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ORIGINAL CONTRIBUTION

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Kinetics and equilibrium of the complexation of Al^{3+} with poly(maleic, acrylic) acid

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Abstract Kinetics and equilibrium of the complexation of Al^{3+} with a polycarboxylic acid (PCA, random copolymer of maleic and acrylic acid with a mean molecular weight of 92 kDa) are investigated by the stopped flow technique and potentiometric titration. The complexation proceeds according to the Eigen–Tamm mechanism, i.e. in first diffusion-controlled step an outer sphere complex is formed. The second rate determining step is the formation of the inner sphere complex, controlled by the exchange rate of hydration water. For this second step the rate constant is $k_1 = 3\,s^{-1}$. It is in the order of magnitude of the water exchange at the Al^{3+} ion as expected for the Eigen–Tamm mechanism. The activation parameters are also determined. Parallel to this direct reaction path a base catalyzed path is found, typical for complexation reactions of hydrolyzable metal ions.

Stable complexes are formed for which the overall association constant $K_{ass} = Q_o(1 + K_i)$ is determined by two parts: a chemical (intrinsic) part, described by the inner sphere association constant $K_i = 3$ and an electrostatically controlled part described by the outer-sphere association quotient Q_o. The evaluation of the kinetic experiments allows to determine the value of $\log(Q_o)$ as a function of pH: $3.3 < \log Q_o < 4.6$. From these data the potential is calculated in the range -67 to -93 mV at pH values between 2 and 4.

For comparison, analogous experiments with the monomeric subunits of the polyacid, glutarate (GA), and tricarballylate (TCA), are performed. The complexation with the monomeric subunits glutaric- and tricarballylic acid can be explained within the classical view of a discrete outer sphere association constant Q_o.

Key words Polyelectrolyte – aluminum – chemical kinetics – metal complexation

Introduction

The mobility of toxic heavy metal ions and Al^{3+} in nature is to a great extent controlled by complexation reactions at natural polyelectrolytes like humic acids [1]. These possess a very complex structure, and thus it is very difficult to investigate the binding mechanisms of metal ions by evaluation of equilibrium and kinetic data. Therefore, studies at defined synthetic polycarboxylic acids are necessary for a basic understanding of the binding mechanisms. Moreover, synthetic polycarboxylic acids are nowadays often used as additives to detergents and they get in large amounts into waters and soils. There they are competitors for natural polyelectrolytes like humic acids and may form complexes with toxic ions like Al^{3+} and heavy metal ions, which are mobilized from soil minerals by the acid rain. In this study the complex formation of Al^{3+} with a synthetic copolymer of maleic- and acrylic acid, denoted in the following as PCA, (Sokalan® BASF-AG, Germany) is investigated.

Investigations on the complexation behavior of Al^{3+} with polyacids are missing to our knowledge whereas the reaction mechanism with small ligands is well understood in aqueous solution. The complexation proceeds according to Eigen's mechanism for metal ion complexation [2–5]. In the first, diffusion-controlled step an outer-sphere complex is formed, where the ligand and the metal ion are separated by the inner hydration shell of Al^{3+}. The second, rate determining step is then the exchange of H_2O from this inner hydration shell. Its rate is determined by the water exchange rate at the metal ion which for Al^{3+} is $k_{ex} = 1.29\,s^{-1}$ [6]; correspondingly for the complexation with low molecular weight carboxylic acids the rate constants are small, but in contrast to transition metal ions like Ni^{2+} they depend on the ligands affinity to H^+, and a linear free energy relation could be proved [5]. A parallel reaction path exists via the hydrolized outer- and inner-sphere complexes which is faster than the direct exchange and becomes dominant at $pH > 3$ [4].

Most of the published investigations on the complexation behavior of polyelectrolytes are concerned with the state of equilibrium of metal ion association and describe it in terms of association constants. Some newer examples comprise the determination of the association of mono-, di-, and trivalent ions with polyelectrolytes, studied by voltammetric techniques [7–9], and the binding of lanthanide ions, investigated by luminiscence spectroscopy [10]. Kinetic studies of metal ion binding at polyelectrolytes are rare. For example Diebler et al. [11, 12] have investigated the complexation of the Ni^{2+}-ion to DNA by means of the *T*-jump method.

In a previous work we have determined the complexation mechanism of Ni^{2+} to a polycarboxylate by combining relaxation measurements with potentiometric titrations [13]. The reaction takes place according to Eigen's two-step mechanism for metal ion complexation [2]. The first step is the formation of the outer-sphere complex analogous to the reaction of metal ions with small ligands. But the value of the outer sphere association constant Q_o, (calculated from the kinetic measurements) is much higher than that for small carboxylates. It was shown that this effect is caused by the high electrical potential of the polyelectrolyte [13]. After the formation of the outer sphere complex the reaction proceeds with the formation of the inner-sphere complex, comprising the release of a water molecule from the inner hydration shell of Ni^{2+} and the formation of the bond to the carboxylate moiety. Its rate constant is of the same order of magnitude as found for reactions with small carboxylates like acetate.

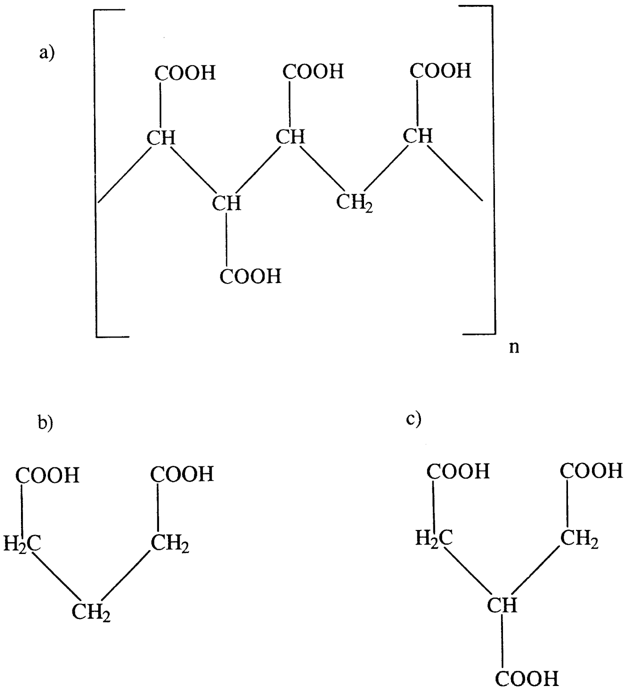


Fig. 1 Structures of the ligands: (a) polycarboxylic acid (PCA), (b) glutaric acid (GA), and (c) tricarballylic acid (TCA)

The aim of this study is to investigate the complexation of Al^{3+} with a commercial polycarboxylic acid (see *Material and Methods*), to elucidate the influence of polyelectrolyte properties like high electric potentials on the binding mechanism. Analogous experiments are performed with glutaric-, and tricarballylic acid, in the following abbreviated as GA and TCA, respectively, which represent the smallest subunits of the polycarboxylic acid (PCA). With those small carboxylic acids no polyelectrolyte effects are expected, i.e. the outer sphere association constant should be a discrete value independent of pH. Thus, it is possible to check the accuracy of the measurements and the correctness of the data evaluation for the polyelectrolyte. Figure 1 shows the structures of the investigated ligands.

