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Catechol derivatives and anion adsorption onto alumina surfaces in aqueous media: influence on the electrokinetic properties

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Abstract

A high state of dispersion of alumina particles can be achieved by using molecules derived from Catechol 1,2(OH)$_2$C$_6$H$_4$, such as Tiron (OH)$_2$C$_6$H$_2$(SO$_3$Na)$_2$ which allows to obtain stable alumina suspensions. In the field of understanding the dispersion mechanism of Tiron and the contribution of each functional group grafted onto the benzene ring of the Tiron molecule, adsorption experiments and surface charge measurements were conducted by using several compounds, containing a benzene ring, and by varying the nature and the number of substituents. The influence of the size and of the charge of the counter ion, electrostatically attracted by a positive charged alumina surface, onto the suspension stability was also studied. Electrokinetic properties of the suspensions versus pH appear to be very useful to characterize the ion adsorption sequence for an oxide surface. With a high immersion heat, an alumina surface better adsorbs ions with a high structuring power for water molecules. This influences the charge developed onto the oxide surface. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Al$_2$O$_3$; Dispersion; Electrokinetic properties; Surfaces; Suspensions

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1. Introduction

Preparation and transformation of concentrated ceramic aqueous suspensions are paramount in the processing of ceramic parts, in particular to control the properties of final products and especially the reliability of these properties. To improve colloidal processing methods such as tape casting or direct coagulation casting (DCC), high powder loadings are required in particular in water based systems, which would be preferred in terms of toxicity and price. For many years, electrolytes[1,2] have often been used as dispersants. They develop highly repulsive potentials and allow the achievement of stable suspensions, because molecules adsorb onto the powder surface and develop surface charges leading to electrostatic stabilisation. Small organic electrolyte molecules do not build a steric barrier between ceramic particles as do polyelectrolytes; so a very high concentration of solid can be achieved in suspensions. For instance, a high state of dispersion of alumina particles can be achieved by using compounds derived from Catechol 1,2(OH)$_2$C$_6$H$_4$, such as Tiron (OH)$_2$C$_6$H$_2$(SO$_3$Na)$_2$; stable alumina suspensions with a concentration of 60 vol.% can thus be obtained.[3] The Catechol molecule, with hard donor groups, has a high affinity for positive ions, such as aluminum ions, leading to a strong adsorption onto oxide surface.

The first part of this work is devoted to understanding the dispersion mechanism of Tiron through adsorption experiments and measurements of surface charge. Several compounds, containing a benzene ring are used to measure the contribution of each functional group grafted onto the benzene ring of the Tiron molecule. In this respect, the influence of molecules of Catechol C$_6$H$_4$ 1,2 (OH)$_2$, 4 Methyl catechol 4CH$_3$C$_6$H$_3$1,2 (OH)$_2$, 1,2 Benzene disulfonic acid C$_6$H$_4$(SO$_3$K)$_2$, 4 Methyl catechol sulfonated 1,2 (OH)$_2$ 4 (CH$_3$) (SO$_3$Na)C$_6$H$_2$ and Tiron (HO)$_2$C$_6$H$_2$(SO$_3$Na)$_2$ on the electrokinetic properties of alumina suspensions versus pH is studied and related to the adsorption behaviour.

As this first study revealed an important contribution of the coverage state of alumina particles surface by the molecule and of the screen effect of the charged molecules

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onto the suspension stability, the second part of this work concerns the influence of the size and charge of the counter ion, electrostatically attracted by a positive charged alumina surface, onto the suspension stability. Objectives of these experiments consist in determining the main parameters which influence the competition between different adsorbates according to the kind of complexation (outer or inner sphere complex). Different electrokinetic properties are obtained using acids (HCl, HNO_3, $HClO_4$, H_2SO_4) of a different nature to decrease alumina suspension pH, prepared with or without dispersant, and to produce positive surface charge.

2. Experimental procedure

2.1. Starting materials

The powder used in this study was the AKP30 alumina (Sumitomo, Japan) with an average particle size of $d_{50} = 0.40$ μm (Sedigraph 5100, Micromeritics) and a specific surface area of 7 m^2 g^{-1} once degased at 300°C during 2 h (N_2 BET). The chemical reagents were supplied by Aldrich (sodium salts and derivatives of benzene) and by Prolabo (Normadose solutions).

2.2. Sulfonation of 4 methylcatechol

To study the influence of the sulfonate groups number grafted on the catechol molecule, no commercial product with only one SO_3^- group was available. Sulfonation of a catechol derivative, the 4 methylcatechol was then carried out.

Ten grams of 4 methylcatechol and 15.8 g of H_2SO_4 were mixed at 50–60°C for 2 h, with magnetic stirring. An excess of 100 mol% of H_2SO_4 was added to ensure complete sulfonation of 4 methylcatechol. The mixture of H_2SO_4 and the acid form of sulfonated 4 methyl catechol was then diluted with water and neutralized by slow NaOH addition to obtain a solution of Na_2SO_4 and of the sulfonated 4 methylcatechol sodium salt. To reduce the solution volume, water was evaporated at 60°C. The absolute ethanol addition led to the Na_2SO_4 precipitation. This salt was removed by centrifugation. After solvent evaporation, sulfonated 4 methylcatechol was obtained as a brown solid. Its chemical and thermogravimetric analysis led to the formula $C_7H_7O_5SNa$, 1.8 H_2O. The pK_a of the more acidic OH group measured at 25°C for an ionic strength of 0.1 M was equal to 8.8.

Because of the methyl group on the para position, only one sulfonate group can be grafted onto the 4 methylcatechol. The ^1H NMR spectrum was consistent with a mixture of the 2 methyl, 4,5 dihydroxy benzene sulfonic acid sodium salt and the 2,3 dihydroxy, 5 methyl benzene sulfonic acid sodium salt in a proportion of 94 and 6 mol%, respectively. Two singlets at $\delta = 7.41$ and at $\delta = 6.87$ were due to two protons free of coupling in positions 2 and 5 onto the benzene ring of the first isomer. Two doublets centred at $\delta = 7.08$ and at $\delta = 6.92$ with a coupling of 2 Hz were due to protons in positions 4 and 6 onto the benzene ring of the second isomer.

