

Effect of cationic surfactant addition on the electrokinetics and stability of silica/kaolinite suspensions in copper hydrometallurgy conditions

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ABSTRACT

The presence of small particles at operating conditions of the hydrometallurgy process forming the crud is a complicated issue. These particles, most often silica and clays, remain in the suspension or float to the top. A potential solution for their elimination could be to promote the sedimentation of the solids by the addition of surfactant. However, such a procedure in these complex systems, with different kinds and sizes of particles, requires the evaluation of the composition and optimal dose of surfactant. In this work, we explore the use of dynamic electrophoretic mobility for indirectly evaluating the adsorption of CTAB on silica/kaolinite mixtures at low pH, high ionic strength, and particle concentration above 3%. The electroacoustic technique (ESA) shows to be suitable to predict the effect of surfactant addition on the individual particles of silica and kaolinite and mixtures of them. The conclusions were in agreement with sizes and sedimentation rate determinations. Moreover, scanning electron microscope (SEM) images confirm the evolution of aggregates and the formation of structures between particles by the addition of CTAB. Since the final aim is the identification of the optimal doses of surfactant in which the described suspensions flocculate and separate from the continuous phase, this investigation can potentially contribute to solve operational problems associated to the generation of crud in the hydrometallurgy process.

1. Introduction

One of the main difficulties in the industrial process of oxidized copper ore beneficiation is the generation of mineral complexes as a consequence of the interactions between particles present in the mineral solid matrix, which are carried by the leaching solution to the next stage of solvent extraction. These interactions are the result of the operational conditions involving low pH and high ionic concentration, naturally leading to aggregation processes eventually producing the formation of crud during solvent extraction (Virmig et al., 2003). Recall that crud is a layer of dispersed particles that forms at interfaces, classically attributed to the presence of small solid particles at the interface between drops of the dispersed phase and the surrounding continuous phase (Ritcey, 1980).

Solid particles exhibiting both hydrophilic and hydrophobic behavior show a particular tendency to generate crud. It can be understood that particles of high density do not cause problems, because they sediment rapidly to the bottom of the separation vessel and can be easily eliminated from the copper solution. The case of small particles is far

more complicated, as they will remain in suspension or float to the top, forming the so-called “fish-eyes”. The materials forming the crud are most often silica and clays (Wang, 2005).

A complicating issue is the instability of the colloids forming the crud, associated to the operating conditions of the hydrometallurgy process (low pH, high ionic strength, and particle concentration above 3%), the most favorable to flocculation because of the reduction of electrostatic repulsive forces (Rowlands and O'Brien, 1995; Kim et al., 2015). This effect is one of the main causes of waste generation, and it is among the main challenges of the metallurgical industry to mitigate the effects of the mineral dragged with the solvent extraction process of heap leaching.

A potential solution is the addition of reagents capable of promoting the sedimentation of the crud particles in different conditions. One possibility is the use of a cationic surfactant in low concentration, in such a way that the stability is modified by a series of different mechanisms associated with surface phenomena, related to: (i) the nature of the structural groups in the solid, (ii) the molecular structure of the surfactant, and (iii) the characteristics of the aqueous phase (Bellmann

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et al., 2007; Atkin et al., 2003). The effects of surfactant addition are multiple. First, upon adsorption of the surfactant molecule, the polar head can neutralize the electrokinetic charge density of the particles, provoking their flocculation. If the molecule only contains a charged, hydrophilic group, the hydrophobic tail would be exposed to the aqueous medium, further reducing the stability by hydrophobic attraction (Rosen, 2012; Paria and Khilar, 2004). Additionally, the presence of surfactants in aqueous media generates an enhanced water repellency associated to the increased solid–liquid interfacial tension and a larger contact between the liquid and the particle, again rising the tendency to flocculate (Thompson and Mcewen, 1983). An advantage of the use of surfactants over inorganic ions of the same charge is that the effects mentioned can be achieved with concentrations far lower than those of ions, the effect being more efficient the longer the surfactant chain (Ottewill, 1968). In this case, bridging flocculation can also take place, by virtue of which a single molecule can connect two particles, if the surface coverage is low, so that uncovered patches can receive the chain end (Kitchner, 1972). For shorter chains, it is also possible that adsorbed molecules can extend into the medium, and interact with other extended molecules; this may happen particularly when the surface coverage is high, so that the surface density of available sites is very low for single molecule bridging (Heinz et al., 2017).

Control of the stability of concentrated slurries is often attained by using polymers, either ionic or nonionic. The most suitable method to follow up and explain changes in the stability of such suspensions is based on the simultaneous determination of particle size and zeta potential by electroacoustic measurements. This has been shown for the case of kaolinite and smectite suspensions by Mpofo et al. (2003), Mpofo et al. 2004a, 2004b). These authors found that polyethylene oxide or polyacrylamide-acrylate were efficient in flocculating and dewatering the clay suspensions, although differences between polymers could be detected and associated to their different chemical functionalities, as demonstrated by zeta potential determinations. Interfacial processes are also important in the field of mineral ore beneficiation by separation of gangue minerals using froth flotation. In this classical technology, the electrical properties of the mineral/solution interface determine the efficiency of the flotation collector adsorption. Determination of such properties can also be carried out by electroacoustics together with direct adsorption measurements, as exemplified in Refs. Pawlik (2005) and Marion et al. (2015).

In the present work, Electrokinetic Sonic Amplitude, ESA, based on the detection and analysis of the pressure wave generated by the application of an alternating electric field to the system, has been used. It is applicable to arbitrary particle contents, as long as the particle density is different from that of medium (Hunter, 1998; Greenwood, 2003). In this manuscript we investigate the use of electrokinetic measurements for indirectly evaluating the adsorption of the surfactant CTAB on silica/kaolinite mixtures under hydrometallurgical conditions.

