

Kinetics of Protonation of Polymethacrylic Acid in Aqueous Solution

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Upon the application of the temperature-jump technique, the protonation of polymethacrylic acid is studied at pH = 7.0 in the presence of bromthymol blue (BTB) as indicator. Rate constants are determined for the proton transfer from carboxylate groups to the dianion of BTB ($k_{\text{ex}} = 3.4 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$), for the association of a proton with a carboxylate group ($k_{\text{L}} = 2.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$), and for association of a proton with the dianion of BTB ($k_{\text{in}} = 5.0 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$).

Introduction

The equilibrium of the binding of metal ions to anionic polyelectrolytes has been studied for many systems¹ since it is of great ecological interest. For the understanding of the mechanism of this process, additional kinetic measurements must be performed, and in a previous study we reported on the kinetics of nickel-complex formation of a polycarboxylic acid in nearly neutral solutions (pH \sim 6). Relaxation times in the range of 0.2–1 ms were observed at 25 °C.² It has been assumed that protonation of the carboxylic groups proceeds much faster, since the protons are not involved in internal hydrogen bridges and thus the reaction should occur with diffusion-controlled speed.³ However, it has been shown already in 1972 by Weiss et al.⁴ that at pH \approx 7 protonation may be relatively slow for polycarboxylic acids, and it may be necessary to take into account the rate of protonation when discussing the kinetics of nickel-complex formation. Therefore we report here on a detailed study of the kinetics of protonation of polymethacrylic acid (abbreviated as PMA), a well-defined polycarboxylic acid.

Experimental Section

Polymethacrylate was purchased from Polymer Standard Service. The sample used in this investigation has a mean molecular weight of $M_w = 64\,000 \text{ g/mol}$ and a polydispersity factor of (M_w/M_n) = 1.02. Either protons or sodium ions are bound to the carboxylic groups (i.e., the sample contains a mixture of acid and sodium salt in which the ratio of acid to sodium salt is not known). All other chemicals are of grade p.a. and are commercially available.

Proton activity was measured using a standard glass electrode. Before each titration of a polyelectrolyte solution, the electrode was numerically calibrated over the whole pH range of interest by titrating a solution of a simple acid (e.g., acetic acid for the range pH < 5.7) with a similar concentration of carboxylic groups. For these reference solutions pH values can be calculated from total ionic concentration, the $\text{p}K_a$ value of the acid, and by applying an appropriate equation for activity

coefficients. In this contribution activity coefficients were estimated by using Davies' equation.⁵

The kinetic measurements were performed using the temperature-jump technique with Joule heating and spectrophotometric detection. 0.1 M KCl (inert electrolyte) was added to the solutions in order to increase their electrical conductivity. Temperature jumps of 2 °C performed from 15 to 17 °C were achieved in 3 μs .

Results

Protonation Equilibria. For the sample of PMA, which is used in this investigation, either protons or sodium ions are bound to the carboxylate groups, and the degree of protonation is not known (see Experimental Section). Therefore in the first step the exact composition of our sample of PMA has to be determined (i.e., in a solution of the sample the fractions of carboxylic acid and of sodium carboxylate have to be determined). This is achieved by titrating the solution with hydrochloric acid and with sodium hydroxide.

The monomeric unit $\{\text{CH}_2\text{-C}(\text{CH}_3)\text{COOH}\}$ of polymethacrylic acid is abbreviated as LH, and the protonation equilibrium may be written as



For the initial concentrations the following definitions are used: A_0 for hydrochloric acid, B_0 for sodium hydroxide, L_0 for carboxylate groups, LH_0 for protonated carboxylate groups; that is, $(L_0 - \text{LH}_0)$ is the initial concentration of sodium carboxylate groups. The actual concentrations are determined by the balanced equations, eqs. 2–4, the balance equation for electrical charges (eq 5) (used instead of the balance equation for protons) where the contribution of the inert electrolyte cancels, and the ion product of water for ionic strength $I = 0.1 \text{ M}$, $T = 17 \text{ °C}$ (M is used as an abbreviation of mol dm^{-3}). Equation 6 is the ionic product of water, where the mean activity coefficient has been estimated by the Davies' formula.⁵ The proton concentration is measured as discussed in the experimental section.

