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Charge reversal of moisturous porous silica colloids by take-up of protons

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ABSTRACT

The net charge of porous Stöber silica colloids is studied using a modified Poisson–Boltzmann theory in a spherical cell, with a focus on the case of water-filled porous silica particles suspended in a non-aqueous solvent. We show that the silica's usual negative surface charge, due to deprotonisation of the Si–OH group, is counteracted by an excess uptake of protons in the water-filled pores of the particle at low enough pH. A small volume fraction of pores suffices to induce a point of zero charge at pH ≈ 4. Based on the difference in Donnan potential between the porous medium and the solvent a relation can be constructed that describes the location of the point of zero charge analytically. The accuracy of this relation is confirmed by numerical calculations. For Stöber silica in water we find a charge reversal below pH ≈ 3, which is in this case solely a result of the selective uptake of cations in the porous network.

1. Introduction

Surfaces of objects that are immersed in a liquid are able to exchange ions with it. The nature of this exchange can either be dissociative, such that the surface releases ions into the liquid, or associative, such that ions adsorb on the surface from the liquid. In either case this exchange results in a net electrostatic charge on the surface. For objects in water this charging is usually quite significant because the high polarity of this particular solvent enables it to contain a high number of ions. In less polar solvents both charging mechanisms are less efficient such that the acquired charge is typically significantly weaker than in water. The competition between (dissociative) proton release and (associative) protonisation in metal hydroxide surfaces like rutile, goethite, and silica leads to a point of zero charge (pzc) that varies over a broad pH range between these materials [1]. For all pH below the pzc of these surfaces, their net charge becomes positive due to the predominant protonisation of the surface. The pzc of silica and the value of the associated dissociation constant related to protonisation, stays nevertheless a point of discussion, as this point is found at very low pH (≈ 2) and its location seems to be dependent on the method used for measuring [2]. Besides, the presence of some particular ion species has proven to be important as well. For example it was shown that the presence of chloride ions shifts the pzc to higher pH [3]. Kosmulski et al. even argue that the presence of a pzc is hard to detect [4] in absence of chloride ions.

An interesting additional feature emerges in organic (oily) solvents. Labib and Williams [5,6] investigated the effect of acidity on various solid metal oxides (including silica) that are immersed in organic liquids, and discovered that the presence of trace amounts of moisture can be very important for the location of the pzc. They showed that their carefully dried samples often displayed a stronger acid-like behavior than their not-so-dry ones. Accordingly, they introduced three regions along the acidity scale of the liquid: (I) low acidity causes the surface to charge negatively, (II) a range in acidity where the sign of the charge is sensitive to the presence of water, and (III) high acidity causes the surface to charge positively.

In this paper, we will introduce a model for the effect of moisture on the electrostatic charge of oil-dispersed Stöber silica colloids. These colloids, synthesised by hydrolyzing tetraethylorthoscilate, are very well-known and have been investigated for many decades now [7]. The work we present here relates to research by Goodwin et al., who showed experimentally that suspensions of Stöber particles in a low-dielectric solvent are very sensitive to small amounts of water and found that the direction of the electrophoretic mobility is actually able to reverse as the water content in the system increases [8]. An important property of Stöber silica is its porosity, which makes that such particles should not always be regarded as solid spheres. The porosity is approximately 10% [9,10] and the form of the porous network allows water to move in [11]. Walcarius et al., as well as Labrosse and Burneau [9], found an average pore diameter of 0.3 nm for Stöber silica. Walcarius et al. [12] showed that this microporous structure is so fine that ion-exclusion effects take place; large ions cannot enter the microporous structure, whilst the smaller ones (e.g. H^+, OH^- or Na^+) easily can [13]. This ion-exclusion effect is also well known for crystalline zeolites [14]. It was shown for microporous silica colloids that the selective uptake of small alkali anions can increase the amount of negative charge of the particles,

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whereas the addition of larger anionic species did not have the same effect as they are not able to enter the microstructure [15]. We argue here that this ionic size selectivity offers an interesting possibility to *reverse* the net charge of Stöber silica suspended in an acidic environment, in this case a low-dielectric solvent in contact with an aqueous solution at a relatively low pH. Given that the bare size of protons (in the form of hydronium ions) is typically (much) smaller than that of the anions, a tendency appears for the silica particles to charge positively due to the alleged selective uptake of positive charge. Using a theoretical framework to calculate the ion densities in equilibrium we will study suspensions of water-containing porous silica colloids in oil. The influence of acidity on the point of zero charge and the magnitude of the charge in such suspensions is investigated.

