Interactions between aluminium ions and acrylic acid–acrylamide copolymers in aqueous solution: 1. Study by ^{27}Al nuclear magnetic resonance

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Aluminium binding to acrylic acid-acrylamide copolymers at different pH values has been studied by ^{27}Al n.m.r. at 104.2 MHz. The study of a pure $AlCl_3$ solution of 1×10^{-3} mol l^{-1} concentration (at 25°C) allowed us, using a computer calculation, to define the concentration of different presumed Al species during the Al^{3+} hydrolysis, when the OH^-/Al varied from 0 to 3. A model is proposed which takes into account the electrostatic interaction between trivalent Al species (Al^{3+} and $Al_{13}(OH)_{27}^{3+}$) and the carboxylate groups of the copolymers. The amount of Al cations bound to the copolymers was then calculated as a function of the pH.

(Keywords: ^{27}Al n.m.r.; acrylic acid–acrylamide copolymers; electrostatic interactions)

INTRODUCTION

The strong interaction of cations with polyions is well known to alter substantially the rheological properties of hydrolysed polyacrylamide used in the tertiary oil recovery process[1–4], and the influence of divalent cations has been extensively studied[5–7]. The purpose of this study is to predict the range of pH where the interaction with aluminium ions is particularly important. Since recent work has shown that the different species of aluminium ions can be detected by ^{27}Al nuclear magnetic resonance (n.m.r.) in $AlCl_3$ solutions[8–15], we have used the same technique to approach the problem.

EXPERIMENTAL

Samples

Three polymer samples were used. Samples AD10 and AD27, provided by Rhône-Poulenc, France, were prepared by photocopolymerization of acrylamide and sodium acrylate. Their acrylate content, measured by potentiometry, elemental analysis and ^{13}C n.m.r., was 1.5 and 17%, respectively[17]. The third sample was a partially hydrolysed polyacrylamide (Pusher 700), of hydrolysis ratio 30%. The molecular weight of the three samples was approximately 5×10^6.

The solutions of $AlCl_3$ (Aldrich) were neutralized by NaOH solutions (Titrisol, Merck).

Potentiometry

The potentiometric measurements were performed with a pH meter, Metrohm 605, using a glass electrode.

^{27}Al n.m.r.

^{27}Al n.m.r. spectra were obtained at 104.23 MHz using a Brucker 400 spectrometer in a Fourier transform mode. The solutions were held in 10 mm o.d. tubes. The substance ($Al(OH)_4^-$) used as intensity reference was dissolved in D_2O (whose deuterium signal placed the field frequency lock) and was contained in the capillary tube of a Wilmad coaxial cell; 90° pulses were used. The pulse interval was sufficient to allow a complete return of the magnetization at equilibrium (pulse interval = 0.08, $T_1 = 0.03$ s). The peak of the reference monomer $Al(OH)_4^-$ is located at 79.9 ppm from the signal of $Al(H_2O)_6^{3+}$. The amount of aluminium bound in each detectable species can be obtained by simple integration. An $Al(OH)_4^-$ solution of well known concentration is used as integration reference.

Preparation of the solutions

$AlCl_3$ solutions of concentrations 10^{-3}, 10^{-2} and 10^{-1} mol l^{-1} were neutralized by addition of small volumes of NaOH solutions of concentration 10 times higher. The neutralized solutions were slightly stirred and kept at room temperature for more than one month. The neutralization ratio ranged between 0 and 3. For solutions of polymer and $AlCl_3$, one must avoid the formation of inhomogeneities or large aggregates, which are generally formed when pure $AlCl_3$ or concentrated solutions of $AlCl_3$ are added to polymer solutions. For this reason we used the following procedure: for given compositions C_p and C_a, the solutions were obtained by mixing equal volumes of a polymer solution of concentration $2C_p$ and an $AlCl_3$ solution of concentration $2C_a$ aged for 14 days, both at the same pH.

