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Hydrolysis and flocculation: a structural approach through small-angle X-ray scattering

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Abstract.— The flocculation of silica by coagulation with hydrolyzed aluminum salt and the flocculation of aluminum salt in the presence of organic acids at pH 6.5 have been studied by using Small-Angle X-ray Scattering. The flocculation of silica at pH 4.5 by isolated Al_{13} is very similar to its flocculation by non-hydrolyzable salt as Ca^{++} ; the fractal dimension D_f of the flocs is 2.20. At pH 7.5, Al_{13} is hydrolyzed and strongly aggregated through hydroxo bridges, and the structure of the flocs is that of Al_{13} aggregates, i.e. $D_f = 1.7$. The flocculation of aluminum in the presence of organics such as acetate, salicylate, lactate and oxalate (organics/Al = 0.25, 0.5 and 1.0) occurs at lower pH values than in the absence of organics. The SAXS curves display a crossover region in the Q-range 0.05 to 0.15 $\text{\AA}^{-1}$, due to the presence of small, loose -Al-OH-Al- aggregates. The simulation of the outermost part of the SAXS curves shows that the organic ligands limit the Al hydrolysis at the stage of the monomers and small oligomers by competing with the OH^- ions. This charge screening results in high coordination numbers and in high density of the flocs ($2.3 \leq D_f \leq 3$).

1. Introduction

Flocculation is a general process by which dispersed particles come together to form large aggregates or settleable flocs. It is one of the most used solid/liquid separation processes [1]. Flocculation under the control of hydrolysis is of importance for many applications. In water treatment, solid/liquid separation of colloidal particles is achieved by addition of inorganic hydrolysable salts [2-4]. Hydrolysis of metal ions is the removal of protons from the hydration shell of the ions by addition of OH^- . It results in nucleation of polycations (Al_{13} in the case of aluminum) by formation of hydroxo bridges between the metal ions [5]. These polycations aggregate by sharing hydroxo bridges. Large flocs are initiated by the formation of small linear aggregates which associate to build a three-dimensional network. Such flocs are able to settle. Sol/gel processes are used to obtain ceramics [6] or transparent alumina films [7]. In the latter case, the aluminum hydrolysis is controlled by adding organic ligands in order to peptize the gel formed at high pH.

The present paper aims at showing that flocculation of colloids by aluminum salts is under the control of hydrolysis. The study of the structure of flocs obtained under different conditions in which hydrolysis can be either hindered, limited or favored, has led us to propose a general model of floc formation. Small-Angle X-ray Scattering (SAXS) is one of the best tools to reveal the structure of flocs. The scattered intensity versus the scattering vector, or the distance distribution function give a direct knowledge of the spatial organization of matter [8]. Two processes have been studied: the flocculation of silica colloids by Al_{13} polycations at various pHs and the flocculation of aluminum salts in the presence of organics at neutral pH.

2. Materials and Methods

Flocculation of silica by Al_{13} clusters and their aggregates

Ludox HS 40 silica colloids have been used. The mean size is 14 nm in diameter as deduced from SAXS [9]. The surface charge is negative at pH higher than 2 [10].

Fig. 1.— SAXS curves and modeled fractal aggregates for Al_{13} aggregates at pH 5 and 6 (from [11]).

Al_{13} was obtained by hydrolysis of 0.1 mol/l aluminum chloride with sodium hydroxide [3]. For a hydrolysis ratio ($R = [NaOH] / [Al]$) $R = 2$ (corresponding to pH = 4), the Al_{13} polycations are isolated. For $R = 2.5$ (corresponding to pH = 5), they form linear fractal aggregates with a fractal dimension $D_f = 1.43$ (Fig.1). At pH higher than 6, more dense aggregates ($D_f = 1.85$) are formed [11].

A 500 ppm suspension of Ludox HS silica colloids was flocculated at pH 4.5 or 7.5 using various concentrations of Al_{13} polycations formed at two hydrolysis ratios ($R = 2.0$ or $R = 2.5$). The total aluminum concentration was $2 \cdot 10^{-3}$ or $4 \cdot 10^{-3}$ mol/l in the pH 4.5 experiment, and $8 \cdot 10^{-3}$ mol/l in the pH 7.5 experiments. The suspensions were stirred at 250 rpm (mean velocity gradient $G = 450 \text{ s}^{-1}$) for 2 min, and then allowed to settle. The settled flocs were collected for SAXS analysis.

