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NMR Relaxation Study of Hydrogen Exchange in Solutions of Polyelectrolytes

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ABSTRACT: Exchange rate measurements of water protons in aqueous solutions of poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMA) by NMR T_2 measurements in $H_2{}^{17}O$ are reported. The polyelectrolyte contribution to the exchange rate is found to depend linearly on the concentration. This indicates that it originates from intramolecular processes, probably proton transfer between COOH and COO^- groups via an intervening water molecule. The corresponding rate constant is an increasing function of the degree of neutralization, largely independent of molecular weight and of the concentration of added salt. The residence time of a proton in a COOH group is calculated from the obtained rate constants and is found to be longer for PMA than for PAA by a factor 5. The influence of added simple salt on the exchange rate is reported. The possibility of obtaining hydrogen ion concentrations and activity coefficients from the experimental exchange rate is demonstrated.

Introduction

An experimental investigation of water proton exchange in solutions of low molecular weight carboxylic acids was reported recently[1]. In the present paper results of ^1H exchange rate measurements using the CarrPurcell NMR method on polyelectrolyte solutions in ^{17}O-enriched water are described. The exchange rate k_{ex} is defined as the inverse mean proton residence time in a water molecule. As in the previous work[1], k_{ex} is obtained from the contribution of the exchange-modulated ^1H–^{17}O scalar coupling to the proton transverse relaxation rate $1/T_2$.

Because the water proton exchange is catalyzed by processes involving the transfer of a proton from a COOH group to a water molecule, k_{ex} may yield information on the proton residence time in a COOH group, τ_{COOH}. Knowledge of τ_{COOH} is important for the interpretation of solvent relaxation data for solutions of high molecular weight compounds.

The polyelectrolytes investigated are poly(acrylic acid) (PAA, $(CH_2(CHCO_2H))_n$) and poly(methacrylic acid) (PMA, $(CH_2(CH_3CCO_2H))_n$). The exchange rate k_{ex} was measured as a function of the polyelectrolyte concentration c_p at a number of α values (α is the degree of neutralization). For PAA, the molecular weight dependence was investigated.

Some measurements of proton exchange in PMA solutions were performed in this laboratory previously,[2] but a quantitative explanation was complicated by the fact that only ^{17}O-enriched water containing 80% deuterium was available, whereas large deuterium isotope effects on the reaction rates are expected.[1] ^{17}O line width experiments on proton exchange in PAA and PMA solutions were reported recently by Halle and Piculell.[3] However, they did not investigate the concentration dependence of the exchange rate systematically, and the method can only give reliable results over a small pH range. Experiments have been reported on proton exchange between polyelectrolytes (PAA and PMA) and indicator molecules by the temperature jump method.[4] Such experiments do not yield direct information on the residence time in COOH groups in the absence of indicator.

In order to partition the experimental k_{ex} into contributions from H_3O^+ catalysis and from polyelectrolyte catalysis, it is necessary to know the H_3O^+ concentration c_{H^+}. For the simple acid solutions studied earlier, c_{H^+} was calculated from known pK and activity corrections.[1] For polyelectrolyte solutions these quantities are not unambiguously and accurately known. To be able to separate H_3O^+- and polyelectrolyte-catalyzed contributions, two alternative approaches were taken:

(a) The exchange rate was measured as a function of c_p in the presence of excess NaCl. Then in the present α-range ($0.3 \leq \alpha \leq 0.8$), c_{H^+} is supposed to be independent of c_p.

(b) For salt-free solutions, c_{H^+} was calculated from the experimental pH and an H_3O^+ activity coefficient estimated from the single-ion activity coefficient γ_{Na^+}, which is known from the literature.

Both methods are shown to yield a polyelectrolyte-catalyzed contribution to k_{ex} (denoted k_{COOH}) that depends linearly on c_p. This indicates that intramolecular processes are responsible for k_{COOH}. The rate constant obtained for polyelectrolyte catalysis will be used to estimate the proton residence time in a COOH group.

Experiments on the influence of added simple salt on the exchange rate are reported. It is shown to be possible in some cases to determine the hydrogen ion concentration and activity coefficient from the experimental exchange rate if the relevant rate constants are known.

Experimental Section

Chemicals and Solutions. All solutions were prepared by weight. The (monomer) aquamolality, $\bar{m}$, is used as a measure of the concentration; i.e., concentrations are given as the number of moles of monomeric units per 55.5 mol of water. Polyelectrolyte concentrations c_p are given as global concentrations, i.e., as $c_{acid} + c_{conjugated\ base}$, unless indicated otherwise. ^{17}O-enriched water was obtained from Monsanto Research Corp. in two fractions containing 43.4 and 52.4 mol % ^{17}O and 31.4 and 35.1 mol % ^{18}O, respectively. The oxygen isotopic composition of these stock solutions was checked by mass spectrometry as described in the previous paper.[1] PAA, degree of polymerization DP = 2100 and DP = 4100, and atactic PMA, DP = 2300, were synthesized and

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fractionated as described before.[5] DP was determined by viscosity measurements in the presence of 0.01 N HCl, using Mark-Houwink relations.[5] PAA of lower molecular weight was obtained as an aqueous solution from Aldrich (catalog no. 19,202.3). The solution was purified by filtration through a G3 glass filter and a Millipore filter scwp 04700, pore diameter 8 μm, and treatment with Norit. Then a series of PAA fractions of increasing molecular weight was separated by fractionated dialysis across a cellulose membrane, among which were fractions with DP = 6.3 and DP = 26 (the use of dialysis as a separation tool for compounds of relatively low molecular weight was originally proposed by Craig and King[6]). In this case DP was determined by vapor pressure measurements. Polyacid concentrations were determined by potentiometric titration. Stock solutions of degrees of neutralization α were then prepared by weight from polyacid solution and sodium hydroxide solution (Merck, Titrisol). Corresponding solutions with added sodium chloride (Baker, 0277) were made. To obtain a concentration series at each α, samples of the stock solutions, to which some $H_2{}^{17}O$ was added in the NMR (10 mm) tubes, were diluted stepwise in the tubes, with NMR measurements in between. The salt-free solutions were diluted with distilled and deionized water to obtain the concentration series. The solutions with excess salt were obtained by dilution with sodium chloride solutions of an aquamolality c_s, c_s was chosen equal to the sodium chloride aquamolality of the initial solution in the NMR tube. This procedure ensured constant NaCl aquamolality in these concentration series. Stock solutions of PAA, $\alpha = 0.489$, $c_p \simeq 0.012\ \bar{m}$, at several sodium chloride concentrations were prepared. For each c_s an NMR sample was prepared from these stock solutions and added $H_2{}^{17}O$. All manipulations involving $H_2{}^{17}O$ were performed at 4 °C to minimize exchange with atmospheric humidity. The final ^{17}O mole fractions ranged from 0.13 to 22.3%.

