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Concentration effects during the formation of poly (acrylic acid)-metal complexes in aqueous solutions

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Summary

The formation of metal complexes between poly (acrylic acid) and divalent, trivalent and tetravalent metal ions was studied. For divalent metal ions, the formation constants determined according to the method of Gregor et al. strongly decrease with increasing ligand concentration in the range 25-280 mM but are nearly insensitive to the ligand to metal concentration ratio. The metal ions were divided in four groups depending on their effect on the pH decrease of the solution. These groups differ from one another by i) the speed of water exchange or ii) by the speed of ligand exchange in the coordination sphere of the metal. The increase of the ligand concentration or of the ligand to metal ratio always led to an increase of the exchange speed of both water and carboxyl groups.

Introduction

Metal complexes of poly (acrylic acid) (PAA) have been investigated since many years. The method of Bjerrum [1] for the determination of the formation constants has been extended to polymer-metal complexes by Gregor et al. [2] and polymers undergoing conformational changes were also studied [3-6]. More recently, the copper complexes of polymers derived from natural amino acids, with various charge density along the main chain, were investigated [7-8]. Complexes of linear and crosslinked PAA were also revisited focusing on the interaction not only with copper but also with nickel, lead and cadmium [9-12]. PAA is often chosen as a model for the complexation of natural humic acids [13] and is used as flocculant in water treatment and sludge thickener [14]. For such applications PAA is used in higher concentrations than in analytical studies. As literature data suggest that the formation constants depend not only on the ligand/metal concentration ratio but also on the ligand concentration, we found necessary to study such effects. In addition, some PAA metal complexes have been used as precursors in the elaboration of ceramics [15-16]. In conditions of high ligand concentrations, the classification of the formation constants for currently studied metal ions could be changed. Therefore and especially in view of the preparation of mixed metal oxides, a precise knowledge of the relative formation constants is required. The present paper reports data on the complexes of PAA with different metal salts (chromium, iron, aluminium, bismuth, vanadium, uranium, nickel, copper, zinc, cobalt, calcium, baryum) including lanthanides (cerium, lanthane, neodynium).

Experimental

Materials

Poly (acrylic acid) (PAA) was a commercial sample (M_w = 450 000) from Aldrich. Acid base titration and thermogravimetric analysis indicated a 6.47 % water content. PAA concentrated stock solutions were prepared and kept in the refrigerator. Dilute solution for analysis were prepared before used and titrated with NaOH in the presence of a supporting electrolyte ($NaClO_4$ 0.1 M) to check their exact concentration. The concentration range of PAA solutions for studies in the presence of metal was 27.8-280 mM. Metal ion stock solutions were prepared from the corresponding metal salt ($CuSO_4$,$5H_2O$; $Ni(ClO_4)_2$,$6H_2O$; $CoCl_2$,$6H_2O$; $ZnCl_2$; $Cr(NO_3)_3$,$9H_2O$; $Fe(NO_3)_3$,$9H_2O$; $Al(NO_3)_3$,$9H_2O$; $BaCl_2$; $Ca(NO_3)_2$,$4H_2O$; $Bi(NO_3)_3$,$5H_2O$; $VOSO_4$,$5H_2O$; $UO_2(NO_3)_2$,$6H_2O$; $Th(NO_3)_4$,$4H_2O$; $CeCl_3$,$7H_2O$; $La(NO_3)_3$,$6H_2O$; $Nd(NO_3)_3$,$6H_2O$) from Aldrich, Merck, Riedel de Häen and Strem. The [ligand]/[metal] concentration ratio R was varied between 1 and 10 by adjusting the metal concentration, keeping the ligand concentration constant in a given set of experiments. No supporting electrolyte was added.

Methods

Protometric titrations were carried out with a Radiometer pH M 65 pHmeter equipped with a combined N65 Schott electrode. The electrode response was checked two times a day using phtalate and borate standard buffers. Titrations were made under nitrogen atmosphere.