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$$[\text{Na}^+] = B_0 + L_0 - \text{LH}_0 \quad (2)$$

$$[\text{Cl}^-] = A_0 \quad (3)$$

$$[\text{LH}] + [\text{L}^-] = L_0 \quad (4)$$

$$[\text{H}^+] + [\text{Na}^+] = [\text{OH}^-] + [\text{L}^-] + [\text{Cl}^-] \quad (5)$$

$$[\text{H}^+][\text{OH}^-] = 1.65 \times 10^{-14} \text{ M}^2 \quad (6)$$

Combining those equations yields eq 7, which is approximated by eqs. 7a,b for highly acidic solutions ($B_0 = 0$; $[\text{H}^+] \gg [\text{OH}^-]$, $[\text{L}^-] = 0$) and for highly basic solutions ($A_0 = 0$, $[\text{H}^+] \ll [\text{OH}^-]$, $[\text{L}^-] = L_0$), respectively.

$$[\text{H}^+] - [\text{OH}^-] = A_0 - B_0 + \text{LH}_0 - L_0 + [\text{L}^-] \quad (7)$$

$$L_0 - \text{LH}_0 = A_0 - [\text{H}^+] \quad (7a)$$

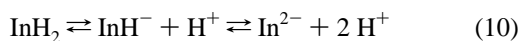
$$\text{LH}_0 = B_0 - [\text{OH}^-] \quad (7b)$$

Thus from the limiting values of $(A_0 - [\text{H}^+])$ and $(B_0 - [\text{OH}^-])$ the values of L_0 and LH_0 are obtained, according to eqs. 7a,b. In this way, L_0 and LH_0 are determined with a reproducibility of $\pm 5\%$, and for our PMA sample we obtained $L_0 = 6.5 \times 10^{-3} \text{ mol/g}$ and $\text{LH}_0 = 2.07 \times 10^{-3} \text{ mol/g}$. A titration curve is shown in Figure 1. The concentrations of LH and L^- can be calculated for each point of a titration curve by eqs 2–7. For polyelectrolytes the protonation of the carboxylate is not described by a dissociation constant, but the dissociation quotient Q_L (defined in eq 8) depends strongly on the pH value of the solution. The results are approximated by a Langmuir–Freundlich isotherm, eq 9, with $K_H = 1.05 \times 10^{-6} \text{ M}$ and $b = 0.68$, as indicated in Figure 2, where the plateaus at high and low pH-values are well-established. However, between data points and isotherm there is a systematic deviation of up to 2%, and a distribution function of $\text{p}K_a$ would lead to a better description of the binding isotherm.⁶

$$Q_L = \frac{k_L'}{k_L} = \frac{[\text{L}^-][\text{H}^+]}{[\text{LH}]} \quad (8)$$

$$[\text{LH}] = L_0 \frac{(K_H[\text{H}^+])^b}{1 + (K_H[\text{H}^+])^b} \quad (9)$$

For the kinetic studies, bromthymol blue has been used as indicator. Abbreviating the indicator by InH_2 , the protonation equilibria are given in eq 10. At 17 °C and $I = 0.1 \text{ M}$, the values $\text{p}K_{\text{In}1} = 1.28$ and $\text{p}K_{\text{In}2} = 6.98$ have been determined in fair agreement with values reported in the literature.⁷