pH measurements were performed with a Radiometer GK-2401C combined glass/Ag-AgCl electrode with saturated KCl salt bridge. The Radiometer pH meter 26 was calibrated at 25.0 °C with buffer solutions 0.025 M KH_2PO_4/Na_2HPO_4 (Radiometer Precision Buffer S1500), pH 6.865, and 0.05 M potassium hydrogen phthalate (Baker, 0197), pH 4.008. The pH and NMR data were obtained from solutions prepared from the same stock solutions. The experimental error is estimated to be ±0.02 pH unit for polyelectrolyte concentrations above 0.02 $\bar{m}$ and for samples with added NaCl and somewhat larger for salt-free solutions of lower concentrations. According to Illingworth,[7] pH measurements with standard combination electrodes are often subject to large (ionic strength dependent) errors, which may be larger than 0.2 pH unit, even for measurements on well-buffered solutions. In connection with previous work,[1] we performed a large number of pH measurements on acetic acid/sodium acetate mixtures at several buffer ratios in the concentration range from 0.004 to 0.3 $\bar{m}$. Comparison of the results with literature values[8] indicated that, with our equipment, the experimental error is not larger than ±0.02 pH unit in that concentration range. However, it was found that stirring of the solution could give rise to large errors in dilute solutions.

Determination of the Exchange Rates. NMR measurements were performed with a home-modified Bruker pulse spectrometer at a field of 1.4 T, where the ^1H resonance frequency is 60 MHz. The temperature was 25.0 ± 0.3 °C. The longitudinal relaxation rate $R_1 = 1/T_1$ was measured by the inversion-recovery method, and the transverse relaxation rate $R_2 = 1/T_2$ was measured by the Carr-Purcell-Meiboom-Gill method. The estimated error margins of R_1 and R_2 are ±3% and ±5%, respectively. The exchange rate k_{ex} was determined from the dependence of R_2 on the Carr-Purcell pulse spacing t_{CP}. The experimental $R_2(t_{CP})$ were fit to the Luz-Meiboom equation,[9] eq 1, if $k_{ex} > 10^4\ s^{-1}$.

$$R_2(t_{CP}) = R_2(0) + \frac{35}{12}P(2\pi J_{OH})^2 k_{eff}^{-1}\left[1 - \frac{2}{t_{CP}k_{eff}}\tanh\frac{t_{CP}k_{eff}}{2}\right] \tag{1}$$

Here, $R_2(0) = \lim_{t_{CP}\to 0} R_2$, $J_{OH} = 86$ Hz[1] is the ^1H-^{17}O scalar coupling constant, P is the ^{17}O mole fraction, $k_{eff} = k_{ex} + R_1(^{17}O)$ is the effective exchange rate,[10] and $R_1(^{17}O)$ is the ^{17}O longitudinal relaxation rate. $R_1(^{17}O) = 141.6\ s^{-1}$ was taken from results on pure H_2O.[11] This should be a good approximation, as the water ^{17}O relaxation rate in PAA and PMA solutions, $c_p = 0.2\ \bar{m}$, at $\alpha = 0$ and $\alpha = 1$ is at most 15% larger than in pure water,[3] whereas in the present experiments the influence of ^{17}O relaxation is important only at much lower concentrations.

If $k_{ex} \leq 10^4\ s^{-1}$ resulted from a fit to eq 1 or was otherwise expected, a numerical method was used to solve the Bloch equations, extended with exchange terms (the Hahn-Maxwell-McConnell equations[12,13]). Further experimental details are described in the previous paper.[1] It could be expected that the assumption

$$R_2(0) = R_1 \tag{2}$$

used there no longer applies in macromolecular solutions, where molecular motions may be present that are not fast compared to the Larmor frequency. The deviations from eq 2 are expected from previous work[14] to be most pronounced in PMA solutions at high concentration and low α. As a check, the $R_1 - R_2$ difference was measured for two PMA solutions in water naturally abundant in ^{17}O at $\alpha = 0.301$ and $\alpha = 0.502$ at concentrations of 0.206 and 0.219 $\bar{m}$, respectively. The $R_1 - R_2$ difference was found to be 0.039 and 0.033 s^{-1}, respectively (that is 10% and 9% of R_1), independent of t_{CP}, thus only just outside the experimental error margin. Then, from the observed total exchange contributions to the transverse relaxation rate, it is estimated that the assumption eq 2 introduces an additional experimental error lower than 1.5% for all experiments. The overall experimental uncertainty in k_{ex} is estimated to be ±5%.

Hydrogen Ion Activity Coefficients. As will be discussed in the Results, values of appropriate operational activity coefficients γ_{H^+} are needed in order to evaluate the H_3O^+-catalyzed exchange rate contribution k_{H^+} (with eq 7) for salt-free solutions. γ_{H^+} were estimated from published sodium ion activity coefficients γ_{Na^+}, as determined in polyelectrolyte solutions with a sodium-selective glass electrode. Costantino et al.[15] have determined γ_{Na^+} in this manner for solutions of atactic PMA, DP = 2900, neutralized by sodium hydroxide to $\alpha = 0.43$, 0.65, and 0.97, respectively, and PAA, DP = 3700, $\alpha = 0.97$. γ_{Na^+} was found to be independent of the concentration in the investigated range $0.006 \leq c_p \leq 0.017$ mol/L and identical for PAA and PMA solutions at $\alpha = 0.97$. Okubo et al.[16] found no concentration dependence of γ_{Na^+} of solutions of PAA, DP = 1700, $\alpha = 1$ in the concentration range $0.008 \leq c_p \leq 0.25$ mol/L and only a slight decrease of γ_{Na^+} at lower concentrations. Their absolute γ_{Na^+}-values are higher than the values of Costantino et al.[15] at $\alpha = 0.97$ by 25-30%. We have taken γ_{H^+} as being constant in the presently investigated concentration range ($0.0025 \leq c_p \leq 0.22\ \bar{m}$), equal for PAA and PMA solutions and independent of molecular weight. We used the results of Costantino et al.[15] because these results pertain to the relevant α-range. Linear interpolation and extrapolation (as $\alpha\gamma_{Na^+}$ vs. α) resulted in $\gamma_{H^+} = 0.56$, 0.35, and 0.25 for $\alpha = 0.3$, 0.5, and 0.8, respectively.