2. Method

2.1. The system

The dispersion under consideration consists of monodisperse Stöber-silica beads that are dispersed in oil. In our description the oil is a low-dielectric solvent that is immiscible with water. All silica beads have a radius a, chosen to be in the colloidal size regime which is somewhere in between several nanometers and a micron. The porosity χ of the particles is defined as the fraction of empty volume inside the beads; we set $\chi = 0.1$ in essentially all calculations below in order to describe Stöber-silica. Throughout this work we will assume that the pores are shaped like cylinders with diameter D. Although in experiments water contamination of the silica is often tried to be avoided, the hygroscopic properties of the material renders this a difficult task in general. In this work we therefore assume that water is able to reside inside the porous network, even if the colloids are suspended in oil. The water could be a remnant of the particle synthesis, moist collected from the air, or could be a trace amount of water that is present in the oil and migrates towards the particles. The strong hydrophillicity of silica ensures that the water inside the pores is not replaced by oil. We will show that the presence of water is important for the net charge of the silica beads as the water-containing porous structure might take up a significant amount of charge, either by charging the Si–OH groups that are in contact with water inside the pores or by a preferential uptake of ions that are small enough to enter the pores [15]. In our model we consider the silica particle to be completely wetted by water such that the complete silica surface, both the internal surface of the pores and the outside surface of the bead, is in contact with water instead of oil. This enables us to calculate all surface chemistry as it is known for a silica–water interface, see Section B.

It turns out to be convenient to treat the ions in our calculations grand-canonically. Experimentally this situation could be realized by the set-up shown in Fig. 1, where water-immiscible oil is in contact with a bulk water reservoir to which a strong acid HX is added. We assume that HX in water completely dissociates into H^+ and X^-, such that the pH, or equivalently the proton concentration

$$\rho_w[\mathrm{M}] = 10^{-\mathrm{pH}} \tag{1}$$

in the water reservoir, can be used as a control parameter. Here M denotes the concentration expressed in moles per liter. We assume for simplicity that H^+ and X^- are the only ions in the system, i.e. we ignore the addition of, for instance, NaCl to the water reservoir. We gauge the electrostatic potential in the water phase to be zero, and consider both the water and the oil as incompressible dielectric fluids with dielectric constants ϵ_w and ϵ_o, respectively, at room temperature T. We also assume diffusive equilibrium between the ions in the bulk water (with concentration $2\rho_w$ as a control parameter), the ions in the bulk oil (with concentration $2\rho_o$ to be calculated below), and the ions inside the silica pores (with a proton concentration to be calculated and a vanishing anion concentration due to the size selectivity of the pores), see section C.

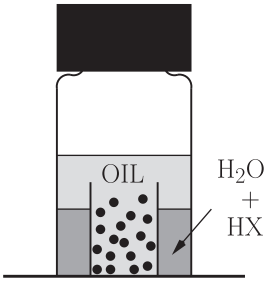

Fig. 1. A schematic view of the described system. The water reservoir is separated from the oil in the center of the set-up via a glass wall. The colloids, which are suspended in oil at the other side of this wall can be observed from below. The pH of the water is controlled by adding an acid HX to the water reservoirs.

In section D we will formulate a spherical Wigner–Seitz cell approximation that allows for explicit numerical calculations of the net charge of the silica particles by coupling the negative silica surface charge and the positive proton uptake in the pores within a Poisson–Bolzmann theory.

2.2. Dissociation of silica in contact with water

The silica–water interface has long been studied, and it is well-known that the charging mechanism of the surface groups at pH values well above 2 is mainly dissociative, causing a negative silica surface charge. The release of protons from Si–OH groups from the surface can be described by the reaction

$$\mathrm{Si{-}OH} \leftrightarrows \mathrm{Si{-}O^-} + \mathrm{H^+}, \tag{2}$$

where H^+ denotes a proton and $\mathrm{Si{-}OH^-}$ a charged surface group. The corresponding dissociation constant in Eq. (2),

$$\mathrm{K_w} = \frac{[\mathrm{Si{-}O^-}][\mathrm{H^+}]}{[\mathrm{Si{-}OH}]}, \tag{3}$$

was measured to be $K_w = 32$ nM [1]. Since the equilibrium constant for protonisation is very small and highly situation dependent, we choose not to include this reaction in this work, quantitative accuracy of our predictions could therefore be limited close to the alleged pzc of ‘dry’ silica at pH 2. Given a local cation (proton) density in the water phase close to the surface, $[\mathrm{H^+}]=\rho_{w,+}(\mathbf{r})$, and writing the local surface charge number density in contact with water as $\sigma_w(\mathbf{r}) = -[\mathrm{Si{-}OH^-}]$, we use Eq. (3) to write

$$\sigma_w(\mathbf{r}) = -\sigma_0 \frac{\mathrm{K_w}}{\rho_{w,+}(\mathbf{r})}, \tag{4}$$

with $\sigma_0 = [\mathrm{Si{-}OH}] + [\mathrm{Si{-}O^-}] \simeq 5\ \mathrm{nm}^{-2}$ the total areal density of dissociated and non-dissociated Si–OH groups on Stöber silica [1,12,16]; this agrees well with the picture that essentially all silicium atoms at the surface carry a Si–OH group. In Eq. (4) it is assumed that the fraction of surface groups that is actually charged is very small compared to the number of available sites, $[\mathrm{Si{-}O^-}] \ll [\mathrm{Si{-}OH}] \approx \sigma_0$, such that the surface charge density is inversely proportional to the local proton concentration [17]. This weak-charging approximation turns out to be valid for the (realistic) parameters that we will consider below.

For the silica–water interface inside the porous silica the same charge mechanism applies as for the outer surface, therefore the porous structure can in principle enable the silica particle to gain more negative charge. However, as we will see next, preferential