Protonation Kinetics. The kinetics of protonation of PMA are studied at $\text{pH} = 7.0$, $T = 17 \text{ }^\circ\text{C}$, and $I = 0.1 \text{ M}$ where the dissociation quotient is $Q_L = 5.3 \times 10^{-7} \text{ M}$. The concentrations of PMA and BTB are varied in the range $6 \times 10^{-5} \text{ M} \leq L_0 \leq 0.065 \text{ M}$ and $1 \times 10^{-5} \text{ M} \leq \text{In}_0 \leq 2 \times 10^{-4} \text{ M}$, respectively. For all solutions a single relaxation effect is observed. In Figure 3 the reciprocal relaxation time is plotted vs L_0 at constant indicator concentration, $\text{In}_0 = 2.5 \times 10^{-5} \text{ M}$. A linear dependence is observed in the range $3 \times 10^{-3} \leq L_0 \leq 0.065 \text{ M}$, but for smaller values of L_0 the reaction rate is much slower

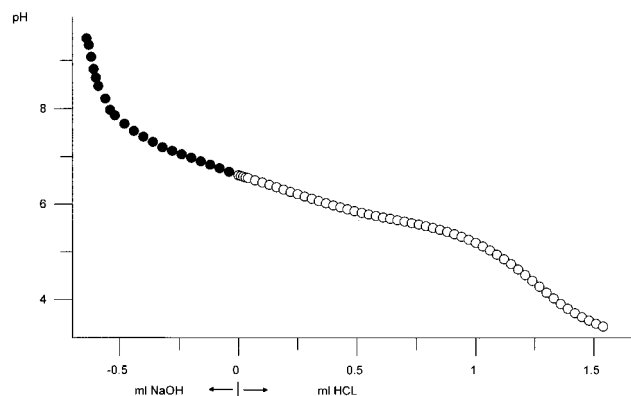


Figure 1. Titration of 30 mL of solution of 1 g L^{-1} PMA with 0.1M NaOH (●) and 0.1 M HCl (○).

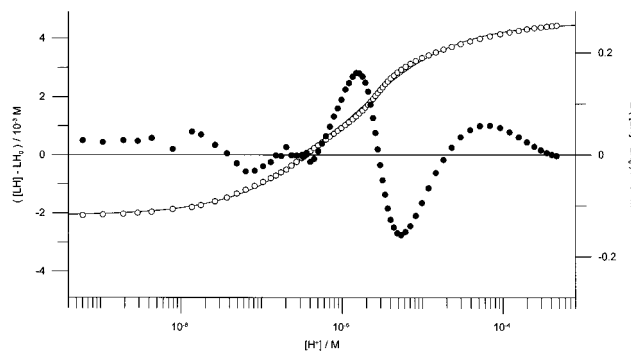


Figure 2. pH dependence of the concentration of protonated carboxylate groups (left hand scale). Data taken from Figure 1. The curve is drawn according to eq 8 with the constants given in the text. The closed circles show the difference between measured data and calculated curve (right hand scale).

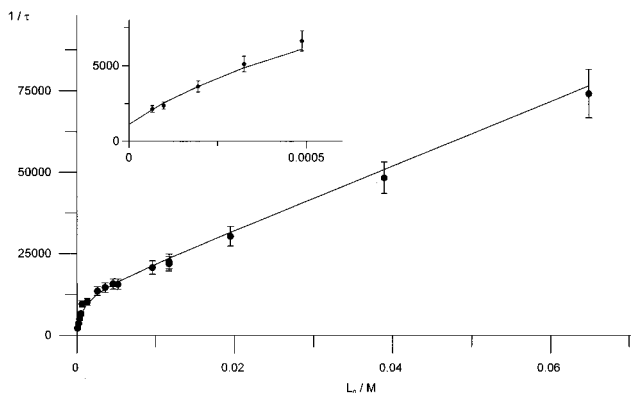
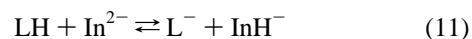


Figure 3. Reciprocal relaxation time vs initial concentration of carboxylate groups at $\text{In}_0 = 2.5 \times 10^{-5} \text{ M}$. The insert shows the values at low concentrations L_0 . The curves are calculated with the data given in Table 1.

than described by the straight line. The dependence of the relaxation time on the concentration of BTB at constant L_0 is shown in Figure 4.

