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# Surface charge density of maghemite nanoparticles: Role of electrostatics in the proton exchange

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## **Abstract**

In the present work, we focus on the surface charge properties of well-defined maghemite ( $\gamma$ - $\text{Fe}_2\text{O}_3$ ) nanoparticles dispersed in water. Due to the acidic properties of surface groups, the nanoparticles surface can be positively or negatively charged depending on the pH. Consequently there are electrostatic repulsion forces between particles that allow stabilizing the suspensions in water. Acid-base titrations of the surface groups starting from acidic, alkaline and neutral pH are performed to access the dependence of the surface charge density with the pH. Titrations are followed by potentiometric and conductimetric measurements. Simultaneous zetametry measurements by acoustophoresis are implemented. The

experimental curves are analyzed using several hypotheses, in particular we assume that the sites on the surface of the particles behave as weak diacids. The interpretation of the experimental determinations of the charge implies to take into account an electrostatic term due to the potential developed at the surface of the particles. Thanks to the complementarity of the potenti-conductimetric titrations and of the zetametry measurements, it is possible to better understand the phenomena of protonation and deprotonation of the colloidal particles as a function of the medium of dispersion (acidic, alkaline, neutral pH and nature of the counterions) and of the nature of the reagent.

## **I- Introduction**

In aqueous medium, colloidal particles are usually stabilized by electrostatic interactions, which strongly depend on the surface charge of the particles. The stability of the suspension is often described in terms of a zeta potential that depends both on the magnitude of the surface charge of the particles and on the ionic strength (the latter determines the range of the electrostatic interactions). The knowledge of the charge properties is therefore important to prepare stabilized dispersions of particles. In this article, magnetic nanocolloidal suspensions are studied in an intermediate concentration range (1.5 volume percent) close to the conditions used for preparing mixed magnetic systems<sup>1</sup>. These nanocolloids have a typical radius of 6nm and are electrostatically stabilized in aqueous solutions. Their surface charge arises from the inherent properties of the oxides on their surface: charges are positive at acidic pH and negative at alkaline pH (at intermediate pH, the charge of the particles decreases, then aggregation process appears). Acid-base titrations can give an access to the surface charge density  $\sigma_0$  of the particles and thus information on the acidic properties (pKa) of surface oxide groups. We are interested here in the influence on the magnitude of  $\sigma_0$  of several parameters, as the pH, the nature of the counter ions of the particles and the reagent used for the titration.

For that, acid-base titrations are followed by simultaneous potentiometric, conductimetric and zetametry measurements.

The determination of the surface charge density is not straightforward and depends on experimental and theoretical approaches that will be discussed in details. A classical model describing the colloidal suspension as a melt of strong acid (the medium of dispersion) and weak diacids (the surface oxides) characterized by two pKa values is used in a first step to analyze the titration curves. However this leads to some differences between the values extracted from the different curves. We explain this in a second step considering an electrostatic contribution in the proton exchange that depends on the surface charge density and therefore on the pH. Complementary zetametry measurements allow us to decide whether the description of the charge of the particles is accurate.

This article is divided in two major parts. The first one gives details on the sample preparation (synthesis and dispersion of the particles), on the characterization techniques implemented and on the theoretical tools used. The second one is dedicated to results and discussions on their interpretation.

## **II- Materials and methods**

### **2.1. Colloidal suspensions**

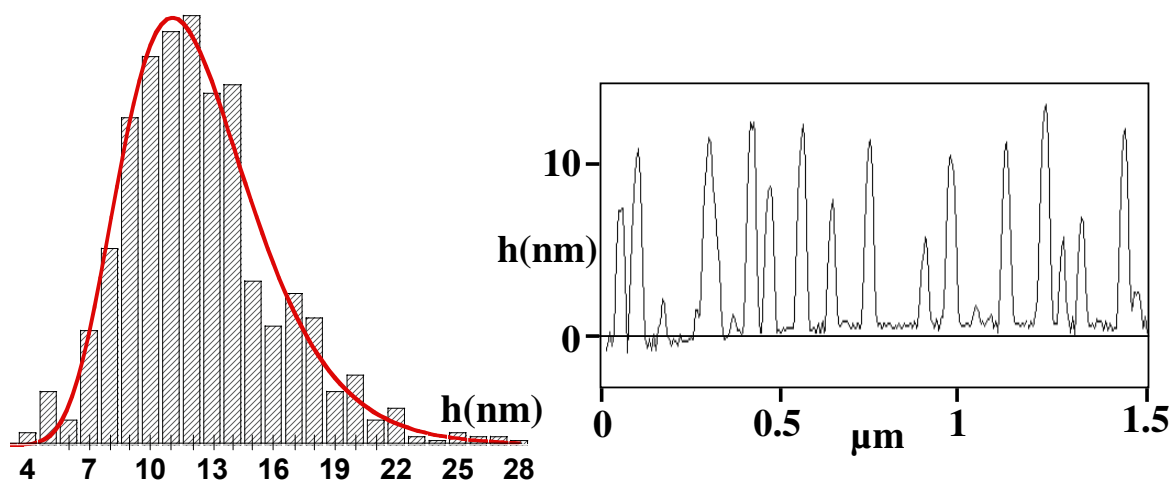
#### **Synthesis and characterisation**

The colloidal suspensions used in this study are composed of nanoparticles of maghemite ( $\gamma$ - $\text{Fe}_2\text{O}_3$ ), a magnetic iron oxide. These nanoparticles are chemically synthesized according to the process described by Massart and al<sup>2</sup> (1987). Briefly, an aqueous mixture of iron(II) chloride and iron(III) chloride is alkalized with concentrated ammonium hydroxide. The precipitate obtained, composed by magnetite ( $\text{Fe}_3\text{O}_4$ ) particles, is separated from the solvent and acidified with nitric acid in order to neutralize the excess of base. Eventually, the particles

are oxidized in maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) in a solution of ferric nitrate at 100 °C. At this step, the size distribution of the particles dispersed in acidic solution lies between diameters  $d$  of 5nm and 20nm. To reduce the polydispersity of the colloidal suspension, the precipitation of the largest particles is achieved by addition of  $\text{HNO}_3$ , which screens the electrostatic repulsion. The supernatant composed of particles of smaller sizes is removed by suction. The fraction with the largest particles is carefully washed with water and acetone (see §2.2) in order to decrease the ionic strength by removing the excess of ions ( $\text{H}^+$ ,  $\text{NO}_3^-$ ). The resulting colloids have an average radius of 6nm. The size distribution of such particles, which can be approximated by a lognormal law, is usually determined from the magnetic properties of the solutions by fitting magnetization curves<sup>3,4</sup> and here also determined from the AFM measurements. The size distribution of particles obtained from the AFM pictures ( $\approx 2000$  particles) exhibits a sharp peak between  $d = 11.5$  and  $12.5$  nm (Figure1). A log normal fit yields an average particle diameter  $d_0 = 12$  nm (with  $\ln d_0 = \langle \ln d \rangle$ ,  $d_0$  being also the median diameter) and a polydispersity  $\sigma_0 = 0.280$ . The volume fraction  $\Phi_{\text{vol}}$  of the particles is evaluated from a chemical titration of iron<sup>5</sup> (eq. 1) and from flame emission spectroscopy after dissolution of the particles in  $\text{HCl}$  ( $12 \text{ mol L}^{-1}$ ).  $\Phi_{\text{vol}}$  is given by:

$$\Phi_{\text{vol}} (\%) = \frac{(2M_{\text{Fe}} + 3M_{\text{O}}) \cdot [\text{Fe}]}{2\rho_{\text{Fe}_2\text{O}_3}} = 1.577 \cdot [\text{Fe}] (\text{mol.L}^{-1}) \quad (1)$$

with  $M$  the molar weigh and  $\rho_{\text{Fe}_2\text{O}_3}$  the density of maghemite ( $4.9 \text{ g.cm}^{-3}$ ). Due to the acidic properties of surface groups, the surface of the nanoparticles can be positively or negatively charged depending on the pH (table 1). Consequently, there are electrostatic repulsion forces between particles that allow stabilizing the suspensions in water at extreme pH. However, the suspensions are not stable for  $3.5 < \text{pH} < 10.5$  because the surface charge density is too low.


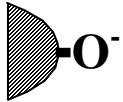


**Figure 1: Left:** Histogram representing the size distribution of maghemite nanoparticles determined from AFM images. The solid line represents a lognormal law fitted to the histogram with a median diameter  $d_0 = 12$  nm and a polydispersity  $\sigma_0 = 0.280$ . **Right:** Example of cross section of an AFM image, which shows the height of the particles, and allows us to build the histogram presented.