Results

Rate Constants k_3. Exchange rates were measured for PAA and PMA solutions as a function of the concentration at several values of α. Results are given in Figure 1 for the concentration series with excess sodium chloride. Results for the concentration series without added salt are given in Figure 2. Experimental pHs of solutions with added salt were concentration independent in the range $0.01 \leq c_p \leq 0.1\ \bar{m}$, within the experimental error margin of ±0.02 pH, and are shown in Table I. pHs of solutions without added salt are given in Figure 3.

The results will be described by using the equation

$$k_{ex} = k_{H^+} + k_{OH^-} + k_{COOH} \tag{3a}$$

where

$$k_{H^+} = \tfrac{1}{3}k_1 c_{H^+} \tag{3b}$$

$$k_{OH^-} = \tfrac{1}{2}k_2 c_{OH^-} \tag{3c}$$

$$k_{COOH} = k_3 c_{COOH}/c_{H_2O} \tag{3d}$$

k_{ex} is the exchange rate, which is defined as the inverse

Table I
Rate Constants k_3 Obtained from Experiments on Solutions with Excess Added Sodium Chloride and on Solutions without Added Salt

		excess-salt expts				expts on salt-free solutions
solution	α	c_s, $\bar{m}$	pH	k_{H^+}, 10^3 s^{-1}	k_3,[a] 10^6 s^{-1}	k_3,[a] 10^6 s^{-1}
PAA, DP = 4100	0.301	0.635	4.18	163	74	61
	0.493	1.48	4.52	51	77	80
	0.785	1.49	5.47	6.5	97	106
PMA, DP = 2300	0.301	0.688	4.99	28	14.6	13.4
	0.502	1.38	5.28	11.0	17.5	16.1
	0.800	1.36	5.94	2.6	21.0	23.3
PAA, DP = 2100	0.449	1.46	4.37	61	66	77
PAA, DP = 26	0.494	1.46	4.63	43	67	72
PAA, DP = 6.3	0.566	1.47	4.60	41	69	

[a] An error margin of ±10% is estimated.

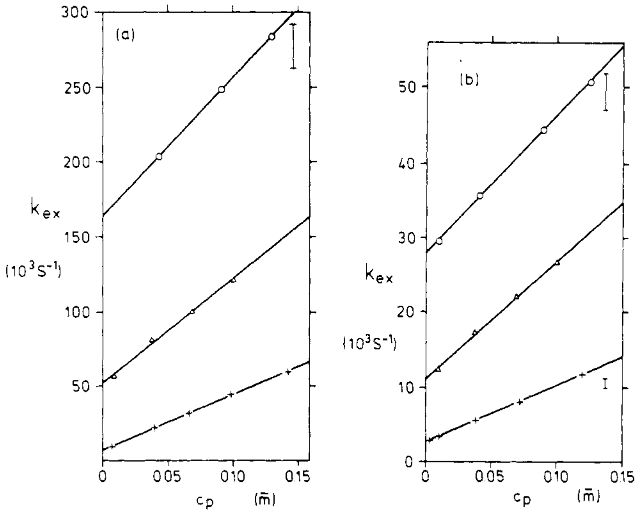

Figure 1. Experimental exchange rates k_{ex} as a function of the polyelectrolyte concentration c_p for solutions with excess NaCl: (a) PAA, DP = 4100, α = 0.301, 0.493, and 0.785, and c_s = 0.635, 1.48, and 1.49 $\bar{m}$ for the curves from top to bottom; (b) PMA, DP = 2300, α = 0.301, 0.502, and 0.800, and c_s = 0.688, 1.38, and 1.36 $\bar{m}$ from top to bottom. The drawn lines correspond to eq 3. The bars denote error margins of ±5%.

mean residence time of a proton in a water molecule. k_1, k_2, and k_3 are the rate constants for H_3O^+-, OH^-, and polyelectrolyte-catalyzed proton exchange, respectively. c_{COOH} is the monoaquamolality of COOH groups, which is approximated by

$$c_{COOH} = (1 - \alpha)c_p \tag{4}$$

The OH^--catalyzed exchange rate contribution k_{OH^-} will, as a first approximation, be calculated from

$$k_{OH^-} = \tfrac{1}{2}k_2 \times 10^{pH-pK_w} \tag{5}$$

From the literature, $k_2 = 3.4 \times 10^9$ s^{-1} $\bar{m}^{-1}$[17] and pK_w = 13.9965[18] (the ionization constant of water at 25 °C) will be used.

The results of the experiments with excess salt will be discussed first. For these experiments, using eq 5, k_{OH^-} is calculated to be less than 0.6% of k_{ex} and will be neglected. As in these experiments the pH is practically independent of c_p, it will be assumed that k_{H^+} is concentration independent. Then, according to eq 3, k_{ex} should depend linearly on c_p. This is seen to be in agreement with the results depicted in Figure 1. From the slope of the straight lines, obtained by least-squares analysis, k_3 was obtained. Results are shown in Table I.

It is seen from the figures that the results are well described by the linear equations. Thus, in contrast to the case of low molecular weight acids,[1] there is no indication of an exchange rate contribution quadratic in the concentration.

For the results on salt-free solutions a different approach is needed to separate the various contributions in eq 3, because here c_{H^+} can be expected to vary strongly as a function of c_p. To eliminate the concentration-dependent

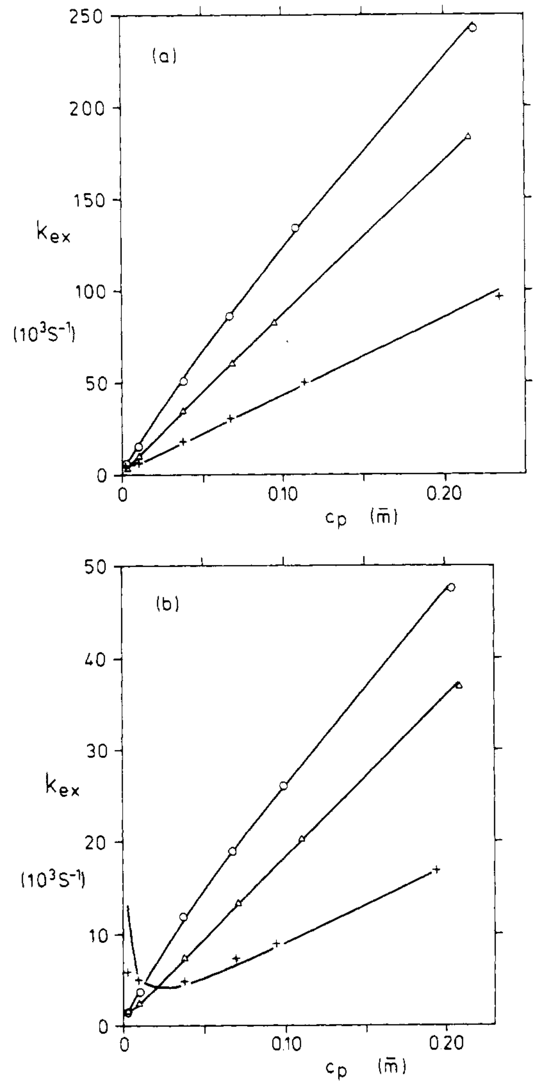

Figure 2. Experimental k_{ex} as a function of c_p for solutions without added NaCl: (a) PAA, DP = 4100, α = 0.301, 0.493, and 0.785, from top to bottom (b) PMA, DP = 2300, α = 0.301, 0.502, and 0.800, from top to bottom. The drawn lines correspond to eq 3.

