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Dispersion of Cu_2O particles in aqueous suspensions containing 4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt

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Abstract

Effect of 4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt's addition upon Cu_2O dispersion properties is studied to clarify dispersant's role in colloidal properties change and its underlying stabilization mechanism, and to quantify processing conditions for the oxide. Dispersing effectiveness was studied through adsorption, rheological and electrophoretic measurements, using as-received and surface charge modified Cu_2O particles. Maximum solid loading attained without dispersant was 73 wt.% (31 vol.%), with corresponding viscosity of 152.5 ± 7.3 Pa s. Addition of dispersant resulted in viscosity between 21.0 Pa s and 5.4 Pa s. No isoelectric point was found for as-received particles' suspensions nor for dispersed suspensions, with particles presenting negative surface charge in all studied pH range, from pH 4 to 10. Adsorption of the organic molecule caused an absolute downshift of 8–25 mV of the electrophoresis curve. Dispersant/Cu_2O interaction was assessed through FTIR analysis. Attained results suggest that, at the natural suspensions pH, dispersant-modified Cu_2O suspensions are stabilized through inner-sphere complexation mechanism, resulting in high dispersion ability.

Keywords: A. Suspensions; D. Transition metal oxides

1. Introduction

Cu_2O has been attracting growing attention over the past years, given its potential use in applications such as catalysis, high-temperature superconductors, antiwear systems and photovoltaic devices [1–5]. Nevertheless, and although several methods for Cu_2O synthesis involve particles' distribution in a liquid host, no work has been carried out regarding Cu_2O dispersion and stabilization properties in fluids, namely in water.

Knowledge and understanding on the dispersion behaviour of cuprous oxide was found necessary by the authors to develop a new fabrication process for aluminium-matrix ceramic reinforced composites which uses ceramic bodies with tailored amounts of alumina and copper oxides (CuO or Cu_2O). In this process, alumina/copper oxide preforms are produced and infiltrated with liquid aluminium. Liquid aluminium reacts with copper oxide giving rise to alumina and copper aluminium oxides and an aluminium–copper alloy (the metallic matrix phase) [6]. Aqueous slip casting was one of the routes used to obtain $Al_2O_3 + Cu_2O$ mixtures' preforms; hence deeper knowledge on the stabilization mechanism and dispersion properties of the individual oxides was thought important. Of course, aluminium oxide dispersion ability in aqueous medium has already been thoroughly studied by several authors using a vast number of dispersants. In as much, the present work aims to contribute to the knowledge of Cu_2O stabilization parameters in aqueous media via colloidal processing route and the effect of dispersant's addition upon Cu_2O dispersion properties is studied in order to clarify its role and the underlying stabilization mechanism, and to quantify processing conditions for the oxide.

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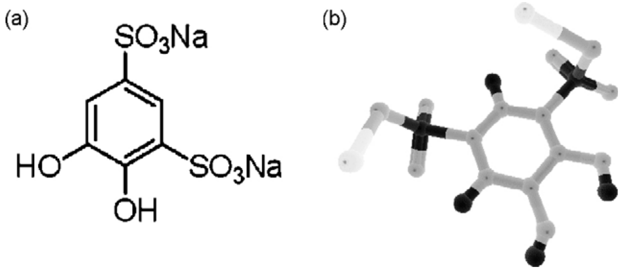

Fig. 1. Tiron's (a) structural formula and (b) 3D view.

As thoroughly known, the stability of any ceramic dispersion depends on the sign and magnitude of the forces acting between the particles suspended in the medium [7]. In aqueous media, the attractive forces hindering dispersion are van der Waals forces, attraction between hydrophobic surfaces and attraction due to electrostatic connection effects between different sign charged particles. Full dispersion can be attained by adding an appropriate dispersant type and amount to the system, so that repulsive interactions are developed to oppose those attractive forces [8,9]. In this work, the chosen surface active agent is 4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt ($C_6H_4O_8S_2Na_2$), commercially known as Tiron (Fig. 1), a surfactant recognized as an extremely effective anionic dispersant in aqueous media for oxides such as Al_2O_3 [10,11], TiO_2 [12,13] and ZrO_2 [12]. Tiron is a low molecular weight weak tetraprotic acid, corresponding to two hydroxyl and two sulfonic groups attached to a benzene ring. The sulfonic acid sites easily give up their protons, resulting in very low $\mathrm{p}K_{\mathrm{a}_1}$ and $\mathrm{p}K_{\mathrm{a}_2}$ values, usually not reported [14]; pK values associated to the hydroxyl acid sites are $\mathrm{p}K_{\mathrm{a}_3} = 7.7$ and $\mathrm{p}K_{\mathrm{a}_4} = 12.6$ [15]. It is an efficient complexing agent for several metallic cations, which enhances its adsorption ability onto particles surfaces of the corresponding metal oxides. Stabilization takes place through chemisorption of the molecule alcohol groups at the metallic oxide surface, resulting in a negatively charged complex [12,13,16]. Additionally, the ionisable sulfonate groups lead to negative charge development [13] and Na^+ cations coordinate around the complexes assisting in their stabilization [17]. Hence, powder's surface becomes highly charged and electric double layer repulsion increases, creating a high repulsive potential between the particles and improving their dispersion ability.