2. Experimental

2.1. Materials

In order to mimic the conditions observed in the copper hydrometallurgical process, the colloidal suspensions investigated are composed by silica and kaolinite particles dispersed in 80 mM solution of copper sulfate at pH 2. The materials used (all from Merck & Co., USA) were: silica (Ludox TMA), natural kaolinite particles, copper sulfate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, sulfuric acid (ACS reagent, 95–98% purity) and the cationic surfactant hexadecyltrimethylammonium bromide (CTAB). The surface area of the solids was measured with a Nova 2200e equipment (Quantachrome Instruments, Anton Paar, Austria). N_2 adsorption was used at 77 K and multipoint studies were performed to obtain the BET surface area (SBET). The results obtained for kaolinite and silica were 15 and 63.2 m^2/g respectively. Water deionized and filtered in a Milli-Q Academic setup, from Millipore France, was used for the preparation

of the solutions. The colloidal suspensions studied in this work were:

1. Silica suspensions in 80 mM CuSO_4 at pH 2.
2. Kaolinite suspensions in 80 mM CuSO_4 at pH 2.
3. Mixtures of kaolinite and silica at the same volume fraction in 80 mM CuSO_4 at pH 2.

2.2. Methods

2.2.1. Particle size

The hydrodynamic radius of the particles was determined by dynamic light scattering by means of a Malvern Zetasizer NanoZS (Malvern Instruments, UK), yielding a number average diameter of 22 ± 7 nm (silica) and 800 ± 130 nm (kaolinite).

2.2.2. Microscopic observations

The structures formed by kaolinite and silica for the different experimental conditions were observed by scanning electron microscopy (Model SU5000, Hitachi, Japan).

2.2.3. Electrokinetic measurements

As mentioned, the characterization of the diffuse layer charge density (approximated by the electrokinetic charge density (Rowlands and O'Brien, 1995) of the suspended particles in solution was carried out by means of the electroacoustic technique known as ESA or Electrokinetic Sonic Amplitude: an alternating electric field (1 to 18 MHz frequency) is applied to the colloidal suspension and the relative movement between particles and media generates a pressure wave that is recorded (Shilov et al., 2004; Dukhin et al., 1999). This technique has been widely used for the interfacial electrical characterization of inorganic particles/solution, in particular in the case of surfactant adsorption on kaolinite (Greenwood et al., 2007).

The electroacoustic measurements provide the dynamic mobility (the alternating-field equivalent to classical electrophoretic mobility), u_d , for each frequency ω of the external field, $E \exp(-i\omega t)$. Recall that the mobility is defined as the ratio between the particle velocity, \mathbf{v}_e , and the applied electric field, \mathbf{E} (Ahualli et al., 2007; O'Brien et al., 1990; O'Brien, 1990; Rider and O'Brien, 1993):

$$\mathbf{v}_e(\omega) = u_d \mathbf{E}(\omega) \quad (1)$$

The dynamic mobility has a complex relation with the zeta potential, ζ , but for thin electrical double layers, this relation can be approximated as:

$$u_d = \frac{2}{3} \frac{\varepsilon_m}{\eta_m} \zeta [1 - C(\omega)] G(\omega) \quad (2)$$

where η_m is the viscosity of the medium, ε_m is its electric permittivity (both values are taken equal to those of water), and $C(\omega)$ is a complex quantity known as the induced dipole coefficient, related to the dipole moment induced by the application of the field, as follows, for spherical particles of radius a :

$$\mathbf{d} = 4\pi\varepsilon_m a^3 C(\omega) \mathbf{E} \quad (3)$$

The typical spectrum of the dynamic mobility shows two relaxations. The one typically occurring at the highest frequency is related with the particle and fluid inertia in the presence of an applied field of frequency ω . Beyond a critical frequency the inertia effect prevents both liquid and particles motion; this effect is represented by the factor $G(\omega)$ in Eq. (3). This inertial critical frequency, ω_{in} , strongly decreases with particle radius as follows (Landau and Lifshitz, 1959):

$$\omega_{in} = \frac{\eta_m}{\rho_m a^2} \quad (4)$$

In this way, the spectrum of the dynamic mobility can provide information on the particle size, and not only on its electrical surface characteristics. The second relaxation is related to the dipole coefficient

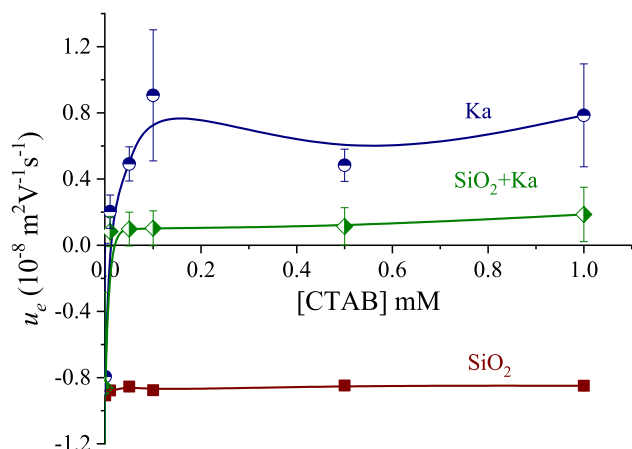


Fig. 1. Electrophoretic mobility (u_e) as a function of CTAB concentration for suspensions of silica (SiO_2), kaolinite (Ka) and a 1:1 mixture ($\text{SiO}_2 + \text{Ka}$), in 80 mM CuSO_4 solutions at pH 2. Error bars correspond to \pm SD ($n = 12$).

$C(\omega)$ frequency dependence (Arroyo et al., 2004; Ahualli et al., 2006). At the MHz range of interest for ESA, we observe the so-called Maxwell-Wagner-O’Konski (MWO) relaxation, which experimentally appears as a mobility rise at a characteristic frequency (Ahualli et al., 2006; Grosse and Delgado, 2010):

$$\omega_{MWO} = \frac{(1 - \phi)K_p + (2 + \phi)K_m}{(1 - \phi)\epsilon_p + (2 + \phi)\epsilon_m} \quad (5)$$

where ϕ is the volume fraction of solids, K_p and ϵ_p are the conductivity and permittivity of the particle, respectively, and K_m conductivity of the medium. We recall that even if the particles are intrinsically non-conducting, their conductivity K_p may be finite, since the excess conductivity of the electrical double layer (known as surface conductivity K^s) contributes an effective particle conductivity, which, for a spherical particle is given by $K_p = K^s/2a$ (Delgado, 2002; Lyklema, 1995). When the frequency of the field is higher than ω_{MWO} , the polarization cannot take place, the dipole coefficient is reduced, and the mobility rises. In short, the dynamic mobility is the AC equivalent to DC electrophoretic mobility, but it provides much more information than a single value as the latter quantity is.