The kinetics are investigated using the stopped flow technique with conductivity detection, which in comparison with relaxation techniques has the great advantage that, in addition to the evaluation of the relaxation times, association constants are also obtainable directly from the reaction amplitudes [5]. The complete reaction scheme describing all steps of the complex formation is rather complicated since it contains three unknown equilibrium constants and four unknown rate constants (see *Reaction model*). Therefore, the evaluation of observable reaction rates and reaction amplitudes must be combined for two independent series of measurements, with varying concentrations of PCA and Al^{3+} and with varying pH, in order to yield the required self-consistent set of coefficients. A comparison of the overall association constant obtained from the kinetic measurements with that obtained from potentiometric titration will prove the validity of reaction scheme and data treatment.

Material and methods

$Al(NO_3)_3 \cdot 9H_2O$, glutaric acid, and tricarballic acid of grade p.A. were obtained from Fluka AG, Switzerland and used without further purification. The polyelectrolyte was provided by BASF AG, Germany (Sokalan®, CP5). It is a random copolymer of acrylic and maleic acid in a ratio of 0.7:0.3 with a mean molecular weight of 92 kDa and a polydispersity factor (M_w/M_n) of 17.7. The original sample, an undefined Na-salt, was brought into its fully protonated form by treating it with an acidic Amberlite cation exchanger in a column, until no further change in pH and conductivity was detectable.

The potentiometric titrations were performed using a Metrohm 605 pH-meter with an accuracy of $\delta pH = \pm 0.03$. The pH-meter was calibrated with standard buffers and a reference titration of a defined sodium acetate solution. Conductivity measurements were performed with the automatic precision brigde B 905 of Wayne Kerr with a relative error in conductivity of ± 0.1%. For the kinetic measurements a self-constructed stopped flow apparatus was used, where the progress of the reaction is monitored by the change in conductivity. The dead time of equipment is 5 ms and a relative change of conductivity of less than 0.01% can be monitored. The reactions were started by mixing the $Al(NO_3)_3$ solution with a solution containing the carboxylic acid. Both solutions were adjusted to the same pH (±0.05) and the same conductivity (±1.0%) using NaOH, HNO_3 and $NaNO_3$. To prevent artefacts caused by a temperature drift the whole assembly is plunged into a thermostated bath with an accuracy of $\delta T = \pm 0.05\,^{\circ}C$. All kinetic measurements and the titrations in presence of Al^{3+} were performed in the range $2.0 < pH < 4.0$ to ensure that only the monohydroxo complex of Al^{3+} is taken into consideration during the base-catalyzed path. Furthermore, it was observed that Al–PCA complex precipitates at pH values above 4.0.

In all stopped flow experiments a great excess of the concentration of carboxylic groups was used to realize the pseudo-first-order conditions. Figure 2 shows a typical experiment. A single-exponential function is fitted to the experimental data. In the following the relative difference in conductivity $\Delta\kappa/\kappa_e = (\kappa_e - \kappa_0)/\kappa_e$ is termed *amplitude* and the rate constant k_{obs}, characteristic for this single-exponential decay, is termed *pseudo-first-order rate constant*. For the evaluation of the amplitudes and relaxation times at least five single runs were accumulated. To obtain the thermodynamic constants the temperature was varied from 15 °C to 35 °C in steps of 5 °C.

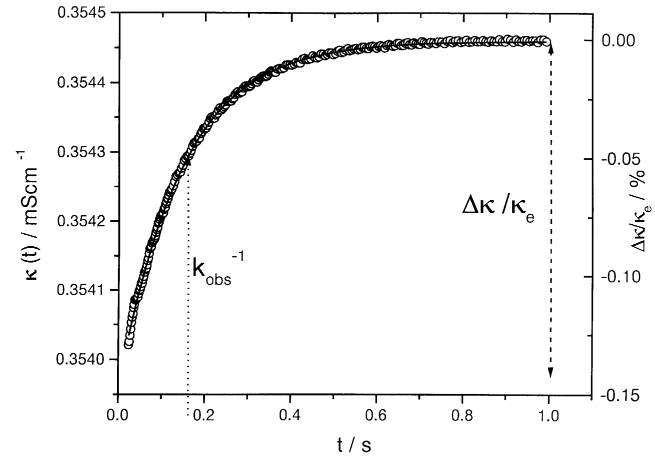


Fig. 2 Change in conductivity at a stopped flow experiment under pseudo-first-order conditions observed for the reaction of 0.1 mM $Al(NO_3)_3$ with 48 mM PCA (as concentration of R–COOH) at $pH = 3.52$ and $T = 25\,^{\circ}C$. k_{obs} is the observed pseudo-first-order rate constant, and $\Delta\kappa/\kappa_e$ is the relative change of the conductivity termed also as *amplitude*, κ_e is the conductivity at equilibrium

Reaction model

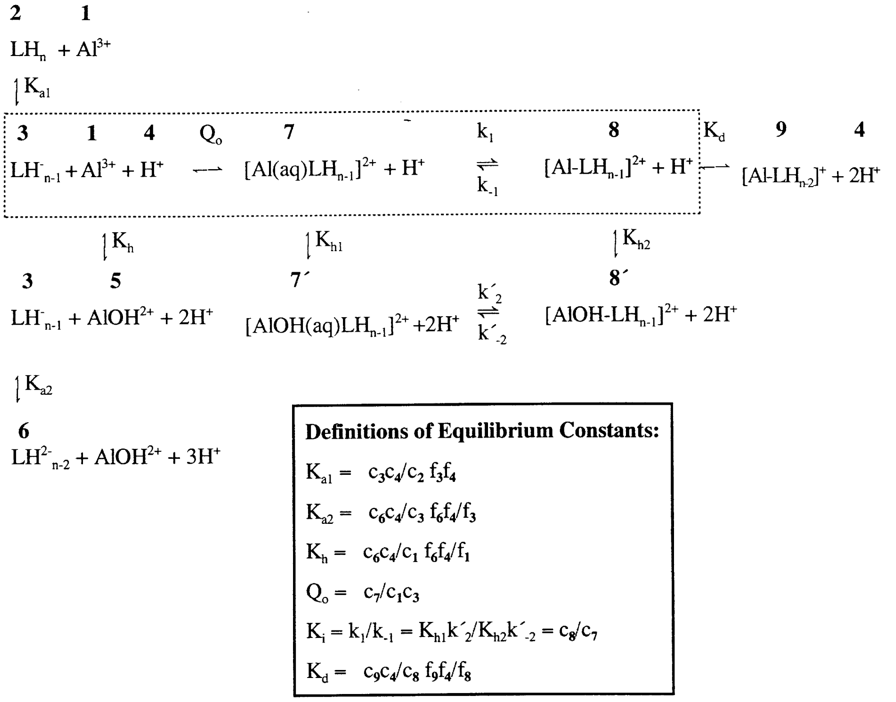
This work deals with the first observable reaction step of the binding of Al^{3+} at PCA (and for comparison at glutaric- and tricarballylic acid), i.e. the formation of the inner sphere complexes. Any possible subsequent reactions like conformational changes or aggregation processes induced by the formation of the inner sphere complexes are slower (see *Results and discussion*) and are not relevant to this study.