RESULTS AND DISCUSSION

Partially neutralized solutions of $AlCl_3$

Theory. It is well known that in partially neutralized solutions of $AlCl_3$, the various steps in the hydrolysis of Al^{3+} lead to the formation of mononuclear ions

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$Al(OH)^{2+}$, $Al(OH)_2^+$ and $Al(OH)_4^-$, polynuclear ions $Al_2(OH)_2^{4+}$ and $Al_{13}(OH)_{27}^{3+}$, and the non-ionic species $Al(OH)_3$ (references 8–15).

The composition of the solution obeys the following equilibrium laws:

$$Al^{3+} + H_2O \rightleftharpoons Al(OH)^{2+} + H^+ \qquad K_{1,1} = 10^{-5.02} \quad (1)$$

$$Al^{3+} + 2H_2O \rightleftharpoons Al(OH)_2^+ + 2H^+ \qquad K_{1,2} = 10^{-8.71} \quad (2)$$

$$Al^{3+} + 3H_2O \rightleftharpoons Al(OH)_3 + 3H^+ \qquad K_{1,3} = 10^{-10.24} \quad (3)$$

$$Al^{3+} + 4H_2O \rightleftharpoons Al(OH)_4^- + 4H^+ \qquad K_{1,4} = 10^{-42} \quad (4)$$

$$2Al^{3+} + 2H_2O \rightleftharpoons Al_2(OH)_2^{4+} + 2H^+ \qquad K_{2,2} = 10^{-6.27} \quad (5)$$

$$13Al^{3+} + 33H_2O \rightleftharpoons AlO_4Al_{12}(OH)_{29}^{2+} + 37H^+ \qquad K_{13,27} = 10^{-127} \quad (6)$$

For each species:

$$(Al_i(OH)_p^{(3i-p)+}) = \frac{(Al^{3+})K_{i,p}f_{1,0}}{f_{i,p}(H)^i} \quad (7)$$

where $f_{i,p}$ is the activity coefficient of $Al_i(OH)_p^{(3i-p)+}$, which can be obtained from the Debye–Huckel expression:

$$\log f_{i,p} = \frac{0.5Z_{i,p}^2 I^{1/2}}{1 + 0.33 r_{i,p} I^{1/2}} \quad (8)$$

r_{ip} represents the radius of the hydrated ion (in Å*):

$$r_{(Al^{3+})} = 9\ \text{Å}; \qquad r_{(Al^+)} = r_{(Al^{2+})} = 5.9\ \text{Å}$$

$$r_{(Al_3^{4+})} = 3.8\ \text{Å}; \qquad r_{(Al_{13}^{3+})} = 19.7\ \text{Å}$$

For a total aluminium concentration, $Al_{tot} = 10^{-3}$ mol l^{-1}, the ionic strength varies from 3×10^{-3} to 6×10^{-3} as a function of the degree of hydrolysis. The activity coefficients have been determined by Bottero *et al.*[8,10] as a function of concentration and neutralization ratio, and we have taken the following average values:

$$f_{1,0} = 0.55; \quad f_{1,1} = 0.75; \quad f_{1,2} = 0.94$$

$$f_{2,2} = 0.75; \quad f_{13,29} = 0.8$$

Moreover, the solubility of the trivalent cations Al^{3+} is limited by the formation of the neutral species $Al(OH)_3$ and by the solubility product K_{sp}:

$$(Al^{3+})(OH^-)^3 < K_{sp} \quad (9)$$

K_{sp} depends on the crystallinity of $Al(OH)_3$ and varies between $10^{-32.34}$ for the amorphous form and $10^{-36.3}$ for gibbsite[18].

A computer calculation taking into account relations (1)–(6) and relation (9) as well as the electroneutrality and material conservation equations allows us to determine the concentration of each aluminium species and the pH of the solution, as already done by Bottero *et al.*[8,9]. These authors neglected the solubility limit of Al^{3+} ions according to relation (9). To obtain the best fit for our experimental ^{27}Al n.m.r. results, we have introduced this expression with a value of $K_{sp} = 1.25 \times 10^{-32}$, a value close to that given for amorphous $Al(OH)_3$. *Figure 1* gives the calculated variations with pH for $Al_{tot} = 10^{-3}$ mol l^{-1}.