2. Experimental

2.1. Materials

Experiments were carried out with commercial cuprous oxide from Riedel (Cu >97%), with measured average particle size (LS 230, Coulter) of 3.5 ± 0.1 μm and measured BET surface area (ASAP 2000, Micromeritics) of 0.90 ± 0.03 m^2/g. Tiron was supplied by Sigma–Aldrich as a powder (impurities less than 1 wt.%, water content 5.4 wt.%) and used as a diluted aqueous solution.

2.2. Powders surface characterisation

Surface coating of Cu_2O powders is common industrial practice to prevent surface oxidation of the stored oxide [18]. Surface characterisation of as-received Cu_2O powders was accomplished through IR spectroscopy (Nicolet 5700 IR, Thermo) with DRIFTS accessory. KBr powder (>99%, FT-IR grade) from Sigma–Aldrich was used as reference material. Cu_2O powder samples over KBr powder were scanned from 4000 cm^{-1} to 400 cm^{-1}, at room temperature. Each collected spectrum was an average of 128 scans. The same procedure was used for dispersant-modified Cu_2O powders surface characterisation.

2.3. Preparation of suspensions

Aqueous suspensions of as-received Cu_2O powders in distilled water were prepared for determination of maximum solid loading without addition of dispersant. In the absence of dispersant, the powders showed strong hydrophobic character, forming dry powder clusters not wetted by water, doubtfully as a result of the applied protective surface coating. Since wetting of the suspending particles by the liquid medium is essential for efficient particles' dispersion [19], removal of surface coating is mandatory. Industrially, this is accomplished through ethanol washing or through dispersant addition, the latter being the procedure implemented in this work. Hence, the effect of Tiron concentrations of approximately 0.1 wt.%, 0.3 wt.%, 0.5 wt.% and 0.7 wt.% (based on dry oxide powder weight) was tested. The dispersant was first mixed with distilled water and powder was added during ultrasonic stirring, which continued for another 5 min, in order to break down particle agglomerates. For chemical equilibrium to be attained, suspensions were stabilized overnight through magnetic stirring. The same procedure was used to prepare reference suspensions with no added dispersant.

2.4. Adsorption studies

The amount of 4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt not adsorbed at oxide particles' surface was determined through UV–visible spectrophotometry (Lambda 6, PerkinElmer), using a quartz cell and D_2 lamp. Calibration curves were built for dispersant solutions in KCl 10^{-1} M, relating the concentration of Tiron in solution with the maximum intensity peak absorbance value. Since the position and intensity of the characteristic adsorption peak for Tiron is pH dependent [20], the pH value of all solutions was adjusted to 4 with HCl 10^{-1} M, guarantying that surface active OH groups are completely associated. The characteristic peak thus determined showed up at 291 ± 0 nm.

Suspensions for adsorption studies were prepared, as described in Section 2.3, in KCl 10^{-1} M (used for setting ionic strength), with 6.3 ± 0.1 wt.% (1.1 ± 0.0 vol.%) solids. A low solid loading was preferred in order to ensure a straightforward flow of the suspensions. Suspensions were then centrifuged at 14,000 rpm for 2 h (Biofuge Stratus, Heraeus) and filtered. The supernatant solutions were adjusted to pH 4 and analyzed at 291 nm. The supernatant of the suspension with no added 4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt was used as baseline. Whenever necessary, solutions where diluted to known concentrations in order to obtain intensity values in the Beer–Lambert linear domain. Comparison of the absorbance value for each supernatant with the calibration curve allowed quantification of the amount of dispersant not adsorbed at the particles surface. Adsorption was then calculated from the difference between the amount of dispersant initially added and that remaining in the supernatant.

Sediments resulting from centrifugation were thoroughly washed with distilled water, dried at 80 °C for 12 h and submitted to DRIFTS, for characterisation of adsorbed-dispersant/Cu_2O interaction mechanism.

2.5. Rheological characterisation

Steady shear rheological measurements upon suspensions with as-determined maximum Cu_2O solid loading and 0–0.7 wt.% Tiron were carried out with a stress controlled rotational rheometer (CSL 500, Carrimed) with cone-and-plate configuration. All measurements took place between 0.1 s^{-1} and 1000 s^{-1}, at 20 °C. In order to convey the same rheological history to all samples, a pre-shear was applied for 1 min at the highest shear rate, prior to each measurement, followed by an equilibrium time of 1 min. The optimal amount of dispersant was attained by determining the concentration which rendered suspensions with minimum viscosity (deflocculation curves), under a fixed shear rate of 50 s^{-1}.