Reaction scheme

This section describes the reaction of Al^{3+} with the investigated anionic ligands, glutarate (GA), tricarballate (TCA), and polycarboxylate (PCA). Figure 3 shows the complete reaction scheme used for all calculations in this work, all equilibrium constants are defined in the lower part of the figure.

(i) First of all the acidity of the ligands must be considered. The deprotonation of the polyelectrolyte PCA can

Fig. 3 (Upper part) reaction scheme for the complexation of Al^{3+} with GA ($n = 2$), TCA, and PCA ($n = 3$). (Lower part) definitions of equilibrium constants used this work



Definitions of Equilibrium Constants:

$K_{a1} = c_3c_4/c_2\, f_3f_4$

$K_{a2} = c_6c_4/c_3\, f_6f_4/f_3$

$K_h = c_6c_4/c_1\, f_6f_4/f_1$

$Q_o = c_7/c_1c_3$

$K_i = k_1/k_{-1} = K_{h1}k'_2/K_{h2}k'_{-2} = c_8/c_7$

$K_d = c_9c_4/c_8\, f_9f_4/f_8$

be described by various models. One way is an intrinsic deprotonation constant ${}^{\mathrm{int}}K_a$, combined with a term describing the electrostatic interaction between protons and polyelectrolyte chain [1], a second possibility is a continuous distribution function of K_a [13, 14]. In this work, a third way is chosen, which is convenient for investigations in a limited pH-range: The deprotonation is approximated by a set of three discrete deprotonation constants, $K_{a,n}$ with $n = 1, 2$, and 3, a model similar to that of Tipping for humic acids [15] and its validity range will be shown in the "Results".

(ii) The second crucial point in the reaction scheme is the description of the outer sphere association, defined in Fig. 3 by Q_0. Q_0 depends only on electrostatic interactions and can be calculated by Eq. (1) [16]

$$Q_o = V_{\mathrm{coll}} N_A \exp\left(-\frac{3e_0\psi_L}{k_B T}\right) , \tag{1}$$

where V_{coll} is the collision volume defined by Eq. (2)

$$V_{\mathrm{coll}} = 4\pi r^3/3 , \tag{2}$$

with the distance of closest approach r. In Eq. (1) ψ_L is the electrical potential of reacting species of the ligand, e.g. "LH_{n-1}^-", e_0, k_B, and T are elementary charge, Boltzmann's constant, and absolute temperature, respectively. For *small* ligands like glutarate and tricarballylate, ψ_L does not vary continuously with pH, i.e. it has discrete values corresponding to their state of ionization. In this case Q_o becomes a real thermodynamic constant and ψ_L may be calculated by Eq. (3)

$$\psi_L = z_L e_0/r\varepsilon , \tag{3}$$

where $z_L e_0$ is the charge of the ligand, r is the distance of closest approach and ε is the dielectric constant of the medium. For the mono- and divalent species of the small ligands GA and TCA $\log(Q_o\, \mathrm{dm}^{-3}\, \mathrm{mol}^{-1})$ is calculated as 1.3 ± 0.3 and 2.1 ± 0.3, where the error is caused by the uncertainty in the distance of closest approach. These data show, that in the pH range of this study (for GA and TCA pH < 3.7) the concentration of outer sphere complexes formed by divalent species of the ligand may be neglected.

In contrast, for *polyelectrolytes*, ψ_L depends on the total charge of the ligand, the ionic strength, the dielectric constant of the medium, the size of the polymer, its shape and its concentration. It varies continuously with pH, since the charge of a polyelectrolyte also varies. In this case Q_o will depend strongly on ionic strength and pH. It will be shown in the next two sections how Q_o and therefore ψ_L may be determined by evaluation of reaction amplitudes $\Delta\kappa/\kappa_e$ and observed pseudo-first-order rate constants k_{obs} of the kinetic measurements (for definitions see Fig. 2).

(iii) The rate-determining step is the formation of the inner sphere complex 8 as shown in Fig. 3. According to the Eigen–Tamm mechanism the rate is determined by the exchange of one H_2O molecule of the inner hydration shell of Al^{3+} by a bond with the ligand, which is described by k_1 and k_{-1}. These rate constants depend on the chemical nature of the metal ion, not on the ligand. Consequently, the rate is strongly dependent on the speciation of Al^{3+}. In earlier studies [4, 5] we could prove that the exchange rate in an outer sphere complex formed by $AlOH^{2+}$ is much faster than at Al^{3+} due to the smaller charge density. Therefore, a base-catalyzed pathway via the species **7′** and **8′** must be taken into consideration although these species exist only in negligible amounts compared to **7** and **8**. Finally, the deprotonation reaction of the inner sphere complex is introduced by the constant K_d.

Table 1 Thermodynamic and kinetic data for the complexation of Al^{3+} with carboxylates at 25 °C

	Glutaric acid [GA]	Tricarballylic acid [TCA]	Polycarboxylic acid [PCA]
pKa_1	4.37 ± 0.05	3.72 ± 0.05	4.0 ± 0.1
pKa_2	5.50 ± 0.1	5.05 ± 0.05	5.9 ± 0.1
pKa_3	—	6.6 ± 0.1	7.8 ± 0.1
pK_d	5.4 ± 1.0	3.5 ± 1.0	3.0 ± 1.0
$\log K_i$	1.15 ± 0.04	1.15 ± 0.04	0.54 ± 0.11
$\log (Q_0\,dm^{-3}\,mol^{-1})$	1.3 ± 0.3*	1.3 ± 0.3*	3.3 to 4.6#
$k_1\,[s^{-1}]$	37 ± 4	19 ± 2	3 ± 1
$k_{-1}[s^{-1}]$	2.7 ± 0.2	1.4 ± 0.1	1.0 ± 0.1
$k_2[mol\,dm^{-3}\,s^{-1}]$	$7.0 \cdot 10^{-2}$	$3.9 \cdot 10^{-2}$	$8.0 \cdot 10^{-4}$
$k_{-2}[mol\,dm^{-3}\,s^{-1}]$	$5.0 \cdot 10^{-3}$	$2.8 \cdot 10^{-3}$	$2.6 \cdot 10^{-4}$
$\Delta H_i^0\,[kJ\,mol^{-1}]$	20 ± 5	28 ± 4	19 ± 2
$\Delta S_i^0\,[J\,K^{-1}\,mol^{-1}]$	90 ± 20	115 ± 20	72 ± 10
$\Delta H_d^0\,[kJ\,mol^{-1}]$	0 ± 5	0 ± 5	0 ± 5
$\Delta S_d^0\,[J\,K^{-1}\,mol^{-1}]$	-100 ± 20	-67 ± 20	-57 ± 15
$\Delta H_1^{\ddagger}\,[kJ\,mol^{-1}]$	70 ± 15	92 ± 15	78 ± 8
$\Delta S_1^{\ddagger}\,[J\,K^{-1}\,mol^{-1}]$	30 ± 20	70 ± 20	20 ± 5
$\Delta H_2^{\ddagger}\,[kJ\,mol^{-1}]$	120 ± 15	70 ± 20	63 ± 12
$\Delta S_2^{\ddagger}\,[J\,K^{-1}\,mol^{-1}]$	90 ± 20	30 ± 30	-100 ± 30

* Calculated by Fuoss equation.

for $2.0 < pH < 4.0$, fitted to experimental data.