It is also well known that the polynuclear species of aluminium are not stable. Turner *et al.*[11,12] have studied the ageing of $AlCl_3$ solutions under different conditions. Their work shows the progressive transformation of Al_{13} ions into colloidal species and especially into $Al(OH)_3$, which is the most stable phase.

Experimental results. Bottero *et al.*[8–10] have performed a systematic study of partially neutralized solutions of $AlCl_3$ by ^{27}Al n.m.r. They show that this technique allows the mononuclear species of aluminium ions to be distinguished from the polynuclear species. It is well known that the fraction of polynuclear species depends on the conditions under which the solutions have been prepared: the rate of neutralization, the stirring used during this process, the ageing time and the temperature. We have not been able to reproduce exactly the conditions used by Bottero *et al.*, so our n.m.r. results are slightly different. In fact, the study of the interactions between polymer and different aluminium species requires a good knowledge of the initial $AlCl_3$ solution. That is why we have reproduced the experiments of Bottero *et al.* On the other hand, we have investigated the ageing of the $AlCl_3$ solutions.

^{27}Al n.m.r. spectra of 10^{-3} M $AlCl_3$ solutions are given in *Figure 2* for various R values (R being the neutralization ratio, $R = (OH^-)/(Al_{tot})$). Apart from the signal taken as reference ($Al(OH)_4^-$), two peaks are observed whose importance varies with R. These signals have been identified[8–10,13–15]: the first signal at 17 ppm from reference is attributed to tetrahedrally coordinated aluminium in the $AlO_4Al_{12}(OH)_n^{p+}$ complex; its intensity is a maximum for $R = 2.3$. The second peak corresponds to monomeric species: $Al(H_2O)_6^{3+}$, $Al(H_2O)_5(OH)^{2+}$ and $Al(H_2O)_4(OH)_2^+$.

Concentrations of mononuclear and polynuclear ions are plotted in *Figure 3* as a function of pH. The behaviour is qualitatively consistent with that described by Bottero *et al.*: decrease of the content of the

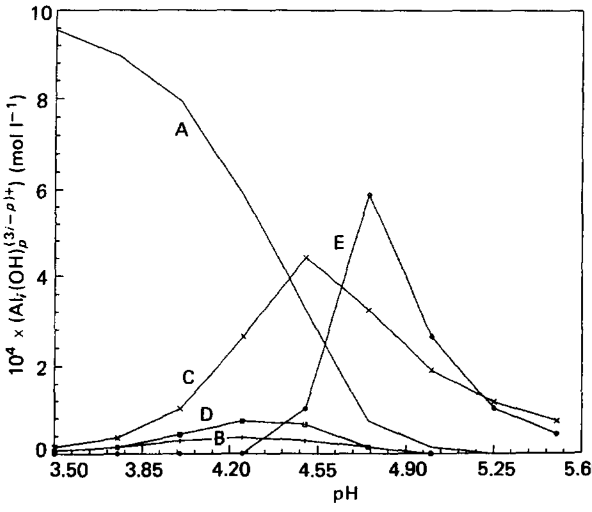

Figure 1 Calculated concentrations of Al^{3+} (curve A), $Al(OH)^{2+}$ (curve B), $Al(OH)_2^+$ (curve C), $Al_2(OH)_2^{4+}$ (curve D) and $Al_{13}(OH)_{29}^{3+}$ (curve E) in 10^{-3} M $AlCl_3$ solutions