A mixture of the two isomers, identified by the chemical formula, 1,2 $(OH)_2$ 4 (CH_3) $(SO_3Na)C_6H_2$ was used to carry out the experiments.

2.3. Preparation of the suspensions

To prepare suspensions for adsorption or zeta potential measurements, the standard procedure consists in deagglomerating the alumina powder in the appropriate aqueous solution containing the test molecule, using ultrasonic treatment (pulsed, 3 min, 600 W, Vibra-cell ultrasonic desintegrator VC 600, Sonic & Materials, USA). In order to reach a chemical equilibrum, suspensions were stabilised for 12 h, using a low-speed rotating roller. The suspensions were prepared and manipulated under laboratory air.

2.4. Adsorption

Adsorption of Tiron, Catechol, $1,2(OH)_2$ $4(CH_3)(SO_3Na)C_6H_2$ and $C_6H_4(SO_3K)_2$ was measured, versus pH, for a fixed amount of 1.310^{-6} mol of compound per square meter of powder added. Slurries were prepared with 3 vol.% solid loading, the solvent being an aqueous solution of NaCl (1×10^{-2} mol l^{-1}) used to fix ionic strength. pH was adjusted using HCl and NaOH solutions. After 12 h of stabilisation, high speed centrifugation allowed to separate the supernatant for analysis. The quantity of non-adsorbed molecule contained in the supernatant was determined by U.V. spectroscopy. The pH of the supernatant containing molecule, the structure of which includes an ionisable alcohol group, was adjusted at pH 4, to retain only the acidic species in solution. The adsorption amount was calculated from the difference between the quantity of dispersant added and that remaining in the supernatant. Table 1 summarizes adsorption wavelength and pK_a of hydroxyl groups for each chemical compound.

2.5. Zeta potential experiments

Zeta potential values of alumina particles in various slurries were measured using Electrokinetic Sonic Amplitude (ESA) measurement (Model ESA8000 Matec, Northborough, MA, USA). This technique and its operating principle have been described previously.[4] Measurements versus pH were carried out with slurries containing a 3.3 vol.% solid loading. According to the kind of experiment, different sodium salts (NaCl, $NaNO_3$, $NaClO_4$, Na_2SO_4) were used to fix ionic

Table 1
Adsorption wavelengths and pK_a of alcohol functions

Compound	λ (nm)	pK_a of alcohol functions
Catechol	275.0	9.3; 13
Tiron	290.3	7.6; 12.5
$C_6H_4(SO_3K)_2$	268.8	
$(OH)_2(CH_3)C_6H_2(SO_3Na)$	284.0	8.8

strength, 1×10^{-2} mol l^{-1} of the required anion was added. To measure zeta potential values over a large pH range, two suspensions were used: the first one from natural pH to acidic pH and the second one for basics. The probe was calibrated using an aqueous suspension of 10 vol.% of Ludox TM (Du Pont, Wilmington, DE, USA). Data recorded with the zeta potential analyser correspond to the measured ultrasonic signal converted into a voltage (ESA). ESA data being directly proportional to electrophoretic mobility of particles, electrokinetic properties variations versus pH will be presented using ESA values.

3. Results and discussion

3.1. Influence of the chemical structure of dispersant

3.1.1. Adsorption

Fig. 1 represents adsorption of the four tested compounds onto the alumina surface versus pH.

The Catechol quantity adsorbed at pH 4, i.e. 1.2×10^{-7} mol m^{-2}, corresponds only to 9% of the amount added (1.3×10^{-6} mol m^{-2}). This value increases with the pH, to reach a plateau at pH 7, when a maximum of 1.04×10^{-6} mol m^{-2} of Catechol is adsorbed, corresponding to 80% of the introduced amount. This concentration continues to be adsorbed to pH 9 and adsorption decreases in basic media to reach the value of 7.3×10^{-7} mol m^{-2} at pH 10. Adsorption experiments, carried out by Hidber et al.,[2] with a high purity αAl_2O_3 powder (HRA 10, Martinswerk, Bergheim, Germany) in the 4–9 pH range and performed by using UV spectroscopy lead to similar results.

The 1,2 benzene disulfonic acid dipotassium salt $C_6H_4(SO_3K)_2$ is not adsorbed in the pH range 9–11. From pH 9, this molecule adsorbed onto alumina particles in larger quantity as the pH became acidic to reach a maximum of 1.04×10^{-6} mol m^{-2} at pH 4.

From pH 4 to 9, the quantity of Tiron and of 1,2 $(OH)_2$ $4(CH_3)(SO_3Na)C_6H_2$ adsorbed is similar. A plateau corresponding to the larger quantity adsorbed, i.e. 1.04×10^{-6} mol m^{-2}, is observed in both cases from pH 4 to 7.5. For a more alkaline pH, the amount adsorbed decreases to pH 9 and seems to reach a plateau of adsorption (8×10^{-7} mol m^{-2}) for 1,2 $(OH)_2$ $4(CH_3)(SO_3Na)C_6H_2$ whereas Tiron adsorption continues to decrease for more alkaline media.

3.1.2. Electrokinetic properties

The influence of the different molecules onto electrokinetic properties of alumina suspensions are shown in Fig. 2. The main features of experimental results are summarized in Table 2.

To complete these data, pH values of alumina suspensions prepared with increasing amounts of Tiron or $(OH)_2$ $4(CH_3)(SO_3Na)C_6H_2$ are reported in Table 3.