Results and discussion

Acid-base properties

The effect of ligand concentration on the titration curves in the absence of metal was first investigated. The concentration range was varied from 24.8 mM to 250 mM i.e. 5 to 50 times higher than the usual range reported in the literature [9-10]. As shown in Figure 1, pH decreases with increasing PAA concentration at a given α value below 1, indicating a stronger polyacid. At the same time, the equivalent point becomes sharper allowing an accurate determination of the equivalent point by the usual methods without the addition of a concentrate strong electrolyte.

The data have been treated in the usual way through Henderson-Hasselbach plots [17-18] i.e. according to: $pH = pK_H^M + n \log(\alpha/(1-\alpha))$

pK_H^M is the pH value at $\alpha = 0.5$ and is usually considered to reflect the average acidity of the polyelectrolyte. n reflects the long range electrostatic interactions and thus usually decreases with increasing added salt concentration [9]

Values of pK_H^M and n obtained in this way are plotted in Figure 2 vs the ligand concentration.

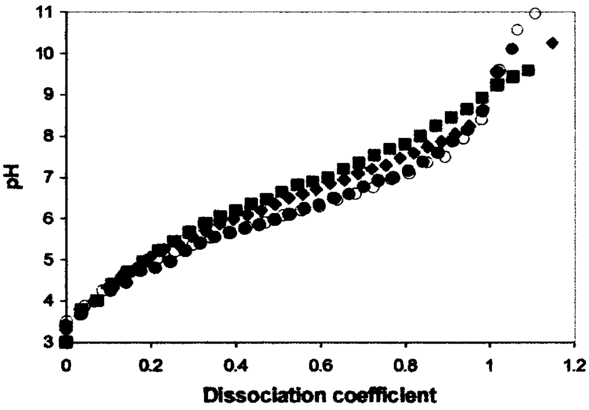

Figure 1. Dependence of the titration curve on the PAA concentration (■) 27.8 mM (◆) 55.6 mM (•) 139 mM (O) 278 mM

PAA behaves as a stronger acid at high concentration in agreement with literature data obtained in the absence of added electrolyte [19]. Note that the values are significantly higher than those obtained in the presence of added electrolyte (no shielding effect) i.e. 5.50 in 0.1 M $NaNO_3$ at [C] = 5 mM [9] and 5.15 in 1 M $NaNO_3$ at [C] = 10 mM [19]

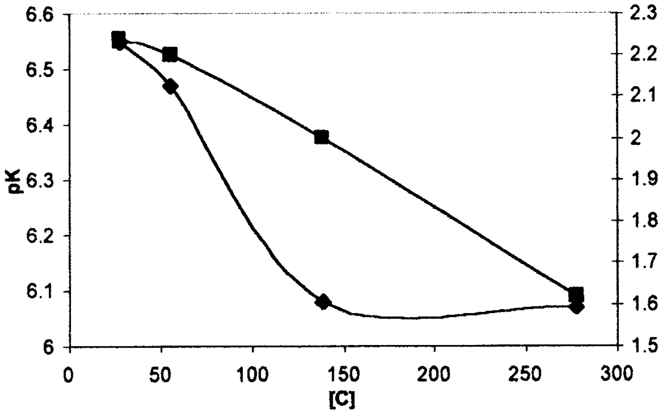

Figure 2. Variation of pK_H^M (◆) and n (■) with concentration ([C] in mM)
Estimated error: on $pK_H^M = \pm 0.05$; on n: = ±0.07

The decrease of n indicates decreasing electrostatic interactions due to the increased concentration of sodium counter-ions. For a PAA concentration of 278 mM, the n value is close to that of 10 mM PAA in the presence of 200mM $NaNO_3$ [19]

