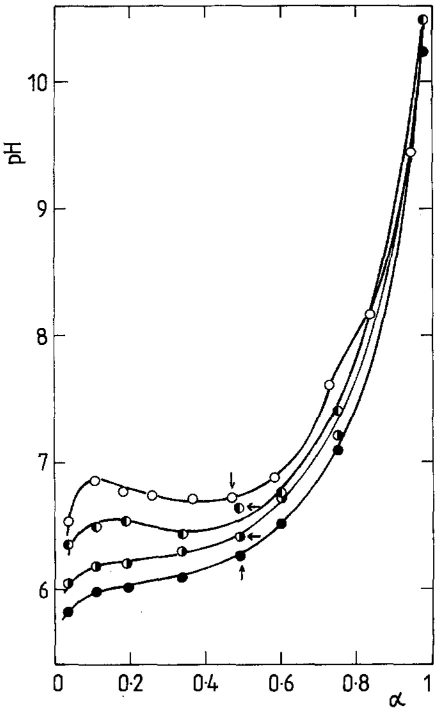

Fig. 3. Changes of pH with the degree of dissociation, α, at various NaCl concentrations: (○) 0, (◐) 0.004, (◑) 0.016, (●) 0.032 M. The arrows indicate point of clarification of the latex dispersion. Latex EM 50

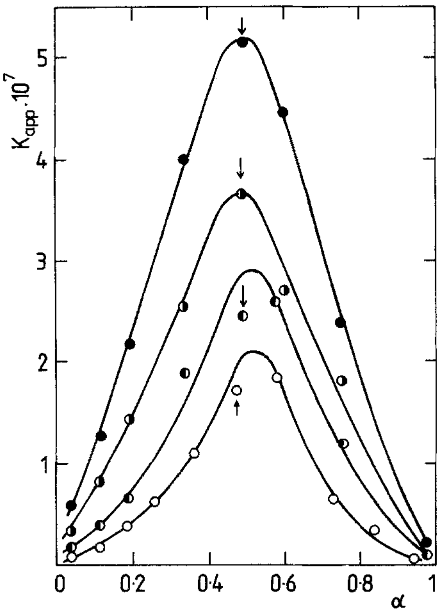

Fig. 5. K_{app} of latex EM 50 as a function of the degree of dissociation, α, at various NaCl concentrations. Symbols are the same as in Fig. 3

strongly extended and, consequently, greatly increase the hydrodynamic volume of the latex particles; then the viscosity of the system is high. In contrast, at higher salt concentrations, K_{app} is larger and thus the pH at a given degree of dissociation decreases with increasing salt concentration. The dissociation is easier even at the beginning of the alkalization as can be seen from the rapid increase of K_{app} at low degrees of dissociation. Consequently, the height of the pH maximum above the pH minimum decreases and at the highest salt concentration pH increases monotonously. At higher salt concentrations, the polymer segments are less extended, their contribution to the hydrodynamic volume of the latex particles is less, and viscosity increases to a limiting value.

4. Conclusions

On the basis of the studies of the alkalization of latices of ethyl acrylate – methacrylic acid copolymers carried out so far it was assumed that a pronounced plateau or even a slight maximum of pH on the titration curves reflect specific changes in the structure of the latex particles. The results of this work indicate that the shape of the titration curves of latices is determined primarily by the concentration of the salt in the dispersion medium. At low salt concentrations, a plateau or even a maximum can be seen on the titration curve while at higher salt concentrations pH increases monotonously like the titration curves of soluble polyacids. At the same salt concentration, however, the section of the titration curve which is typical of structural changes of the particles, always lies above the titration curves of the hypothetical soluble polymer of the same composition. This phenomenon is a consequence of the gradual accessibility of the carboxylic groups to the dispersion medium during changes of the latex particle structure. Compared to the soluble copolymer, a smaller number of carboxylic groups is accessible to the dispersion medium at a given degree of dissociation.

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