### **Influence of the nature of the counter-ions**

For the experiment presented here, we use the following types of suspensions: the particles associated with their counter ions dispersed in both acidic and alkaline medium. The concentration of the ions in the suspensions (ionic strength) and their nature are parameters that also control the stability of the colloidal suspensions (see figure 2). For instance divalent cations like sulphate ( $\text{SO}_4^{2-}$ ) screen the electrostatic interactions (by adsorption) leading to the aggregation of the nanoparticles whereas univalent and larger ions like nitrate ( $\text{NO}_3^-$ ) or perchlorate ions ( $\text{ClO}_4^-$ ) are suitable for electrostatically stabilized suspensions. Moreover, chloride ion ( $\text{Cl}^-$ ) (very small) is a complexing agent of iron and leads to a fast dissolution of the particles in acidic medium. Therefore we dispersed the nanoparticles in perchloric acid ( $\text{HClO}_4$ ) and nitric acid ( $\text{HNO}_3$ ) between pH 1 and 3.5. (Below pH = 1.5, iron oxides are not thermodynamically stable and start to dissolve but the kinetics of dissolution is very slow). In

order to obtain stabilized colloidal suspension of negatively charged particles, tetramethylammonium hydroxide ( $\text{TMA}^+ \text{OH}^-$ ; Sigma Aldrich) is used within the 10-13 pH range. In fact, NaOH cannot be used to prepare stabilized suspensions because sodium ( $\text{Na}^+$ ) counter-ions (very small) are flocculating agents of our system in alkaline medium. Thus the number of counter ions that can be used is limited because of the constraints related to the colloidal stability.

Particles	pH range of stability	Stabilizing Counterions	Non-Stabilizing Counterions	Reagent
 $\text{-OH}_2^+$	1.0-3.5	$\text{NO}_3^-$ $\text{ClO}_4^-$	$\text{Cl}^-$ (dissolution) $\text{SO}_4^{2-}$ $\text{PO}_4^{3-}$	NaOH TMAOH
 $\text{-O}^-$	10.0-13.0	$\text{TMA}^+$ (alkyl) $_n \text{N}^+$	$\text{Na}^+$	$\text{HNO}_3$ $\text{HClO}_4$

**Table 1:** Characteristics of the colloidal dispersion in acidic medium (positively charged particles) and in alkaline medium (negatively charged particles): pH range of stability, stabilizing counterions, non-stabilizing counterions. Fourth column: reagents used for the titrations.

## 2.2. Determination of the surface charge density of the nanoparticles

When dispersed in aqueous media, iron oxide nanoparticles acquire a surface charge as a result of the Brønsted acid-base behaviour of the surface oxides (surface sites). The simplest hypothesis to describe the sites on the surface is to assume identical sites which behave as weak diacids. Their pH-dependent protonation/deprotonation process can then be described by the following equilibria (2) and (3) where M is the metal of the spinel type nanoparticles





In order to determine the structural charge and the zeta potential of our nanoparticles we have performed simultaneously potentiometric-conductimetric acid-base titrations as proposed in reference<sup>6</sup> and zetametry measurements on each colloidal sample (80 mL) at a volume fraction  $\Phi_{\text{vol}}(\%) = 1.5$  under CO<sub>2</sub>-free atmosphere. The simultaneous measurements (zetaprobe, conductivity and pH electrode, temperature probe, burettes) impose the volume of 80ml. The volume fraction  $\Phi_{\text{vol}}(\%) = 1.5$  is a compromise : it is high enough in order to distinguish the titrations of strong and weak acids in the conductivity curves; it is low enough to keep an efficient homogenization whatever the pH. Indeed, at higher volume fraction and at intermediate pH, the particles precipitate and form a thixotropic phase which hinders homogenization.

### **Titration procedure**

In this study we perform several titrations through distinct experiments (not successive) from acidic medium (pH = 2) to alkaline medium (forward titration), from alkaline (pH = 12) to acidic medium (backward titration) and from the neutral pH (assimilated to the point of zero charge (PZC) of the particles) to acidic or alkaline media. The initial pH is adjusted to pH = 2 in the forward titration, to pH = 12 in the backward titration and to pH ~ 7 in the case of the titration starting from the PZC of the particles. In the forward titrations we use tetramethylammonium hydroxide ( $[\text{TMAOH}] = 1 \pm 0.05 \text{ mol L}^{-1}$ ) as strong alkaline reagent (pKa > 13), whereas in the backward ones, we use nitric and perchloric acid at the same concentration. All reagents used in these investigations are of analytical grade (VWR International France). After each experiment, the concentrations of the reagents (TMAOH, HClO<sub>4</sub> and HNO<sub>3</sub>) are checked by acid base titration with HCl and NaOH (1.0 mol L<sup>-1</sup>, Normadose VWR). Before titrations, alkaline reagents are stirred and degassed by purified argon for 10 min to prevent the carbonation phenomena.

### **Potentiometric-conductimetric method**

Both the potentiometric-conductimetric techniques and reagent additions in the suspension are carried out by using a DT 1200 analyzer (Dispersion technology, USA) which includes electrochemical probes, thermometer and electronic burettes. The immersion-type conductimetric cell is calibrated by using KCl solutions of known conductivities while the pH electrode is used after calibration by three buffer solutions (pH 4, 7 and 10). As particles coagulate in the intermediate range of pH, the diffusion of the potential determining ions in the medium, and therefore the electrochemical readings, can be affected. Therefore, we apply an efficient magnetic stirring for all experiments in order to minimize these sources of inaccuracy.

### **Zetametry**

Maghemite based “ferrofluids” absorb in the visible spectrum (solutions are black reddish) and appear opaque at high volume fractions. Thus we cannot apply standard techniques based on Doppler effect to measure the zeta potential of our particles like in laser zetametry. We use the acoustophoresis, a technique based on the signal produced between two electrodes when the charged suspension is exposed to an ultrasonic wave. The instrument, DT 1200, measures the induced current (amplitude and phase) named CVI (Colloidal Vibration Intensity) between the electrodes. The software deduces the electrophoretic mobility and therefore the zeta potential (classical theory: Helmholtz-Smoluchowski equation<sup>7</sup>) from CVI. It has to be notified that the zeta potential values used in this study are the ones given directly by the apparatus. The determination of the electrophoretic mobility of the particles from the CVI requires a calibration of the apparatus by a colloid of well known electrokinetic properties. The calibration is performed using a colloidal suspension of ludox<sup>®</sup> (TM-50 Sigma Aldrich)

at  $\Phi_{\text{weight}}(\%)=10$  (silica particles: 30nm, KCl ( $0.01 \text{ mol L}^{-1}$ ), pH = 9,  $\zeta(\text{mV}) = -38$ ). Several parameters, measured or taken from tables, are necessary: the volume fraction of the particles, the dielectric constant, the sound speed, the density of both the particles and the solvent, as well as the compressibility and the viscosity of the solvent. Concerning our systems, the relationship between CVI and zeta potential is independent of the size as far as the size is lower than  $100\text{nm}^8$ .

Eventually, the signal of the supported salt is an additional factor which could influence the value of the calculated zeta potential. A procedure exists to correct the zeta potential by measuring the signal which comes from the salt. In our system, such measurements show that the effect of salt (here the ionic strength is less than  $0.08 \text{ mol L}^{-1}$ ) on the zeta potential value is negligible.

### **2.3 Preparation of the samples**

Throughout all experiments carried out in this study, the same sample of ferrofluid is used and no additional salt is dissolved in the suspension (the ionic strength depends only on the concentration of the acidic or alkaline species in the suspension, the charged particles plus the counter-ions in their vicinity). Maghemite particles once synthesized are stabilized in nitric acid within the pH range 1.5-1.8. Consequently, in order to disperse the particles in the appropriate medium (acidic:  $\text{HClO}_4$ ,  $\text{HNO}_3$ , alkaline: TMAOH or neutral) and finally to adjust the pH and therefore the ionic strength values by eliminating undesirable ions, the suspensions undergo chemical and physical treatments. The protocols used are described under.

**- Sample at pH=12: transfer from acidic medium  $\text{HNO}_3$  toward alkaline medium TMAOH**

TMAOH is added to a suspension of particles in a nitric acid solution until a concentration of  $0.5 \text{ mol L}^{-1}$  is reached in order to reverse the surface charge of the particles. The suspension is vigorously stirred and heated at  $100^\circ\text{C}$  during 15 minutes. The particles are then dispersed in alkaline medium, their counterions are  $\text{TMA}^+$ , and  $\text{TMA}^+\text{NO}_3^-$  pairs remain in the solution. To remove these ions, acetone (Normapure grade) is added in order to destabilise the suspension. In fact the change in the dielectric constant of the medium weakens the repulsion forces between particles and leads to the destabilisation of the suspensions. Under the action of the gravitational and magnetic forces, the aggregated particles sediment at the bottom of the container. The supernatant containing water, ions and acetone is removed by suction. The precipitate is carefully washed by successive additions of acetone followed by suction in order to eliminate ions  $\text{TMA}^+$ ,  $\text{NO}_3^-$  and  $\text{OH}^-$  in excess. Diethyl ether is poured on the precipitate to remove acetone by precipitation/suction. Then water is added: the precipitate disperses immediately in water, and the diethyl ether, non miscible with water, separates. This organic phase is removed by suction and the remaining solvent dissolved in water is eliminated by slight heating. Finally, a solution of TMAOH ( $10^{-2} \text{ mol L}^{-1}$ ) is poured in the concentrated suspension in order to adjust the pH and the volume fraction of the sample.