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* Å = 10^{-10} nm

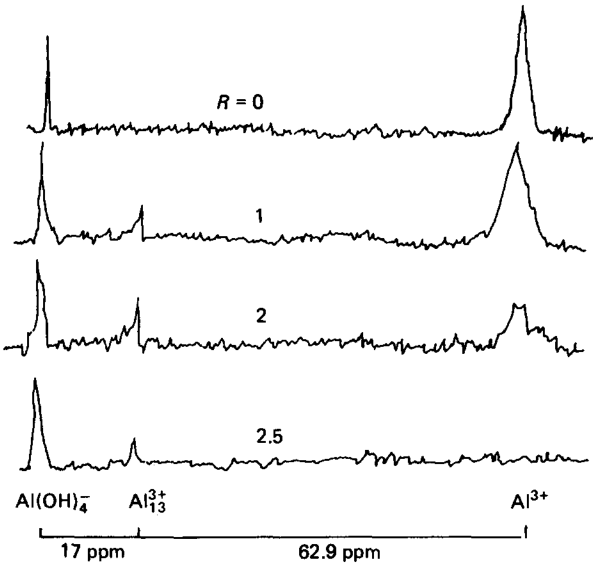

Figure 2 ^{27}Al n.m.r. spectra of 10^{-3} M $AlCl_3$ solutions at different neutralization ratios, R

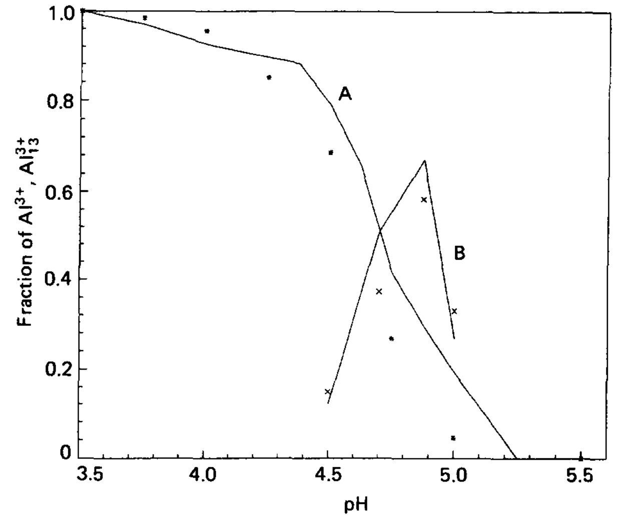

Figure 3 Fractions of mono (curve A, *) and polynuclear ions (curve B, ×) in 10^{-3} M $AlCl_3$ solutions as calculated (curves) and measured by ^{27}Al n.m.r. (*, ×)

monomeric species and a maximum in the concentration of polynuclear ions for $R=2.3$. Nevertheless, the sum of the contents of the different types of ions is $<100\%$ for $R>2$, which suggests that part of the Al is bound in Al_{13} aggregates or in $Al(OH)_3$ species which are undetectable by n.m.r. (Bottero *et al.* found the same result for $R>2.5$).

This behaviour leads us to introduce the expression for solubility limit, equation (9), into our calculations. In *Figure 3*, good agreement between experimental and calculated results can be observed.

N.m.r. spectra of aged $AlCl_3$ solutions have been registered at different time intervals. While the concentration of mono-ions remains constant, one can observe the progressive disappearance of Al_{13} ions with ageing time (see *Figure 4*). After two months, the solutions must only contain mononuclear ions and different forms (amorphous or crystalline) of $Al(OH)_3$. A similar evolution was noted by Turner[11,12], using other techniques. This result shows the importance of working with $AlCl_3$ solutions prepared under well defined and reproducible conditions and having the same ageing time.

Solutions of polymer and $AlCl_3$

Interaction model. Acrylamide–acrylic acid copolymers are polyacids who pK_a is an increasing function of ionization degree. Various theoretical models have been proposed in order to predict such a variation as a function of the electrical potential of the polyion. Practically, Mandel[19] has proposed an expression for pK_a in simple polynomial form:

$$pK_a = pK_0 + A_1\alpha + A_2\alpha^2 + \ldots \qquad (10)$$

Determination of the values pK_0, A_1 and A_2 for these polymers has been the objective of two different systematic studies[5,20]. We will use the data of reference 5.

