XVI International Mineral Processing and Recycling Conference
28-30 May 2025, Belgrade, Serbia

DOI: 10.5937/IMPRC25422V Original research article

INFLUENCE OF CATIONIC SURFACTANTS ON THE ELECTROKINETIC PROPERTIES AND STABILITY OF SILICA-KAOLINITE SUSPENSIONS UNDER COPPER HYDROMETALLURGY CONDITIONS

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ABSTRACT – Small particles, such as silica and clays, complicate hydrometallurgy by forming crud that floats or remains suspended. Adding surfactants may promote sedimentation, but requires evaluating their composition and dosage. This study uses dynamic electrophoretic mobility to assess CTAB adsorption on silica/kaolinite mixtures under low pH, high ionic strength, and particle concentrations above 3%. Electroacoustic analysis predicts surfactant effects on individual and mixed particles, aligning with sedimentation rates and size measurements. SEM images confirm aggregate formation with CTAB. Identifying optimal surfactant doses to flocculate and separate particles addresses operational issues caused by crud in hydrometallurgy processes.

Keywords: Clay, Copper mining, Electroacoustics, Surfactants, Stability.

INTRODUCTION

A major challenge in oxidized copper ore beneficiation is the formation of mineral complexes due to particle interactions in the solid matrix, carried by the leaching solution to solvent extraction. These interactions, driven by low pH and high ionic concentration, lead to aggregation and crud formation—a dispersed particle layer complicating separation processes [1, 2].

A solution involves using low-concentration cationic surfactants to modify particle stability. Surfactants adsorb onto particles, neutralizing electrokinetic charge, promoting flocculation, and destabilizing particles via hydrophobic attraction. They outperform inorganic ions by achieving these effects at lower concentrations, with longer chains enabling bridging flocculation. Polymers like polyethylene oxide and polyacrylamide-acrylate also effectively control slurry stability, evaluated through particle size and zeta potential measurements. Electroacoustic techniques provide simultaneous insights into particle size and electrokinetic properties.

Interfacial properties are crucial in processes like froth flotation, where mineral-solution interface charges determine efficiency. Electroacoustic methods and adsorption measurements effectively study these interactions. This study applies the Electrokinetic

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Sonic Amplitude (ESA) technique to assess CTAB adsorption on silica/kaolinite mixtures under hydrometallurgical conditions of low pH, high ionic strength, and high particle concentrations—key factors in crud formation.

By evaluating CTAB adsorption, the study offers strategies to control particle aggregation, mitigating crud formation and improving mineral extraction and separation efficiency.

EXPERIMENTAL

Materials

To replicate conditions in copper hydrometallurgy, the colloidal suspensions consist of silica and kaolinite particles dispersed in 80 mM copper sulfate solution at pH 2. Materials (Merck & Co., USA) included Ludox TMA silica, natural kaolinite, $CuSO_4 \cdot 5H_2O$, sulfuric acid (95–98% purity), and the cationic surfactant CTAB. Surface areas of kaolinite (15 m^2/g) and silica (63.2 m^2/g) were determined using N_2 adsorption at 77 K with BET analysis (Nova 2200e, Quantachrome Instruments). Solutions were prepared with Milli-Q deionized water. The colloidal suspensions studied were as follows:

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/silica at the same volume fraction, 80 mM $CuSO_4$ at pH 2.

Methods

Particle size

The hydrodynamic radius of the particles was determined by dy namic 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).

Microscopic observations

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

Electrokinetic measurements

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

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

RESULTS AND DISCUSSION

Electrophoretic mobility

The electrical surface properties of silica, kaolinite, and their mixtures were analyzed by observing the effect of CTAB concentration (up to 1 mM, near the critical micelle concentration) on the electrophoretic mobility (u_e) of particle suspensions under hydrometallurgical conditions (80 mM $CuSO_4$, pH 2).

Fig. 1 shows that silica's mobility remains largely unchanged as CTAB increases, contrasting with studies indicating strong CTAB affinity for silica at various pH levels [3]. The minimal mobility reduction, saturating at low CTAB concentrations, may result from the small particle size and high hydrophilicity limiting CTAB adsorption.