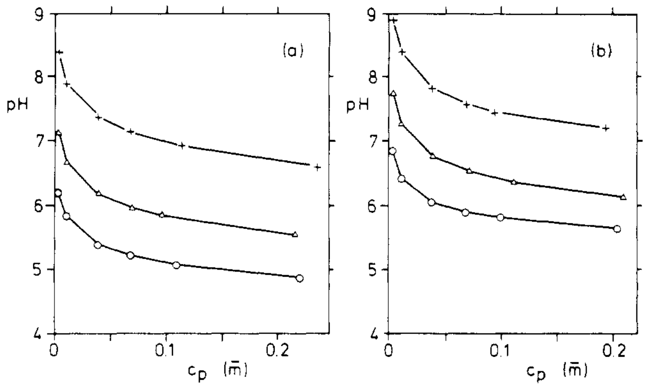

Figure 3. Experimental pH as a function of c_p for solutions of (a) PAA, DP = 4100, α = 0.785, 0.493, and 0.301, for the curves from top to bottom and (b) PMA, DP = 2300, α = 0.800, 0.502, and 0.301, from top to bottom.

k_{H^+} contribution, corrected exchange rates k_c are defined by

$$k_c = k_{ex} - k_{H^+} \tag{6}$$

k_{H^+} is calculated from the experimental pH according to

$$k_{H^+} = \frac{1}{3}k_1\left(\frac{1}{\gamma_{H^+}}\right)10^{-pH} \tag{7}$$

Here, $k_1 = (9.6 \pm 0.5) \times 10^9$ s^{-1} $\bar{m}^{-1}$[1] and γ_{H^+} is the appropriate operational hydrogen single-ion activity coefficient, defined by

$$\gamma_{H^+} = 10^{-pH}/c_{H^+} \tag{8}$$

Unfortunately, in polyelectrolyte solutions γ_{H^+} is not known. It can only be estimated from related quantities that may be determined experimentally in a direct manner. As explained in the Experimental Section, γ_{H^+} was taken equal to the sodium ion activity coefficient, as determined for PMA solutions,[15] from measurements with a sodium-selective glass electrode and calomel electrode with a KCl salt bridge. From uncertainty margins in γ_{Na^+} and k_1 of ±10% and ±5%, respectively, and an uncertainty margin in the experimental pH of ±0.02 pH, the calculated k_{H^+} is thought to be accurate to within ±12%.

Values of k_c are depicted in Figure 4. The relationship between k_c and c_p appears in most cases to be linear, with the appropriate straight lines going through the origin. This is in agreement with eq 3 and 6, if k_3 is concentration independent and k_{OH^-} is negligible. The deviations from such a straight line through the origin at higher α's and lower concentrations are expected to be caused by the increase of k_{OH^-} with decreasing concentration. For the solutions of PMA, α = 0.8, k_{OH^-} is important even at the higher concentrations, as will be discussed later. It is noted that a possible quadratic term in the rate equation is not indicated; this is in agreement with the results of the experiments with excess salt. For the experiments at α = 0.3, the correction for H_3O^+-catalyzed exchange is rather important (30–40% of k_{ex}). Therefore, some systematic error in the calculation of k_{H^+} could possibly be thought to obscure deviations from a linear dependence of k_c on c_p. However, the results at α = 0.5 and for PAA at α = 0.8, where the correction is smaller, strongly indicate linearity. Accordingly, we will again use eq 3 to obtain k_3 values, which are then calculated from

$$k_3 = (k_c - k_{OH^-})\frac{c_{H_2O}}{c_p(1-\alpha)} \tag{9}$$

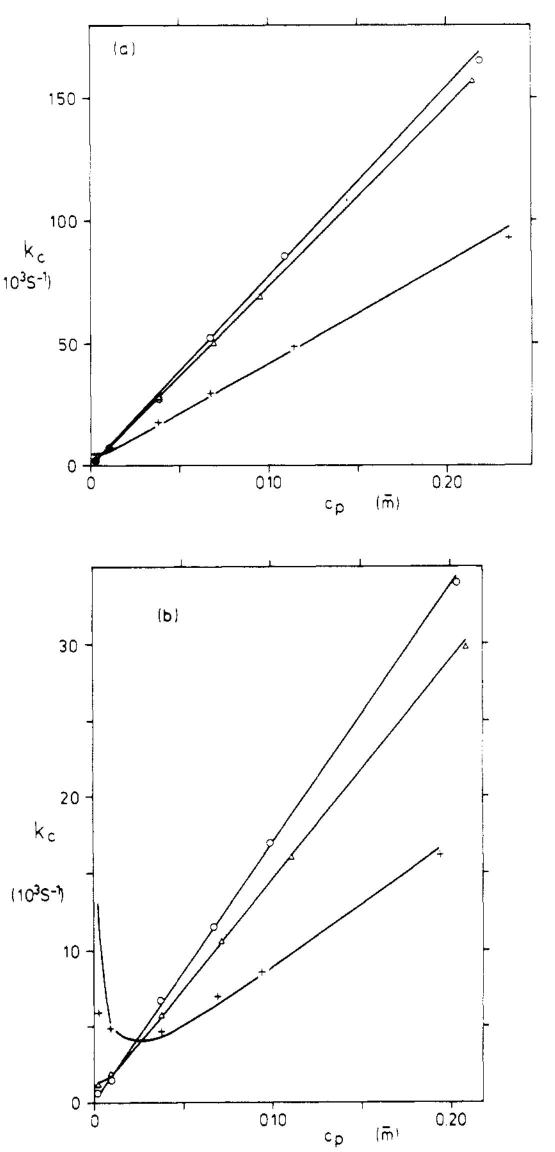

Figure 4. Exchange rates corrected for H_3O^+ catalysis ($k_c = k_{ex} - k_{H^+}$) as a function of c_p for solutions of (a) PAA, DP = 4100, α = 0.301, 0.493, and 0.785, for the curves from top to bottom and (b) PMA, DP = 2300, α = 0.301, 0.502, and 0.801, from top to bottom. The drawn lines are calculated according to eq 3 and 6. The bars denote error margins, calculated from the uncertainty margins in calculated k_{H^+} and experimental k_{ex} of ±12% and ±5%, respectively.