If C_p is the concentration of polymer in g cm^{-3} and C_{ip} the molar concentration of carboxylate groups, then

$$\alpha = (COO^-)/(C_{ip}) \qquad (11)$$

$$K_a = (COO^-)(H^+)/[C_{ip} - (COO^-)] \qquad (12)$$

At each step of the calculation by successive approximation, new values of K_a must be determined from the actual value of α.

At a given pH, the polymer, more or less dissociated, will be in the presence of different aluminium ions. As a first step we will only consider electrostatic interactions between the cationic species of Al and the carboxylate groups. In fact, hydrogen bonds including acrylamide functions and non-ionic $Al(OH)_3$ could also be expected at higher pH but this form of interaction cannot be detected by n.m.r. Then different equilibria could be considered:

$$---COO^- + Al(OH)_2^+ \rightleftharpoons COOAl(OH)_2 \qquad (a)$$

$$---COO^- + Al(OH)^{2+} \rightleftharpoons COOAl(OH)^+ \qquad (b)$$

$$2---COO^- + Al(OH)^{2+} \rightleftharpoons COO_2Al(OH) \qquad (c)$$

$$4---COO^- + Al_2(OH)_2^{4+} \rightleftharpoons COO_4Al_2(OH)_2 \qquad (d)$$

$$---COO^- + Al^{3+} \rightleftharpoons COOAl^{2+} \qquad (e)$$

$$2---COO^- + Al^{3+} \rightleftharpoons COO_2Al^+ \qquad (f)$$

$$3---COO^- + Al^{3+} \rightleftharpoons COO_3Al \qquad (g)$$

$$3---COO^- + Al_{13}^{7+} \rightleftharpoons COO_3Al_{13} \qquad (h)$$

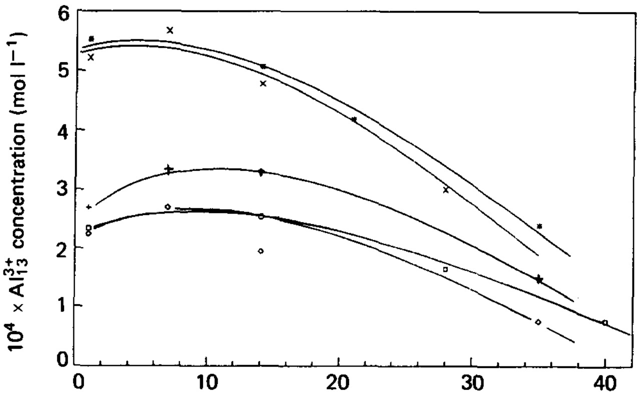

Figure 4 Effect of ageing time on concentration of polynuclear ions in 10^{-3} M $AlCl_3$ solutions at different neutralization ratios, R: (◇) 0.5; (□) 1; (×) 1.5; (*) 2; (+) 2.5

It is difficult to take into account all these equilibria, so the following approximations will be made:

1 Since the $Al(OH)_2^+$ ion probably behaves as a monovalent cation of the type Na^+ or K^+, one can neglect its interaction with the polyion: it is known that the condensation phenomena described in the Manning theory[21] can only be important for values of the charge parameter, ζ, which correspond to a carboxylate group content $>35\%$, at pH 7. This limit is not attained with the polymers under study.

2 The $Al(OH)^{2+}$ and $Al_2(OH)_2^{4+}$ ions are expected to interact strongly with the polymer charged groups, but as shown in *Figure 1* their concentration is very low and one can assume that their fixation on the polyion will slightly modify the global system.

3 The strongest interaction includes the trivalent cations, mono and polynuclear. Since our ageing studies had shown that the concentration of mono-ions remains constant while the content of Al_{13} tends to zero with time, we investigated two cases: first, the case where only Al^{3+} ions are present in the solutions, which corresponds to aged solutions – the calculation is then performed by taking into account equilibrium (g), which is assumed to be predominant over equilibria (e) and (f); second, the case where the two types of trivalent cations can be present in fresh $AlCl_3$ solutions (14 days ageing) – Equilibria (g) and (h) are introduced into the computations.

