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POLYELECTROLYTE COMPLEXATION AT OXIDE-WATER INTERFACES INFLUENCE ON COLLOIDAL STABILITY

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The present study aimed at the colloidal stability at short terms of aluminium oxide particles in aqueous suspensions containing polyacrylic acid and complexing aluminium ions resulting from the oxide dissolution at initial pH 5. Carboxylic acid groups were found to strongly interact with aluminium ions and form a oxide-polymer complex. The kinetics of polymer adsorption was obtained by determining the concentrations of complexed polyacid or polyacid free of aluminium ion which are non adsorbed and remain in the supernatant as a function of time. The adsorption mechanism was found to depend on the carboxylic acid to aluminium ion ratio. For low value of this ratio, the polyelectrolyte rapidly adsorbed in the form of a polyion highly complexed with the initially solubilized aluminium ions. For high value of the ratio, the adsorption was long delayed and the polyacid underwent an aluminium-hydrogen ion exchange, the extent of which depended on the oxide dissolution rate as evidenced by increase of the pH of the suspension.

INTRODUCTION

The interactions of polyelectrolytes with minerals and clays constitute a puzzling domain of investigation insofar as the liquid phase generally contains ions of various nature and electrical charge, and the colloid itself may be subjected to different types of phenomena such as dissolution or accretion. Such interactions may develop in the aquatic environment when the colloids are suspended in a medium

of a given electrochemical composition—the equilibrium conditions being imposed by the liquid phase—or in sediments and muds, when the electrochemical characteristics are locally imposed by the "solid" phase. In the latter situation, the large surface area developed by the small colloids exerts a paramount influence on the characteristics of the interstitial water [1]. The colloidal stability in suspensions, sediments and muds strongly depends on the nature of the interaction developed at the solid-liquid interfaces [2].

1 MATERIALS AND METHODS

1.1 Aluminium oxide

α -alumina was kindly provided by *Aluminium-Péchiney*. The mean particle size was 1.54 μm and the specific surface area was 3 m^2/g . The sample is partially soluble in 0.001 M KCl aqueous solution and the resulting aluminium ion concentration is 3×10^{-4} N at pH 5.0. The oxide presents no further dissolution when 0.4 g of dry power is suspended in 50 ml of the "synthetic" supernatant (0.001 M KCl + 3×10^{-4} N AlCl_3 at pH 4.06) and the "equilibrium" pH which is instantaneously established is 5.0.

1.2 Polymer

The fractionated sample of polyacrylic acid (PAA) of molecular weight 9.6×10^5 strongly interacts with aluminium ions and the maximal degree of complexation is close to 0.60 in the liquid phase containing 0.001 M KCl + 3×10^{-4} N AlCl_3 at pH 5.0.

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1.3 Analysis of the supernatant

The concentrations of the different chemical species present in the liquid phase suspending the oxide (free aluminium ions [Al-f], non complexed carboxylate groups [COO⁻-f] and free plus complexed carboxylate groups [COO⁻]) were determined by titration with NaOH, taking advantage of the different shapes of the titration curves obtained under conditions of excess of aluminium ions, excess of carboxylic acid groups and equal concentrations of the two species [3].

1.4 Zeta potential

The zeta potential was calculated using the Smoluchowski equation and the electrophoretic mobility determined by the Malvern method (Malvern Zeta Sizer III).

2 RESULTS AND DISCUSSION

2.1 Kinetics of the polyelectrolyte adsorption

Results obtained for the two situations of excess aluminium ions and excess polymer, i.e. below and above an initial dosage of 2.5 mg/m² are fully different.

The first situation corresponds to (i) sufficient concentration of initially solubilized aluminium ions for complexation of the carboxylic acid groups and (ii) no polymer in the liquid phase owing to fast adsorption of complexed polyelectrolyte. The adsorbed polymer protects the aluminium oxide from further dissolution.

The second situation corresponds to excess polyelectrolyte. The degree of initial complexation is simply related to the relative polymer dosage (3×10^{-4})/[COO⁻]. In Figure 1, the concentrations of the different constituents—free polymer, total polymer and complexed aluminium ions—are expressed in terms of the normality of the aqueous solution on the left ordinate. The concentrations of free and total polymer in the supernatant solution are expressed in terms of the amount of non adsorbed polymer per unit area of the alumina surface (mg/m²) on the right ordinate.

General conclusions are obvious. The concentration of free polyelectrolytes decreases more rapidly than the total (free + complexed) concentration showing the occurrence of complexation prior to adsorption. Non or low complexed polyelectrolytes only adsorb with the progress of complexation. The delay increases with the amount of polymer added indicating that the aluminium ions originate from the dissolution of the colloidal alumina.