Reaction amplitudes

The reaction amplitudes of the stopped flow experiments are defined as the overall difference in conductivity κ between the states immediately after mixing and at equilibrium (Fig. 2). They are determined by the total concentrations of ligand and aluminium, the pH, the ionic strength and the values of the equilibrium constants Q_o, K_i and K_d, defined in the reaction scheme in Fig. 3. The amplitudes can be calculated theoretically according to the additivity rule [4, 5]:

$$\Delta\kappa = \kappa_e - \kappa_s = \sum_{i=1}^{n} z_i c_{i,e} \lambda_{i,0} f_\lambda - \sum_{i=1}^{n} z_i c_{i,s} \lambda_{i,0} f_\lambda \, . \tag{4}$$

In Eq. (4) c_i are the concentrations of the participating species, z_i their charge, $\lambda_{i,0}$ their limiting equivalent conductivity and f_λ their mean conductivity coefficient. The indices "e" and "s" indicate the equilibrium and the start conditions. Equation (4) allows to calculate the amplitudes by solving numerically the nonlinear system of equations set up from all involved mole balances and equilibrium constants (Table 1), where κ_s is obtained simply by setting $K_i = 0$ [5, 14]. Then Q_o, K_i and K_d are obtainable by least-square fitting of Eq. (4) with variation of these parameters. Since it turned out that Q_o and K_i cannot be determined independently by exclusive evaluation of the amplitudes, the observed reaction rate constants are included in the analysis as it will be described in the next section.

Reaction kinetics

The kinetics of the formation of inner sphere complexes are described by the reaction scheme in Fig. 3 and the rate equation is given in Eq. (5)

$$\frac{d(c_8(t) + c_9(t))}{dt} = k_1\,c_7(t) - k_{-1}\,c_8(t) + \frac{k_2}{c_4(t)}\,c_7(t) - \frac{k_{-2}}{c_4(t)}\,c_8(t) \, , \tag{5}$$

with the rate constants $k_2 = k_2' K_{h1}$ and $k_{-2} = k'_{-2} K_{h2}$. Equation (5) is linearized and integrated with the assumption of pseudo-first-order conditions [5, 16]. Then the observed pseudo-first-order rate constant k_{obs} of a single exponentially decaying function reads

$$k_{obs} = \left(k_{-1} + \frac{k_{-2}}{c_4} \frac{f_{II}}{f_I^2} \right) \frac{((x_8/x_9) - K_i(x_7/x_9))}{(1 + (x_8/x_9))} \equiv k_b(pH) F(x) \, , \tag{6}$$

where x_i are the deviations of the concentrations $c_i(t)$ from their equilibrium values $c_i\,(c_i(t) = c_i + x_i(t))$ and f_i are activity coefficients. The term $F(x)$ depends only on the mole balances and the equilibrium constants, not on time, and may be calculated from the composition of each solution. Equation (6) is used for analysis of the reaction time $1/\tau$ in two ways:

(i) *at constant pH*: k_b(pH) stays constant and the term $F(x)$ now depends only on the total concentrations of Al^{3+} and ligand and the values of Q_o and K_i. Thus these constants can be fitted to measured relaxation rate constants k_{obs} for solutions with varying concentrations of Al^{3+} and ligand.

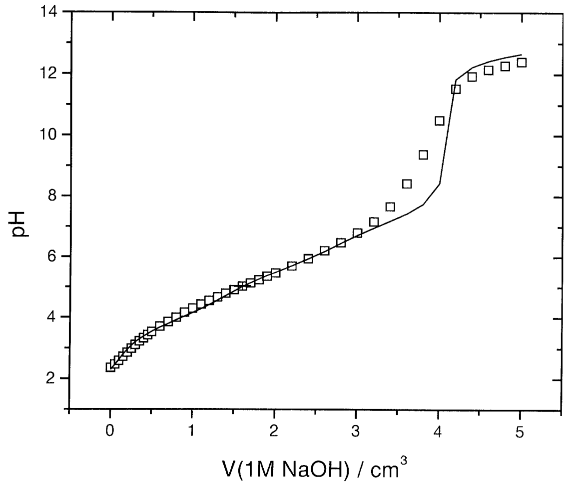
(ii) *at constant concentrations of Al^{3+} and ligand*: by plotting $k_{obs}/F(x)$ versus the activity corrected reciprocal concentration of $H^+(aq)$ the rate constant k_{-1} and k_{-2} can be determined from the intercept and the slope of a regression line.

Results and discussion

Titration curves

Figure 4 shows the titration of PCA with NaOH and the fit with the discrete 3-pK model ($pK_{a,1} = 3.95$, $pK_{a,2} = 5.9$ and $pK_{a,3} = 7.8$). This model is comparable to Tipping's "model V", which describes the deprotonation of natural polyelectrolytes by two sets of each of the four coefficients [15]. The deviations at $pH > 6.0$ are caused most probably by the counterion condensation [17], but are not relevant for this work, since all stopped flow experiments are performed at $pH < 4$. From the three discrete deprotonation coefficients (see also Table 1) a mean coefficient can be calculated, which is of the same order of magnitude as the maximum of the continuous distribution function assigned by Hermeier et al. [13], proving that this treatment is also valid. Furthermore the polymer is treated as a polymer containing a three protonic subunit with no interaction between different subunits, since the pH range of this study is restricted to $pH < 4.0$. The corresponding results obtained for GA and TCA are also summarized in Table 1. In contrast to PCA no deviations of the calculated and the experimental titration curve occur over the whole pH-range.

Fig. 4 Titration of 25 cm^3 0.157 M PCA (with respect to carboxy-residues) with 1 N NaOH



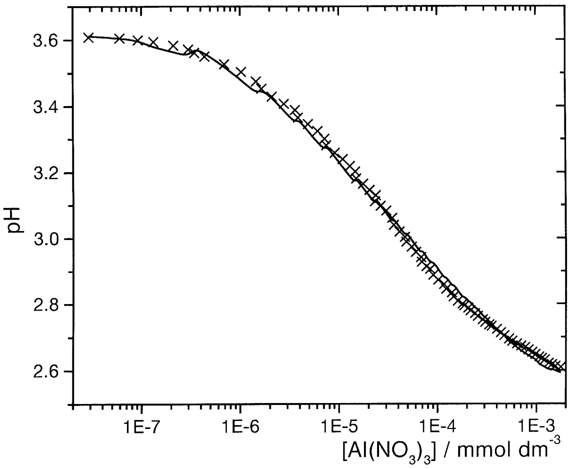


Fig. 5 Titration of 0.016 M PCA (with respect to carboxy residues) with $Al(NO_3)_3$ starting at pH = 3.6. The line represents the best fit with $K_{ass} = 10^{5.1}\,dm^3\,mol^{-1}$ and $K_d = 10^{-3.0}\,mol\,dm^{-3}$

It should be noted here that this approach does not intend to give a model which is valid for the whole pH-range accessible for the study of metal complexation of PCA in aqueous solution. The sample used in this study is rather polydisperse, but the reported acidity coefficients for PCA describe well the behavior of PCA in the pH- and concentration range employed in this study. The values are useful for the calculation of the degree of neutralization and the fraction of unprotonated residues, necessary for the calculation of the conductivity for the evaluation of amplitudes, as described in Eq. (4).