This series of assumptions constitutes a first approach to the problem. In fact there is no direct evidence for $Al(OH)_2^+$ behaving as an alkaline cation or for the predominance of equilibrium (g) over equilibria (e) and (f). These hypotheses seem to us the most convenient in simplifying the problem by reducing the number of equilibrium constants.

Calculated curves. The experimental results show that the pH variation when one mixes the polymer and $AlCl_3$ solutions (both at the same pH, pH_i) may be neglected. We assume that the pH of the mixture is pH_i.

1 Aged Al solution. We have to resolve simultaneously the equations corresponding to equilibria (a)–(f) and equations (9)–(11). We also consider equilibrium (g) with a constant K_i, chosen arbitrarily at first and adjusted later to obtain the best fit to the experimental results. So we add two other equations as follows:

$$Al_{tot} = (\Sigma i Al_i(OH)_p^{3i-p}) + Al(COO)_3 \qquad (13)$$

$$C_{ip} = (COO^-) + (COOH) + 3(Al(COO)_3) \qquad (14)$$

Our calculation program allows us to calculate, by a step by step method, the concentrations of different Al ions, $Al(COO)_3$ complexes and (COO^-) 'free' groups as a function of pH. Some results are given in *Figure 5* for the same polymer concentration but different degrees of hydrolysis. The amount of Al^{3+} is found to decrease with increasing degree of hydrolysis, τ, while for all τ values the concentration of $Al(COO)_3$ complexes reaches a maximum for a pH near to 4.3. Such behaviour can easily be understood: for the low pH (pH 4), (Al^{3+}) is a maximum but the carboxylate groups are weakly dissociated and for pH 5 (Al^{3+}) tends to zero.

2 Fresh $AlCl_3$ solutions. In this case both Al^{3+} and Al_{13}^{3+} ions are present, so we will take into account the equation corresponding to equilibrium (h) with a new constant K_0 to be defined.

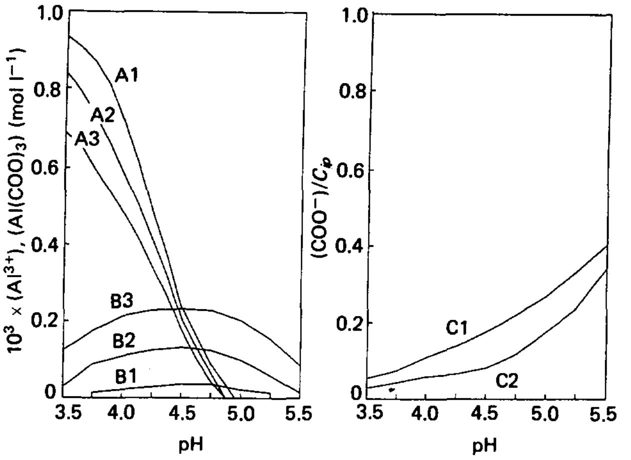

Figure 5 Polymer–aluminium interactions: calculations for aged $AlCl_3$ solutions (10^{-3} mol l^{-1}) with $K_i = 10^{14}$. Curves A, concentration of Al^{3+}: 1, without polymer; 2 and 3, with 0.25 g l^{-1} of AD27 ($\tau = 17\%$) and Pusher 700 ($\tau = 30\%$), respectively. Curves B, concentration of $Al(COO)_3$ complexes with 0.25 g l^{-1} of: 1, AD 10 ($\tau = 2\%$); 2, AD 27; and 3, Pusher 700. Curves C, fraction of free COO^- groups: 1, pure Pusher 700 solution (0.25 g l^{-1}); 2, with 10^{-3} M $AlCl_3$