In the interest of this work, it is convenient to consider the relationship between the dynamic mobility measured for a mixture of two kinds of particles (dynamic mobility and volume fraction of each of them given by $u_{d,i}$, ϕ_i ($i = 1, 2$), respectively), and the contributions of the individual species of the mixture. As demonstrated in Jimenez et al. (2007), the ESA signal (as determined by the complex amplitude of the sonic wave, A_{ESA}) measured is the superposition of that of the individual components, weighted by the density contrast between the particle and the medium, $\Delta\rho_i = \rho_i - \rho_m$:

$$A_{ESA} = \sum_{i=1}^2 \phi_i \frac{\Delta\rho_i}{\rho_m} u_{d,i} \quad (6)$$

The electrokinetic characterization was carried out in two phases. As a first approximation, the DC electrophoretic mobility of dilute suspensions was measured in the Zetasizer NanoZS. Then, the dynamic mobility was measured using the AcoustoSizer Ilc ESA apparatus (Colloidal Dynamics, USA). Since the ionic concentration of the suspensions is rather high, background correction of raw data was carried out in all cases, for the correct determination of u_d .

2.2.4. Stability tests

In order to evaluate the stability of the suspensions, a sedimentation test was carried out using a 6705 UV/VIS spectrophotometer (Jenwat, UK). The sedimentation was followed by recording the optical

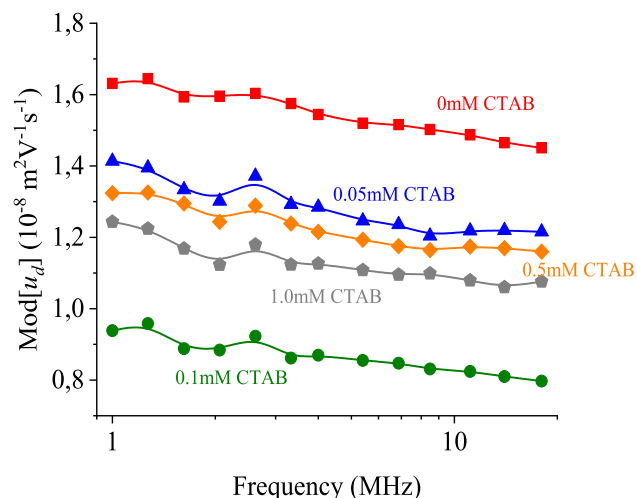


Fig. 2. Experimental data of the modulus of the dynamic mobility as a function of frequency for silica suspensions, in 80 mM CuSO_4 solutions at pH 2, for the indicated CTAB concentrations. The relative standard deviation (not shown for clarity) of each data point ranges between 0.3 and 2.4%.

absorbance as a function of time. The wavelength was set at 470 nm.

3. Results and discussion

3.1. DC electrophoretic mobility

An overview of the electrical surface properties of the particles investigated (silica, kaolinite and their mixtures), can be achieved by observing the effect of CTAB concentration (up to the critical micelle concentration, close to 1 mM) on the electrophoretic mobility u_e of dilute suspensions of the particles, always keeping the hydrometallurgical conditions (80 mM CuSO_4 solutions at pH 2).

Fig. 1 shows the results: note, first of all, that the electrophoretic mobility of silica particles does not show significant changes as the concentration of CTAB increases (Fig. 1). This is in contrast with literature evidences that find that colloidal silica has good affinity for CTAB over a wide pH range (Elias et al., 2016), so that the absolute value of the (negative) mobility decreases with the addition of surfactant. In our case, the reduction of mobility is small and saturates at very low CTAB concentration. The small size of the particles and their hydrophilicity may limit the adsorption of CTAB on silica in our experiments.

On the contrary, the electrophoretic mobility of kaolinite particles undergoes significant changes under the addition of CTAB. Furthermore, a change in the polarity of the particle charge can be appreciated that can be interpreted as a result of overcharging, due to the successful adsorption of surfactant, in agreement with Kamal et al. and Figdore et al. (Kamal et al., 2017; Figdore, 1982), who reported that a low pH condition increases the adsorption capacity. These results allow inferring that low doses of CTAB could suffice to neutralize the charge of kaolinite and force its aggregation in the hydrometallurgical crud. Regarding the silica-kaolinite mixtures, they have intermediate values of mobility, more shifted towards those of kaolinite, probably due to its predominant contribution to the light scattering of the mixture. It is difficult to deduce from this data whether CTAB is adsorbed preferentially on any of the particle types, and hence whether the surfactant alters possible interactions between particles. This will be explored in the following sections.

3.2. Dynamic electrophoretic mobility of individual particles

Electroacoustic measurements of 2.5% silica suspensions in 80 mM CuSO_4 and pH 2, as a function of the CTAB concentration are plotted in

Table 1

Zeta potential (ζ) of silica particles in 80 mM CuSO₄ and pH 2, as obtained from DC electrophoresis and from electroacoustic measurements.

[CTAB], mM	ζ (mV) (DC electrophoresis)	ζ (mV) (ESA)
0.00	-18.4 ± 0.4	-20.0 ± 0.5
0.05	-10.9 ± 0.2	-14.0 ± 0.5
0.10	-11.2 ± 0.4	-13.5 ± 0.5
0.50	-10.8 ± 0.3	-12.0 ± 0.5
1.00	-10.9 ± 0.5	-11.5 ± 0.5

Table 2

Zeta potential (ζ) of kaolinite particles in 80 mM CuSO₄ and pH 2, as obtained from DC electrophoresis and from electroacoustic measurements.