To determine the association constant of the polymer with Al^{3+}, a solution of 16 mM PCA (with respect to monomer units) is titrated with a solution of $Al(NO_3)_3$, and the results are shown in Fig. 5. It should be noted here that the evaluation of the titration curves does not differentiate between outer- and inner-sphere complexes due to their identical stoichiometry. Only an overall association constant K_{ass} may be obtained as defined by Eq. (7).

$$K_{ass} = \frac{c_7 + c_8}{c_1 c_3} = Q_o(1 + K_i) \; . \qquad (7)$$

The best fit of the titration curve is given with values of log ($K_{ass}\,dm^3\,mol^{-1}$) = 5.0 ± 0.1 and log ($K_d\,mol^{-1}\,dm^{-3}$) = −3 ± 1 and assuming monodentate binding of Al^{3+} at $pH < 3.6$. The corresponding results for GA and TCA are log ($K_{ass}\,dm^3\,mol^{-1}$) = 2.8 ± 0.1 for both GA and TCA, and log ($K_d\,mol\,dm^{-3}$) = −5.4 ± 0.1 and −3.5, respectively (see Table 1).

The values of the dissociation constant K_d have to be compared with the second deprotonation constant $K_{a,2}$. In case of GA the acidity of the second carboxylic group does not increase in a significant way, i.e. the formation of the inner sphere complex at one carboxy group does not influence the release of H^+ from the second one. In case of TCA the acidity of the second carboxylic group increases by one order of magnitude, and at PCA this effect is even more pronounced. In case of GA the carboxylate groups are separated by a distance of more than four C–C bond- lengths which is too far to show a significant effect. Closer distances as in TCA and PCA yield an increase in acidity.

The main difference between the polyacid PCA and its monomeric subunits (GA and TCA) is the large value of K_{ass}. This is caused by higher electrostatic interactions of the polymer with the metal ions due to the polyelectrolyte effect and will be discussed in detail later. A differentiation between the contributions of Q_o and K_i to K_{ass} is not possible by only evaluation of titration curves, for this purpose the kinetic experiments must be evaluated as shown below.

Kinetics

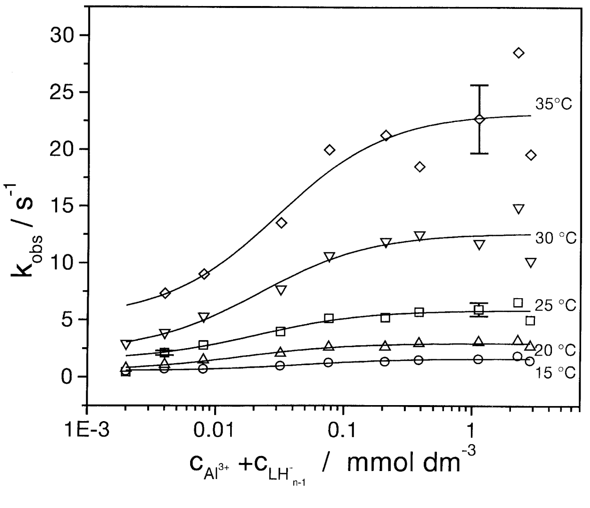
All stopped flow experiments of the complexation of Al^{3+} with PCA, GA, and TCA show a single-exponentially decaying reaction in the time range between 10 ms and 1 s at temperatures between 15 °C and 35 °C characterized by amplitude ($\Delta\kappa/\kappa_e$) and pseudo-first-order rate constant k_{obs}, as defined in Fig. 2. These effects show an apparent activation energy of approximately 100 kJ mol^{-1}, which is typical for the formation of monodentate complexes of Al^{3+} in solution.

For GA and TCA no subsequent slower reaction is observed indicating that bidentate complexes of Al^{3+} with GA and TCA are not formed. This is the expected behavior since chelation would lead to an eight-membered ring, which is not stable [5]. In contrast to this, for the reaction of Al^{3+} with PCA at higher pH values, a longer, nonexponentially decaying effect with relatively small (compared to the first relaxation effect) amplitude is observable. It is well known that conformational changes may influence the conductivity (Ref. [18], and references quoted therein). However, in the stopped flow experiments presented here, solutions of $Al(NO_3)_3$ and PCA are mixed at equal pH and conductivity, and the mixing will not induce conformational changes. These may occur as a consequence of Al^{3+}-complexation, and the first observable effect is unambigously the formation of the Al^{3+}-inner sphere complex. Thus, this study intends to focus on the basic steps occurring when Al^{3+} comes into contact with the polyelectrolyte in solution, i.e. the outer sphere association and the formation of the inner sphere complex as shown in Fig. 3. Those steps must be understood and described by rate- and equilibrium parameters, before subsequent reaction steps like conformational changes induced by the complexation of Al^{3+} are investigated.

Evaluation of k_{obs} at constant pH

In order to validate the reaction scheme in Fig. 3, at first, stopped flow experiments were performed with different concentrations of metal and ligand at constant pH of 3.55 ± 0.05. At this pH the PCA is locally (within the 3-carboxylate subunit) singly deprotonated and the reaction proceeds via the outer sphere complex **7**. The same is valid for GA and TCA. As derived in the chapter *Reaction Model*, Eq. (6) is fitted to the experimental data for k_{obs}, by variation of Q_o, K_i and k_b (for details see [14]) implying the calculation of all c_i and x_i/x_9 by solving the corresponding system of equations. The resulting parameters as well as the corresponding enthalpies and entropies are listed in Table 1. Values for k_b are not included in Table 1. k_b depends on pH and has no further meaning in contrast to the rate constant k_1 and k_2, which can only be obtained from pH-dependent measurements as will be shown below. The results for PCA are illustrated in Fig. 6, where k_{obs} at pH = 3.55 is plotted versus $(c_1 + c_3)$. Since the data of k_{obs} show a curved course in the given range $(c_1 + c_3)$ it is possible to fit independently the three parameters, if the plot is linear, only two parameters (K_i and k_b) are independently fittable [14]. This is the case for the complexation of Al^{3+} with GA and TCA, where the value of Q_o is calculated by Fuoss's equation [16] (Eq. (1) including

Fig. 6 Results of stopped flow experiments at constant pH: dependence of k_{obs} for the complexation of Al^{3+} with PCA on the concentration of $(Al^{3+} + LH^-_{n-1})$ at pH = 3.55 at different temperatures. The lines represent the fit of Eq. (6) (for $T = 25\,°C$, $k_b = 1.6\,s^{-1}$, $Q_0 = 10^{4.5}\,dm^3\,mol^{-1}$ and $K_i = 3$)



Eqs. (2) and (3) as $\log (Q_o \, dm^3 \, mol^{-1}) = 1.3$. The results are given in Table 1.