Flocculation of Al solutions by organic ligands.

Solutions of 0.1 mol/l $AlCl_3 \cdot 6H_2O$ were mixed with organic acids (acetic, oxalic, salicylic or lactic acid) at pH 3.5, and at L/M (total ligand concentration / total aluminum concentration) ratios of 0.25, 0.5 and 1. The solutions were hydrolyzed up to pH 7.0 by adding 1 mol/l NaOH under vigorous stirring. The formation of colloids and precipitates was monitored by continuous turbidity measurement using a Hach turbidimeter calibrated in Nephelometric Turbidity Units (NTU). After settling, the flocs were collected for SAXS analysis. Solid state ^{27}Al NMR spectra (Fig. 2) have shown that such precipitates contain mainly hexacoordinated Al, and secondarily Al_{13} detected by the resonance of tetracoordinated Al at 62.9 ppm [12].

SAXS data recording

The sample holder for the settled flocs was a 0.8 mm cell fitted with Kapton film windows.

Synchrotron radiation of the DCI storage ring of LURE (Université de Paris Sud, Orsay France) was used for its high intensity associated with point collimation. The collected data covered the Q-range from 10^{-3} to $0.4 \text{ \AA}^{-1}$ (Q is the scattering vector: $Q = 4\pi \sin \theta / \lambda$, with 2θ the scattering angle and $\lambda = 1.6 \text{ \AA}$). The data were recorded for 2 hours. More thorough scattering spectra in the Q-range $0.1 \text{ \AA}^{-1} < Q <$

$0.6 \text{ \AA}^{-1}$ have been recorded on a laboratory apparatus equipped with a Rigaku rotating anode. In this case the time required for recording the data was 24 h.

SAXS data analysis

The scattered intensity $I(Q)$ is:

$$I(Q) = K I_0(Q) \cdot S(Q) \quad (1)$$

where K is a scale constant, $I_0(Q)$ the scattering intensity due to the subunits, and $S(Q)$ the interference function which depends on the interparticle arrangement within the floc. $S(Q)$ is valid within the $1/L \leq Q \leq 1/R$ range, where L is the size of the floc and R the size of the subunit. If the flocs are mass fractals [13] with fractal dimension D_f , then

$$I(Q) / I_0(Q) \approx S(Q) \approx Q^{-D_f} \quad (2)$$

Fig. 2.— Solid-state ^{27}Al NMR spectra of freeze-dried Al-organic precipitates at pH 7.0 (from [12]).

In the case of large flocs such as the heteroflocs $\text{SiO}_2/\text{Al}_{13}$, the distance distribution function $P(r)$ has been calculated strictly within the experimental Q -range, thus delimiting a maximum experimental volume V_w (smaller than the real floc volume) calculated from the $Q_{\min}$ value:

$$V_w = \frac{4}{3} \pi \left(\frac{\pi/2}{Q_{\min}} \right)^3 \quad (3)$$

The size of the SiO_2 subunit particle was derived from the scattering curve of a dilute sol [9]. The derived theoretical scattering curve of the SiO_2 subunits $I_0(Q)$ was used to normalize the experimental curves and to extrapolate them to $Q = 1.5 \text{ \AA}^{-1}$ in order to avoid Fourier ripples in $P(r)$.

The volume of matter V_m within the experimental volume V_w was derived from $P(r)$. The V_m/V_0 ratio, where V_0 is the volume of a single SiO_2 particle ($V_0 = 2.5 \cdot 10^{-18} \text{ cm}^3$), leads to the number N of silica particles in the experimental volume. Then the local density ρ can be calculated [8]:

$$\rho = N \cdot m_0 / V_w \quad (4)$$

where m_0 is the mass of a single silica particle.

In the case of the Al-organics precipitates, the nature of the subunits is unknown. However, the outermost part of the scattering curves could be modeled by taking into account the oligomeric species formed during the hydrolysis of aluminum chloride: monomers, dimers, trimers and Al_{13} [13-16].

3. Results

Flocculation of silica colloids by Al_{13} .