[CTAB], mM	ζ (mV) (DC electrophoresis)	ζ (mV) (ESA)
0.00	-10.1 ± 0.2	-13.0 ± 0.2
0.05	+6.2 ± 0.5	+6.3 ± 0.3
0.10	+11.5 ± 0.5	+11.3 ± 0.5
0.50	+6.2 ± 0.3	+6.5 ± 0.5
1.00	+9.9 ± 0.2	+10.1 ± 0.4

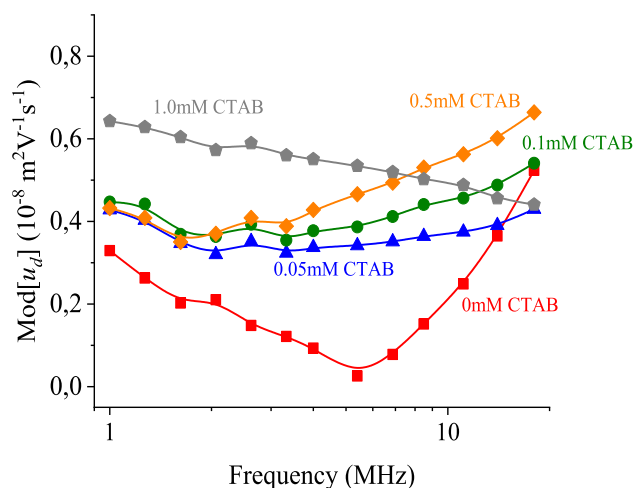


Fig. 3. Experimental data of the modulus of the dynamic mobility as a function of frequency for kaolinite suspensions, in 80 mM CuSO₄ solutions at pH 2, for the indicated CTAB concentrations. The relative standard deviation (not shown for clarity) of each data point ranges between 0.3 and 3%.

Fig. 2. Modelling the particles as spheres, it was possible to use well tested dynamic mobility theories (Ahualli et al., 2006; Ahualli et al., 2006) for fitting the $u_d(\omega)$ spectra (and in fact also the static electrophoretic data of Fig. 1) and obtaining the zeta potentials. The results are detailed in Table 1. The agreement between the two kinds of evaluations is clear and gives reliability to our conclusions, based mostly on dynamic mobility.

Note in Fig. 2 that in the entire surfactant concentration range the mobility decreases monotonically, that is, the MWO elevation is not observed. Two arguments could be offered to explain this fact: on one side, the zeta potential of the particles must be low because of the high ionic strength involved, and hence the MWO relaxation is of little significance. On the other side, it is precisely the low charge that brings about particle aggregation and subsequent increase of the average size. According to Eq. (4), such increase in radius will provoke a lower inertia relaxation frequency. Since the size distribution is likely polydisperse in such case, we can expect that the relaxation will actually expand over a wide band in frequency, manifesting in the modest decline found in the frequency range accessible. Regarding the effect of CTAB addition on the

zeta potential, Table 2 shows that such effect is not very significant, and appears as a small decrease in $|\zeta|$.

Regarding the dynamic mobility of kaolinite, data are presented in Fig. 3. Recall that kaolinite presents a platelet structure with SiO₂ tetrahedral sheets adjacent to octahedral alumina Al(OH)₂ ones by sharing oxygen atoms (Iler, 1973). In addition to isomorphous substitution of Si⁴⁺ by Al³⁺ in the silica layers producing a negative structural charge, silica faces will coexist with alumina surfaces, strongly affecting the aggregation of the kaolinite particles, and their interaction with ions or other species in the medium (Gupta and Miller, 2010; Gupta et al., 2011; Valenzuela-Elgueta et al., 2019; Hu et al., 2003). This structural condition promotes the adsorption of the positive surfactant on the negative silica faces, and therefore the modification of the charge density. In fact, the modulus of the mobility can be fitted by using increasingly more positive values of zeta potential upon the addition of CTAB, according to the classical electrophoresis results (Fig. 1).

Considering now the trends in Fig. 3, one can observe that, without the addition of surfactant, the suspension shows a mobility rise coherent with an MWO relaxation. This occurs whether the charge of the particles is positive or negative, but it is more pronounced before the addition of CTAB, indicating a more highly charged surface. We confirm that the presence of the cationic surfactant reduces the charge by progressive neutralization of its originally negative values (see Fig. 1 and Table 2). Only for high CTAB concentration can we observe a reappearance of the MWO rise, associated in this case to positive electrokinetic charge density. Note, however, that this tendency is not observed at the maximum tested concentration of CTAB, 1 mM, in this case, the inertial effect associated with the generation of large aggregates is observed. Recall that the mobility spectrum strongly depends on the size of particles in such a way that above the inertial frequency, given by Eq. (4), the particles cannot follow the applied electric field and the mobility tends to zero. The larger the charged entities, the lower the inertial frequency is. The behaviour shown is compatible with a significant particle-particle aggregation leading to a very reduced inertial relaxation frequency. As a consequence, such relaxation dominates the spectrum, as a signal of aggregates presence. Overall, the results obtained with DC electrophoresis and dynamic mobility are again coherent, in terms of the values of the zeta potentials obtained from both sets of data, as shown in Table 2. We can confirm that the addition of surfactant has a greater effect on kaolinite than in silica particles, and that a change of particle size is produced when the surfactant is added to kaolinite,