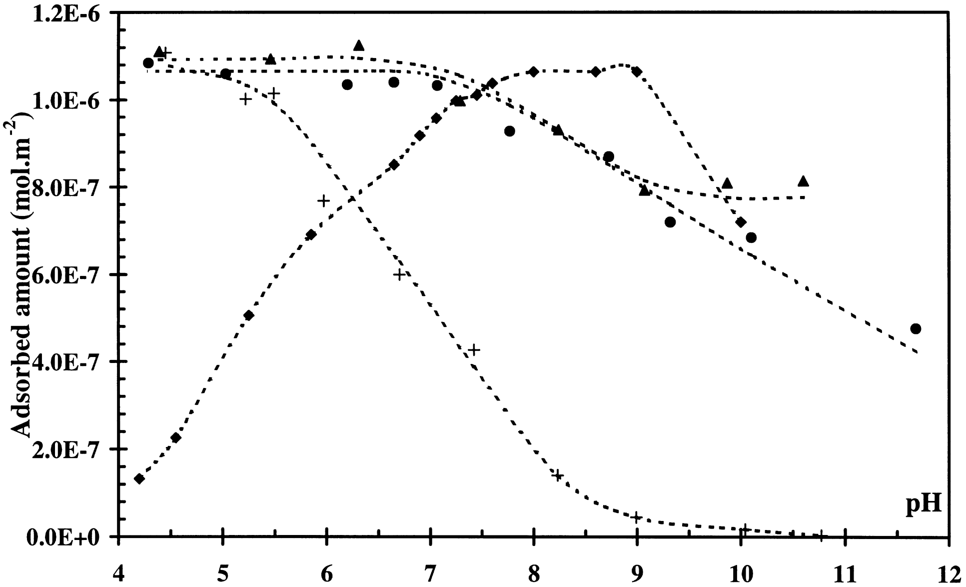


Fig. 1. Adsorption versus pH onto alumina surface of (●) Tiron, $(HO)_2C_6H_2(SO_3Na)_2$. H_2O, (+) 1,2 Benzene disulfonic acid, $C_6H_4(SO_3K)_2$, (▲) $(OH)_2(CH_3)(SO_3Na)C_6H_2$, (◆) Catechol C_6H_4 1,2 $(OH)_2$.

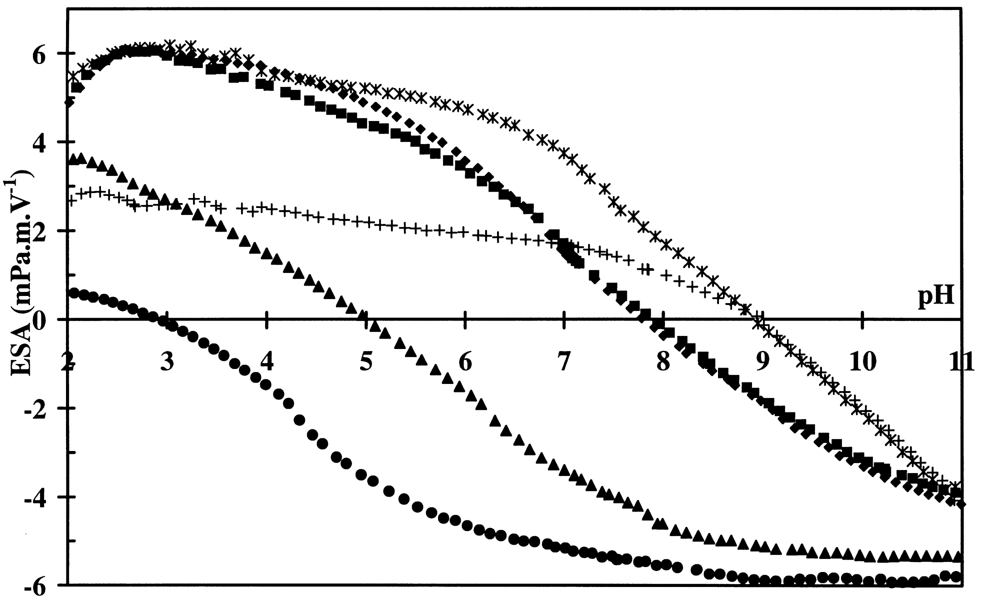


Fig. 2. ESA data versus pH for an alumina suspension (∗) with no additive, with 1.3×10^{-6} mol m^{-2} of (+)1,2 Benzene disulfonic acid, $C_6H_4(SO_3K)_2$, (◆) Catechol, C_6H_4 1,2 $(OH)_2$, (■) 4 Methyl catechol, $CH_3C_6H_3$ 1,2 $(OH)_2$ (▲)$(OH)_2(CH_3)(SO_3Na)C_6H_2$, (●) Tiron $(HO)_2C_6H_2$ $(SO_3Na)_2$.

Table 2
Electrokinetic properties of aqueous alumina suspensions

Additives: 1.3×10^{-6} mol m^{-2} introduced	Natural pH	ZPC	ESA pH = 9 (mPa.m V^{-1})	pK_a of the OH groups of the additive[5] T = 25°C, IS = 0.1 M
None	7.6	9	0	
$(HO)_2C_6H_4$	6.6	7.8	−1.6	9.3, 13
$(OH)_2(CH_3)C_6H_3$	6.6	7.8	−1.6	9.4, 13
$C_6H_4(SO_3K)_2$	8	9	0	
$(OH)_2(CH_3)(SO_3Na)C_6H_2$	8.5	5	−3.8	8.8
$(HO)_2(SO_3Na)_2C_6H_2$	8.3	3	−4.2	7.6, 12.5

3.1.2.1. Without dispersant. Without dispersant, the natural pH of AKP30 suspension is 7.6 and the surface charge is positive (2.6 mPa.m V^{-1}). From the smaller value of ESA signal (−3.2 mPa.m V^{-1}) measured at pH 11, the surface charge increases linearly (ZPC = 9) up to pH 7. For values of pH lower than 7 (ESA = 4 mPa.m V^{-1}), the density of positive surface charge increases more slowly and the ESA signal measured at pH 3 is equal to 6 mPa.m V^{-1}.