The concentrations of protons and hydroxyl ions are negligibly small compared to those of indicator and carboxylate groups. Therefore, a single relaxation effect is expected, which is caused by the reaction described in eq 11.



Regarding the reaction rate, it must be considered that reaction 11 may proceed by three different path: (i) by direct proton

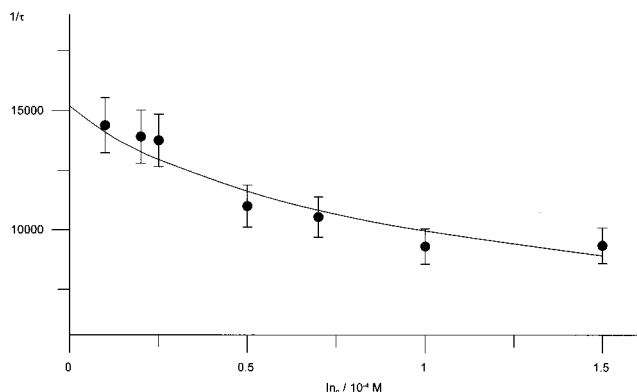


Figure 4. Reciprocal relaxation vs initial concentration of BTB at $L_0 = 1.6 \times 10^{-3}$ M. The curve is calculated with the data given in Table 1.

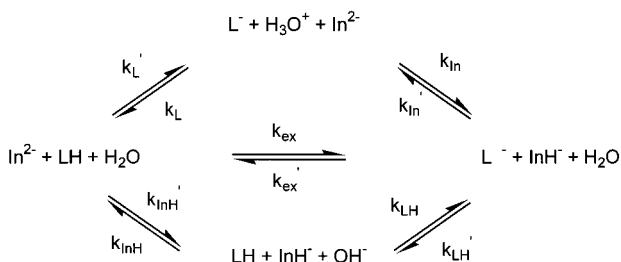


Figure 5. Scheme of proton transfer reactions between carboxylate groups, indicator and water.

transfer from carboxylate group to indicator dianion, (ii) by deprotonation of the carboxylic acid followed by protonation of the indicator, (iii) by proton transfer from water to the indicator dianion followed by the deprotonation of the carboxylic acid. This leads to the reaction scheme in Figure 5. For the calculation of the relaxation time the polyelectrolytic character of the ligand is neglected i.e., the approximation of independent binding sites L^- is made where all binding sites have the same dissociation quotient Q_L and where the reaction proceeds with the rate constants k_L' and k_L . (Q_L is not a dissociation constant, since it depends on the pH value of the solution.) Equations 12 and 13 are the rate laws for LH and InH^- , respectively.

$$\frac{d[InH^-]}{dt} = k_{In}[In^{2-}][H^+] - k_{In}'[InH^-] + k_{ex}[In^{2-}][LH] - k_{ex}'[L^-][InH^-] + k_{InH}'[In^{2-}] - k_{InH}[InH^-][OH^-] \quad (12)$$

$$\frac{d[LH]}{dt} = k_L[L^-][H^+] - k_L'[LH] + k_{ex}'[L^-][InH^-] - k_{ex}[In^{2-}][LH] + k_{LH}'[L^-] - k_{LH}[LH][OH^-] \quad (13)$$

(The index “i” of the rate constant k_i refers to that compound, which reacts in the bimolecular reaction with protons or hydroxyl ions.) Since the concentrations of H^+ and OH^- are relatively very small, they may be calculated as functions of concentrations and rate constants applying the Bodenstein approximation, eq 14, (equivalent to the quasi-stationary state assumption). For acidic and basic solutions we obtain eqs 15 and 16, respectively. Introducing these equations into eq 12 leads directly to eq 17 for the relaxation time, where the proton exchange quotient Q_{ex} is defined in eq 18.