**- Sample at pH=2: transfer from alkaline medium TMAOH toward acidic medium  $\text{HClO}_4$**

We do not perform the transfer of the particles from the nitric acid medium to the perchloric acid medium directly. In a first step, the suspension in  $\text{HNO}_3$  is transferred into alkaline medium as described above. In a second step, a perchloric acid solution is added to the suspension until a concentration of  $0.5 \text{ mol L}^{-1}$  is reached. The particles are then dispersed in acidic medium, their positive charges are compensated by  $\text{ClO}_4^-$  counter ions, and  $\text{TMA}^+\text{ClO}_4^-$  pairs remain in the solution. Contrary to suspensions of negatively charged

particles in TMAOH (pH = 13) and of positively charged particles in HNO<sub>3</sub> at pH = 1, which can be easily destabilized by addition of acetone, it is very difficult to precipitate particles dispersed in HClO<sub>4</sub> at pH = 1. Therefore, suspensions in HClO<sub>4</sub> are destabilized by addition of concentrated perchloric acid (12 mol L<sup>-1</sup>) until precipitation. Indeed, the ionic strength becomes so large, that the electrostatic interactions between particles are highly screened, leading to the precipitation of particles. However it is difficult to reduce this high ionic strength by successive washing of the precipitate with acetone. In this system, it is thus easier, although longer, to control the pH and the ionic strength I of the suspension with the technique of dialysis (note that this technique can also be used for the other systems). The suspension is packed into a dialysis tube (Spectra/Por-12000-14000) plunged in a solution adjusted to the selected pH. The wall of the dialysis tube is a membrane which is permeable to the small molecules and the ions, whereas the particles and the macromolecules cannot pass through this membrane. The osmotic pressure outside the tube has to be adjusted to prevent the outside solution to pass inside the tube and make it inflate and burst. A polymer Dextran: 500000 g mol<sup>-1</sup> (Amersham Biosciences) is dissolved ( $\Phi_{\text{weight}} = 5\%$ ) in the outer solution. After several days, the inner pH in the dialysis tube stabilizes at a value which depends on the pH of the outside solution.

### **- Sample at the neutral pH**

Starting from alkaline or acidic medium, the colloidal suspensions are neutralized respectively with HNO<sub>3</sub> or NaOH till pH ~ 7 is reached. At pH ~7 (near the PZC) the magnitude of the structural charge of the particles tends toward zero, thus particles flocculate. The precipitate is carefully washed with water till the conductivity of the supernatant (removed by suction) is close to that of de-ionized water.

## 2.4 Determination of the surface charge density of the particles

The total concentration of protons bound to the oxides at the surface of the particles can be experimentally determined from potentiometric-conductimetric titrations. The colloidal suspensions are a mixture of weak acidities (the surface sites of the nanoparticles) and of strong acidities in the medium of dispersion (or strong base in alkaline medium). In a common acid-base titration of a mixture of a strong acid with weak polyacids, measurements of conductivity make it possible to determine with precision the equivalence points corresponding to the neutralization of all the acidic and basic functions if the pKa values are distinct ( $\Delta pK_a = pK_{a1} - pK_{a2} > 2$ ). A similar interpretation can be applied in colloidal suspensions if we assume that: **(I)** all surface sites are amphoteric oxides, so that they exchange protons according to equations (2) and (3) **(II)** all the surface sites are identical **(III)** the sites are weak acids **(IV)** the two acidities of each site are weak enough ( $pK_{a1} \gg 2$ ,  $pK_{a2} \ll 12$ ) and they are distinct ( $\Delta pK_a > 2$ ) **(V)** the sites are independent, which means that there is no influence of one site on the other sites **(VI)** at  $pH = 2$  and  $pH = 12$ , the charge is at saturation (all sites are charged) thus the number of charges per particle is the same at  $pH = 2$  and  $pH = 12$ . We shall discuss the validity of these hypotheses later on.

### Titration of surface acidities

Considering these assumptions, there are therefore at least two equivalence points (EP) in the forward and the backward titration. First an EP that corresponds to the neutralization of the strong acid or base and then a second EP that corresponds to the neutralization of all weak diacid groups. These EP are usually determined from first derivative of the pH curve, or from the abrupt changes of slope of the conductivity curves. The total concentration of adsorbed protons  $[H^+]_{ads}$  is determined from the amount of reagent ( $C_{reagent} = 1 \text{ mol L}^{-1}$ ) which is added to the suspension between the first and the second equivalence point.

In the case of titrations starting from acidic, alkaline and neutral pH, it is also possible to evaluate the number of protons bound to the surface of the particle by comparing the pH measured after the addition of the reagent to the solution and the pH expected if no particles are present. For an alkaline reagent (TMAOH), this difference  $\Delta nOH^-$  is calculated according to the equation (4):

$$nOH^-_{dropped} + nOH^-_{initial} = (nOH^-_{free}) + (nH^+_{initial} - nH^+_{free}) + \Delta nOH^-$$

(4)

$nOH^-_{initial}$  and  $nH^+_{initial}$  are respectively the amount of hydroxide ions and of protons (mol) that are initially present in solution,  $nOH^-_{free}$  and  $nH^+_{free}$  are the hydroxide ions and the protons that remain free after the addition of reagent ( $nOH^-_{dropped}$ ). Symmetrical expressions can be obtained for an acidic reagent.

For the titrations performed between acidic and alkaline pH ( $pH = 2 \rightarrow 12$ ), the amount of protons removed at the surface of the particles ( $nH^+_{ads}$ ) corresponds to  $\Delta nOH^-$ . The total concentration  $C_T$  of the charges at the surface of the particle is therefore the half of the total number of bound protons determined from the titration ( $C_T = [H^+]_{ads} / 2$ ) if we assume the hypotheses formulated above.

For the titrations performed from the neutral pH,  $C_T$  is directly accessible ( $C_T = [H^+]_{ads}$ ) without considering the assumptions (III), (V) and (VI) described above. We thus consider that the neutral pH corresponds to a point of zero charge at which no charge subsists (PZC) on the surface of the particles and that the protons or hydroxides can reach the whole surface of the particles.

### Surface charge density calculation

In the framework of the previous hypotheses, the surface charge density  $\sigma_0$  is a function of pH and depends on the relative amount of sites positively ( $MOH_2^+$ ) and negatively charged

( $MO^-$ ) at the surface of the particles according to the equation (5) with  $F$  the faraday constant,  $V_{\text{solution}}$  the volume of the solution,  $S_{\text{particles}}$  the total surface of the particles.

$$\sigma_0 = \frac{F \times V_{\text{solution}}}{S_{\text{particles}}} \times \left( [MOH_2^+] - [MO^-] \right) \quad (5)$$

The maximum surface charge density of particles ( $\sigma_0^{\text{sat}}$ :  $C \text{ m}^{-2}$ ) obtained at  $\text{pH} = 2$  or  $12$  is determined from the  $C_T$  ( $\text{mol m}^{-3}$ ) value:

$$\sigma_0^{\text{sat}} = \frac{Q_{\text{total}}}{S_{\text{particules}}} = \frac{(C_T \times V_{\text{solution}} \times F)}{(4\pi a^2 \times \Phi_{\text{vol}}(\%) \times V_{\text{solution}}) / (4/3\pi a^3 \times 100)} = \frac{100F \times C_T \times a}{3\Phi_{\text{vol}}(\%)} \quad (6)$$

with  $\Phi_{\text{vol}}(\%)$  the volume fraction of particles and  $a(\text{m})$  the radius of particles. As the sizes of the particles are polydisperse,  $a$  is a mean size, therefore  $\sigma_0^{\text{sat}}$  is a mean charge density. This is a first approach which will be improved later on, however other studies are necessary before to be able to really take into account the size polydispersity in the determination of the surface charge density because we do not know yet the evolution of the surface charge density with the size. Nevertheless, to avoid an impact of this polydispersity on the comparison of the different experiments performed, the same particles have been used here for all the experiments, and it has been checked regularly that no evolution of their size distribution occurred.

### III- Determination of the surface charge density: Results and Discussion

#### 3.1. Mixture of strong and weak acids: classic analysis

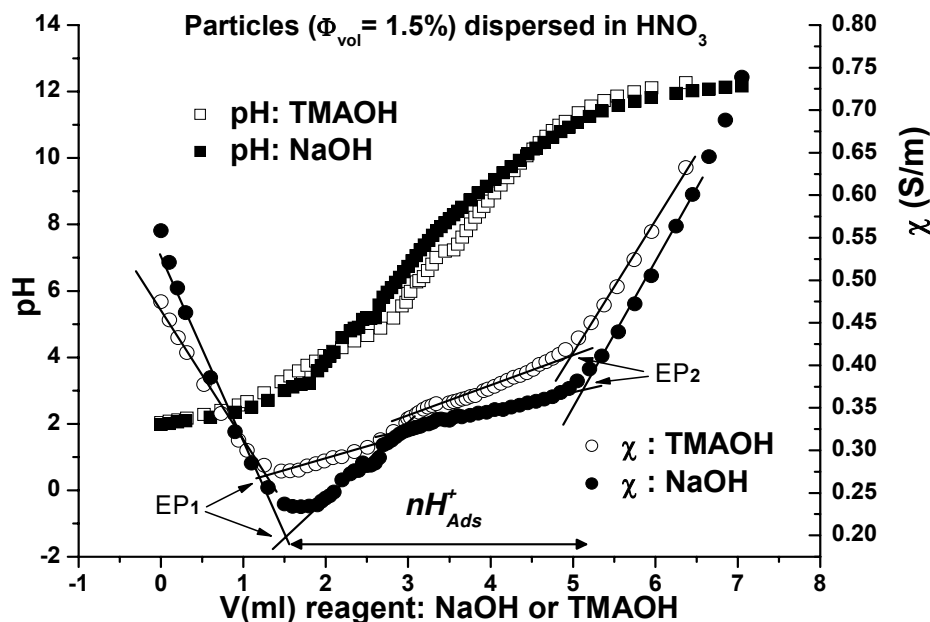
In a first approach, we use the assumptions (I) to (VI) to interpret the titration experiments and deduce the surface charge density.