Table 3
pH of alumina suspensions with increasing amount of Tiron and 1,2 $(OH)_2$ $4(CH_3)$ $(SO_3Na)C_6H_2$

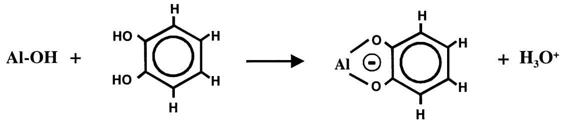
Concentration of additive (mol m^{-2})	pH (Tiron)	pH ($(OH)(CH_3)(SO_3Na)C_6H_2$)
0	7.6	7.6
2.15×10^{-7}	8.6	8.7
4.3×10^{-7}	8.9	8.9
6.45×10^{-7}	8.8	8.9
8.6×10^{-7}	8.6	8.8
1.3×10^{-6}	8.3	8.5

Theoretical models, such as the single site triple layer model (TLM)[6] allow to describe surface chemical reactions of oxide minerals in aqueous media. Adsorption is assumed to occur at amphoteric surface hydroxyls groups, which are uniformly distributed over oxide surface and are considered energetically equivalent. The charge on oxide surface is essentially due to adsorption (pH < ZPC) or desorption (pH > ZPC) of protons and these protolysis reactions govern electrokinetic properties of alumina suspension. At pH 7, a large number of available hydroxyl surface groups should be protonated and this protonation continues to occur as pH decreases but more slowly. By considering the acid volume added to decrease the pH, ionic strength remains constant to pH 3. For a pH < 3, the alumina solubility becomes more effective[7] releasing aluminum ions in the suspension which contribute with Cl^- and H^+ ions to increase ionic strength in the suspension and to compress the diffuse electrical double layer. In basic media, the alumina dissolution should be taken into account for pH > 10.5.[7] The soluble species $Al(OH)_4^-$, a monovalent anion, is less efficient to increase ionic strength in the suspension and no longer influences electrokinetic properties of alumina suspension below pH 11.

3.1.2.2. With added molecules

a. Catechol. Addition of 1.3×10^{-6} mol m^{-2} of Catechol in an alumina suspension leads to a pH decrease from 7.6 to 6.6. At this natural pH, the surface charge is positive (2.7 mPa.m V^{-1}) but the charge density is smaller than at pH 6.6 for the pure alumina suspension (4.2 mPa.m V^{-1}). The Catechol adsorption leads to a ZPC shift of over 1.2 pH units and the difference between the ESA signal for a pure alumina suspension and for a Catechol one remains constant between pH 7 and 8.5. Electrokinetic properties of the Catechol suspension become similar to those of a pure alumina suspension at pH > 10.5 and from pH 5 to more acidic pHs.

Adsorption measurements show a strong Catechol adsorption onto the particles surface between pH 7 and 9. This strong adsorption should be due to the formation of an inner sphere complex between metal ion on surface and alcohol groups of the molecule, according to this following surface reaction:[8]



In this reaction, Catechol adsorption leads to a more acidic suspension and to a negative contribution to the surface charge. This contribution remains constant between pH 7 and 8.5 corresponding to the range of maximum adsorption pH. Hydronium ions produced when Catechol adsorbs should likely contribute to pH decrease and to ionisation of the available hydroxyl surface groups at pH 7. From pH 7 to acidic pH, the decrease of the negative contribution to the surface charge can be attributed to the progressive desorption of Catechol. Similar phenomena are observed from pH 9 to 11; Catechol is desorbed too. This similar tendency observed for basic pHs show that Catechol is strongly adsorbed only around the alumina powder ZPC. This phenomenon has also been observed when Catechol is adsorbed onto TiO_2 surface.[9]

b. 4 MethylCatechol. Electrokinetic properties of suspension prepared with 4 methylCatechol are similar to those obtained with Catechol, curves are superimposed in all the pH range studied. The graft of a neutral group onto the Catechol molecule does not modify its adsorption properties onto alumina surface. Some studies concerning adsorption of Catechol derivatives with NO_2 groups confirm these results.[10]

The methyl group as additional substituent onto the para position of Catechol molecule permits to graft only one sulfonate group in sulfuric acid media. The compound 1,2 $(OH)_2$ $4(CH_3)(SO_3Na)C_6H_2$ was prepared as previously described. It was used to study the influence of the sulfonate groups number onto electrokinetic properties of alumina suspensions prepared with molecules specifically adsorbed as Catechol.

c. 1,2 Benzenedisulfonic acid, dipotassium salt. At pH > 7.6, a very small amount of 1,2 benzene disulfonic acid dipotassium salt is adsorbed onto alumina surface; then natural pH and ZPC of the suspension are not affected. From pH 11 to 9, this compound does not influence electrokinetic properties of the alumina suspension. For pH < ZPC, the $C_6H_4(SO_3K)_2$ molecule adsorbs onto alumina surface and decreases the density of positive surface charge, whatever the pH. As no influence is observed on ZPC, adsorption of this molecule should occur as an outer sphere complex stabilised by electrostatic attraction. This molecule should only neutralize a fraction of protonated hydroxyl groups, probably because of the steric hindrance of the molecule. Nevertheless, some hydroxyl groups may remain available and may be ionised.

d. Tiron and $(OH)_2$ $4(CH_3)(SO_3Na)C_6H_2$. pH values of alumina suspensions prepared with increasing amount of Tiron or of 1,2 $(OH)_2$ $4(CH_3)(SO_3)C_6H_2$, increase from an addition of 2.15×10^{-7} to 6.45×10^{-7} mol m^{-2} then decrease for larger amounts added (Table 3). At pH 9, adsorption of these two molecules leads to a negative surface charge with a high density (Fig. 2). This charge decreases as pH becomes acidic. The decrease is faster for suspension prepared with $(OH)_2$ $4(CH_3)(SO_3Na)C_6H_2$ than it is for one prepared with Tiron, leading to a higher IEP (i.e. 5) than 3 for suspension prepared with Tiron. An inflexion point is observed at pH = 4.3 and ESA = −2.3 mPa.m V^{-1} for the Tiron curve and at pH = 6.5 and ESA = −2.7 mPa.m V^{-1} for 1,2 $(OH)_2$ $4(CH_3)$ $(SO_3)C_6H_2$ curve. After this point, the negative amplitude of ESA signal decreases linearly. For pH > 9, the density of negative charge, higher for Tiron (−5.9 mPa.m V^{-1}) than for 1,2 $(OH)_2$ $4(CH_3)$ $(SO_3)C_6H_2$ (−5.2 mPa.m V^{-1}), remains constant for both.