$$\frac{d[LH]}{dt} = - \frac{d[InH^-]}{dt} \quad (14)$$

$$[H^+] = \frac{k_L'[LH] + k_{In}'[InH^-]}{k_L[L^-] + k_{In}[In^{2-}]} \quad (15)$$

$$[OH^-] = \frac{k_{InH}'[In^{2-}] + k_{LH}'[L^-]}{k_{InH}[InH^-] + k_{LH}[LH]} \quad (16)$$

$$\frac{1}{\tau} = \left(k_{ex} + \frac{k_L'k_{In}}{k_L[L^-] + k_{In}[In^{2-}]} + \frac{k_{InH}'k_{LH}}{k_{InH}[InH^-] + k_{LH}[LH]} \right) \times ([LH] + [In^{2-}] + Q_{ex}([InH^-] + [L^-])) \quad (17)$$

$$Q_{ex} = \frac{k_{ex}'}{k_{ex}} = \frac{[LH][In^{2-}]}{[L^-][InH^-]} = \frac{K_{In2}}{Q_L} \quad (18)$$

$$\frac{1}{\tau} = \left(k_{ex} + \frac{k_L'k_{In}}{k_L\alpha_L L_0 + k_{In}\alpha_{In} In_0} \right) ((1 - \alpha_L)L_0 + \alpha_{In} In_0 + Q_{ex}(\alpha_L L_0 + (1 - \alpha_{In}) In_0)) \quad (19)$$

The last term of the sum in the first brackets of eq 17 may be neglected at pH = 7, as will be worked out in the Discussion section. Thus eq 17 may be reduced to eq 19, where furthermore the degrees of dissociation α_L and α_{In} of LH and InH^- , respectively, are introduced. For all solutions, α_L and α_{In} have the same values, since the kinetics are studied at constant proton concentration, and they can be calculated from the values of Q_{ex} and K_{In2} obtained from the measurements at equilibrium. The rate constants are evaluated in the following way: at high concentrations L_0 , all terms proportional to In_0 may be neglected in eq 19, and for this range eq 20 may be applied,

$$\frac{1}{\tau} = k_{In} Q_L \left(\frac{1}{\alpha_L} - 1 + Q_{ex} \right) + k_{ex} (1 - \alpha_L + Q_{ex} \alpha_L) L_0 \quad (20)$$

describing a linear dependence of $1/\tau$ on L_0 , which is observed for $L_0 > 2 \times 10^{-3}$ M. From the intercept and slope of the straight line the rate constants $k_{In} = (4.8 \pm 0.7) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and $k_{ex} = (3.4 \pm 0.3) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ are calculated. Since the error in k_{ex} is relatively small, this value is used in the next step, where eq 19 is fitted to the data $L_0 < 3 \times 10^{-3}$ M. This fit yields $k_{In} = (6.2 \pm 1.0) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and $k_L' = (8.8 \pm 1.2) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$. Finally, eq 19 is fitted to the data in Figure 4, again using the already known value of k_{ex} , and $k_{In} = (5.3 \pm 1.0) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and $k_L' = (10.5 \pm 1.2) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ are calculated. The coincidence of the differently determined values of k_{In} and k_L' supports strongly the proposed reaction scheme in Figure 5. The backward rate constants are calculated from the values of Q_L , Q_{ex} , and K_{In2} . All constants are summarized in Table 1, and the curves in Figures 3 and 4 are calculated by eq 19 using the above-mentioned values.