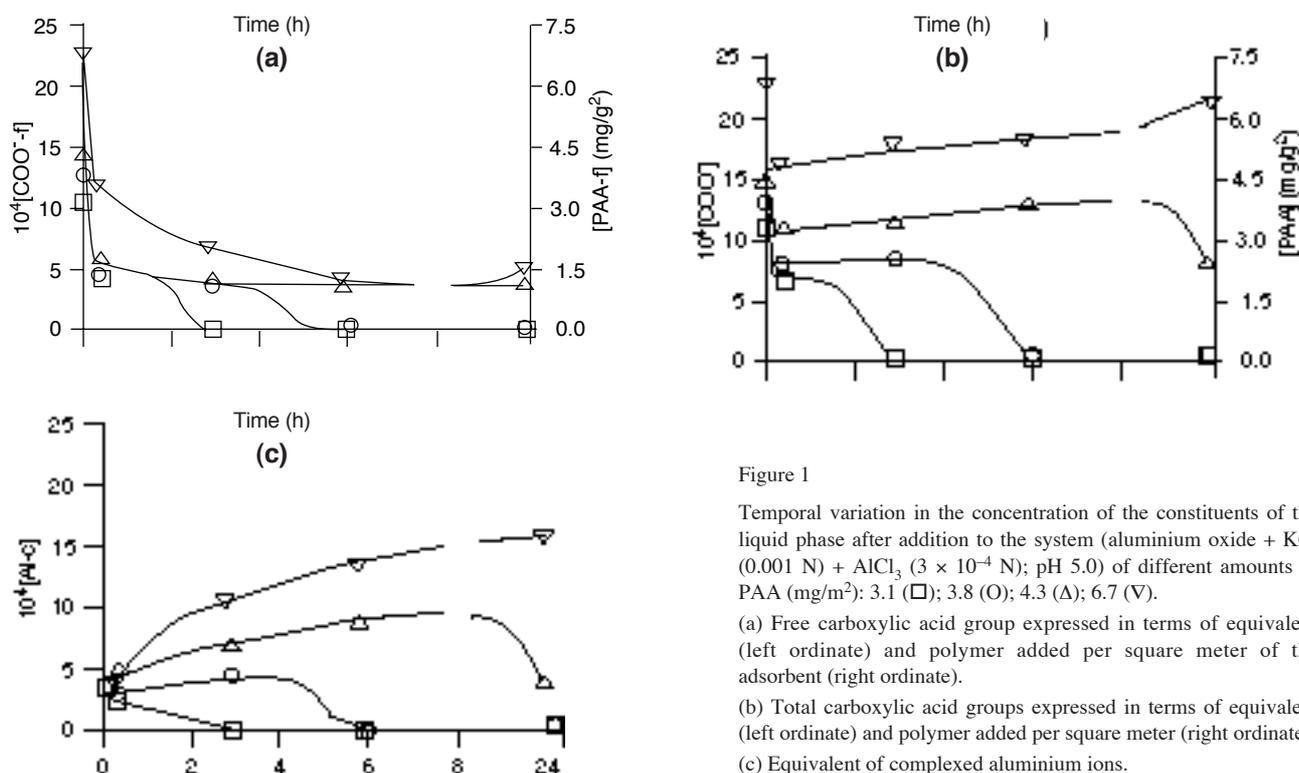


Figure 1

Temporal variation in the concentration of the constituents of the liquid phase after addition to the system (aluminium oxide + KCl (0.001 N) + AlCl₃ (3×10^{-4} N); pH 5.0) of different amounts of PAA (mg/m²): 3.1 (□); 3.8 (O); 4.3 (Δ); 6.7 (∇).

(a) Free carboxylic acid group expressed in terms of equivalent (left ordinate) and polymer added per square meter of the adsorbent (right ordinate).

(b) Total carboxylic acid groups expressed in terms of equivalent (left ordinate) and polymer added per square meter (right ordinate).

(c) Equivalent of complexed aluminium ions.

2.2 Zeta potential of the alumina-polyelectrolyte complex

Figure 2 shows the zeta potential of the polyelectrolyte coated alumina particles as a function of time for different initial polymer dosages expressed in mg/m^2 . Below $4.5 \text{ mg}/\text{m}^2$, the initial drop in zeta potential increases with the polymer dosage, but this does not correspond to the equilibrium value. The zeta potential increases slowly after 5-10 h, and seems to be stable after 24 h. The transition period may correspond to a modification of adsorption characteristics. Above $4.5 \text{ mg}/\text{m}^2$, the initial drop remains more or less constant for 24 h. There is a close correlation between the time dependence of the adsorption and that of the zeta potential. Adsorption of polyelectrolyte characterised by a large degree of complexation gives rise to positively charged polymeric interfaces. On the contrary, adsorption of polyelectrolytes characterised by a lower degree of complexation leads to surfaces characterised by negative values of the zeta potential. For values of the polymer dosage smaller than $5 \text{ mg}/\text{m}^2$, the period required to reach the initial pH 5 parallels that of the zeta potential. For values larger than $5 \text{ mg}/\text{m}^2$, the pH increases with time during the period corresponding to the polymer-induced dissolution of the oxide.