As for Catechol, the same adsorption mechanism can be used [Eq. (1)], an inner sphere complex is built between alcohol groups of the molecule and hydroxyl surface groups. This complex creates a negative charge which contributes in addition to that of ionised sulfonate groups, to the negative surface charge observed onto the particles surface. With two sulfonate groups, Tiron addition in the suspension leads to a higher density of negative charge.

The Tiron adsorption has been discussed in a previous work.[3] Adsorption isotherms established at pH 5, 7, 9 and 11 showed that Tiron is strongly adsorbed onto particles surface at neutral and acidic pH. However, the value observed on the plateau increases when pH becomes more acidic. The electrostatic interactions between the surface, positively charged in acidic media or negatively charged in basic media because of free OH groups ionisation, and the negative molecule enhance its adsorption for acidic pHs and is detrimental for basic pHs. Adsorption of 1,2 $(OH)_2$ $4(CH_3)(SO_3Na)C_6H_2$ shows the same behaviour, except that with only one sulfonate group, the molecule is less repulsed by the negative alumina surface at basic pHs. It adsorbs in a larger amount than Tiron (Fig. 1).

The maximum amount of compound adsorbed i.e. 1.04×10^{-6} mol m^{-2}, the same whatever the chemical structure, does not depend on the nature and on the number of substituents on the benzene ring. This maximum amount represents the total coverage of the AKP30 alumina surface by this kind of molecule. This total coverage is reached with the two kinds of adsorption, namely the inner and/or the outer sphere complex. The inflexion point observed on ESA signal variations versus pH for suspensions prepared with Tiron and 1,2 $(OH)_2$ $4(CH_3)(SO_3)C_6H_2$ can illustrate the transition between two adsorption mechanisms. The strong adsorption of ionised molecule by the positive surface and the total coverage of the surface by the 1,2 benzene disulfonic acid adsorbed as outer sphere complex suggest that Tiron and 1,2 $(OH)_2$ $4(CH_3)$ $(SO_3)C_6H_2$ could be adsorbed as outer sphere complex too in acidic media. When ESA signal reaches the value of 2.3 mPa.m V^{-1}, which corresponds to a sufficient density of free OH_2^+ groups, adsorption as ion pairs is enhanced and the additional amount of molecule adsorbed from this ESA value does not lead to an additional negative contribution to the surface charge. It can explain the linear variation of the ESA signal from the inflexion point.

The increase of natural pH of suspension after a small addition of Tiron or 1,2 $(OH)_2$ $4(CH_3)$ $(SO_3)C_6H_2$, which are weak acids, can be explained by hydronium ions adsorption onto alumina surface, this is enhanced by the screen effect of the adsorbed negative molecules. These hydronium ions protonate free hydroxyl groups at the alumina surface and should increase the positive contribution to the surface charge. This effect should be favoured by Tiron, the structure of which includes two sulfonate groups. This can explain the small difference observed between the two ESA signals measured between pH 8.5 and 9. This phenomenon seems to have more influence on surface charge than on pH. As Tiron and $(OH)_2(CH_3)(SO_3Na)C_6H_2$ are weak acids, the non adsorbed quantity of dispersant which remains in the solvent for an initial amount of 1.3×10^{-6} mol m^{-2} decreases the suspension pH.

To conclude this paragraph, formation of inner sphere complex onto oxide surface leads to a stronger adsorption which can be enhanced by electrostatic attraction, if the molecule is ionised. This shows that an electrolyte could be an efficient dispersant if functional groups which permit a strong adsorption are different from functional groups which create the surface charge.

3.2. B. Alumina suspensions in acidic media, anion influence

The objective of this second phase of the study was to determine the influence of the anion included in the chemical structure of the salt used to fix the ionic strength and of the acid used to change the pH onto electrokinetic properties of aqueous alumina suspensions.

3.2.1. Experimental results

3.2.1.1. Without dispersant. Four strong acids, three monovalent HCl, HNO_3 and $HClO_4$ and one bivalent H_2SO_4, were used to change the pH of pure alumina suspensions. Suspensions were prepared with an aqueous solution of the sodium salt including the same anion as the acid used. Fig. 3a shows electrokinetic properties versus alumina suspensions pH prepared at an ionic strength fixed with 1×10^{-2} mol l^{-1} of the anion. Fig. 3b compares electrokinetic properties variations of alumina suspensions prepared with different concentrations of SO_4^{2-} ions.

Before addition of any salt, alumina suspension pH and ESA signal were measured at 7.2 and 5.3 mPa.m V^{-1}, respectively. Concerning monovalent anions, whatever the salt added, the natural pH of the suspension is equal to 7.6 with an identical value of the ESA signal (2.2 mPa.m V^{-1}) at this pH. From pH 7.6 to 2, the use of HNO_3 or of HCl leads to the same variations of the suspension electrokinetic properties. The decrease of surface charge for pH < 3 seems to be due to an ionic strength increase which compresses the diffuse electrical double layer around each particle, thus reducing the potential. When perchlorate acid is added to alumina suspension, surface charge density increases more rapidly versus pH than with the two previous anions, the ESA amplitude difference becomes higher when the pH decreases (i.e. 0 mPa.m.V^{-1} at pH 7.5, 0.8 mPa.m V^{-1} at pH 5.5, 1.6 mPa.m V^{-1} at pH 3.5). ESA signal reaches a maximum of 7 mPa.m V^{-1} at pH 3.