Discussion

For the scheme given in Figure 5, all rate constants are evaluated for the upper triangle (i.e., for the direct proton transfer and for the acidic reaction path). For the lower reaction path (i.e. for the basic path) upper limits of the rate constants may be estimated by assuming that the reactions involved proceed with diffusion-controlled rates in the energetically downward

TABLE 1: Parameters Obtained for the Reaction of PMA with BTB as Described in Figure 5 at pH = 7.0, T = 17 °C, I = 0.1 M

reaction	parameter
$L^- + H^+ \rightleftharpoons LH$	$Q_L = (5.3 \pm 1) \times 10^{-7} M$ $k_L = (2.1 \pm 0.7) \times 10^9 M^{-1} s^{-1}$ $k_L' = (1.1 \pm 0.4) \times 10^3 s^{-1}$
$In^{2-} + H^+ \rightleftharpoons InH^-$	$K_{In2} = (1.0 \pm 0.2) \times 10^{-7} M$ $k_{In} = (5.0 \pm 1.0) \times 10^{10} M^{-1} s^{-1}$ $k_{In}' = (5.0 \pm 1.8) \times 10^3 s^{-1}$
$LH + In^{2-} \rightleftharpoons L^- + InH^-$	$Q_{ex} = 0.2 \pm 0.04$ $k_{ex} = (3.4 \pm 0.4) \times 10^6 M^{-1} s^{-1}$ $k_{ex}' = (6.8 \pm 0.6) \times 10^5 M^{-1} s^{-1}$

direction. This assumption leads to $k_{InH} \approx 5 \times 10^9 M^{-1} s^{-1}$ and $k_{LH} \leq k_L = 2.1 \times 10^9 M^{-1} s^{-1}$, and the rate constants for the backward reactions $k_{InH}' \approx 4.8 \times 10^2 s^{-1}$ and $k_{LH}' \leq 40 s^{-1}$ are given by the equilibrium constants K_{In2} and Q_L . Inserting those values into eq 17 justifies the neglect of the lower reaction path when calculating the relaxation time at pH = 7.

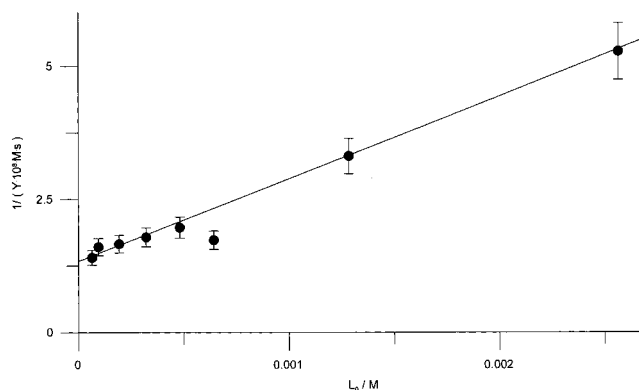
Preliminary measurements showed that at pH ~ 7 the relaxation time depends only weakly on the pH value of the solution: a change of δ pH = 0.03 causes a change of approximately 5% in the relaxation time. The reproducibilities of τ and pH are $\pm 5\%$ and ± 0.03 , respectively. Therefore we assume an overall error of $\pm 10\%$ in the relaxation time at pH = 7.

The rate constants are obtained by fitting eq 19 to the relaxation times, where both k_L' and k_{In} are contained in one term. In order to show that those constants can be determined separately with high accuracy, eq 19 is rearranged to give eq 21 with Y defined in eq 22. Figure 3 shows a linear dependence of $1/\tau$ on L_0 in the broad range $0.003 M \leq L_0 \leq 0.068 M$, and $k_{ex} = 3.4 \times 10^6 M^{-1} s^{-1}$ is obtained from the slope according to eq 20. With this value of k_{ex} , the points in Figure 6 are calculated yielding an excellent straight line, and from the intercept and slope k_L' and k_{In} are calculated. The value of k_{In} obtained in this way agrees well with the value obtained from the intercept of the straight line in Figure 3.

$$\frac{1}{Y} = \frac{\alpha_L L_0}{Q_L k_{In}} + \frac{\alpha_{In} In_0}{k_L'} \quad (21)$$

$$Y = \frac{1}{\tau((1 - \alpha_L)L_0 + \alpha_{In}In_0 + Q_{ex}(\alpha_L L_0 + (1 - \alpha_{In})In_0))} - k_{ex} \quad (22)$$