The results show clearly that for PCA it is possible by means of kinetic experiments to distinguish between the contributions of K_i (the chemical part, $\Delta G^\circ_{i,\,PCA} = -4 \, kJ \, mol^{-1}$) and Q_o (the electrostatic part $\Delta G^\circ_{o,\,PCA} = -26 \, kJ \, mol^{-1}$) to the overall association free enthalpy. K_i is of the same order of magnitude as observed for many other small organic ligands [4, 5] and also for GA and TCA. It is determined by the free enthalpy of interaction of Al^{3+} with a carboxy-group. The association constant K_{ass} according to Eq. (7) is calculated from these kinetic results as $\log (K_{ass} \, dm^3 \, mol^{-1}) = 5.1$. The agreement with that obtained from the titration proves unambigously the validity of the data evaluation.

The most striking difference is the contribution of Q_o: for GA and TCA all results are described with $\log Q_o = 1.3 \, dm^3 \, mol^{-1}$. For PCA, Q_o increases strongly although the degree of deprotonation is not very different at pH = 3.55. This proves that the polyelectrolytic nature of the PCA influences considerably the association of Al^{3+} by the strong electrostatic interaction between the trivalent cation and the PCA. Assuming a radius of the polyacid of 0.4 ± 0.1 nm and a radius of the hydrated Al^{3+} ion of 0.3 nm, the collision volume is calculated from Eq. (2) as $1.4 \, nm^3$ and from Eq. (1) the electrical potential of the polyelectrolyte is obtained as $\psi_L = -91 \pm 8 \, mV$. The error is mainly caused by the uncertainty in the distance of closest approach and the error in Q_o (see Fig. 8). The value of ψ_L fits well to that obtained for the association of the bivalent cation Ni^{2+} [13], and to values determined by the incorporation of potential-sensitive dyes into polyelectrolyte chains [19].

Amplitude evaluation at variable pH

Amplitudes are defined as the relative change of conductivity during the formation of the inner sphere complexes. They are determined by two opposite effects. Firstly the conductivity decreases due to charge neutralization, and secondly it increases as a result of reestablishing of the deprotonation reactions described by K_{a1}, K_{a2} and K_{a3}, and the release of H^+ due to the reaction from species **8** to **9** (see Fig. 3). These effects will dominate the amplitude since the equivalent conductivity of H^+ is much larger than that of Al^{3+}, so the amplitudes as defined by Eq. (4) will be positive. To determine Q_o(pH) a second series of stopped flow experiments is performed at variable pH. The outer sphere complexation coefficient Q_o is fitted to the experimental amplitude data by a least squares procedure with variation of Q_o (pH) and using Eq. (4) for the theoretical calculation of the change of conductivity.

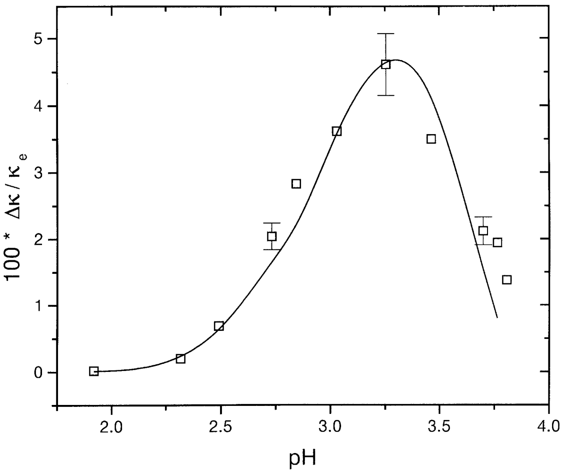


Fig. 7 Results of stopped flow experiments at variable pH: relative amplitudes $\Delta\kappa/\kappa_e$ as a function of pH at $T = 25\,^\circ C$ and total concentrations of $Al(NO_3)_3$ of $0.0001 \, mol \, dm^{-3}$ and of PCA of $0.008 \, mol \, dm^{-3}$ (with respect to carboxy residues). The line represents the best fit of Eq. (4) to the data with the assumption that Q_0 depends on pH (see Fig. 8)

The conductivity of a polyelectrolyte solution is generally a very complex quantity [18]. But for this purpose, only the changes of conductivity are of interest, so the apparent limiting value of conductivity of free carboxy-residues may be estimated as 35 and $70 \, cm^2 \, \Omega^{-1} \, mol^{-1}$ for PCA^- and PCA^{2-}, respectively. Numerical calculations have shown that the variation of λ°_{PCA} in the range of ± 20% has a negligible influence on the amplitudes as calculated by Eq. (4). The amplitudes are dominated by the disappearance of Al^{3+} due to complexation and the release of H^+. The data of λ° for the other participating species are taken from the literature [4, 5, 20] and are estimated from the ion sizes for the GA and TCA species.

Figure 7 shows measured amplitudes and the best fits with $2.9 \le \log Q_o \le 4.5$ at $1.9 < pH < 3.75$, and Fig. 8 demonstrates the increase of Q_o with pH for $T = 25\,^\circ C$; these best fit data are used for the calculation of amplitudes in Fig. 7. This procedure fits well the data from pH = 2–3.6. The amplitudes are positive, i.e. the conductivity increases during the formation of the inner sphere complexes **8** and **9**. This means that the charge neutralization during the reaction of the anionic ligand with the Al^{3+}-cation is overcompensated by the release of H^+, induced by the binding of Al^{3+} and is described by the deprotonation constant K_d. Beyond pH = 3.6 the experimental amplitudes are more positive than the calculated ones. The reason is the insufficient description of the polymer by a set of three discrete deprotonation constants plus a discrete deprotonation constant K_d of the inner sphere

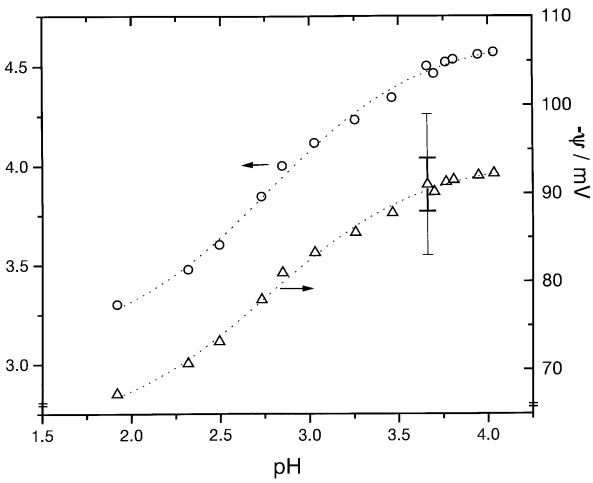


Fig. 8 Dependence of $\log Q_0$(○) and of the potential (acc. Eq. (1)) at the polyelectrolyte (△) on pH. The bold errorbar is the random error of ψ due to the uncertainty of Q_0 and the thin errorbar represents the systematic uncertainty due to the distance of closest approach r in Eq. (2)

complex. The true degree of deprotonation of the PCA is higher than calculated by the set of discrete constants, even if this set describes well the titration curve within this pH-range. This shows one great advantage of kinetic experiments: The analysis of the change of a physical quantity yields much more exact data than the calculation of its absolute value, due to unknown systematic errors. So kinetic experiments are much more sensitive with respect to the reaction mechanism than the analysis of titration curves.