Sulfate anions lead to very different electrokinetic properties of alumina suspension. A small concentration of 1×10^{-3} mol l^{-1} of SO_4^{2-} added leads to a strong increase of the suspension pH from 7.2 to 8.4 and to a strong decrease of the positive ESA amplitude from 5.3 to 0.5 mPa.m V^{-1} (Fig. 3b). A gradual addition of sulfate ions to 1×10^{-2} mol l^{-1} in the suspension continues to increase the pH to a value of 8.7. ESA signal becomes negative with a low amplitude (i.e.−0.5 mPa.m V^{-1}). An expanded scale for ESA signal was used to better observe the surface charge variations versus pH. Whatever the SO_4^{2-} ions concentration, from natural pH to pH 7, H_2SO_4 addition leads to a positive contribution to the surface charge. The amplitude of this contribution decreases when ionic strength is high. For ionic strength fixed at 0.5×10^{-2} mol l^{-1} of SO_4^{2-}, the surface charge becomes positive at pH > 8.2 and remains negative for

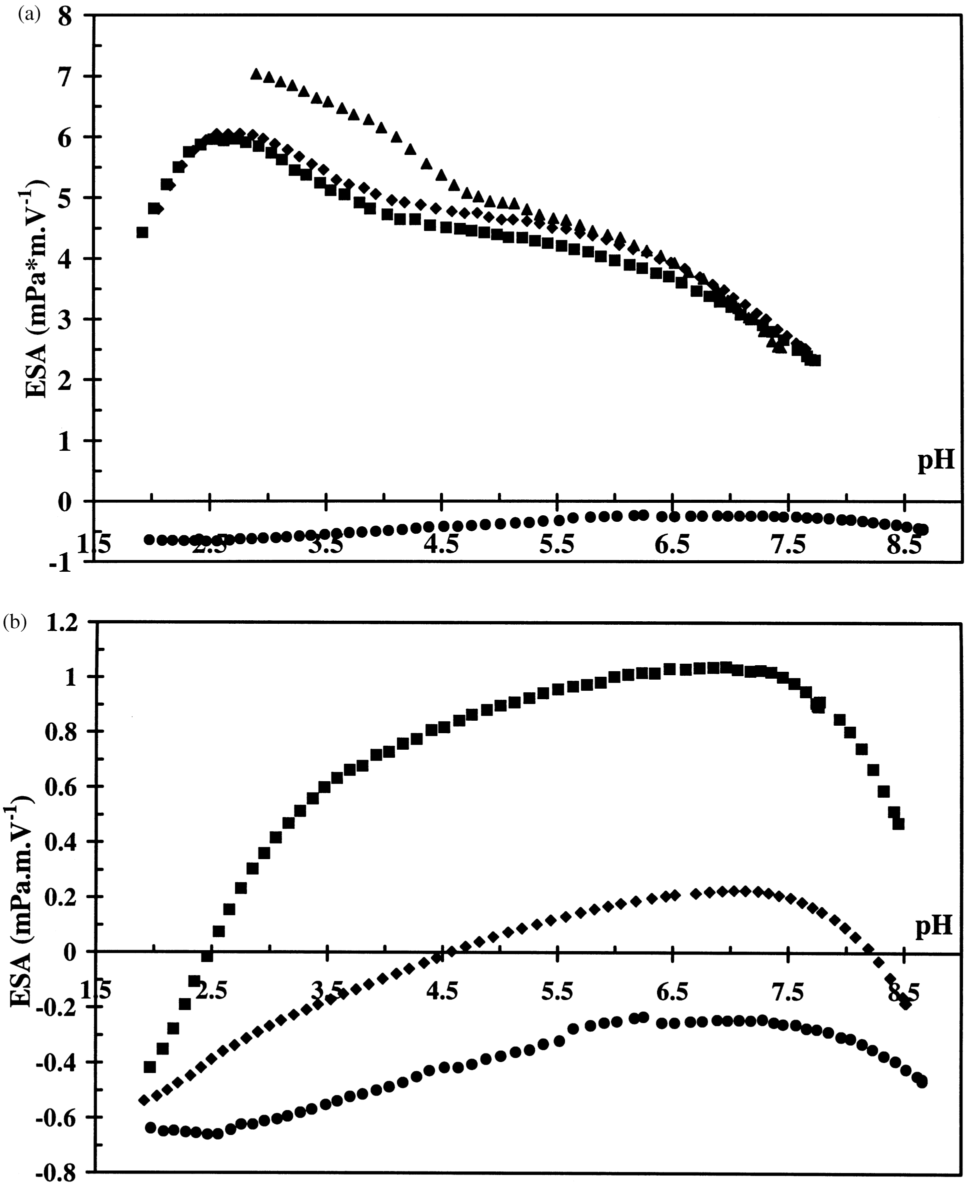


Fig. 3. (a) ESA data versus pH of alumina suspensions acidified with (■) HCl, (◆) HNO_3, (▲) $HClO_4$, (●) H_2SO_4. The ionic strength was fixed with 1×10^{-2} mol l^{-1} of the anion of the sodium salt including the same anion as the acid used. (b) ESA data versus pH of alumina suspensions acidified with H_2SO_4 for an ionic strength fixed with (■) 10^{-3} mol l^{-1}, (◆) 0.5×10^{-2} mol l^{-1} of Na_2SO_4.

an ionic strength of 1×10^{-2} mol l^{-1}. As pH becomes acid ($pH<7$), ESA signal decreases and for an ionic strength of 1×10^{-3} mol l^{-1} and 0.5×10^{-2} mol l^{-1}, the surface charge becomes negative for a $pH<2.5$ and 4.6, respectively.