The flocs formed at pH 4.5 and at pH 7.5 with Al concentrations of $2 \cdot 10^{-3}$, $4 \cdot 10^{-3}$ and $8 \cdot 10^{-3}$ mol/l settled very quickly. Their size ranged between 20 and 600 μm , as measured by light diffraction with a Malvern Mastersizer. In the plots $\log I(Q)$ vs. $\log(Q)$ (Fig. 3), $\log(Q)$ values higher than -1.5 correspond to the scattering by the silica subunit. For $\log(Q)$ values lower than -1.6, the curves displayed a linear portion. The curves corresponding to $R = 2.5$ and pH 4.5 also displayed a concavity resulting from local repulsions between subunits [17]. There was no significant difference between the scattering curves recorded at $2 \cdot 10^{-3}$ or $4 \cdot 10^{-3}$ mol/l (Fig. 3). The fractal dimension D_f was higher for $R = 2.5$ than for $R = 2.0$, and was lower for pH 7.5 than for pH 4.5 (Table I). The local density ρ varied in the same way as D_f .

Fig. 3.— SAXS curves of silica flocs - at pH 4.5 for $R=2$ and $R=2.5$ (see arrows); full lines: $[Al] = 2 \cdot 10^{-3}$ and dotted lines: $[Al] = 4 \cdot 10^{-3}$ mol/l) - at pH 7.5 (bold line) $[Al] = 8 \cdot 10^{-3}$ mol/l.

Table I.— Values of the fractal dimension D_f calculated from the slopes of the SAXS curves in Fig. 3, and of the local density ρ calculated from the $P(r)$ curves and eq. 4.

	$R = 2.0$		$R = 2.5$	
pH	4.5	7.5	4.5	7.5
D_f	2.06	1.75	2.20	2.06
$\rho \times 10^{-2}$ (g/cm ³)	7.8	5.2	11.3	8.7

Flocculation from Al-organic acids mixtures

Organic ligands always caused higher turbidity than chloride, and at lower pH, as exemplified in Figure 4 for $L/M = 0.5$. Lactate and acetate caused moderate turbidity increase, whereas salicylate and oxalate caused very high turbidity. The increase in turbidity was observed at pH ranging from 3.5 to 4.8 with organic acids, whereas it occurred at pH 6.0 with aluminium chloride. Liquid-state ^{27}Al NMR studies have shown that organic ligands hinder the formation of Al_{13} in the pH range from 3.5 to 6.5. This effect ranked as follows: oxalate > salicylate > acetate > lactate [18,19].

The outermost part of the SAXS curves of precipitated Al-organics differed markedly from that of pure precipitated Al_{13} (Fig. 5). This supports the liquid- and solid-state ^{27}Al NMR results, which established the poor formation of Al_{13} in the presence of organic acids due to their strong affinity for

aluminum oligomers [12,18,19]. Therefore, the subunits building the aggregates were assumed to be the monomer, the dimer, the trimer, and secondarily the Al_{13} . They were assumed to be spheres of radius 1.88 Å for the monomer and 2.97 Å for the dimer and the trimer, as calculated from the distances between the aluminum and oxygen atoms [20]; the radius of Al_{13} was taken as 7 Å [14]. The slope of the scattering curves in the 0.1 to 0.6 Å⁻¹ Q-range was close to -1 (Fig. 5). Therefore, the subunits were assumed to be locally aggregated within short linear chains.

Fig. 4.— Evolution of the turbidity of Al chloride and Al-organic acids mixtures at $L/M = 0.5$ with the pH (from [12]).

With these assumptions the outermost part of the scattering curves could be simulated. X-ray scattering by organics is negligible. However, their presence within the aggregates has been taken into account by introducing 1 to 3 Å spacings between the spheres. Calculated scattering by monomers, dimers, trimers and Al_{13} were combined in various proportions according to the NMR results, in order to derive the scattering curves $I_0(Q)$ of 2 to 5 membered chains, which are the real observable basic units of the precipitates.

Fig. 5.— Outermost part of the SAXS curves: (a) of Al_{13} and Al-organics precipitates at $L/M = 0.5$; (b) fitted scattering curve of Al-lactate precipitates at $L/M = 0.5$ and 1.

The best fits to the experimental scattering curves were obtained with models including a huge majority of monomers (70 to 97 %), low amounts of dimers and trimers (0 to 30 %), and Al_{13} in very low amounts in the case of lactate and salicylate (4 and 13 %) (Table II).