Now the values of the rate constants must be discussed. Diffusion-controlled rates are expected for the protonation reaction of In^{2-} and L^- , since the protons are not involved in internal hydrogen bridges. The value $k_{In} = 5 \times 10^{10} M^{-1} s^{-1}$ agrees with this expectation for a reaction between ions with $z_+z_- = -2$. It is smaller by a factor of approximately 2 compared to the rate constant for the protonation of the sulfate ion, and this difference may be due to the large separation of the two negative charges in the bromthymol blue dianion. For the carboxylate groups the value $k_L = 2.1 \times 10^9 M^{-1} s^{-1}$ is smaller than expected for the diffusion controlled reaction between two ions with $z_+z_- = -1$. However, there are three facts, which may contribute to a reduction of the reaction rate, but cannot be taken into account quantitatively so far. (i) The polyelectrolyte chain of PMA may be regarded as a charged rod with high surface potential, which strongly attracts counter ions.

**Figure 6.** Results of the kinetic measurements for small concentrations of L_0 according to eq 21.

Therefore it is well-shielded by the potassium ions of the inert electrolyte added to the solutions, and thus the effective charge is substantially reduced. (ii) PMA may have a coiled conformation, with the consequence that many binding sites are not accessible to protons. (iii) Diffusion-controlled rate constants have been estimated so far for spherical ions, and the different geometry of the present process may influence the rate of reaction. In order to discriminate between these possibilities, (i) kinetics are studied at different ionic strength, (ii) light scattering of solutions of PMA is measured, and (iii) calculations are performed for the estimation of diffusion rates of small ions in the environment of rod like or coiled anionic polyelectrolytes.

The values of k_{ex} and k_{ex}' are much smaller than the diffusion-controlled values. They may be discussed in the Brönsted log k vs pK relation. For the proton transfer from water to In^{2-} we have pK = -1.7 and $\log(k/M^{-1} s^{-1}) = 2.0$ (taking into account the concentration of water), and the corresponding values for the proton transfer from LH to In^{2-} are pK = 6.3 and $\log(k/M^{-1} s^{-1}) = 5.8$. This means, that the difference of 8 in pK relates to an difference of about 4 in log k corresponding to a slope of 0.5 in the Brönsted plot. For the protonation of L^- a difference of 8.7 in pK relates to a difference of about 4.5 in log k corresponding to a slope of 0.52 in the Brönsted plot. For a discussion of the slopes measurements with other proton donors are needed.

The relaxation times reported by Weiss et al.⁴ for the protonation of PMA are in fair agreement with our data. However, their measurements are restricted to a relatively small concentration range, where the strong curvature is observed in Figure 3. Weiss et al.⁴ assume a linear dependence in this range, and therefore they obtain a larger value for the proton exchange, $k_{ex} = 2 \times 10^7 M^{-1} s^{-1}$. For the protonation of the indicator, they report a value of $k_{In} = 3 \times 10^{10} M^{-1} s^{-1}$ and the protonation of the carboxylate groups has been assumed to be too fast to be measured.

There remains a final problem: In our evaluation it is assumed that the protonation sites are independent from each other and that all of them have the same dissociation quotient. This is a very rough assumption, and distribution functions should be introduced for the rate constants as they already have been introduced for equilibrium constants.⁶ The dependence of the rate constants on the corresponding dissociation constants can be estimated according to the theory of Eigen.³ However, further measurements at different pH values are necessary before

the influence of distribution functions in the rate equations may be reasonably discussed.

Summarizing, the rate of protonation of polymethacrylate can be calculated using the information obtained in this investigation. Thus the influence of protonation can be quantitatively taken into account, when the kinetics of metal ion binding to this polyelectrolyte are studied.

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