#### Potential-conductimetric titrations from $\text{pH}=2$

Titration in figure 2 are performed in colloidal suspensions initially dispersed in acidic media  $\text{HNO}_3$  without any added salt from  $\text{pH} = 2.0$  to  $\text{pH} = 12.0$ , by addition of alkaline reagents,



either TMAOH or NaOH (1 mol L<sup>-1</sup>). The concentration of protons bound to the particles, [H<sup>+</sup>]<sub>ads</sub>, deduced from the determination of the equivalence points, is 47 mmol L<sup>-1</sup> at Φ<sub>vol</sub>(%) = 1.5 if the initial pH is 2.0. If we consider that C<sub>T</sub> = [H<sup>+</sup>]<sub>ads</sub> / 2, this corresponds to a charge density at saturation σ<sub>0</sub><sup>sat</sup> = 0.30 C m<sup>-2</sup> at pH = 2.0. This latter assumption is in good agreement with the change in the slope of the conductivity curves at the half-equivalence point that may be related to the beginning of the titration of the second surface acidity of the particles. The charge density of maghemite nanoparticles determined in HNO<sub>3</sub> is in good agreement with the charge density at saturation σ<sub>0</sub><sup>sat</sup> = 0.326 C m<sup>-2</sup> of cobalt ferrite determined by Campos and al<sup>6</sup> using the same procedure (CoFe<sub>2</sub>O<sub>4</sub>, Φ<sub>vol</sub>(%) = 1.5, HNO<sub>3</sub> pH = 2, reagent NaOH). However, from titrations of hematite<sup>9</sup> (α-Fe<sub>2</sub>O<sub>3</sub>, spheres of diameter 120 nm, HNO<sub>3</sub> pH = 4, reagent NaOH), a lower value of the charge density is determined at the ionic strength 10<sup>-2</sup> mol L<sup>-1</sup> and pH = 4, but of the same order of magnitude, σ<sub>0</sub><sup>sat</sup> = 0.19 C m<sup>-2</sup>.



**Figure 2:** Potentio-conductimetric titration of colloidal suspensions Φ<sub>vol</sub>(%) = 1.5 dispersed in HNO<sub>3</sub> at pH = 2.0, with TMAOH (1 mol L<sup>-1</sup>) (open symbols) and in HNO<sub>3</sub> pH = 1.9 with

NaOH (1 mol L<sup>-1</sup>) (**full symbols**). Determination of the equivalence points, **EP1** and **EP2**, and therefore of the number of protons ( $nH^+_{ads}$ ) bound to the particles, from the conductimetric curves ( $\chi$ (S/m): **circles**).

Concerning the values of the conductivity, the quantitative analysis is rather complicated and beyond the scopes of the present work, which is mainly concerned with the variations of the conductivity. Using the hypotheses **(I)** to **(VI)** (see § 2.4.) as Campos et al, we can make a first analysis of the results obtained with two different counterions, Na<sup>+</sup> and TMA<sup>+</sup> and explain the variation of the conductivity with the volume of reagent dropped into the suspension. In this framework, the strong variations before EP1 are exclusively attributed to a consumption of free protons, and the strong variations after EP2 are due to the addition of alkaline reagent which is assumed to remain free in the solution. The slight variations between EP1 and EP2 are related to the exchange of charged species with the surface of the particles. Between EP1 and the PZC (neutral pH), condensed nitrate counterions are released in the solution while decreasing the charge of the particle by addition of alkaline reagent, and new free charged species (TMA<sup>+</sup> or Na<sup>+</sup>) are added to the solution. Thus the conductivity is expected to increase. Between the PZC and EP2, the amount of negative charges on the surface should progressively increase when alkaline reagent is added, new free charged species (TMA<sup>+</sup> or Na<sup>+</sup>) are added to the solution but one part should condense on the surface of the particle. The increase of the conductivity between PZC and EP2 is thus smaller than between EP1 and PZC. However, several differences between the two systems NaOH or TMAOH appear on the curves of conductivity.

**(i)** The different initial conductivities for the two titrations ( $\chi \sim 0.55$  S/m for the titration with NaOH and  $\chi \sim 0.475$  S/m for the titration with TMAOH), thus the different positions of the points EP1, are explained by the difference of initial pH ( $\Delta pH = 0.1$ ).

(ii) The shape of the conductivity curves between the two equivalence points EP1 and EP2 changes depending on whether TMAOH or NaOH is used as the reactant. Firstly, the increase of conductivity between EP1 and PZC is higher with NaOH than with TMAOH, because the individual molar conductivity of  $\text{Na}^+$  is greater than that of  $\text{TMA}^+$  ( $\lambda^\circ\text{Na}^+ = 5.01 \text{ mS mol}^{-1} \text{ m}^2$ ,  $\lambda^\circ\text{TMA}^+ = 4.49 \text{ mS mol}^{-1} \text{ m}^2$  at  $25^\circ\text{C}$ ). Secondly, increasing the pH above  $\text{pH} > 7$ , the particles remain aggregated whatever the pH if one uses NaOH, whereas the particles can be individually redispersed for high pH if one uses TMAOH. This may be due to the higher condensation of the small  $\text{Na}^+$  ions compared with the big  $\text{TMA}^+$  ions. As the condensed  $\text{Na}^+$  no longer contribute to the conductivity  $\chi$ , the slope of  $\chi$  between PZC and EP2 is smaller with  $\text{Na}^+$  than with  $\text{TMA}^+$ . Despite this difference of aggregation between the two systems (NaOH and TMAOH), the same surface charge density is obtained from both titrations, which means that aggregation does not impede charge determination.

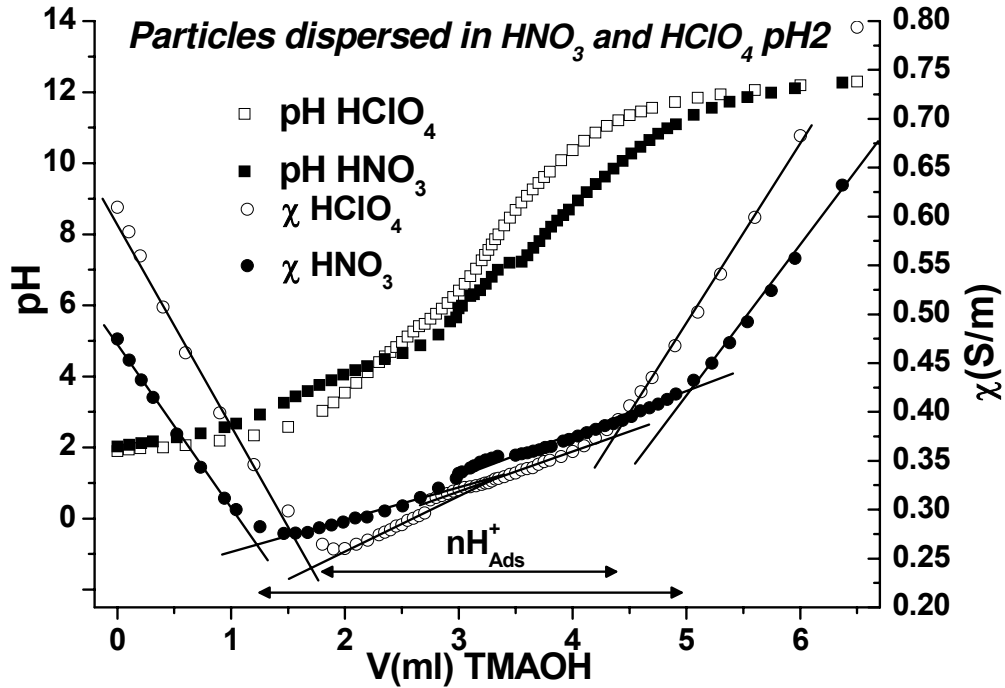
The change in the slope of the conductivity around the neutral pH is assumed to be related to the end of the titration of the first surface acidity of the particles as described in the experimental part. By considering independent acidic groups on the surface of the particles, the  $\text{pK}_a$  value for the first and the second acidity correspond to the pH at the half-equivalence. For particles dispersed in  $\text{HNO}_3$  at  $\text{pH} = 2.0$ , the  $\text{pK}_a$  determined from the potentiometric curve are  $\text{pK}_{a1} = 4.4$  and  $\text{pK}_{a2} = 9.3$ . For free acidic or alkaline species, such a difference in the  $\text{pK}_a$  values should lead to high variations of pH with the volume of reactant dropped into the solution. It is not the case with the acidic groups located on the surface of the particles.

### **Influence of the nature of the counter ions**

We probe here the influence of the nature of the counter ions on the magnitude of the structural charge of the particles. For that we compare the different systems consisting in particles dispersed in  $\text{HClO}_4$  and  $\text{HNO}_3$  titrated by TMAOH or NaOH, and particles dispersed

in TMAOH and titrated by HClO<sub>4</sub> or HNO<sub>3</sub>. In the literature, a difference in the magnitude of the structural charge of the particles while changing NO<sub>3</sub><sup>-</sup> for ClO<sub>4</sub><sup>-</sup> has already been observed on Goethite (α-FeOOH)<sup>10</sup>, and on rutile nanoparticles (TiO<sub>2</sub>, rod-like: length 200nm, width 45nm,  $\sigma_0^{\text{sat}}(\text{NO}_3^-) = 0.075 \text{ C m}^{-2}$ ,  $\sigma_0^{\text{sat}}(\text{ClO}_4^-) = 0.05 \text{ C m}^{-2}$ )<sup>11</sup>. In these studies, the influence of several anions on the surface charge density is investigated on systems positively charged below the point of zero charge (PZC). Titrations performed on these systems emphasize that proton adsorption decreases in the order Cl<sup>-</sup> > NO<sub>3</sub><sup>-</sup> > ClO<sub>4</sub><sup>-</sup>. This order corresponds to the Hofmeister series describing the difference in the charge density of colloidal particles according to the nature of the counter ion.