Under the presumption of a local cylindric form of the polymer, a linear charge density on the surface of the polymer and a collision volume of $V_{\mathrm{coll}} = 1.4\,\mathrm{nm}^3$, Eqs. (1) and (2) allow to compute the electrical potential ψ of the polyelectrolyte as a function of pH. The right-hand ordinate of Fig. 8 shows the decrease of ψ from -67 mV at pH = 2 to -92 mV at pH = 4. The bold errorbar represents the random uncertainty caused by the error in Q_o and the thin errorbar the additional systematic uncertainty due to the collision volume. This course of the potential is expected: with increasing degree of ionization it will increase, but at larger values of ψ_L the association of counterions (Na^+, Al^{3+}) will shield the charges more effectively and prevent the polyelectrolyte from too high potentials.

The results for the complexation of Al^{3+} with the subunits of polyacid: GA and TCA are given in Table 1. The experimental amplitudes can be described with *constant* values of $Q_o = 20\,\mathrm{dm}^3\,\mathrm{mol}^{-1}$, as calculated by Eqs. (1) to (3) and $K_i = 14 \pm 1$ for 25 °C, showing that no polyelectrolyte effect occurs. The data compiled in Table 1 correspond well to those obtained for many other small carboxylic- and aminoacids [4, 5], and need not be discussed further.

The values of K_d, representing the deprotonation of the inner sphere complex **8**, do not vary with temperature within experimental error for PCA, GA and TCA. So $\Delta H_d = 0 \pm 20\,\mathrm{kJ\,mol}^{-1}$, and the free enthalpy is dominated by the decrease of entropy: $-60\,\mathrm{J\,mol}^{-1}\,\mathrm{K}^{-1} > \Delta S_d > -100\,\mathrm{J\,mol}^{-1}\,\mathrm{K}^{-1}$ (Table 1), reflecting a strong increase of order with the deprotonation. Most probably an association of the second carboxylic group with the metal ion via bridging H_2O-molecules is responsible for this effect. A direct bonding is very unlikely since no slow reaction effect is measured that could be contributed to the chelation, as it is observed for other small organic ligands like NTA [5].

Evaluation of k_{obs} at variable pH

A plot of $k_{\mathrm{obs}}/F(x)$ (Eq. (6)) versus the corrected reciprocal proton concentration $1/c_4 f_{\mathrm{II}}/f_{\mathrm{I}}^2$ yields the rate constants k_{-1} and k_{-2}. The term $F(x)$ is calculated from mass balances and fast preequilibria (for definitions see Fig. 3). Assuming a pH-independent outer sphere quotient Q_o does not lead to a linear relation (Fig. 9, (□)). Only with the data obtained for Q_o as a function of pH as shown in Fig. 8, the relation between $k_{\mathrm{obs}}/F(x)$ and $1/c_4 f_{\mathrm{II}} f_{\mathrm{I}}^2$ becomes linear (Fig. 9 (■)), and so it proves the validity of the reaction scheme depicted in Fig. 3 for the complexation of Al^{3+} at PCA. The intercept and the slope yield the rate constants k_{-1} and k_{-2} and their dependence on temperature yield the activation parameters as summarized in Table 2. The product $K_i k_{-1}$ yields the value $k_1 = 3.1\,\mathrm{s}^{-1}$, which is of the same order of magnitude as the rate constant for the water exchange at Al^{3+} (aq), which is $1.29\,\mathrm{s}^{-1}$ [6]. This proves the validity of the theory of Eigen and Tamm for the complexing of Al^{3+} at PCA, see section "*reaction scheme*".

For the small ligands GA and TCA the plots of $k_{\mathrm{obs}}/F(x)$ versus $1/c_4 f_{\mathrm{II}}/f_{\mathrm{I}}^2$ are linear with a constant value of Q_o, like for the evaluation of the amplitudes. The obtained rate constants and activation parameters are summarized in Table 2, they fit well in the range as observed for other small organic ligands. The forward rate constants $k_1 = 37\,\mathrm{s}^{-1}$ for GA and $19\,\mathrm{s}^{-1}$ for TCA are higher than expected from the Eigen–Tamm theory. The reason is, as proved for many other small ligands, the distortion of the inner hydration shell of Al^{3+} by the ligand [5]. This leads to an increase of the water exchange rate proportional to the affinity of the ligand to H^+, and as a consequence to a linear free energy relation between $\log K_{a1}$ and $\log k_1$. The value of k_1 for the PCA does not fit in this linear free energy relation, for an acid with $pK_{a1} = 4$ k_1 should be

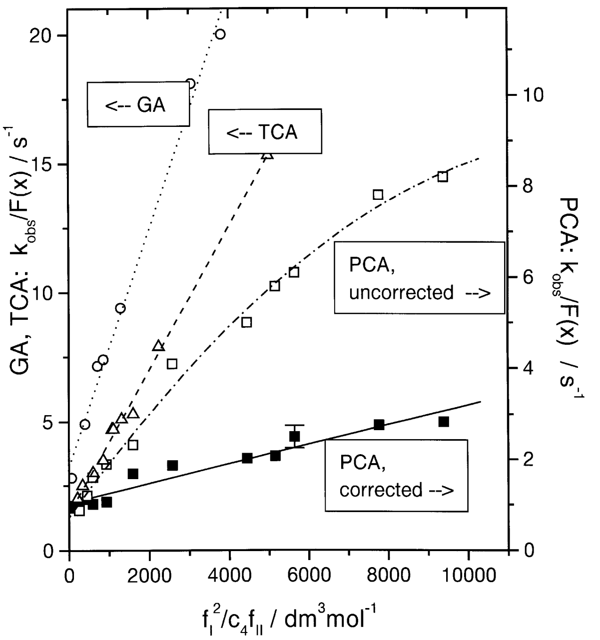


Fig. 9 Results of stopped flow experiments at variable pH: plots of $k_{\mathrm{obs}}/F(x)$ versus $f_{\mathrm{II}}/c_4 f_{\mathrm{I}}$ according to Eq. (6) for the pH-dependent stopped flow measurements at $T = 25\,^{\circ}\mathrm{C}$ for the formation of the inner-sphere complex of Al^{3+} with glutaric acid (Ga, ··· o ···), tricarballyic acid (TCA, - - -△- - -) and polycarboxylic acid (PCA, —■—). The lines are the best linear fits, the intercepts yield k_{-1}, the slopes k_{-2}. Also shown is a plot of $k_{\mathrm{obs}}/F(x)$ versus $f_{\mathrm{II}}/c_4 f_{\mathrm{I}}$ for PCA with *constant* Q_0: curved line (·—·—□—·—·), indicating that this assumption is not valid

greater. Or vice versa: for $k_1 = 3.1\,\mathrm{s}^{-1}$ a value of $\mathrm{p}K_{\mathrm{a1}} \approx 3$ would be expected. This is probably a consequence of the insufficient modeling of the polyacid by a set of three discrete deprotonation coefficients. All obtained activation enthalpies ΔH_i are typical for the small and highly charged Al^{3+} ion, and the positive activation entropies indicate the dissociative nature of the reaction mechanism which is of the I_{D} type [2].