Metal complexes

As expected, the titration curves in the presence of metal exhibit a decrease of pH at a given α value, which depends on the nature of the metal and on the R-value. Some examples of this effect are shown in Figure 3 for divalent ions or pseudo divalent ions like VO^{2+}. The pH decrease is even more important for Al^{3+} or Cr^{3+}.
According to Gregor et al [2] this pH decrease is due to the displacement of the following equilibria assumed for divalent metal ions only:

$$2\ RCOOH + Cu^{2+} \rightarrow (RCOO)_2Cu + 2H^+ \qquad B_2 \qquad (1)$$

$$RCOOH \rightarrow RCOO^- + H^+ \qquad Ka \qquad (2)$$

$$2RCOO^- + Cu^{2+} \rightarrow (RCOO)_2Cu \qquad K_2 \qquad (3)$$

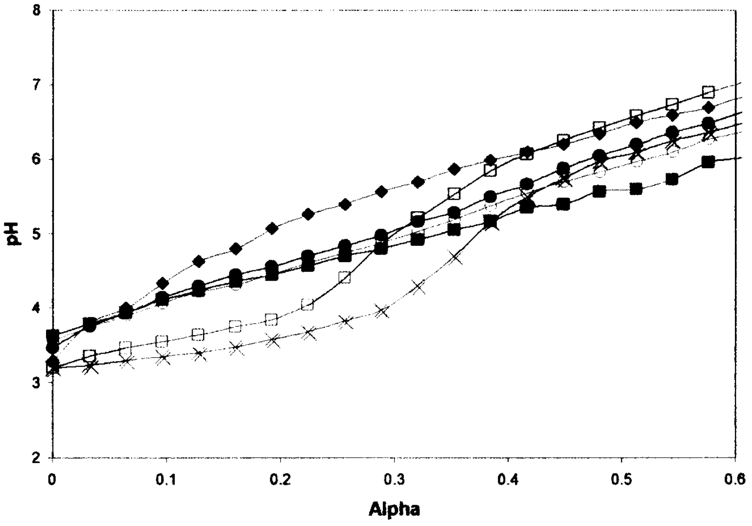

Figure 3. pH decrease of PAA solutions in the presence of metal : (◆) no metal; (•) Co^{2+}; (○) Zn^{2+}; (■) Ni^{2+}; (□) Cu^{2+}; (×) VO^{2+}

The theory of Gregor et al. [2], expressed by Eqs (1-3) neglects the contribution of complexes involving more than two carboxyl groups. Within this assumption, the formation constant B_2 may be deduced from the variation of n the average number of ligands per metal ion vs a function of pH (formation curve as shown in Figure 4) by taking twice the abscissa value at n = 1 and calculating then K_2 by:

$$K_2 = B_2/(K_H^M)^2 \qquad (4)$$

Or $$\log_{10}K_2 = \log_{10}B_2 + 2 * pK_H^M$$

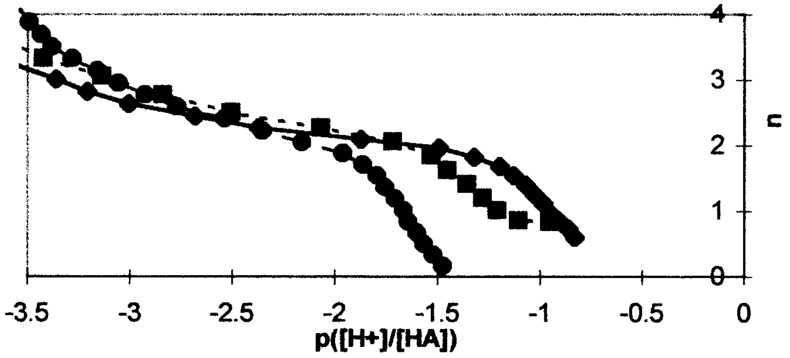

Figure 4. Formation curves for PAA-copper at R=5; PAA concentration: (◆) 27.8 mM (■) 55.6 mM (•) 139 mM

Figure 4 shows as an example a distinct concentration effect on the formation curve and thus on the values of the formation constants.

Effect of ligand concentration

B_2 and K_2 data for usually studied metal ions are reported in Table 1.