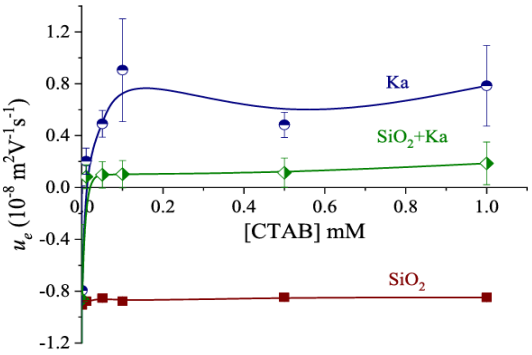

Figure 1 Electrophoretic mobility (u_e) as a function of CTAB concentration for suspensions of silica (SiO_2), kaolinite (Ka) and a 1:1 mixture (SiO_2 +Ka), in 80 mM $CuSO_4$ solutions at pH 2. Error bars correspond to ±SD (n =12)

Conversely, kaolinite exhibits significant mobility changes with CTAB addition, including a charge polarity reversal due to overcharging from effective surfactant adsorption. This aligns with reports [4, 5] that low pH enhances adsorption, suggesting low CTAB doses can neutralize kaolinite charge and promote aggregation in crud.

For silica-kaolinite mixtures, mobility values lie between those of individual particles, skewed toward kaolinite, likely due to its dominant light scattering contribution. It remains unclear if CTAB preferentially adsorbs on specific particles or alters their interactions, an aspect explored in subsequent sections.

Dynamic electrophoretic mobility of individual particles

Electroacoustic measurements of 2.5% silica suspensions in 80 mM $CuSO_4$ (pH 2) were analyzed using dynamic mobility theories to determine zeta potentials (Table 1). The results align with static electrophoretic data, confirming reliability. Mobility decreases monotonically with CTAB, likely due to low zeta potential from high ionic strength and particle aggregation, which increases size and lowers relaxation frequency.

Table 1 Zeta potential (ζ) of silica particles in 80 mM $CuSO_4$ and pH 2, as obtained from DC electrophoresis and from electroacoustic measurements

[CTAB], mM	ζ mV (DC electrophoretic)	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

CTAB has minimal impact on silica's zeta potential (Table 2), causing only slight decreases in |ζ|. In contrast, kaolinite shows a stronger response due to its silica and alumina layers. CTAB adsorption on negatively charged silica faces increases zeta potential and alters charge density. Fig. 3 shows kaolinite mobility rising without CTAB due to MWO relaxation, indicating highly charged surfaces. CTAB addition neutralizes the negative charge, with high concentrations reversing polarity. At 1 mM CTAB, aggregation dominates, reducing relaxation frequency and mobility.

Table 2 Zeta potential (ζ) of kaolinite particles in 80 mM $CuSO_4$ and pH 2, as obtained from DC electrophoresis and from electroacoustic measurements

[CTAB], mM	ζ mV (DC electrophoretic)	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	+10.2 ± 0.4

Kaolinite's structure promotes CTAB adsorption on its silica faces, enhancing aggregation and altering size distribution, as shown by zeta potential (Table 2) and dynamic mobility data. In contrast, silica's high hydrophilicity and small size limit surfactant interaction. Overall, CTAB significantly affects kaolinite, proving effective for modifying clay particle behavior in suspension.

Dynamic mobility of Silica/Kaolinite mixtures

Adding CTAB (Fig. 2) shifts mobility toward kaolinite's behavior as CTAB concentration increases. At 0.1 mM CTAB, mobility resembles silica's, suggesting significant silica coating on alumina, driven by silica's higher negative charge and selective siloxane adsorption on kaolinite edges at low pH. These silica-kaolinite interactions, not captured in the model, explain deviations between predictions and observations.

Higher CTAB concentrations reduce charge differences between kaolinite faces and edges, halting silica-kaolinite interactions. Kaolinite dominates again, with mobility decreasing at high frequencies, indicating large aggregate formation.