In the present study, the results seem similar: from the conductivity curves (see figure 5) performed in colloidal suspensions (dispersed in acidic media before the addition of TMAOH 1 mol L<sup>-1</sup>) without any salt added, different values of [H<sup>+</sup>]<sub>ads</sub> are evaluated in HNO<sub>3</sub> and HClO<sub>4</sub>, respectively 47 mmol L<sup>-1</sup> and 32 mmol L<sup>-1</sup>. Note that the titrations were performed twice for each acid and gave reproducible results. This value 32mmol L<sup>-1</sup> corresponds to a charge density at saturation  $\sigma_0^{\text{sat}} = 0.20 \text{ C m}^{-2}$  in HClO<sub>4</sub> at pH =1.9 ( $\sigma_0^{\text{sat}} = 0.30 \text{ C m}^{-2}$  in HNO<sub>3</sub>).



**Figure 3:** Potentio-conductimetric titration of colloidal suspensions ( $\Phi_{\text{vol}}(\%) = 1.5$ ) dispersed in  $\text{HClO}_4$  pH = 1.9 (**open symbols**) and  $\text{HNO}_3$  at pH = 2.0 (**full symbols**), with TMAOH ( $1\text{mol L}^{-1}$ ). The conductimetric measurements (**circles**) performed in  $\text{HNO}_3$  and  $\text{HClO}_4$  emphasize the non negligible difference in the amount of protons bound to the surface of the particles ( $n\text{H}^+_{\text{ads}}$ ).

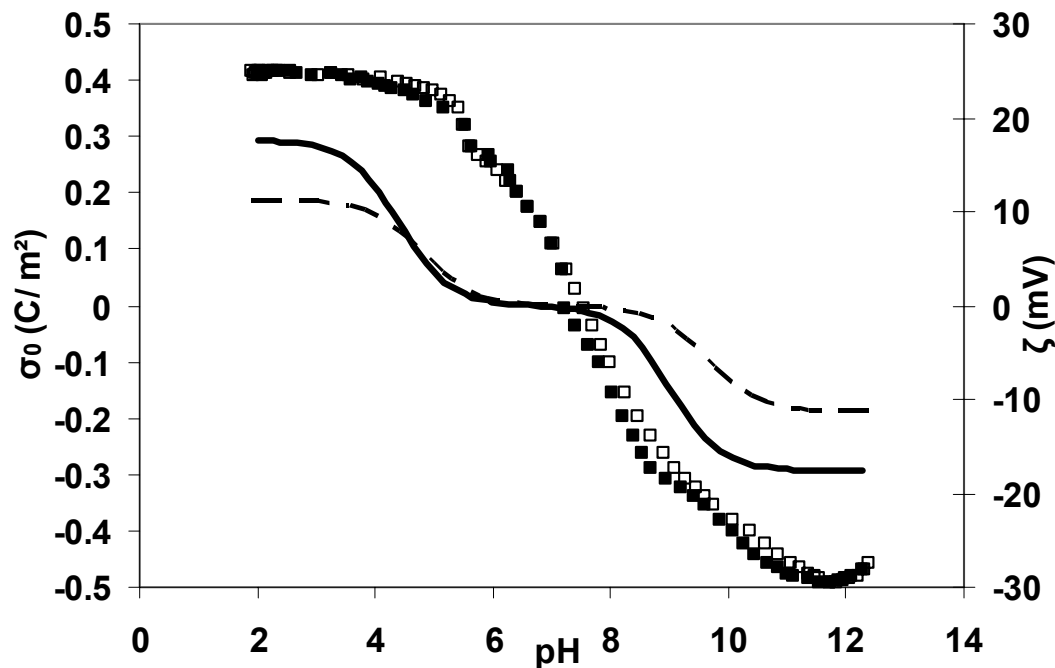
However, the amount of TMAOH added to neutralize the free protons in the suspension dispersed in  $\text{HClO}_4$  is higher than in  $\text{HNO}_3$  (see Figure 3). Using  $V_{\text{TMAOH}}$  at EP1, we expect  $\Delta\text{pH} = 0.2$  and  $\Delta\chi = 0.24 \text{ Sm}^{-1}$  between the two colloidal suspensions before titrations, values higher than the experimental ones ( $\Delta\text{pH} = 0.1$  and  $\Delta\chi = 0.13 \text{ Sm}^{-1}$ ). Moreover the amount of reagent dropped from EP<sub>2</sub> ( $V = 4.35\text{mL}$ , pH = 9.8) to the end of the titration at pH = 12.4 does not correspond to the variation of pH measured in the suspension. For both systems, the incoherences between the variations of pH and conductivity with the amount of reactant dropped question the fact that all the sites on the surface of the particles are titrated between EP1 and EP2.

## Determination of $\sigma_0$ (C m<sup>-2</sup>) versus pH. Comparison with zeta potential

Knowing the surface charge density at saturation  $\sigma_0^{\text{sat}}$  in HNO<sub>3</sub> and HClO<sub>4</sub>, it is possible to deduce the variation of  $\sigma_0$  with the pH of the medium according to (7) using the assumptions (I) to (VI) described in §2.4 :

$$\sigma_o = V_{\text{solution}} \cdot \frac{F}{S_{\text{particles}}} \left( \frac{10^{-2\text{pH}} - Ka_1 Ka_2}{10^{-2\text{pH}} + Ka \cdot 10^{-\text{pH}} + Ka_1 Ka_2} \right) \cdot C_T \quad (7)$$

with  $V_{\text{solution}}$  the volume of the solution (m<sup>3</sup>),  $S_{\text{particles}}$  the surface of the particles (m<sup>2</sup>),  $Ka_1$  and  $Ka_2$  the acidity constants related to the equilibria (2) and (3) and  $C_T$  the total concentration of sites (mol m<sup>-3</sup>). The pKa values used for the calculation are determined from the potentiometric curves: we find pKa<sub>1</sub> = 4.6, pKa<sub>2</sub> = 9.3 for HNO<sub>3</sub> and pKa<sub>1</sub> = 4.8, pKa<sub>2</sub> = 9.6 for HClO<sub>4</sub>. The figure 4 shows the variation with the pH of the surface charge density calculated in HNO<sub>3</sub> and HClO<sub>4</sub> and its comparison with the zeta potential determined by acoustophoresis. Whereas the profile of the surface charge density differs in the two media HNO<sub>3</sub> and HClO<sub>4</sub>, the profile of the zeta potential appears to be similar. Moreover, considering that the ionic strengths in colloidal suspensions dispersed at pH = 2 in HNO<sub>3</sub> and HClO<sub>4</sub> are similar, if the zeta potential values are the same in both systems, one can expect that the surface charge density at saturation at pH = 2 is identical in both media. Similar conclusions can be drawn at pH = 12. At  $\Phi_{\text{vol}}(\%) = 1.5$ , zeta potential measurements of particles dispersed in acidic medium at pH = 2.0 without added salt were found to be +25mV with a high reproducibility. This value in magnitude is slightly lower than the zeta potential of -30 mV for negatively charged particles at  $\Phi_{\text{vol}}(\%) = 1.5$  at pH = 12.0 without added salt, which is not consistent with the assumption of similar charge at pH = 2 and at pH = 12. That result questions the hypothesis of an influence of the nature of the counter-ion on the magnitude of the surface charge density, and raises the question of the validity of the interpretation of the titrations based on the assumptions (I) to (VI).



**Figure 4:** Surface charge density of the particles  $\sigma_0(\text{C m}^{-2})$  dispersed in  $\text{HNO}_3$  (**full line**) and  $\text{HClO}_4$  (**dashed line**) calculated with Eq. 7 ( $\text{HNO}_3$ :  $\text{pK}_{a1} = 4.6$ ,  $\text{pK}_{a2} = 9.3$ ;  $\text{HClO}_4$ :  $\text{pK}_{a1} = 4.78$ ,  $\text{pK}_{a2} = 9.6$ ) and hypotheses **(I)** to **(VI)** (see text). **Squares:** Zeta potential determined from acoustophoresis during titrations with TMAOH beginning from  $\text{pH} = 2.0$  for both systems ( $\text{HNO}_3$ : **open symbols**,  $\text{HClO}_4$ : **full symbols**).