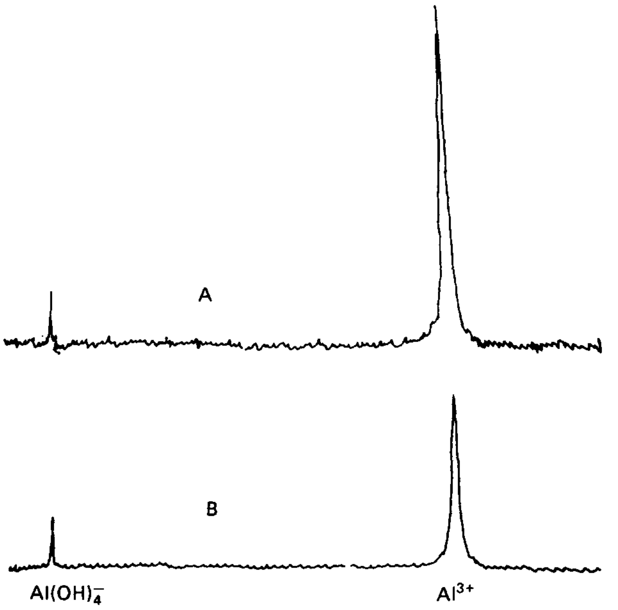

Figure 6 ^{27}Al n.m.r. spectra of $AlCl_3$ solutions (10^{-3} mol l^{-1}) without polymer (curve A) and with 0.5 g l^{-1} of AD10 (curve B)

Equations (13) and (14) must be changed as follows:

$$Al_{tot} = (\Sigma i Al_i(OH)_p) + Al(COO)_3 + 13Al_{13}(COO)_3 \qquad (13')$$

$$C_{ip} = (COO^-) + (COOH) + 3Al(COO)_3 + 3Al_{13}(COO)_3 \qquad (14')$$

Some calculated curves are shown together with experimental results in *Figures 8* and *9*. We have reported the amount of the monomeric ions 'bound' into $Al(COO)_3$ complexes or into Al_{13} form. In fact, when the Al_{13} ions interact with carboxylate groups, equilibrium (f) goes to the right and the number of monomeric ions decreases. This representation is slightly different from

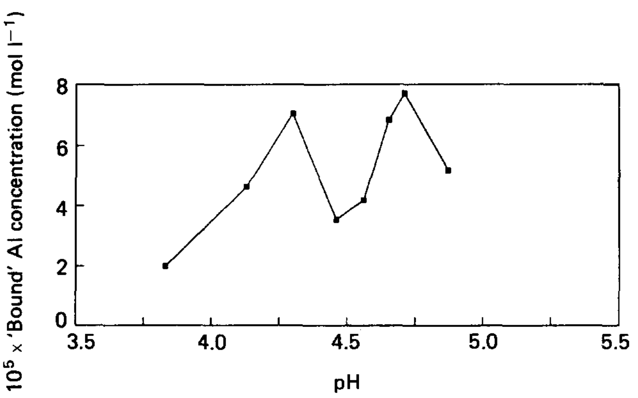

Figure 7 Polymer–aluminium interactions: concentration of 'bound' monomeric Al ions for 10^{-3} M $AlCl_3$ and 0.5 g l^{-1} AD10 as a function of pH (n.m.r. results)

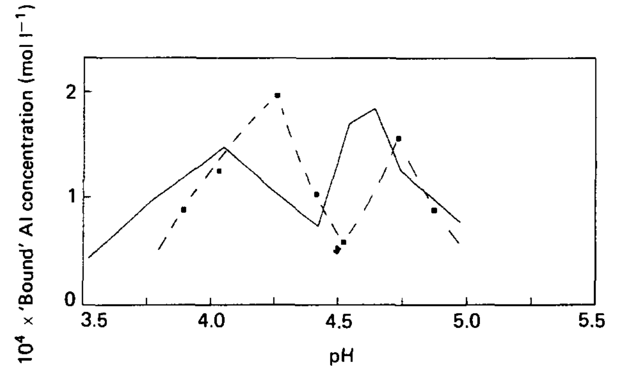

Figure 8 Polymer–aluminium interactions: concentration of 'bound' monomeric Al ions for 10^{-3} M $AlCl_3$ and 0.25 g l^{-1} AD27 as a function of pH (n.m.r. results (☒) and curves calculated with $K_i = 10^{14}$ and $K_0 = 10^{16}$)

that of *Figure 5* and can easily be compared with the experimental results.