To minimize the influence of the uncertainty in the calculated k_{H^+} and k_{OH^-}, the average k_3 at each α was taken for concentrations where this influence is the least important: It was required that $k_{H^+} < 0.4k_{ex}$ and $k_{OH^-} < 0.005k_{ex}$, or for PMA, α = 0.800, where the second criterion is not satisfied in the experimental concentration range, $k_{OH^-} < 0.06k_{ex}$. This procedure implies that the lower two to four concentrations in each series are not used in the k_3 calculation. The drawn lines in Figure 2 correspond to eq 3, and those in Figure 4 correspond to eq 6 and 3, with k_3 from the last column of Table I. The agreement with experimental values is seen to be good, except for the lowest concentration of PMA, α = 0.8, where k_{OH^-} is expected to be dominant. This is thought to be related to the approximate character of eq 5 and possibly to the uncertainty in k_2 (values in the range (3.1–5.5) × 10^9 s^{-1} (mol/L)$^{-1}$ have been reported.[9,17,19] k_3 values obtained from experiments with and without excess salt are very similar (Table I), indicating that k_3 does not strongly depend on c_s.

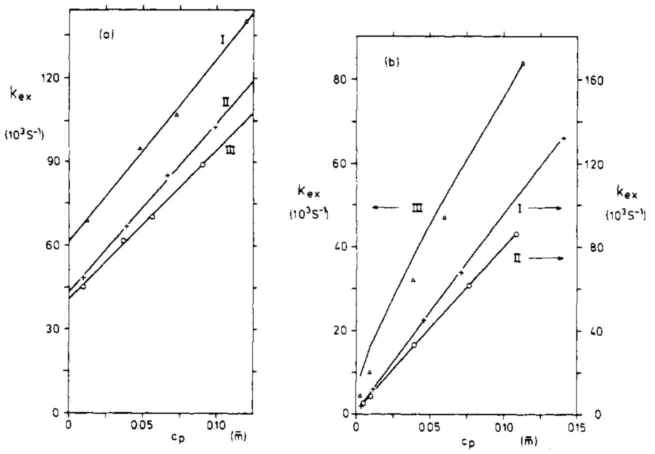

Figure 5. Results of experiments on solutions of PAA. Curves denoted by I, II, and III correspond to (I) DP = 2100, α = 0.449, (II) DP = 26, α = 0.494, and (III) DP = 6.3, α = 0.566. (a) Exchange rates k_{ex} for excess-salt experiments; c_s = 1.46, 1.46, and 1.47 $\bar{m}$ for curves I, II, and III, respectively. (b) Exchange rates k_{ex} for salt-free solutions. The drawn lines correspond to eq 3.

It is concluded that the use of γ_{Na^+} as an estimate of γ_{H^+} in eq 7and the use of k_1 from the value for dilute acetic acid solutions yield a consistent and plausible description of the experimental results via eq 3. However, if a possible influence of the polyelectrolyte on k_1 is anticipated, upper and lower bounds on k_1 can in some cases be established in the following manner. k_1 may be calculated from (see eq 3)

$$k_1 = \frac{3}{c_{H^+}}\left\{k_{ex} - k_{OH^-} - k_3\frac{c_{COOH}}{c_{H_2O}}\right\} \tag{10}$$

Here, c_{H^+} may be calculated from eq 8, with γ_{H^+} taken equal to γ_{Na^+} as before. In eq 10, k_3 is now varied in the range $0 \leq k_3 \leq k_{3,max}$, where the largest possible k_3 value, $k_{3,max}$, is obtained from k_{ex} at the highest concentration in a series (taking $k_1 = 0$ at that concentration). Then, taking into account uncertainty margins in k_{ex} of ±5% and in γ_{H^+} of ±10%, it follows that $4 \times 10^9 \leq k_1 \leq 16 \times 10^9$ s^{-1} $\bar{m}^{-1}$ for PAA, α = 0.3, c_p = 0.0029 $\bar{m}$. For PMA, α = 0.3, c_p = 0.0022 $\bar{m}$, it follows that $8 \times 10^9 \leq k_1 \leq 18 \times 10^9$ s^{-1} $\bar{m}^{-1}$. From this it is concluded that in these solutions k_1 cannot be drastically different from the value $k_1 = 9.6 \times 10^9$ s^{-1} $\bar{m}^{-1}$ obtained from experiments on acetic acid solutions. For solutions in the higher concentration or α-range, k_1 cannot be confined to a reasonably narrow range in this manner. However, there is no indication of a drastic influence on k_1 of added solute. This is in agreement with the rather weak dependence of k_1 on NaCl concentration, reported previously.[1]

Influence of the Degree of Polymerization. The procedures described in the previous section were also applied to solutions of PAA of lower degrees of polymerization. Results are depicted in Figures 5 and 6. The pH of the excess-salt solutions was again found to be independent of c_p. The k_3 values obtained are shown in Table I.

A linear dependence of k_c on c_p, in agreement with eq 3, is again obtained (see Figure 6b), except for PAA, DP = 6.3. From the negative values of k_c at low concentrations for DP = 6.3, depicted in Figure 6b, it is concluded that the applied activity corrections are inadequate there. This is not surprising in view of the low degree of polymerization. The data in Table I show that the molecular weight dependence of k_3, down to low degrees of polymerization, is unimportant.