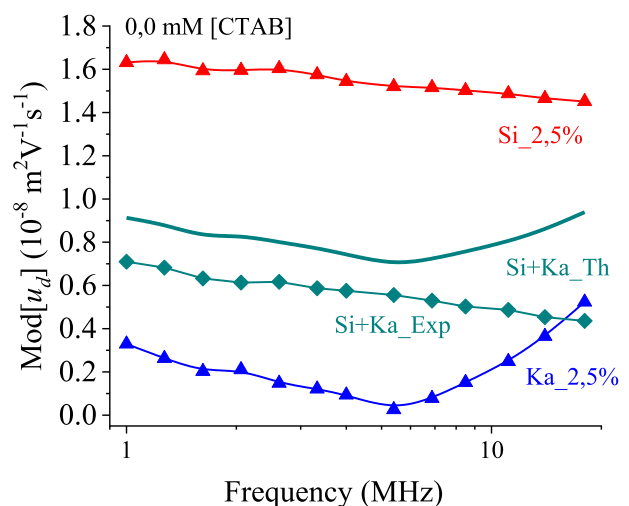


Fig. 4. Frequency dependence of the modulus of the dynamic mobility of suspensions containing 2.5% silica (Si_{2,5%}), 2.5% kaolinite (Ka_{2,5%}), and their mixture (Si + Ka_Exp), including the theoretical predictions of Eq. (6) (Si + Ka_Th). The relative standard deviation (not shown for clarity) of each data point ranges between 0.1 and 2.2%.

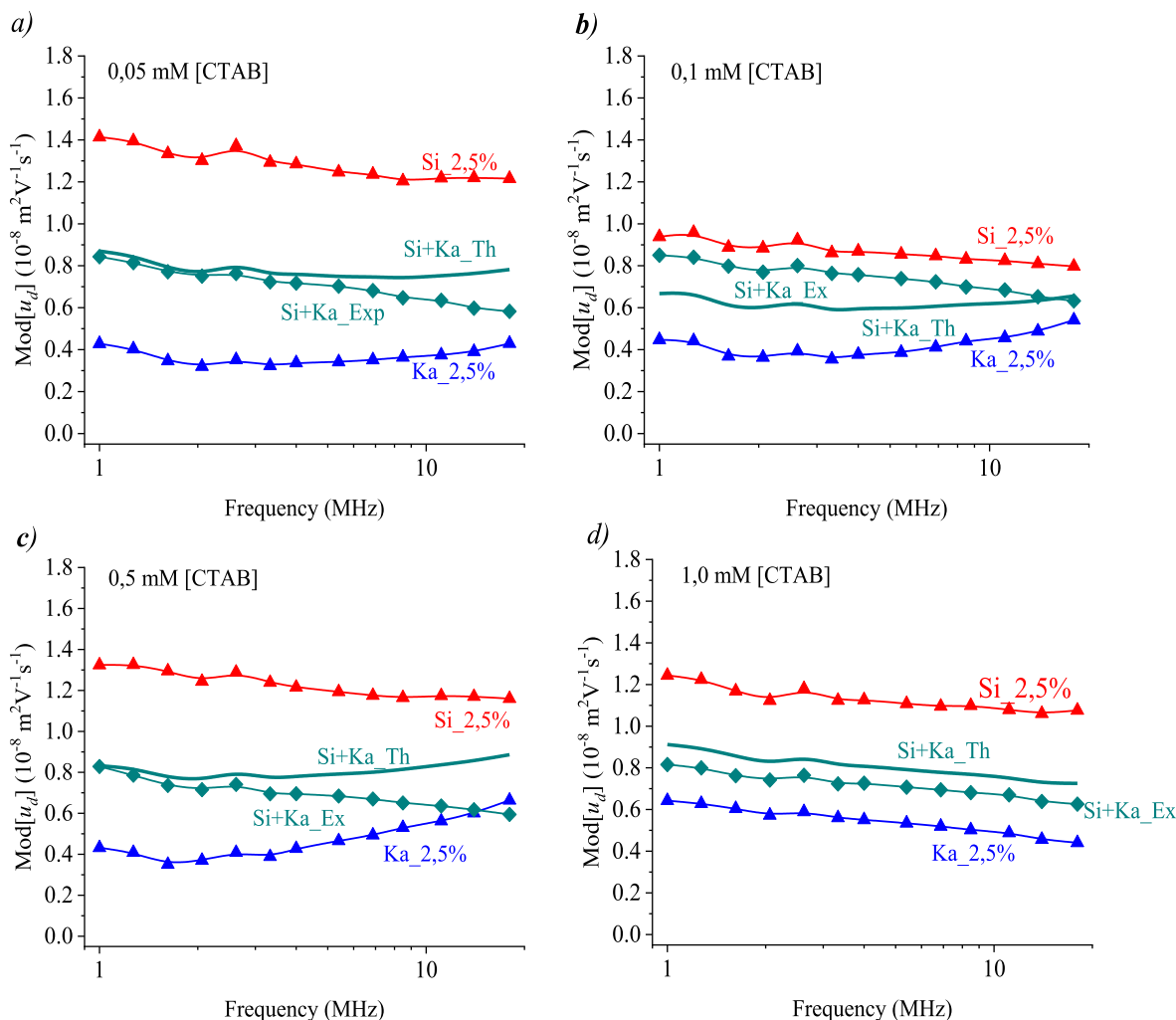


Fig. 5. Frequency dependence of the modulus of the dynamic mobility of suspensions containing 2.5% silica (Si 2,5%), 2.5% kaolinite (Ka 2,5%), and their mixture (Si + Ka_Ex), including the theoretical predictions of Eq. (6) (Si + Ka_Th), for different CTAB concentrations, as indicated. The relative standard deviation (not shown for clarity) of each data point ranges between 0.2 and 3%.

demonstrating the ease of adsorption of CTAB on the silica-type faces in this clay. This behavior is promoted by the structural characteristics of the kaolinite particles, which have a complex distribution of charge density resulting in the formation of multiple structures under certain conditions (Kumar et al., 2016; Preocanin et al., 2016).