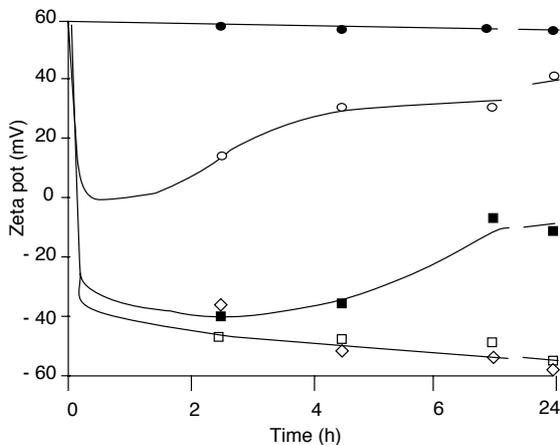


Figure 2

Temporal variation in the zeta potential of the colloidal in the presence of different amounts of added PAA (mg/m^2): 0 (●); 2.0 (○); 4.0 (■); 6.0 (□) and 8.0 (◇).

2.3 Stability of the colloidal alumina-polyelectrolyte complex

The height of the colloidal suspension was recorded after a given constant period for different orthokinetic flocculation experiments. The effect of both the period of stirring (corresponding to the period in which the adsorption changes and/or the adsorbed polymer changes its charge and

conformation) and the amount of polymer added were investigated. In Figure 3, when the height of the suspended phase is close to zero the suspension is fully destabilised while peptised particles do not settle. After a period of stirring of less than 3-5 h, the suspension flocculated when the polymer dosage was less than $2.5 \text{ mg}/\text{m}^2$. After 24 h, the instability range was very limited around the value of $4 \text{ mg}/\text{m}^2$. We note that there is a correlation between the instability domain and the period in which the zeta potential is close to zero. Owing to the aluminum ion complexation, the adsorbed polymer layer behaves like a polyampholyte which bears an excess of positively charged surface groups when the adsorbed polymer is fully complexed and an excess of negatively charged groups when the polymer is slightly complexed.

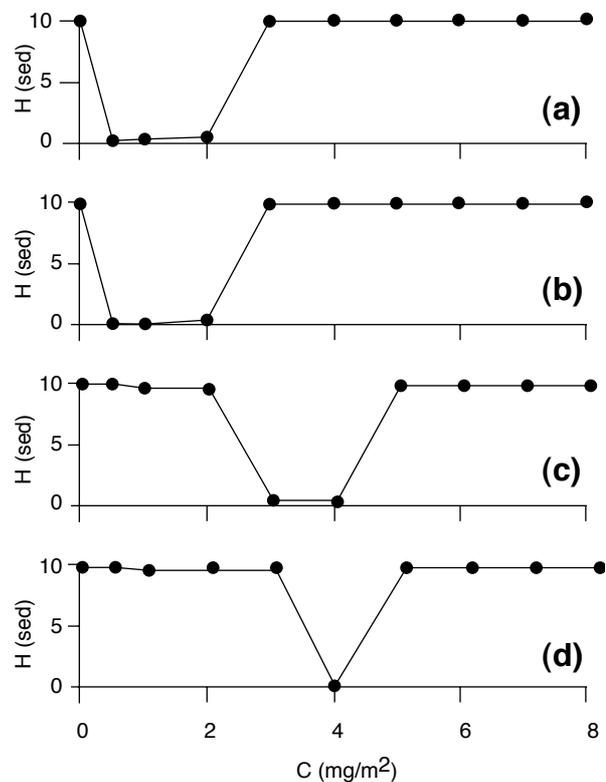


Figure 3

Height of the suspension as a function of the amount of PAA (mg/m^2) added to the system (aluminium oxide + KCl (0.001 N) + AlCl_3 (3×10^{-4} N); pH 5.0) after different periods of stirring: (a) 10 min; (b) 2 h; (c) 6 h and (d) 24 h.

CONCLUSION

Polyelectrolyte adsorption does not correspond to the classical view of a homopolymer adsorbing on an inert

adsorbent when plurivalent ions compete with monovalent and hydrogen ions for the ionised groups. Ion-exchange processes contribute to the modification of polymer composition and solubility [4]. This study on the interaction of synthetic polyelectrolytes with a soluble oxide, which involves the dissolution of the oxides and the adsorption of the complexed species, may provide a new insight into the possible interaction of such polymers and the constituents (or pollutants) of muds. It may give an information on the changes at short terms of the rheological properties of muds.

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