Table 1. Values of B_2 and K_2 for PAA complexes with various divalent metal ions at different ligand concentration (R = 5) (Estimated error on $\log_{10}K_2 = \pm 0.10$)

PAA concentration and pK_H^M value	Metal ion	$\log_{10} B_2$	$\log_{10} K_2$	K_2
27.8 mM 6.55	Cu^{2+}	-1,9	11,20	1,58E+11
	Ni^{2+}	-3,73	9,30	2,34E+09
	Co^{2+}	-3,30	9,80	6,34E+09
	Zn^{2+}	-3,75	9,35	2,24E+09
	VO^{2+}	-1.69	10.90	7.98E+10
55.6 mM 6.47	Cu^{2+}	-2,2	10,74	5,50E+10
	Ni^{2+}	-4,05	8,89	7,76E+08
	Co^{2+}	-3,67	9,27	1,86E+09
	Zn^{2+}	-4,19	8,75	5,62E+08
139 mM 6.08	Cu^{2+}	-3,24	8,92	8,32E+08
278 mM 6.07	Cu^{2+}	-3,9	8,24	1,74E+08

The values of K_2 indicate the formation of very stable complexes. In peculiar, they are much more stable than those issued from the metal salts as $ZnCl^+$, $ZnCl_2$ or $ZnCl_3^-$. For example log K for the formation of $ZnCl_3^-$ is -0.3 [20] and such complexes are quantitatively displaced by the polymer complex.

They are significantly higher than those obtained in the presence of added electrolyte [9,21-23] (K_2 = 6.6 for Cu and 5.5 for Ni in the presence of 0.1 M $NaNO_3$ [9]) in agreement with previous observations [2,7]. The order of the formation constants i.e. Cu> Co>Ni, Zn seems insensitive to concentration effects. The value for the pseudo divalent ion VO^{2+} is intermediate between Cu^{2+} and Ni^{2+}. The most important result is the remarkable decrease of the formation constant K_2 with increasing the concentration of the ligand at constant R-value. This trend is also observed for B_2 and is thus independent on the variation of pK_H^M. For copper the complex is one thousand times less stable when the ligand concentration is ten times higher. In this concentration range, beyond C^*, the polymer chains interpenetrate and intermolecular complexes less stable than intramolecular ones are favored.

Two PAA-copper complexes were prepared in the same conditions (α = 0.4 and R = 5) changing only the ligand concentrations (C = 27.8 and 139 mM) and were recovered and analyzed. In the low concentration complex, the ligand to metal ratio was the same as in the initial mixture i.e. R = 5. In the high concentration complex this ratio was only 2.3 indicating that some steric hindrance prevents the ligand to highly coordinate to the metal ion. This effect has been investigated in details in the case of cerium-PAA complexes in order to prepare cerium oxide catalysts and the results will be reported later.

Influence of the ligand to metal ratio R

As some literature data suggest that the formation constants could depend on the ligand to metal ratio this effect was investigated only for divalent and pseudo divalent metal ions. Typical results are given in Table 2 for Cu^{2+} and VO^{2+}. Taking into account the experimental error on Log K_2 (estimated to ± 0.10) the values can be considered as independent on R

Table 2. Variation of B_2 and K_2 for Cu^{2+} and VO^{2+}PAA complexes on changing the ligand to metal ratio R. [Ligand] = 27.8 mM

Metal ion	R	$\log_{10} B_2$	$\log_{10} K_2$	K_2
Cu^{2+}	10	-1,87	11.23	1.71^{E}+11
	5	-1.90	11.20	1.59^{E}+11
	2	-1.91	11.19	1.56^{E}+11
VO^{2+}	10	-1.63	11.47	2.96^{E}+11
	5	-1.69	11.41	2.58^{E}+11
	2	-1.37	11.73	5.39^{E}+11

Influence of the valency of the metal

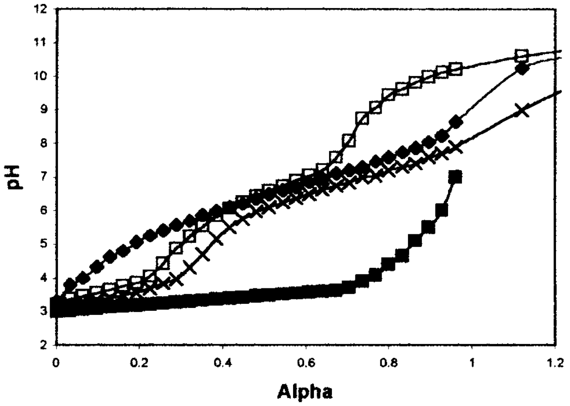

Figure 5. Titration curves of PAA in the presence of: (◆) no metal; (□) Cu^{2+}; (×) Bi^{3+}; (■) Th^{4+}