Table II.— Composition of the models used to fit the outermost experimental SAXS curves. mon.: monomers, olig.: oligomers (dimers or trimers).

Acids	lactate		acetate		salicylate		oxalate			
L/M	0.5 or 1.0		0.5 or 1.0		0.25 or 0.5		0.25		1.0	
model	mon.	Al_{13}	mon.	olig.	mon.	Al_{13}	mon.	olig.	mon.	olig.
% Al	96	4	87	13	90	10	94	6	70	30

From these data, $S(Q)$ was calculated and $\log S(Q)$ vs. $\log(Q)$ was plotted (Fig. 6). The curves displayed a linear part in the Q -range 0.01 to 0.05 $\text{\AA}^{-1}$, from which the fractal dimension of the aggregates was calculated (Table III). A crossover region ranging from $Q = 0.05$ to $Q = 0.15 \text{ \AA}^{-1}$ joined this linear part and the Q -domain relative to the subunit scattering.

5. Discussion.

The features observed on both investigated systems can be generalized in a model which accounts for the hydrolysis of aluminum salts in combination with the growth of clusters. This is a general scheme for sol-gel-precipitate processes [6]. The growth of aggregates is based on random diffusion, leading to fractal aggregates with D_f values depending on the number and localization of the reactive clustering sites [13,21]. In the hydrolysis mechanisms, the presence of ligands other than OH or O leading to hydroxo- or oxo-bonds, can strongly modify the structure of the aggregates or precipitates. Both examples of this study reveal the role of the hydroxo- or oxo-bonds on the structure of heteroprecipitates.

The heteroflocculation of SiO_2 colloids by Al-OH polymers depends on the hydrolysis level of aluminum. At pH 4.5, for which hydrolysis and growth of Al-OH aggregates are limited, the corners of Al_{13} are essentially H_2O molecules. The fractal dimension of the flocs results from the high affinity of Al_{13} for the silica surface. Some SiO_4 surface sites are exchanged by AlO_4 , and the Al-OH polymers "adsorbed" onto silica become potential sites for clustering. Non-universal D_f values are obtained: $D_f = 2.06$ or 2.20 (Table I), indicating that the coordination number of each SiO_2 colloid is high and results from its affinity for Al_{13} and the conformation and size of Al_{13} aggregates (Fig. 1). The flocculation mechanisms of silica by Al-OH polymers, i.e. charge screening [22], is very similar to that observed with Ca^{++} cations or low molecular weight cationic macromolecules [23-25].

Fig. 6.— $\log S(Q)$ - $\log Q$ plots for $L/M = 0.5$ and different L.

At pH = 7.5, the hydrolysis and aggregation of aluminum are strongly forwarded. The size of Al_{13} aggregates is much larger than that of SiO_2 colloids. In this case, the affinity between these species leads to the adsorption of single silica particles on the Al_{13} aggregates. Thus, the structure of the resulting flocs is only slightly modified by the presence of silica and the fractal dimension is close to that of Al_{13} aggregates. The hydrolysis of aluminum is the only limiting step of heteroflocculation.

Organic ligands compete with the OH^- ions for the hydrolysis sites of aluminum in replacing bridging OH bonds by organic bonds. Therefore, the nucleation of Al species and growth of aggregates are modified, according to the ligand/Al ratio [18,19]. The precipitates formed at pH = 7 do not present universal growth patterns: the fractal dimension values range from 2.3 to 3 (Table III).

Table III.— D_f values of Al-organics precipitates at different L/M ratios.

Acids	acetate		oxalate		salicylate		lactate	
L/M	0.5	1.0	0.25	1.0	0.25	0.5	0.5	1.0
D_f	2.59	2.77	2.30	2.92	2.47	2.92	2.60	2.42

The increase of D_f with L/M indicates that the structure of the precipitates become more compact with increasing number of ligands bound to Al monomers and oligomers. The densification of the precipitates is maximum ($D_f = 2.92$) with the chelating and potentially bridging oxalate and salicylate. The crossover region on the SAXS curves is more or less extended (Fig. 6). It reveals the presence of small clusters with a less dense structure. As shown on figure 6, the crossover is more extended at low ligand/Al ratios. It shows that -Al-OH-Al- aggregates coexist with -L-Al-L- aggregates in which L are organic-ligands.

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