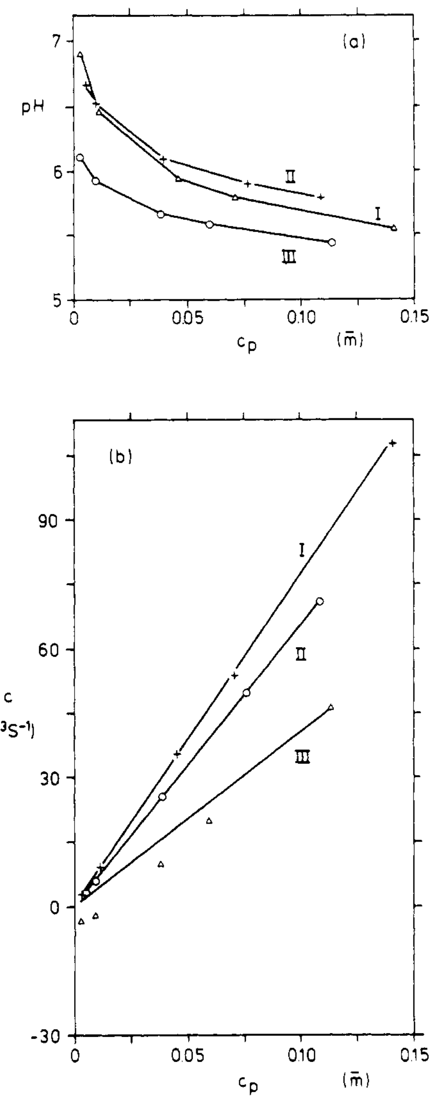

Figure 6. Results of experiments on solutions of PAA. Curves denoted by I, II, and III refer to the same solutions as in Figure 5. (a) Experimental pH for salt-free solutions. (b) Corrected exchange rates k_c for salt-free solutions. The drawn lines correspond to eq 3 and 6.

Influence of Added Salt. In Figure 7 results are depicted of experiments on solutions of PAA, DP = 4100, α = 0.489, $c_p \simeq 0.011$ $\bar{m}$, as a function of the concentration of added sodium chloride, c_s. It is seen that both the exchange rate and the pH are strongly dependent on c_s.

These results will be used to demonstrate that, in principle, it is possible to obtain hydrogen ion concentrations and activity coefficients from the experimental exchange rate. For this purpose eq 11 and 12 will be used.

$$c_{H^+} = (k_{H^+})_{exptl}/(\tfrac{1}{3}k_1) \tag{11}$$

Here, $(k_{H^+})_{exptl}$ is the experimentally determined H_3O^+-catalyzed exchange rate contribution.

$$(k_{H^+})_{exptl} = k_{ex} - k_2 \times 10^{pH-pK_w} - k_3\frac{c_{COOH}}{c_{H_2O}} \tag{12}$$

From c_{H^+} and experimental pH the hydrogen ion activity coefficient may then be obtained from eq 8. Significant results can only be obtained if the k_2 term is a minor correction, if an independent estimate of k_3 is available, and if $(k_{H^+})_{exptl}$ is a substantial part of k_{ex}. In the case of the added-salt experiments discussed in this section, these requirements are met. Here, $k_3 = 80 \times 10^6$ s^{-1} is taken from

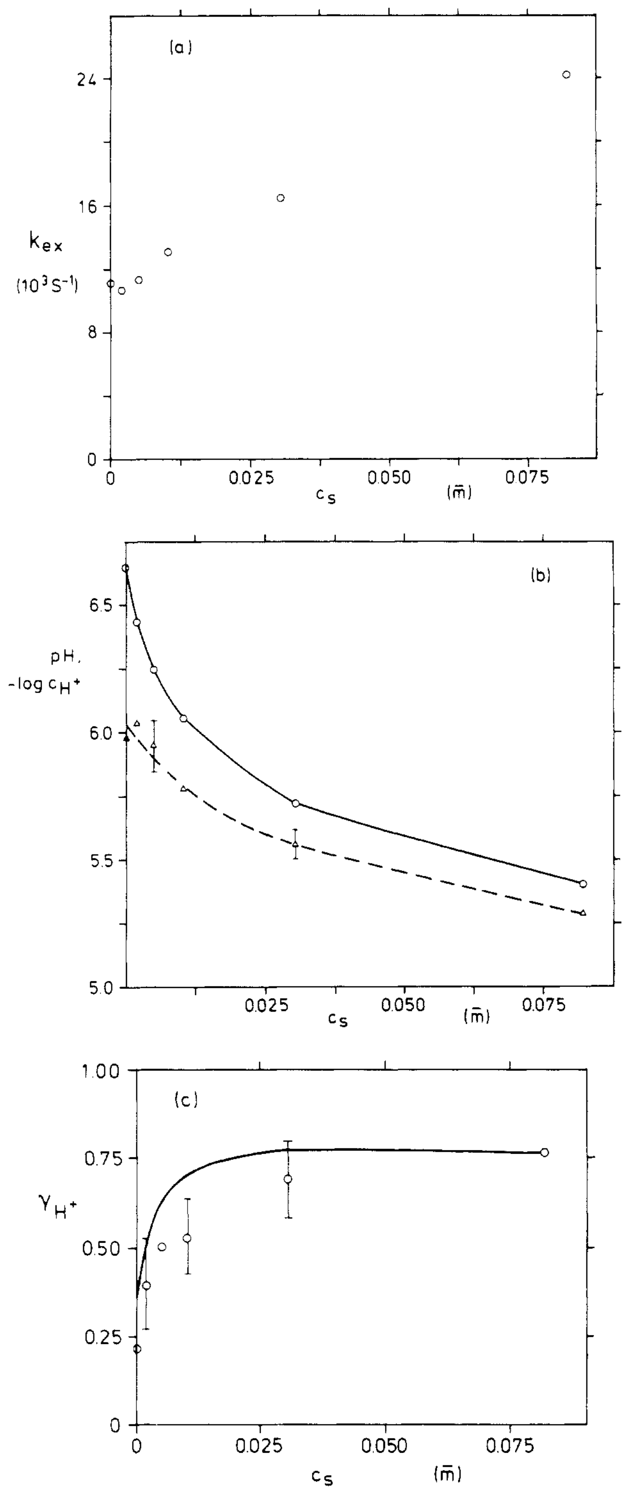

Figure 7. Results of experiments on solutions of PAA, DP = 4100, $\alpha = 0.489$, $c_p \simeq 0.011\ \bar{m}$, as a function of the concentration of added sodium chloride, c_s: (a) experimental exchange rates k_{ex}; (b) experimental pH (○) and $-\log c_{H^+}$ (△) calculated according to eq 11; (c) hydrogen ion activity coefficients γ_{H^+} calculated from eq 8 and 11. The solid line was calculated according to the additivity rule, eq 13.

the value for salt-free PAA solutions at the same α (see Table I).