3.3. Dynamic mobility of Silica/Kaolinite mixtures

Studies of suspensions combining different types of particles are well justified in hydrometallurgical process. We intend to find information as to whether the effect of CTAB addition will be just the combination of the effects on each kind of particles invidually considered, or if the surfactant will have an effect on particle mixed structures beyond linear superposition. To that aim, we will consider in this section the dynamic mobility of the mixed samples containing the two mineral species in the suspension at the same weight fraction as in the separate studies carried out till this point, that is, 2.5% of each colloid, or 5% total solids content. The conditions of solution are the same as above mentioned: 80 mM solutions of CuSO₄ and pH 2. The dynamic mobility of suspensions of silica and kaolinite with no CTAB added is shown in Fig. 4. The results show that the mobility is close to the superposition model predictions, at least at low frequencies. At high frequency, the mobility is found to decrease with frequency, thus differing from the calculated weighted average, which shows an increase associated to the MWO process. This

suggests that aggregation between the positive surfaces of kaolinite and negative silica particles is taking place, a feature not considered of course in our model. The aggregation will reinforce the role of the inertial decrease over the MWO rise.

We now wonder to what extent these processes are influenced by the addition of CTAB. Fig. 5 shows the dynamic mobility results obtained for mixed suspensions for CTAB concentrations between 0.05 and 1 mM. It is possible to observe that the divergence above mentioned between predictions and data at high frequencies is reproduced when CTAB is added, and also that, as the surfactant addition increases, the model prediction is mainly influenced by the dynamic mobility of the kaolinite. However, for 0.1 mM CTAB the spectrum of the mixture is closer to that of silica suggesting a significant coating of silica on alumina, which can be explained by silica being more negative and kaolinite more positive (Tables 1 and 2) for such concentration. The latter effect is attributable to the stronger changes of the charge that the surface of this mineral suffers. In previous works, it was found that at low pH siloxane chains can undergo selective adsorption onto the kaolinite edges (Valenzuela-Elgueta et al., 2019), since attractions between silica and alumina faces are dominant (Gupta et al., 2011), and hence mostly edge surfaces are exposed to the silica nanoparticles. This kind of interaction cannot be predicted by the model and therefore a separation between predictions and experimental results can be appreciated. When the concentration of CTAB is increased, the charge difference between kaolinite faces and

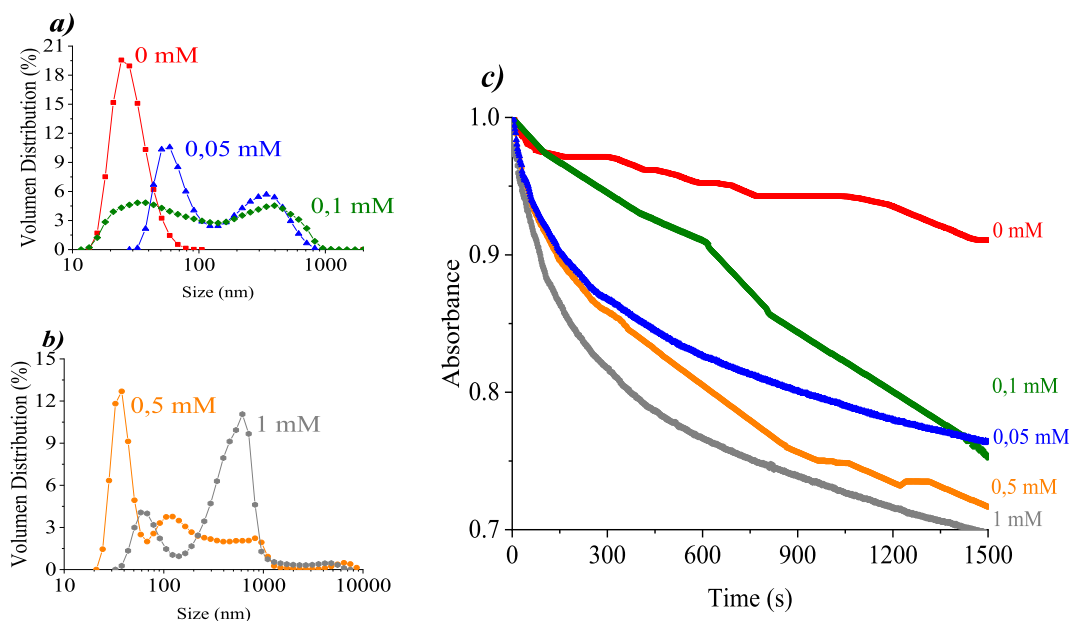


Fig. 6. Effect of surfactant addition on the size distribution and absorbance kinetics for 2.5% silica suspensions. a) Size distribution for 0, 0.05 and 0.1 mM CTAB; b) size distribution for 0.5 and 1 mM of CTAB; c) Sedimentation tests (optical absorbance as a function of time) for the indicated CTAB concentrations.

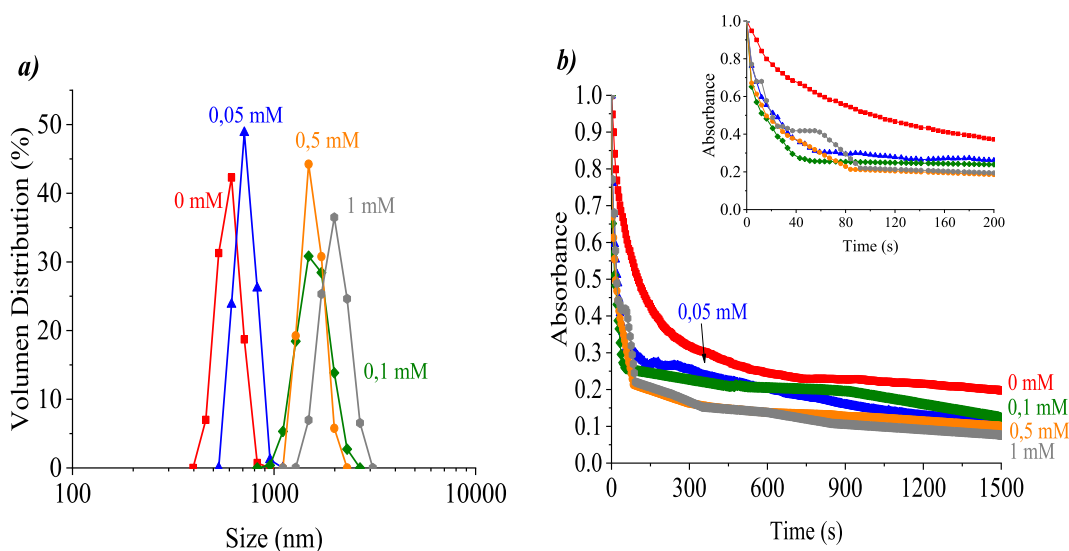


Fig. 7. Same as Fig. 6, but for kaolinite suspensions. a) Size distribution, and b) sedimentation tests (optical absorbance as a function of time) for the indicated CTAB concentrations. Inset in b): first 200 s of sedimentation.

edges is less significant, and the phenomenon cannot proceed, so that kaolinite is again dominant, and the averaging procedure of the model is closely followed, including the fact that the experimental values of dynamic mobility decay with frequency, indicating formation of large aggregates.