In the case of metal ions with a valency higher than 2, the calculations of a formation constant using the theory of Gregor et al.[2] is somewhat hazardous. Nevertheless whatever the number of equilibria to add to Eqs (1)-(3), the formation of the complex always induces a decrease of pH which depends on the strength of interaction between the ligand and the metal. Figure 5 shows typical titration curves obtained with metal ions having different valencies.

In a previous work [24] we have shown that the different metal ions interacting with PAA may be divided in four groups depending on the shape of the curve ΔpH vs α, ΔpH being the pH decrease obtained by: pH(PAA) – pH(PAA-metal).

These four groups were defined at rather low ligand concentration (20-30 mM) and may be characterized as follows (Figure 6):

- Group a: includes Cr^{3+}: Low speed of water exchange and ligand exchange. Strong pH decrease at the beginning of the curve ($\alpha = 0$)
- Group b: Fe^{3+}, Al^{3+}, Bi^{3+}, VO^{2+}, UO_2^{2+}. Medium speed of water exchange and slow ligand exchange. Strong pH decrease at the beginning of the curve (α=0).
- Group c: this group includes metal ions frequently investigated in the literature: Ni^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}, Ba^{2+}, Ca^{2+}. Rapid water exchange and slow ligand exchange. Weak pH decrease at $\alpha = 0$.

- Group d: Lanthanides : Ce^{3+}, La^{3+}, Nd^{3+}. Rapid water and ligand exchanges. Strong pH decrease at the beginning of the curve.

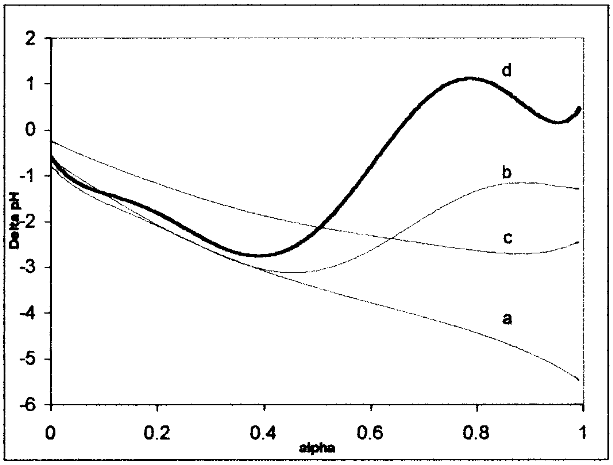

Figure 6. Curves ΔpH vs α for the different groups of metals

The titration curves were obtained for the above fifteen metal ions, for ligand concentrations of 27.8; 55.6 and 139 mM and also for ligand to metal ratios of 1 and 5.

The results may be summarized as follows:

The increase of R or the increase of the ligand concentration shifted the metal ions from one group to another: group a to group c; group b to group c and group c to group d i.e towards the behavior of the lanthanide group characterized by high exchange speed for the two kinds of ligand: water and carboxyl group. This is undoubtedly related to changes in the mobility of water in the vicinity of the polymer chain. For example, copper, nickel, cobalt or zinc at [ligand] = 139 mM behave as the lanthanides at 27.8 mM. Bismuth, iron, aluminium at 139 mM behave as copper at 27.8 mM

Conclusion

Distinct concentration effects occur during the formation of metal complexes with PAA. This concerns mainly the absolute values of the formation constants that can drastically decrease. But generally speaking, and not only for divalent ions, the behavior of the complexes in terms of acido-basicity is deeply modified. In view of the preparation of mixed complexes, such information may be useful. In peculiar, formation constants have to be measured in the conditions to be used for the preparation of the complexes.

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