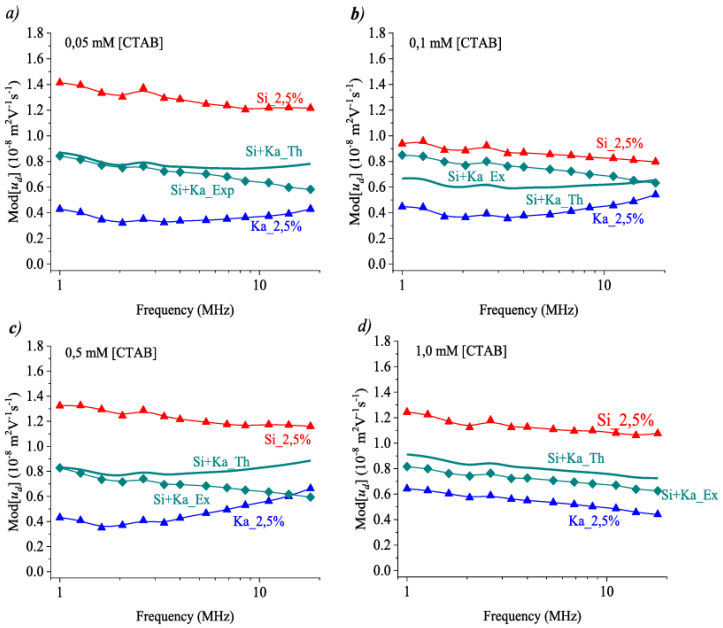

Figure 2 Frequency dependence of the modulus of the dynamic mobility of suspensions containing 2.5% silica (Si_2,5%), 2.5% kaolinite (Ka_2,5%), and their mixture (Si + Ka_Ex), including the theoretical predictions

Size distribution and stability test

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. The stability data corresponding to the mixed suspensions are plotted in Fig. 3a (size distribution) and 3b (time variation of absorbance).

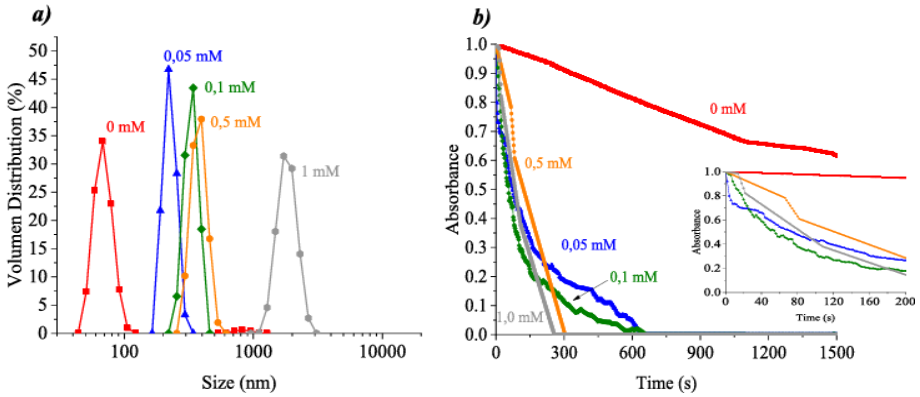

Figure 3 Same as Fig. 7, but for mixed suspensions containing 2.5% silica and 2.5% kaolinite

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. 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.

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 [5].

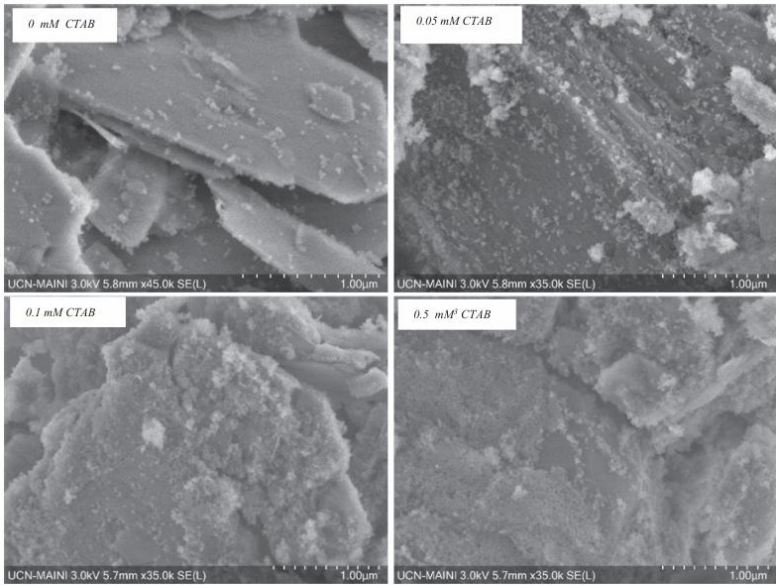

Figure 4 SEM images for the applied surfactant concentration range

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.

CONCLUSIONS

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.

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