### 3.2. Validity of the previous analysis

#### Potential-conductimetric titrations from $\text{pH}=12$

To elucidate the existence of an influence of the nature of the counterion on the charge of the particles, we performed titrations of a colloidal suspension ( $\Phi_{\text{Vol}}(\%) = 1.5$ ) in TMAOH  $\text{pH} = 12.0$  by  $\text{HClO}_4$  and  $\text{HNO}_3$  ( $1 \text{ mol L}^{-1}$ ). The influence of the ions  $\text{ClO}_4^-$  or  $\text{NO}_3^-$  on the potential-conductimetric curves should appear when the particles are positive ( $\text{pH} < 7$ ). For both titrations with  $\text{HClO}_4$  and  $\text{HNO}_3$ , although the first equivalence point is not accurately determined given that the initial conductivity is low at  $\text{pH} = 12.0$  (data not shown), the amount of protons, determined by the titration, that adsorb on negatively charged particles

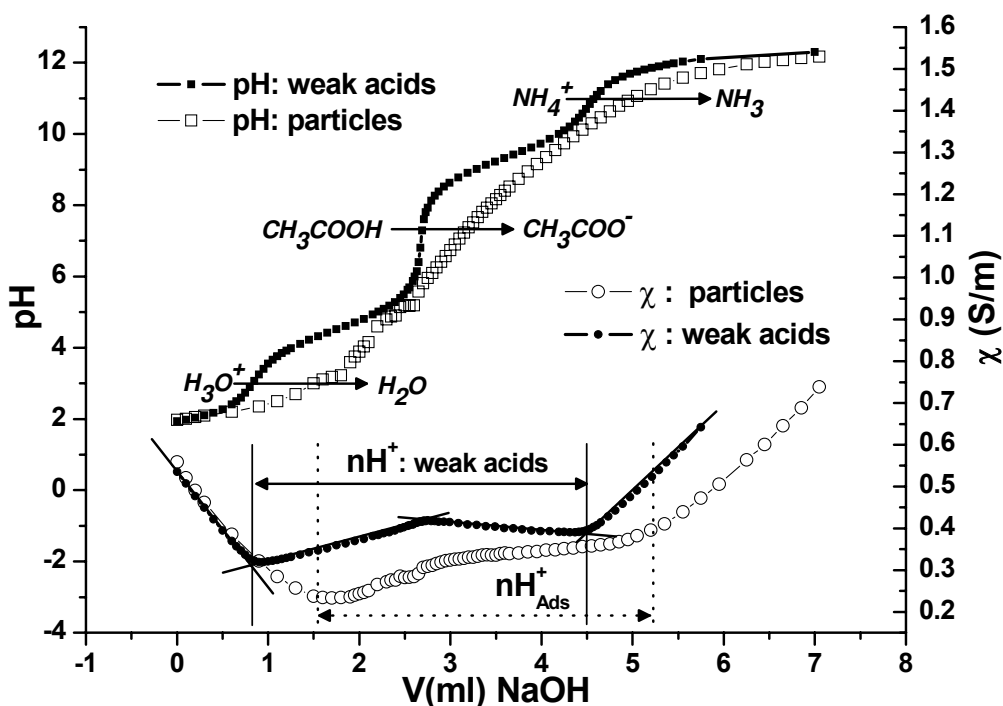
leads to the same surface charge density. Moreover, the magnitude of the surface charge density determined is  $0.3 \text{ C.m}^{-2}$ , as previously found for the particles dispersed in  $\text{HNO}_3$  at  $\text{pH} = 2.0$ . These results confirm that there is no influence of the nature of these counter-ions on the magnitude of the surface charge density.

### **Equivalent system with independent acidities and two distinct pKa.**

As a comparison, we performed a titration of a solution of  $\text{CH}_3\text{COONH}_4$  and  $\text{HNO}_3$  at  $\text{pH} = 2.0$  by  $\text{NaOH}$ . The salt  $\text{CH}_3\text{COONH}_4$  is chosen because the pKa values of the pairs  $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$  ( $\text{pKa} = 4.75$ ) and  $\text{NH}_4^+/\text{NH}_3$  ( $\text{pKa} = 9$ ) are very close to those of the particles. At  $\text{pH} = 2$ , the weak acidic groups  $\text{CH}_3\text{COOH}$  and  $\text{NH}_4^+$  are not dissociated. The concentration of  $\text{CH}_3\text{COONH}_4$  ( $23 \text{ mmol L}^{-1}$ ) dissolved in  $\text{HNO}_3$  is equivalent to the concentration of the protons ( $46 \text{ mmol L}^{-1}$ ) bound to the particles ( $\Phi_{\text{vol}}(\%) = 1.5$ ) dispersed in  $\text{HNO}_3$  at  $\text{pH} = 2$ . In figure 5, three high variations of pH appear on the potentiometric curve and three marked changes in the slope of the conductivity curve. The EP associated to these variations is in good agreement with the amount of alkaline reagent required to neutralize first  $10^{-2} \text{ mol L}^{-1}$  of strong acid ( $\text{HNO}_3$ ), then  $23 \text{ mmol L}^{-1}$  of  $\text{CH}_3\text{COOH}$ , and finally  $23 \text{ mmol L}^{-1}$  of  $\text{NH}_4^+$ .

On the contrary, in the case of particles titrated with  $\text{NaOH}$ , the potentiometric curve does not exhibit any marked variation and the changes in the slope of the conductivity curve are not well marked either. This is the reason why it becomes difficult to determine accurately the position of the EP even from conductivity. Moreover, for the particles, the volume of reagent dropped at EP1 corresponds to an amount of alkaline reagent much greater than the initial amount of free protons determined by the pH measurement before the titration. This means that, before EP1 one probably titrates not only the strong acid in solution but also some sites on the particles.



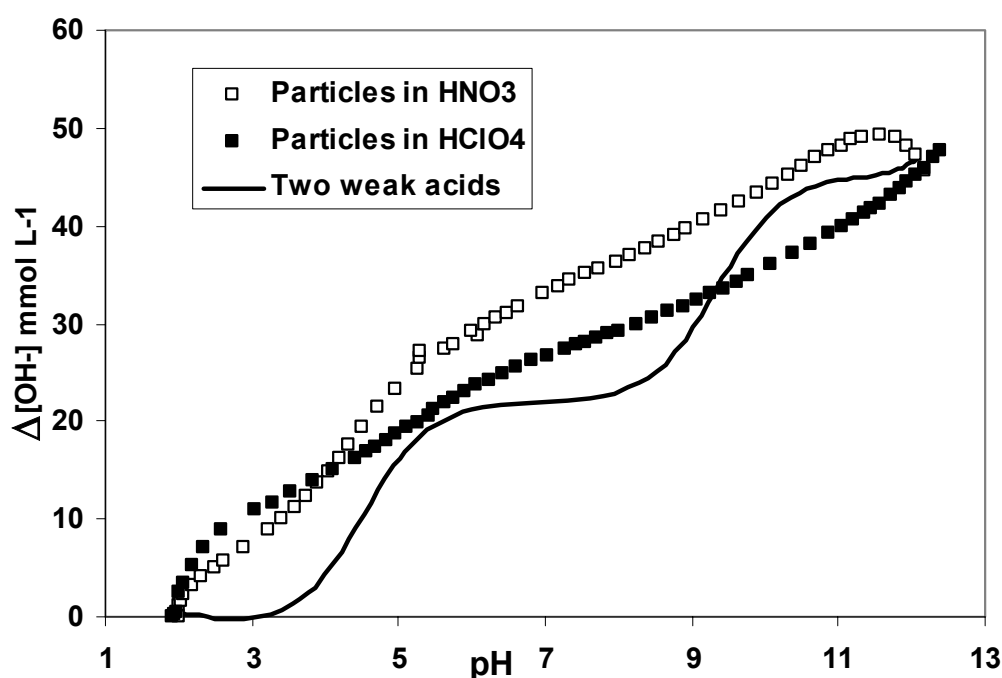


**Figure 5:** Potentio-conductimetric titrations with NaOH ( $1 \text{ mol L}^{-1}$ ): Comparison between a colloidal suspension (open symbols)  $\Phi_{\text{vol}}(\%) = 1.5$  dispersed in  $\text{HNO}_3$  at  $\text{pH}=2.0$  and a solution of  $\text{CH}_3\text{COO}/\text{NH}_4$  ( $23 \text{ mmol L}^{-1}$ ) and  $\text{HNO}_3$  at  $\text{pH}= 2.0$  (full symbols):  $\text{pK}_a \text{NH}_4^+/\text{NH}_3= 9$ ,  $\text{pK}_a \text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^- = 4.75$ . The amount of weak acidities ( $n\text{H}^+$ ) is compared with the amount of protons bound to the surface of the particles ( $n\text{H}^+_{\text{ads}}$ ).

### Interpretation of the potentiometric curves

As the equivalence points determined from conductimetry are not accurate, we analyze the potentiometric curves with Eq (4) (see § 2.4.) in order to determine  $\Delta n\text{OH}^-$ , which gives the number of protons linked to the particles. Figure 6 plots  $\Delta[\text{OH}^-]$  ( $\Delta n\text{OH}^-$  per volume) versus pH for particles dispersed in  $\text{HNO}_3$  and  $\text{HClO}_4$  at  $\text{pH} = 2$ . For  $\text{CH}_3\text{COONH}_4$  in  $\text{HNO}_3$  at  $\text{pH} = 2$ ,  $\Delta[\text{OH}^-]$  plotted for comparison, corresponds to the amount of alkaline reagent that reacts with the weak acidities. As  $\Delta[\text{OH}^-]$  at  $\text{pH} = 12$  is the same for the curves in Figure 6, it means that the number of protons bound on the particles surface is identical in both colloidal

suspensions. However, the profiles are very different from the equivalent system with independent weak acidities ( $\text{CH}_3\text{COOH}$ ,  $\text{NH}_4^+$ ), which invalidates the hypothesis **(IV)** and **(V)** where independent acidic sites with two distinct acidities are considered. Moreover, before the point called EP1, a large part of the amount of alkaline reagent dropped reacts with the protons on the surface of the particles, which questions the previous description, in particular whether the saturation of the charge at  $\text{pH} = 2$  is achieved or not.