For an ionic strength fixed at 1×10^{-2} mol l^{-1} of anion, to decrease the suspension pH from 7.5 to 3, a proton concentration of 4.55×10^{-3} mol l^{-1} is required whatever the monovalent salt and the mono acid used and 5.9×10^{-3} mol l^{-1} is required with sulfuric acid.

3.2.1.2. With Tiron addition. Electrokinetic properties of an alumina suspension prepared with 1.3×10^{-6} mol m^{-2} of Tiron were studied in acidic media with SO_4^{2-} as background anion. In Fig. 4, results are compared to those obtained with Cl^- (paragraph A). The salt (NaCl or Na_2SO_4) added to fix ionic strength does not influence the natural pH (8.3) of a suspension stabilised with Tiron and the two acids (H_2SO_4 and HCl) leads to the same electrokinetic properties in a pH range between 5.5 and 8.3. For values of pH lower than 5.5, ESA signal increases more slowly with H_2SO_4 than with NaCl and the density of surface charge remains negative in all the pH range studied. At pH = 3, the IEP reached with HCl, the amplitude of ESA signal is equal to −2.6 mPa.m V^{-1}.

3.2.2. Discussion

The bare radius and the hydration enthalpy of the anions are reported in Table 4.[11]

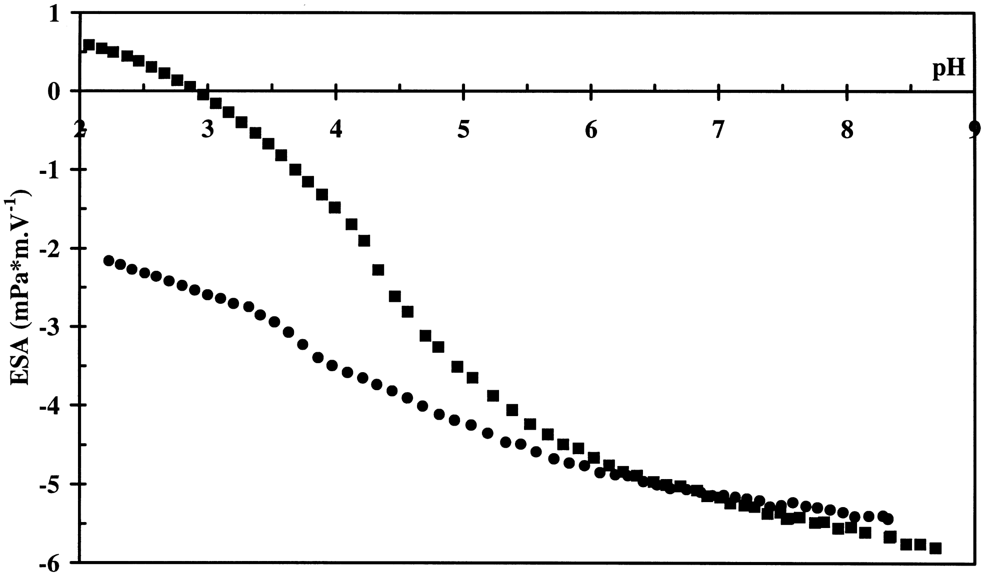


Fig. 4. ESA data versus pH of an alumina suspension with 1.3×10^{-6} mol l^{-1} of Tiron $(HO)_2C_6H_2(SO_3Na)_2$ acidified with (■) HCl, (●) H_2SO_4. The ionic strength was fixed with 1×10^{-2} mol l^{-1} of the anion of the sodium salt including the same anion as the acid used.

3.2.2.1. Natural pH of alumina suspensions. The natural pH of an aqueous alumina suspension depends on the valence of the anion used to fix the ionic strength. Powder surface reacts with water, producing hydronium ions; they lead to an acidic pH and are adsorbed onto particle surface, protonate the hydroxyl surface groups and then produce a positive surface charge. Then, anions of the electrolyte, added in the solvent to fix ionic strength, are electrostatically attracted. Previous studies[12] concerning anion adsorption at oxide/water interfaces showed that the monovalent anions studied in this work (Cl^-, NO_3^-, ClO_4^-) adsorb by forming outer sphere complexes with oxide surfaces. The sulfate complexation mechanism by oxide surfaces appears to be more complex to determine accurately. The standard methods of characterization (i.e. potentiometric titration, modeling of adsorption data)[13,14] lead to similar conclusions concerning the pH and ionic strength influence on SO_4^{2-} adsorption. This anion adsorbs only onto a positively charged surface such as goethite, hematite and alumina surfaces and that adsorption decreases at high ionic strength. These methods prove to be insufficient to investigate the complexation mechanism. To elucidate interactions that occur in aqueous goethite suspensions, Peak et al.[15] conducted in-situ experimentation ATR-FTIR spectroscopy. With this powerful analytical tool, they showed that sulfate adsorption occurs via a continuum of both outer-sphere and inner-sphere complexation onto goethite surface. The outer sphere complexation dominates in the pH range between 8.4 and 5, at low ionic strength, and inner sphere complexation becomes important in acidic media, with high ionic strength. The inner sphere complex was identified as a monodentate bisulfate surface complex shown in the following surface reaction via a ligand exchange between protonated hydroxyl group and sulfate anion.

Table 4
Bare radius (nm) and enthalpy of hydration (kJ mol^{-1}) of Cl^-, NO_3^-, ClO_4^-, SO_4^{2-}

Anion	Radius (nm)	Enthalpy of hydration (kJ mol^{-1})
Cl^-	0.172	−381
NO_3^-	0.179	−314
ClO_4^-	0.240	−229
SO_4^{2-}	0.258	−1059

$$\text{Fe-OH}_2^+ + SO_4^{2-} \rightarrow \text{Fe-O} - SO_3\text{-H}^+ + H_2O$$

In acidic media (3 < pH < 5), Hug[16] detected the same inner sphere complex onto the hematite surface and for more basic pHs, he suggests the contribution of outer complexation to obtain a good fit of its adsorption data. As hematite and alumina have the same cristallographic structure and a similar ZPC as goethite, the mechanisms of SO_4^{2-} adsorption determined onto goethite and hematite surfaces can be used to interpret the electrokinetic data of alumina suspensions.