Values of $-\log c_{H^+}$, calculated from eq 11, are depicted in Figure 7b. Uncertainty margins in this figure were calculated from the uncertainty margins in k_{ex} and k_3 of ±5% and ±10%, respectively. It is seen that the addition of small quantities of salt leads to a decrease of $-\log c_{H^+}$, similar to, but less pronounced than, the decrease of pH. In Figure 7c the $\gamma_{H^+}(c_s)$ obtained from eq 8 and 11 are compared with values calculated from the additivity rule, eq 13, which often gives a reasonable estimate of counterion activity coefficients γ_c in polyelectrolyte solutions with added salt.[20]

$$\gamma_c = \frac{c_s\gamma_s + c_e\gamma_p}{c_s + c_e} \tag{13}$$

Here, c_s and c_e are the concentrations of counterions from added simple salt and polyelectrolyte and γ_s and γ_p are the activity coefficients of the ions in salt solutions without polyelectrolyte and in salt-free polyelectrolyte solution, respectively. $\gamma_p = 0.35$ was taken from γ_{Na^+} reported by Costantino et al.[15] and γ_s was taken from ref 21. Experimental γ_{H^+} is seen to be in semiquantitative agreement with the additivity rule, the large error margin in γ_{H^+} not allowing detailed conclusions. The results show the initial low value and the pronounced increase of γ_{H^+} as a result of the addition of a small amount of simple salt, typical for activity coefficients of counterions in polyelectrolyte solutions.

The above results show the possibility of obtaining hydrogen ion concentrations and activity coefficients from the experimental exchange rate. The uncertainty in such results would probably be smaller for experiments at lower concentrations and α-values, because then the uncertainty in calculated k_{COOH} will be less important.

Discussion

General. In the polyelectrolyte solutions investigated it was found that the polyelectrolyte contribution to the water proton exchange rate, k_{COOH}, is a linear function of c_p, both in salt-free and in excess-salt solutions. From this observation it is concluded that k_{COOH} is dominantly caused by intramolecular reactions. This is contrary to the situation with low molecular weight carboxylic acid solutions, where intermolecular proton transfer via solvent between COOH and COO⁻ groups was found to be important over a similar concentration range.

The rate constant k_3 for intramolecularly catalyzed water proton exchange in acetic acid solutions, which is attributed to the cyclic process $COOH + nH_2O \rightleftarrows COOH + nH_2O$,[22] was previously determined to be $(8.6 \pm 2.3) \times 10^6$ s^{-1}.[1] For PAA solutions k_3 was found to be 61×10^6 s^{-1} or higher (Table I). It is improbable that the cyclic exchange process would be much faster for PAA than for acetic acid, where it was found to be relatively unimportant. Thus, as suggested previously,[3] an important contribution to k_3 is thought to occur as a result of proton transfer via solvent between COOH and COO⁻ groups on the same polymer chain.

From the increase of k_3 with α, which is found for both salt-free and excess-salt PAA solutions (see Figure 8), it is concluded that the average number of nearby COO⁻ groups to which a proton may be transferred from a particular COOH group is probably an increasing function of α.

$(k_3)_{PMA}$ was found to be about 5 times smaller than $(k_3)_{PAA}$ over the whole α range. Here, it is not a priori clear that transfer between COOH and COO⁻ groups is the dominant mechanism, because $(k_3)_{PMA}$ is only about 2 times larger than $(k_3)_{\text{acetic acid}}$. However, the α-dependences of $(k_3)_{PMA}$ and $(k_3)_{PAA}$ are similar, suggesting a similar mechanism. For PMA, as compared to PAA, the dissociation constant is smaller, the reorientations of the polymeric COOH groups are slower,[14,23] and the presence of the CH_3 groups may interfere with the formation of a favorable hydrogen bond configuration, necessary for the occurrence of proton transfer. All of these factors may be envisioned to lead to a smaller k_3 for PMA.

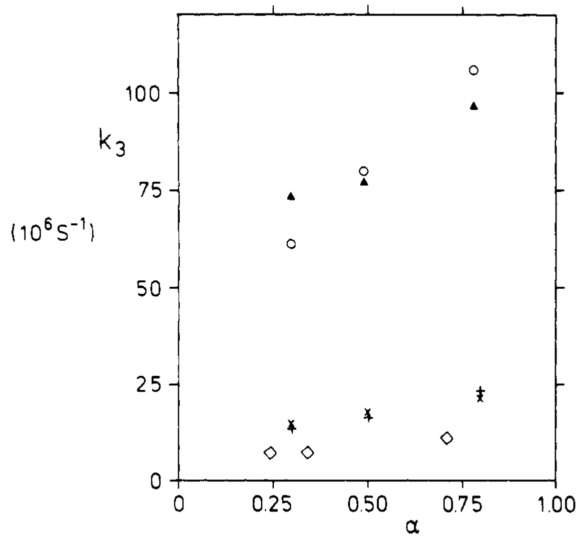

Figure 8. Rate constants for polyelectrolyte-catalyzed hydrogen exchange, k_3, as a function of α, obtained from experiments on solutions of (▲) PAA, DP = 4100, with excess salt, (○) PAA, DP = 4100, without added salt, (×) PMA, DP = 2300, with excess salt, (+) PMA, DP = 2300, without added salt, and (◇) PMA, DP = 5200, without added salt, in 80% D_2O (from ref 2).

Comparison with Previous Results. In previous work[2] ^1H exchange rates were determined in solutions of PMA, DP = 5200, in ^{17}O-enriched H_2O/D_2O mixtures at a deuterium mole fraction $x = 0.806$. k_3 values were obtained by the use of an approximate correction for H_3O^+ catalysis. These k_3 values are depicted in Figure 8 also. The increase of k_3 with α is again apparent, whereas the absolute values are lower by about a factor of 0.6. This may be attributed to the deuterium isotope effect on k_3. Linear extrapolation to $x = 1$ yields a total isotope effect on k_3 for H transfer of 0.5, which is equal to the isotope effect on the rate constants for acetic acid catalyzed H exchange of 0.51 ± 0.07[1] within the experimental error.

Halle and Piculell[3] have investigated proton exchange in PAA and PMA solutions from ^{17}O line width measurements as a function of the pH. With this method a significant exchange broadening is only obtained in the pH range 6–8. They have interpreted their results with an equation analogous to our eq 3 (their eq 5 and 7, with $r = 2k_{ex}$).

Experiments on pure water and on $1.50 \times 10^{-3}\ \bar{m}$ PAA (DP = 3200) and $10.2 \times 10^{-3}\ \bar{m}$ PMA (DP = 90) solutions were performed. Activity corrections were not taken into account, and an α-independent rate constant for COOH-catalyzed exchange was assumed. The results were, in our notation, $(k_3)_{PAA} = 179 \times 10^6\ s^{-1}$ and $(k_3)_{PMA} = 32.3 \times 10^6\ s^{-1}$. These values are almost 2 times higher than the average values obtained in this work. Taking into account activity corrections would lead to lower k_3 values, bringing the values of Halle and Piculell in better agreement with the present results. Their ratio $(k_3)_{PAA}/(k_3)_{PMA} = 5.5$ is about the same ratio that we obtained.