**Figure 6:** Amount of alkaline reagent that has reacted with the particles in the suspension or with the independent weak acids (system  $\text{CH}_3\text{COONH}_4$  in  $\text{HNO}_3$ ) in solution as a function of pH. **Open symbols:** particles dispersed in  $\text{HNO}_3$   $\text{pH} = 2.0$ , **full symbols:** particles dispersed in  $\text{HClO}_4$   $\text{pH} = 1.9$ , **line:**  $\text{CH}_3\text{COONH}_4$  ( $23 \text{ mmol L}^{-1}$ ) and  $\text{HNO}_3$  at  $\text{pH} = 2.0$ .

### 3.3. Influence of the electrostatics in the proton exchange process.

In order to explain the discrepancy between the titration curves performed from extreme pH values and the interpretations of the conductivity curves, and also to describe more accurately

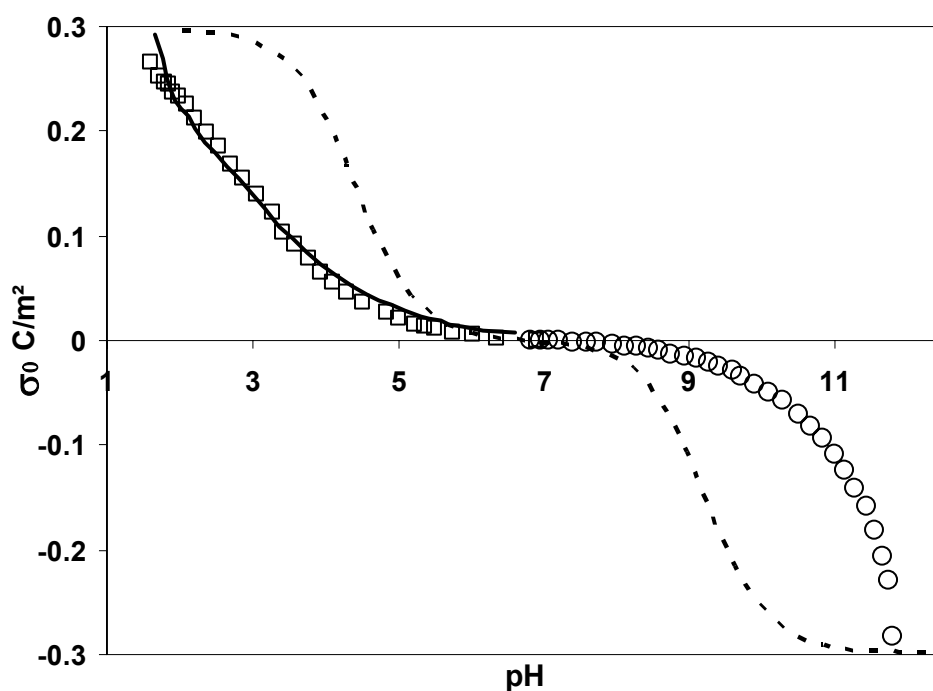
the variation of  $\sigma_0$  with pH, another titration protocol is used and an additional term taking into account the electric field developed by the particles is introduced.

### **Experimental determination of $\sigma_0$ (C m<sup>-2</sup>) versus pH: titrations from the PZC**

The titration between pH = 2 and pH = 12 does not allow us to access the experimental variation of  $\sigma_0$  with the pH, even from the potentiometric curves. Only a calculated  $\sigma_0$  can be obtained assuming several hypotheses among which the symmetrical charge between pH = 2 and 12. To bypass this assumption, we perform titrations from an initial pH close to the neutral pH to acidic and alkaline pH, as detailed in the experimental part. The surface charge density at each pH is calculated assuming that no charge subsists at the initial pH, therefore no counter ions subsist in the solution either. This assumption is reasonable since the conductivity of the precipitated suspension is close to the conductivity of water at the initial pH. On figure 7, surface charge densities determined from titrations from the PZC using HNO<sub>3</sub>, HClO<sub>4</sub> and TMAOH as reagent are presented and compared to  $\sigma_0$  (Cm<sup>-2</sup>) calculated using Eq. (7) and a symmetrical charge density  $\sigma_0 = 0.3 \text{ C m}^{-2}$  at pH = 2 and 12. The profile of  $\sigma_0$  (C m<sup>-2</sup>) between the PZC and the acidic pH (protonation curve) appears to be the same whatever the reagent used (HNO<sub>3</sub> or HClO<sub>4</sub>) as already observed with the forward and the backward titrations analyzed as in Figure 6 (backward titrations not shown). However the evolution of the experimental  $\sigma_0$  with the pH is not well predicted by the profile of  $\sigma_0$  calculated with Eq (7).

In the alkaline part, the evolution of the experimental  $\sigma_0$  versus the pH is different, and the surface charge density at extreme pH close to pH=12 seems to be larger than that near pH=2, meaning that the charge is not symmetrical with respect to the PZC. Moreover, the charge densities  $\sigma_0 = 0.22 \text{ C m}^{-2}$  and  $\sigma_0 = 0.35 \text{ C m}^{-2}$  obtained respectively at pH = 2.0 and pH = 12.0

are not exactly similar to the surface charge densities determined from the potentiometric curves in the forward and the backward titrations ( $\sigma_0 = 0.30 \text{ C m}^{-2}$ ). Note that the error on the pH measurements performed near the extreme values and in colloidal suspensions may lead to an important error on the determination of the amount of protons that are bound to or removed from the particles. Therefore, we limit our analysis to the range  $2 < \text{pH} < 12$ . Despite these possible errors, the total amount of protons linked to the particles deduced from Figure 7 corresponds to an equivalent concentration  $[\text{H}^+]_{\text{ads}} = 50 \text{ mmol L}^{-1}$ , is in good agreement with the value of  $47 \text{ mmol L}^{-1}$  obtained in § 3.1.



**Figure 7:** Surface charge density of particles as a function of the pH:

- determined from potentiometric titration of colloidal suspension  $\Phi_{\text{vol}}(\%) = 1.5$ , from the PZC to pH = 1.5 (**open squares and full line**) and from the PZC to pH = 12.5 (**open circles**).  $\text{HNO}_3$   $1 \text{ mol L}^{-1}$ ,  $\text{HClO}_4$   $1 \text{ mol L}^{-1}$  and  $\text{TMAOH}$   $1 \text{ mol L}^{-1}$  were used as reagent.
- calculated (**dashed line**) with Eq (7) with:  $\text{pK}_{\text{a}1} = 5.4$ ,  $\text{pK}_{\text{a}2} = 9.3$ , a surface charge density at pH = 2.0 and 12.0,  $\sigma_0 = 0.3 \text{ C m}^{-2}$ .

## Theoretical determination of $\sigma_0(\text{C m}^{-2})$ versus pH

Let us consider a model based on a site dissociation model taking into account the potential developed at the surface of the particles. It implies that the sites on the particles are equivalent, however no longer independent. Several authors interested in the dissociation properties of acid groups at the surface of colloidal silica<sup>12</sup>, latex particles<sup>13</sup> and acrylamide-acrylic acid copolymers<sup>14</sup>, emphasize the existence of such an additional contribution of electrostatic nature  $\Delta G_{el}$  in the dissociation process of poly(-base, -acid). We note  $K_{a1}^0$  and  $K_{a2}^0$  the thermodynamic constants (8) associated to the acid base equilibria (2) and (3), constants which correspond to the acidity of the surface when the global charge tends toward zero, thus here near the PZC. Note that we consider here concentrations and not activities.  $\alpha_1$  and  $\alpha_2$  are the dissociation coefficients.

$$K_1^0 = \frac{[-MOH][H^+]}{[-MOH_2^+]} = \frac{\alpha_1 [H^+]}{1 - \alpha_1} \quad \text{and} \quad K_2^0 = \frac{[-MOH][H^+]}{[-MOH_2^+]} = \frac{\alpha_2 [H^+]}{1 - \alpha_2} \quad (8)$$

The changes in the free energy of the dissociation process  $\Delta G_{el}$  in the case of poly-acids induce a change in the apparent dissociation constants  $K_{a1}$  and  $K_{a2}$  according to the equation (9) with R the molar gas constant:

$$pKa = pK_a^0 + 0.4343 \frac{\Delta G_{el}}{R \cdot T} \quad (9)$$

$\Delta G_{el}$  can be expressed in terms of the electrostatic potential<sup>15,16</sup>,  $\psi_d$ , at the surface of the particle, with e the elementary charge and  $N_A$  the Avogadro number:

$$\Delta G_{el} = -eN_A \psi_d \quad (10)$$

Although  $\psi_d$  is called here the surface potential, it is actually localized on the outer Helmholtz plane (oHp) in a description of the ionic atmosphere of the particles with surface amphoteric oxide groups<sup>17</sup> according to a double layer model (Gouy-Chapman-Stern model). The plane oHp is the plane defined by the counter ions condensed on the surface of the particles.