3.4. Size distribution and stability tests

In order to assess the effects of surfactant addition to the stability of suspensions of pure silica and kaolinite and their mixtures, changes in particle size distribution and sedimentation rate were measured as a function of the dose of surfactant, applied in hydrometallurgy conditions. Fig. 6a,b shows the CTAB effect on the hydrodynamic diameter distributions of silica suspensions; note how from a purely monomodal system before addition of CTAB, the system shifts to a multimodal condition, with a population around 800 nm in diameter growing when

the concentration of the surfactant is increased. Such a size increment manifests (Fig. 6c) in a clearly faster sedimentation rate, both observations being attributable to the flocculating effect of the surfactant (Ottewill, 1968).

Fig. 7 shows that the behavior of kaolinite suspensions is very similar, although in this system the populations remain monomodal as the average diameter increases upon CTAB addition. The combination of the cationic nature of the CTAB, low pH and high ionic concentration explain the significant increase in average size (Liu et al., 2018; Ucbeyiy Sahinkaya and Ozkan, 2011). The low surface area of the kaolinite (15 m²/g), is the cause of the immediate effect of the low doses of CTAB on the electrokinetic charge density, and the subsequent aggregation.

The stability data corresponding to the mixed suspensions are plotted in Fig. 8a (size distribution) and 8b (time variation of absorbance).

The results obtained for kaolinite alone in Fig. 7 are magnified by the

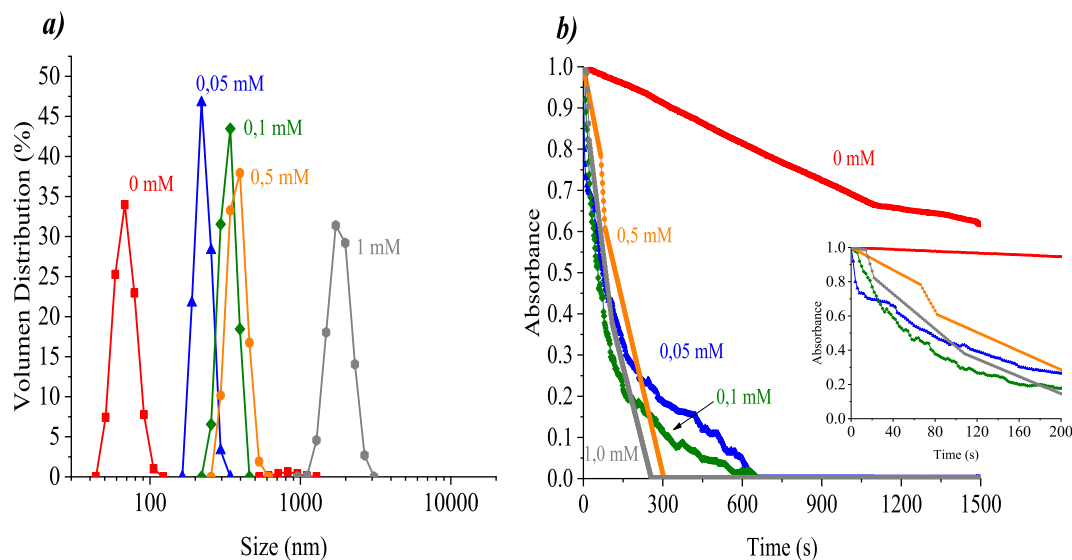


Fig. 8. Same as Fig. 7, but for mixed suspensions containing 2.5% silica and 2.5% kaolinite.

addition of silica nanoparticles: the population of particles at the highest CTAB concentration is centered in a larger diameter when silica is added. The sedimentation rate is also much faster in mixed systems, which undergo practically full sedimentation in less than five minutes, something not found in the individual components (Figs. 6, 7). It is suggested that in the presence of increasing CTAB concentrations the adsorption of silica on kaolinite is favored, as above mentioned, and this provokes the formation of structures at the experimental conditions (low pH and high ionic strength), which have been previously studied by several authors. The structure formation was ascribed to the generation of siloxane complexes, acting as a kind of binder between the larger particles, thus enhancing the flocculating effect of the surfactant.

It is very important to emphasize that the results of the sedimentation experiments complement each other and at the same time confirm the results of dynamic mobility. Both Fig. 2 and Fig. 3 show the effect of the surfactant on the mobility spectrum of the individual particles, and it is observed that, although the zeta potential that best fits these data does not change substantially (Tables 1 and 2), the dynamic mobility curves are altered with the addition of CTAB. The key of the electroacoustic technique is that the behavior of mobility with frequency is also sensitive to size and therefore to the possible formation of aggregates. The same arguments can be applied to the bimodal suspensions, Fig. 5, explaining a faster sedimentation than the individual particles.

3.5. Microscopic observations

In order to obtain an empirical proof of the hypothesized structures, a morphological analysis of the samples was performed by Scanning Electron Microscope observations. Fig. 9 shows the SEM images obtained for the various concentrations of surfactant used.