We have found by these calculations two maxima in the amount of 'bound' monomeric ions, for pH = 4 and pH = 4.6. Comparing this result with *Figure 1*, it is obvious that these maxima correspond to the highest values of Al^{3+} and Al_{13}^{7+} concentration, respectively.

Experimental results. We have only studied the second case, where freshly prepared $AlCl_3$ solutions (aged for 14 days) are used.

We compared the n.m.r. signal of the same concentration of aluminium (10^{-3} mol l^{-1}) at a given pH in the absence and in the presence of different acrylamide–acrylic acid copolymers. The signal from the monomeric species allows us to evaluate the number of monomeric Al ions which have disappeared when the polymer solution is added (subsequently referred to as Al 'bound'). We cannot do the same thing with polynuclear species because their signal is not strong enough. In *Figure 6*, the decrease in the amount of monomeric species is clearly shown in the n.m.r. spectra, by addition of AD10 in $AlCl_3$ solution.

In *Figures 7–9*, the concentration of bound monomeric Al ions is represented as a function of pH for three different systems. Calculated curves obtained with the best pair of values K_i, K_0 are compared with experimental results.

The following remarks can be made. First, as expected from calculations, n.m.r. experiments show that the amount of aluminium bound onto the polymer increases with increasing degree of hydrolysis of the polymer, and two maxima in this binding are observed. The experimental and calculated results are in qualitatively good agreement. Second, nevertheless, there are shifts between the pH values of these maxima; in fact these shifts do not exceed 0.2 pH. Such differences could easily be explained by the numerous assumptions introduced in the calculations.

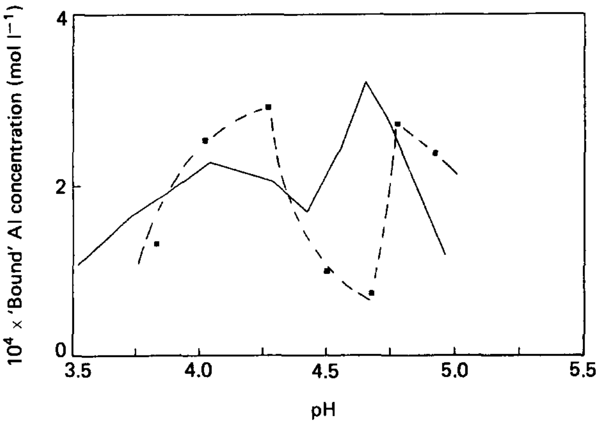

Figure 9 Polymer–aluminium interactions: concentration of 'bound' monomeric Al ions for 10^{-3} M $AlCl_3$ and 0.25 g l^{-1} Pusher 700 as a function of pH (n.m.r. results (☒) and curves calculated with $K_i = 10^{14}$ and $K_0 = 10^{16}$)

CONCLUSIONS

Our results on Al^{3+} hydrolysis are close to those found in the literature. The difference lies in the exact determination of the concentration of the polynuclear ions Al_{13}, whose structure and evolution depend on many conditions. For interactions between aluminium ions and ionic copolymers, the simple model proposed gives a good account of the n.m.r. results. It allows the prediction of the pH range where the maximum interaction must be observed and calculation of the number of carboxylate groups neutralized by the binding of the aluminium ions. Nevertheless, in such a model, only electrostatic interactions are taken into account and hydrogen bonds are neglected. We will show in a subsequent paper that all these types of interaction must be considered in order to explain viscometric behaviour and phase separation phenomena, particularly in the neutral range of pH.

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