For natural suspension pH, by forming outer sphere complex with protonated hydroxyl groups, adsorption of the different anions balances the positive surface charge, but with a valence of 2, a small concentration of SO_4^{2-} (1×10^{-3} mol l^{-1}) is sufficient to neutralize the positive charge. The screen effect of a bivalent anion adsorbed onto the surface likely leads to a better adsorption of the hydronium ions of the solvent. It can also explain the higher natural pH measured with sulfate addition as opposed to monovalent anions addition.

Nevertheless, even though the same adsorption mechanism is considered, these ions do not have the same affinity for alumina surface. A review of literature data shows that a surface with a high enthalpy of immersion as Al_2O_3 better adsorbs structure maker ions and a given surface bearing a positive electrical charge is always more structure maker than the same one negatively charged. According to the values of hydration enthalpy (Table 4), the adsorption sequence of anions studied here onto the positive alumina surface should be the following: $SO_4^{2-} > Cl^- > NO_3^- > ClO_4^-$. With a valence of 2 and a higher adsorption constant, SO_4^{2-} leads to the complete neutralization of OH_2^+ groups present on the surface and monovalent ions to a partial neutralization.

3.2.2.2. behaviour in relation to pH. As pH decreases, hydronium ions added onto an alumina surface protonate available hydroxyl groups, which enhances anion adsorption. By using monovalent anions, the density of positive charge increases as pH becomes acidic (Fig. 3a). This confirms that monovalent anions do not cover all the density of OH_2^+ groups because of a low adsorption constant for the alumina surface and the influence of the anion nature becomes sensitive as the density of OH_2^+ groups increases; Cl^- and NO_3^-, better adsorbed than ClO_4^-, can neutralize a higher density of OH_2^+ and lead to a smaller positive surface charge.

Protonation of free hydroxyl groups is also observed with sulfuric acid addition through the small positive contribution done to the surface charge from natural pH to pH 7. At this pH, SO_4^{2-} adsorption should continue to occur as outer sphere complexation and does not entirely counterbalance the density of protonated hydroxyl groups even with a concentration of 1×10^{-2} mol l^{-1} of SO_4^{2-}. For pH < 7, the hydroxyl groups protonation continues to occur slowly (paragraph A) and adsorption of SO_4^{2-} ions leads to a negative contribution to the surface charge (Fig. 3b). Acidic media enhances sulfate ions adsorption which then enhances proton adsorption because the concentration of H_2SO_4 required to diminish the pH from 5 to 3 is equal to 1.52×10^{-3} mol l^{-1} and 1.29×10^{-3} mol l^{-1} for 1×10^{-2} mol l^{-1} and 0.5×10^{-2} mol l^{-1} of Na_2SO_4 respectively. The formation of a monodentate bisulfate surface complex [Eq.(2)] from pH 7 is concurrent with the observed decrease of ESA amplitude: by exchanging a OH_2^+ group for a neutral ligand, this kind of adsorption permits to decrease the positive contribution to the surface charge.

The comparison between electrokinetic properties of suspensions prepared with disulfonic acid $C_6H_4(SO_3K)_2$ and those acidified with H_2SO_4 confirms that because of its steric hindrance and its low solvation by the water molecules, disulfonic acid does not neutralize all the OH_2^+ density and that the electrostatic force of attraction between molecule and surface is not the main parameter which governs anion adsorption.

Concentrated alumina suspensions can be prepared by decreasing pH because of high repulsive potential created by the protonation of hydroxyl groups. A monoacid with a large anion such as ClO_4^- appears to be the most efficient agent. Rheological experiments are underway to confirm these concluding remarks.

3.2.2.3. With Tiron addition. At natural pH of a suspension stabilised with Tiron, salt anions, used to fix ionic strength, are repulsed from the negatively charged surface. Their influence onto the surface charge is only observed for pH values lower than 5.5, when OH_2^+ concentration becomes high enough to permit a significant adsorption. Moreover, the hydronium ions quantity required to decrease the pH from 8.3 to 5.5 (1.9×10^{-3} mol l^{-1}) is the same whatever the acid used. But, as observed in experiments carried out without Tiron addition, a higher concentration of hydronium ions is necessary to decrease the suspension pH from 5.5 to 3 with sulfuric acid (3.8×10^{-3} mol $l^{-1} > 2.0\times10^{-3}$ mol l^{-1}), the pH range for which the anion adsorption is effective. In this pH range, the monodentate bisulfate complex formation, which permits to diminish the positive contribution to the surface charge due to the hydroxyl groups protonation, is in agreement with the interpretation of electrokinetic properties and titration results observed.

4. Summary

The main parameters which control Tiron adsorption onto alumina surface have been determined by using adsorption isotherms and electrophoretic mobility measurements. Each substituent onto the benzene ring contributes to give this molecule the ability to disperse alumina powder efficiently in water. Specific adsorption, such as inner sphere complex, and coulombic interactions between the molecule and the positive electrical charge of the surface, lead to the total surface coverage by Tiron in acidic media.

Electrokinetic properties of suspensions versus pH appear to be very useful to characterize the ion adsorption sequence for an oxide surface. With a high heat of immersion, an alumina surface better adsorbs strongly solvated anions by water molecules. This influences the charge developed onto oxide surface. The comparison of parameters such as pH, surface charge and volume of titrant permits to understand and interpret phenomena which occur on the oxide/water interface and explain how dispersion is affected during practical activities.

To complete this work, the quantitative triple layer model would be apply to evaluate the influence of the organic and inorganic anions adsorption on the protonation level.

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