The picture corresponding to 0 mM CTAB shows that silica nanoparticles have an apparent preference for adhering primarily to kaolinite edges, as described in our previous work (Kamal et al., 2017). By adding the CTAB surfactant, the silica and kaolinite form aggregates between themselves and also it is possible to observe silica aggregates to adhere onto the kaolinite surface in a heterogeneous form. It can be noted that, by increasing the surfactant concentration, the aggregation becomes massive, forming more complex structures. These results are consistent with what was observed in the evolution of the particle size distribution and with the behavior shown in the stability tests.

4. Conclusions

The effects of surfactant adsorption in systems with different kinds of particles (silica, kaolinite and their mixtures) have been studied. According to the results obtained for 2.5% silica particles in 80 mM CuSO_4 and pH 2 suspensions, the surfactant addition scarcely modifies the dynamic mobility and zeta potential. However, a flocculating effect is observed by measuring particle size and sedimentation rate, more pronounced, the higher surfactant concentration. This phenomenon is attributable to the flocculating effect associated with low surfactant concentrations under the operation conditions.

The dynamic mobility of kaolinite suspensions has been investigated in the same conditions, and in this case a change was produced in the polarity of the particle charge when CTAB concentration is increased. Even more, the mobility rise corresponding to a Maxwell-Wagner-O'Konski relaxation changes with the electrokinetic charge density, and at the highest CTAB concentration the inertial relaxation suggests an increment of particle size. This result is coherent with the average particle size determinations and, consequently, with the increase in sedimentation rate.

Finally, the behavior of silica/kaolinite mixtures has been studied under surfactant addition. The differences at high frequency between model predictions (calculated as the weighted average of the two kinds of particles) and experimental results show that aggregation between kaolinite and silica particles is taking place. This conclusion is ascertained by size distribution spectra and sedimentation rate. Also, SEM images reveal the evolution of the aggregates forming increasingly complex structures as CTAB is added.

CRediT authorship contribution statement

J. Valenzuela-Elgueta: Methodology, Software, Validation, Writing - original draft. **A.V. Delgado:** Conceptualization, Investigation, Writing - review & editing, Funding acquisition. **S. Ahualli:** Conceptualization, Investigation, Software, Visualization, Writing - review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

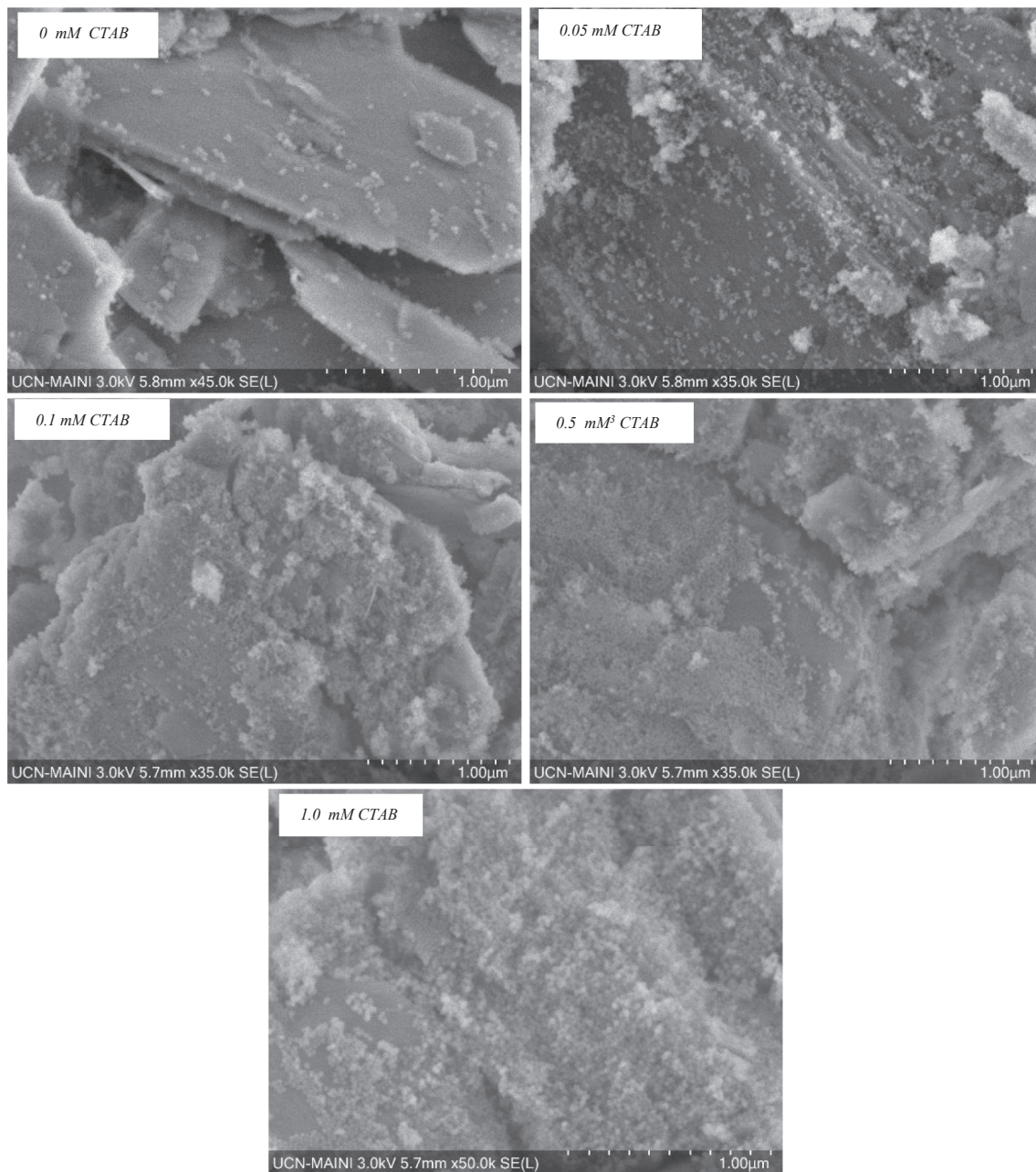


Fig. 9. SEM images for the applied surfactant concentration range.

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