Differences are observed for the base-catalyzed step. Both the reaction rates of the subunits (GA and TCA) and the rates for the PCA differ in one order of magnitude. This shows that the base-catalyzed step does not contribute significantly at PCA. The reason is clear: The large negative potential of the polyelectrolyte prevents the hydrolysis of Al^{3+} in the vicinity of the polymer strands by repelling of OH^- or enriching of H^+, respectively.

Conclusions

The complexation of Al^{3+} with the ligands glutaric acid (GA), tricarballylic acid (TCA) and a random copolymer of maleic- and acrylic acid (PCA) has been investigated by titration and by applying the stopped-flow technique. For all ligands a single exponentially decaying relaxation effect in the 10 ms–1 s range is observed that can be attributed unambigously to the formation of monodentate inner sphere complexes. For PCA a slower, nonexponential reaction mode is observed caused by subsequent processes: the charges of the polyelectrolyte become partially neutralized by the formation of the inner sphere complexes, and therefore conformational changes are probable, which are accompanied by changes in electrical conductance. But these effects are not relevant to this study, since for the understanding of these processes it is necessary to understand the basic process taking place when Al^{3+} comes in contact with the polycarboxylic acid. All observed reaction rates and amplitudes in the 10 ms–1s range are fully explained by a reaction model based on the Eigen–Tamm mechanism for metal ion complexation. The central feature of the model is the variation of the outer sphere association coefficients Q_{o} with the charge of the polyelectrolyte. Thus, Q_{o} is fitted to the experimental data for observed rate constants and amplitudes in the pH-range from 2 to 4. Summarizing this study, the following points should be stated:

(i) Al^{3+} forms a stable inner sphere complex with the polyelectrolyte (PCA), with a mean association constant $\log (K_{\mathrm{ass}}\,\mathrm{dm}^3\,\mathrm{mol}^{-1}) = 5$. The major part of the association free energy is caused by the electrostatic interaction between the polyelectrolyte and the trivalent metal ion. The inner sphere complex is monodentate, however a weak association of the second carboxy group by a $\mathrm{H_2O}$ bridge is probable. The inner sphere complex induces the deprotonation of neighboring COOH groups, the deprotonation constant for Al–PCA is $\mathrm{p}K_{\mathrm{d}} = 3.0$, for Al–TCA and Al–GA it is $\mathrm{p}K_{\mathrm{d}} = 3.5$ and $\mathrm{p}K_{\mathrm{d}} = 5.4$, respectively.

(ii) For all investigated ligands the reaction proceeds via the Eigen–Tamm two-step mechanism for metal ions. The first step consists of the association of the hydrated Al^{3+}-ion to the ligand. The association coefficient Q_{o} for this outer sphere complex is controlled by the electrostatic interaction and may be calculated for GA and TCA from the Fuoss theory as $20\,\mathrm{dm}^3\,\mathrm{mol}^{-1}$. For PCA this coefficient increases with pH and the degree of ionization. It increases strongly up to $10^{4.5}\,\mathrm{dm}^3\,\mathrm{mol}^{-1}$ due to the large negative electrical potential of the polyelectrolyte.

(iii) The potential of the polyelectrolyte is calculated to range from $-67\,\mathrm{mV}$ at $\mathrm{pH} = 2$ to $-93\,\mathrm{mV}$ at $\mathrm{pH} = 4$.

(iv) The rate-determing step for the inner sphere complexation consists of the release of a $\mathrm{H_2O}$ molecule from the inner hydration shell of Al^{3+} and its replacement by a carboxy-group of the ligands. The rate constants found are $k_1 = 3.1$, 19, and $37\,\mathrm{s}^{-1}$, for PCA, TCA, and GA, respectively. This release is influenced by the affinity of the reacting carboxy-groups for H^+, which distorts the symmetry of the inner hydration shell of Al^{3+} and therefore accelerates the exchange of the hydration water. The positive activation entropy indicates the lowered degree of hydration of the intermediate complex.

(v) The reactions accompanying the formation of inner sphere Al^{3+}-complexes (deprotonation of the polymer) may be modeled approximately by treating PCA as a three protic acid in the pH range of investigation. However, at higher degrees of deprotonation, occurring at $pH > 3.6$, this model reaches its limits. A polyelectrolyte model calculating explicitly the electrostatic potential as a function of size and shape of the polyelectrolyte, its charge and its conductivity as a function of pH, and ionic strength would be preferable. But the application of such a model would exceed considerably the scope of this work, since the task here is to elucidate the binding mechanism of Al^{3+} at a polyelectrolyte by the evaluation of kinetic experiments.

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References

1. Buffle J (1989) Complexation Reactions in Aquatic Systems. Ellis Horwood Ltd, Chichester, UK
2. Eigen M (1993) Pure Appl Chem 6:97
3. Wikins RG (1991) Kinetics and Mechanisms of Transition Metal Complexes. VCH, Weinheim
4. Pohlmeier A, Thesing U, Knoche W (1994) Ber Bunsenges Phys Chem 97:10
5. Pohlmeier A, Knoche W (1996) Int J Chem Kin 28:125
6. Hugi-Cleary DL, Helm L, Merbach A (1985) Helv Chim Acta 68:545
7. Ciszkowska M, Osteryoung JG (1996) J Phys Chem 100:4630
8. Yoshikawa M, Anson FC (1996) J Phys Chem 100:4199
9. Jiang R, Anson FC (1992) J Phys Chem 96:10565
10. Lis S, Wang Z, Choppin GR (1995) Inorg Chim Acta 239:139
11. Diebler H, Secco F, Venturini M (1987) Biophys Chem 26:193
12. Diebler H, Secco F, Venturini M (1991) J Inorg Biochem 42:67
13. Hermeier I, Herzig M, Knoche W, Pohlmeier A, Narres HD (1996) Ber Bunsenges Phys Chem 100:788
14. Fenn-Barrabass C (1996) PhD thesis, University of Bielefeld, Germany
15. Tipping E (1993) Environ Sci Technol 27:520
16. Strehlow H, Knoche W (1972) Fundamentals of Chemical Relaxation. VCH, Weinheim, Germany
17. Manning GS (1978) Quart Rev Biophys 2:179
18. Van Leeuwen HP, Cleven RFMJ, Valenta P (1991) Pure Appl Chem 63:1251
19. Morishima Y, Higushi Y, Kamachi M (1991) J Polymer Sci A29:677
20. Landolt-Bornstein (1960) Zahlenwerte und Funktionen, Vol II, Part 7. Springer Verlag, Berlin, Germany