Weiss et al.[4] have studied proton transfer between PAA and PMA on the one hand and the indicator phenol red on the other by the temperature jump (relaxation) method. They report a rate constant of $(2 \pm 1) \times 10^7\ s^{-1}\ (mol/L)^{-1}$ independent of α, both for PAA (DP = 1000) and PMA (DP = 1000). This confirms that carboxylic groups on polyelectrolytes may be involved in fast proton-exchange processes. As a plausible explanation of the fact that a single relaxation time of the chemical equilibrium was obtained in all cases, they proposed that fast proton exchange between different parts of the polyelectrolyte might take place via a system of hydrogen bonds along the chain. Our results clearly indicate that such a process takes place via intervening water molecules. Without this intervention no contribution to the exchange rate k_{ex} would be observed.

Table II
Residence Times in COOH and COOD Groups, τ_{COOH} and τ_{COOD}, in Salt-Free Solutions of PAA (DP = 4100) and PMA (DP = 2300) and $\tau_\perp$ Values for Anisotropic Rotational Diffusion Models Used in the Literature

solution	α	τ_{COOH}[a] in H_2O, ns	τ_{COOD}[b] in D_2O, ns	$\tau_\perp$, ns
PAA	0.8	4.7	17	
	0.3	8.2	30	
	0			17[c]
PMA	0.8	21	77	
	0.3	37	134	
	0.35			32[d]
	0			115[d]

[a] Calculated from eq 14, with $n = 1$ and k_3 from Table I, last column. [b] Calculated from eq 15. [c] For PAA, DP = 19 000, at 28 °C.[23] [d] For PMA, DP = 4700, at 28 °C.[14]

Proton Residence Time in a COOH Group. If the average number of water molecules via which a proton is transferred in the processes responsible for k_{COOH} is denoted n, the residence time of a proton in a COOH group, τ_{COOH}, is given by

$$\tau_{COOH} = [2k_3/n]^{-1} \qquad (14)$$

For the cyclic process involving COOH only, $n = 2$ has been proposed. For the transfer between COO^- and COOH in acetic acid solutions, $n = 1$ was indicated from the observed deuterium isotope effects on the rate constant.[1] For PAA the second process is supposed to be dominant; for PMA it is expected to have at least an important contribution to k_3. Accordingly, we will use eq 14, with $n = 1$. Results on τ_{COOH} are shown in Table II.

It is noted that n could be larger as well as smaller than 1. The latter is possible if direct proton transfer between COOH and COO^- groups, which is not detected by the method used here, is also important.

In our laboratory a number of studies were performed on the results of solvent deuterium relaxation measurements on polyelectrolyte solutions in D_2O.[14,23,24] In the interpretation of these experiments the COOD motions were described in a model of axially symmetric anisotropic rotational diffusion. It was assumed that the residence time of a deuteron in a COOD group is much larger than the longer correlation time in the rotational diffusion model, $\tau_\perp$. The validity of this assumption will now be discussed.

The deuterium isotope effect on $(k_3)_{PMA}$ obtained from a comparison of the present values in H_2O with previously determined values in 80% D_2O[2] and the corresponding isotope effect obtained for acetic acid[1] were found to be equal within the experimental accuracy. Therefore, in the calculation of τ_{COOD} in D_2O from k_3 values in H_2O it will be assumed that the isotope effects on τ_{COOH} for the investigated polyelectrolytes and for acetic acid are equal. For acetic acid solutions

$$(\tau_{COOD})_{D_2O} = 3.6(\tau_{COOH})_{H_2O} \qquad (15)$$

has been obtained.[1] The resulting COOD residence times are shown in Table II.

The anisotropic rotational diffusion models discussed above were applied to PAA solutions for $\alpha = 0$[23] and to PMA solutions for $0 \leq \alpha \leq 0.35$.[14] Upper limits of the deduced $\tau_\perp$ are given in the last column of Table II. From this table it may be concluded that the loss of correlation of the quadrupole interaction responsible for deuterium relaxation in a COOD group is dominantly caused by the rotational motions. Thus the slow-exchange limit with respect to the molecular motions may indeed be assumed to be valid approximately. Still, the deuterium exchange should probably be taken into account by at least a correction on the obtained $\tau_\perp$.

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Registry No. Poly(acrylic acid) (homopolymer), 9003-01-4; poly(methacrylic acid) (homopolymer), 25087-26-7.

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Molecular and Crystal Structure of Dextrans: A Combined Electron and X-ray Diffraction Study. 1. The Anhydrous High-Temperature Polymorph[†]

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ABSTRACT: The crystal and molecular structure of an anhydrous polymorph of a linear, synthetic dextran has been determined through a combined electron and X-ray diffraction analysis and stereochemical model refinement. Electron diffraction data corrected for beam damage were obtained from lamellar single crystals grown from dilute solution and included $hk0$ data to a resolution of 1.1 Å, as well as selected higher layer reflections. The X-ray data in the form of powder patterns were recorded from collections of the same crystals. The structure crystallizes in a monoclinic unit cell with parameters a = 9.22 Å, b = 9.22 Å, c (chain axis) = 7.78 Å, and β = 91.3°. The space group is $P2_1$ with the b axis unique. Two antiparallel-packed molecular chains pass through the unit cell, and the asymmetric unit contains two glucopyranose residues. The base plane of the unit cell is not at right angles to the chain axes. The conformation of the molecule is relatively extended and ribbon-like, with successive glucopyranose residues in a near-twofold screw relationship. The chain conformation is stabilized by one intramolecular hydrogen bond per glucose residue. The chains of like polarity pack into sheets with extensive intrasheet hydrogen bonding. The sheets, packed antiparallel, are likewise extensively bonded together by intersheet hydrogen bonds. The conformational angles ϕ, ψ, and ω show the ϕ angle to be governed by the exo-anomeric effect and the O(6) rotation to be gt. Although the structure resides in a stereochemical energy minimum, the actual conformation could not be predicted by energy minimization methods. The structure solution was straightforward using combined electron diffraction and powder X-ray data, with final residuals R''(electron diffraction) = 0.189 and R(X-ray) = 0.101.

Introduction

During the past 15 years, the crystal structures of many naturally occurring α- and β-(1–3)- and -(1–4)-linked polysaccharides have been determined.[1-7] Both homopolymers and heteropolymers—either in linkage or in sugar residue—are included in this list.[5-7] Many polymorphs, hydrates, and complexes have been characterized, and as a result, a considerable body of information now exists on the structure of these classes of polysaccharides. In the course of these studies, sophisticated procedures for polymer crystal structure refinement have been developed, dealing both with the interpretation of fiber X-ray diffraction data and with stereochemical model analysis.[8]

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