Considering a spherical particle of radius  $a$  in a symmetrical 1-1 type electrolyte solution, Ohshima et al<sup>18</sup> proposed a method to determine the electric potential  $\psi(r)$  at a distance  $r$  ( $r \geq a$ ) from the centre of the particle.

$$\frac{d^2\psi}{dr^2} + \frac{2}{r} \frac{d\psi}{dr} = \frac{2e \cdot c}{\varepsilon_r \cdot \varepsilon_0} \sinh\left(\frac{e \cdot \psi}{k_B \cdot T}\right) \quad (11)$$

The equation (11) satisfies the spherical Poisson Boltzmann (P.B.) equation, with  $c$  electrolyte concentration,  $\varepsilon_r$ : relative permittivity of the solution (78.5: relative permittivity of water),  $\varepsilon_0$ : the permittivity of a vacuum and  $k_B$ : Boltzmann constant. A simple approximate analytical solution to the spherical P.B. equation allows linking the surface charge density of the particle  $\sigma_0$  to the surface potential  $\psi_d$ :

$$\sigma_0 \cdot \frac{F_A}{\varepsilon_r \cdot \varepsilon_0 \cdot R \cdot T \cdot \kappa} = 2 \cdot \sinh\left(\frac{Y_d}{2}\right) \cdot \left(1 + \frac{2}{\kappa \cdot a \cdot \cosh^2(Y_d/4)} + \frac{8 \ln(\cosh(Y_d/4))}{(\kappa \cdot a)^2 \cdot \cosh^2(Y_d/2)}\right)^{1/2} \quad (12)$$

with  $Y_d$  the reduced potential  $Y_d = F_A \cdot \psi_d / R \cdot T$ ,  $F_A$  the Faraday constant,  $R$  the molar gas constant and  $\kappa$  the Debye parameter for a 1-1 electrolyte given by (13):

$$\kappa = \left(\frac{2 \cdot c \cdot 10^{-3} \cdot F_A^2}{\varepsilon_r \cdot \varepsilon_0 \cdot R \cdot T}\right)^{1/2} \quad (13)$$

Thus it is possible to calculate  $\sigma_0$  ( $C \cdot m^{-2}$ ) as a function of  $\psi_d$  for each acid base equilibrium, and then to deduce the dissociation coefficients  $\alpha_1$  and  $\alpha_2$  according to (14):

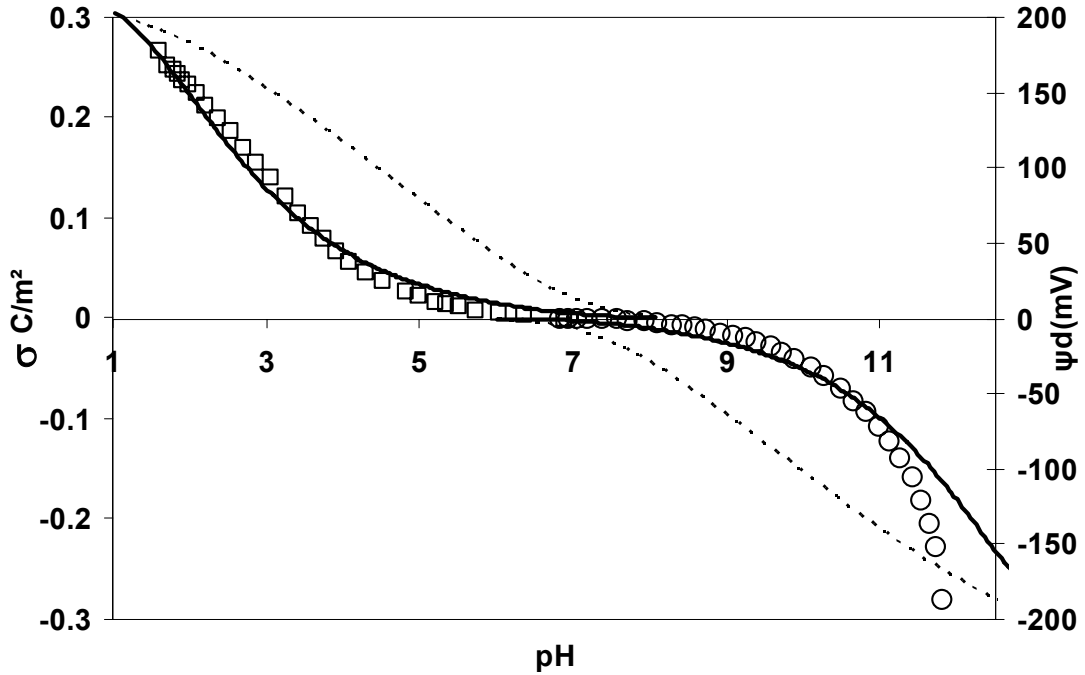
$$\sigma_0 = (1 - \alpha_1) \cdot e \cdot N_s \quad \text{and} \quad \sigma_0 = -\alpha_2 \cdot e \cdot N_s \quad (14)$$

$N_s$  ( $number \cdot m^{-2}$ ) corresponds to the total amount of sites binding protons at the surface of the particle.  $\alpha_1=0$  signifies that all sites are  $(-M-OH_2^+)$  and  $\sigma_0$  is positive, conversely  $\alpha_2=1$  signifies that all sites are  $(-M-O^-)$  and  $\sigma_0$  is negative.

Knowing the dependence between  $\sigma_0$  and  $(\alpha_1, \alpha_2)$ , it is possible to establish the dependence of  $\sigma_0$  with the pH according to the equation (15), with the adjustable parameters  $pKa_1^0$  et  $pKa_2^0$ :

$$pH = pK_a^0 - \log \frac{1-\alpha}{\alpha} + 0.4343 \frac{\Delta G_{el}}{RT} \quad (15)$$

$pK_{a1}^{\circ}$  and  $pK_{a2}^{\circ}$  relative to the equilibrium (2) and (3) can be extrapolated from  $pK_a=f(\alpha)$  ( $\alpha$  is obtained from  $\sigma_{exp}$  with (14),  $pK_a$  from (15), suffix 1 is for the acidic part, suffix 2 for the alkaline part). This gives  $pK_{1}^{\circ} = 4.5$  and  $pK_{2}^{\circ} = 9$  for particles initially dispersed in  $HNO_3$ . However, the extrapolation is not accurate because of the strong variations of  $pK_a$  close to  $pK_a^{\circ}$ . Therefore we prefer to determine  $pK_a^{\circ}$  from the fit of  $\sigma_0=f(pH)$ . This gives  $pK_{a1}^{\circ} = 5.4$  and  $pK_{a2}^{\circ} = 9$ , values not so far from those determined in the potentiometric titrations considering independent acidic groups.



**Figure 8:** Dependence of the structural charge  $\sigma_0(C m^{-2})$  with the pH: **open symbols:**  $\sigma_0$  determined experimentally from the potentiometric titration. **Full line:** Simulation of  $\sigma_0$  during the titration:  $c = 0.01mol L^{-1}$ ,  $pK_{1}^{\circ} = 5.4$  and  $pK_{2}^{\circ} = 9$ ,  $N_s = 2.1$  charges  $nm^{-2}$ . **Dashed line:**  $\psi_d(mV)$  the surface potential determined from the Poisson-Boltzmann equation for a spherical particle.

The good agreement of the simulation and the experimental results on figure 8 emphasizes the necessity to take into account the electrostatic contribution in order to accurately determine the surface charge density of the particles.

### **Conclusion and perspectives**

In this study, we determined the surface charge density of well defined nanocolloids by implementing simultaneous potentiometric titration technique and zetametry. The physico-chemical conditions of synthesis and dispersion of the colloidal particles are very well defined and allow preparing suspensions in acidic, alkaline or neutral pH under controlled conditions of ionic strength, volume fraction and of the nature of the counterions. Titrations starting from acidic, alkaline and neutral pH and simultaneous zetametry measurements, allowed us to accurately determine the surface charge density of the particles. For the titrations starting from acidic and alkaline media, potentiometric measurements as well as zetametry measurements showed that the surface charge density of the nanoparticles is neither influenced by the nature of the counter ions ( $\text{ClO}_4^-$ ,  $\text{NO}_3^-$ ), nor by the nature of the reagent ( $\text{TMA}^+$ ,  $\text{Na}^+$ ). Additional titrations starting from the neutral pH give us a direct access to the variation of the surface charge density with the pH. It confirms that the colloidal particles are not fully charged at  $\text{pH} = 2$  and  $\text{pH} = 12$  and that the surface charge density at  $\text{pH} = 12$  is more important than at  $\text{pH} = 2$  as raised by zetametry measurements.

The properties of the surface oxide groups are studied as a function of the pH of the medium of dispersion (acidic, alkaline, neutral), of the nature of the counterions, and of the nature of the reagent. Different thermodynamical models are applied to describe the proton exchanges between the surface of the particles and the solution. In a first step, we show that a model with independent acidities does not adequately describe the experimental titrations curves and the experimentally determined charge of the particles. In a second step, we take into account the



electrostatic field generated by the particle itself during the protonation. This model well explains the gradual variation of the charge with the pH experimentally determined: it is indeed more difficult to add charges on an already charged particle than on an uncharged or weakly charged particle.

The complementarity of the techniques used (simultaneous potentiometric titrations and zetametry) allowed us to understand the protonation and the deprotonation of the surface of the colloidal particles and therefore to define their stability range. The next step will be to understand the link between the structural charge, the effective charge, which is the overall charge after condensation of the counter ions, and the zeta potential.

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