2.6. Electrophoretic characterisation

Colloidal suspensions containing approximately 5 wt.% (0.9 vol.%) solids were prepared by dispersion of as-received and Tiron-treated Cu_2O particles in KCl 10^{-3} M aqueous solution, followed by overnight hydration. XRD analysis showed that no new crystalline phases were formed on hydration. Dispersant's concentration tested corresponded to the minimum on the deflocculation curve. Zeta potential of diluted samples was measured (Coulter Delsa 440SX) as a function of pH, at 25 ± 0.2 °C. HCl 10^{-2} M or KOH 10^{-2} M was used for pH adjustment.

3. Results and discussion

3.1. As-received powders surface characterisation

Surface coating identification of as-received Cu_2O powders was assessed through DRIFTS (Fig. 2). Corresponding peak assignment is rendered in Table 1. The broad bands above 3000 cm^{-1} relate to the presence of adsorbed water. Bands at 1130 cm^{-1}, 796 cm^{-1} and 634 cm^{-1} were assigned to Cu_2O, in good agreement with other authors [21–23]. The remaining bands were credited to surface coating: the presence of CH_3 and CH_2 bands (approximately 1:1 intensities), together with the absence of CH_2 rocking, point towards a polymeric backbone of alternating CH_2 and CH groups, with each repeating unit containing a pendant CH_3 group, in good agreement with the polypropylene molecule or similar [24].

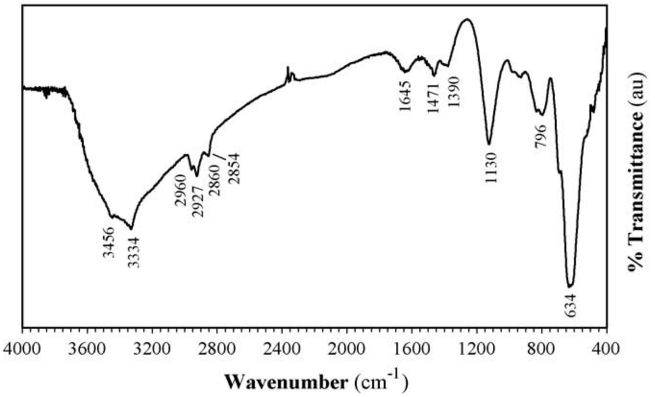

Fig. 2. DRIFTS spectra for as-received Cu_2O powders.

Table 1
As-received Cu_2O DRIFTS spectra band assignment.

Band position (cm^{-1})	Band assignment
>3000	O–H stretch (water)
2956	C–H asymmetric stretch (CH_3)
2926	C–H asymmetric stretch (CH_2)
2868	C–H symmetric stretch (CH_3)
2854	C–H symmetric stretch (CH_2)
1645	O–H scissors (water)
1464	C–H scissors (CH_2) C–H asymmetric bend (CH_3)
1379	C–H umbrella mode (CH_3)
1130	Cu(I)–O (Cu_2O)
796	Cu(I)–O (Cu_2O)
634	Cu(I)–O (Cu_2O)

3.2. Adsorption characterisation

Attained maximum solid loading was approximately 73 wt.% (31 vol.%), with a corresponding pH value of 7.35. The distilled water used in preparing the suspensions presented a pH value of 5.86 ± 0.07. This variation suggests that the organic coating upon the oxide surface is discontinuous, allowing interaction between the oxide surface and water molecules and hydration of OH surface groups.

Both as-received and Tiron surface modified Cu_2O suspensions presented shear-thinning rheological behaviour. Shear-thinning is characteristic of suspensions with solids volume fractions typically bellow 50 vol.% [19], and corresponds to a gradual rupture of the flocs' network formed by the particles. With increasing shear stress the liquid entrapped inside the flocs is released and a more ordered structure forms in the flow direction, resulting in a decrease of viscosity [25]. Flow curves for each suspension were adjusted with the Sisko model [25] to establish viscosity values, and dispersant concentrations resulting in minimum viscosity were used in building the deflocculation curve (Fig. 3). As-received Cu_2O suspensions presented viscosity values of 152.5 ± 7.3 Pa s.

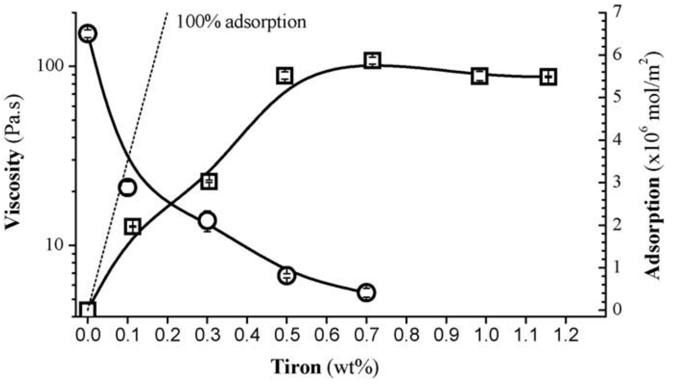

Fig. 3. Deflocculation curve, under a fixed shear rate of 50 s^{-1} (○). Adsorption curve (□): adsorbed Tiron vs. Tiron's initial concentration in suspensions; dashed line refers to theoretical 100% Tiron adsorption.

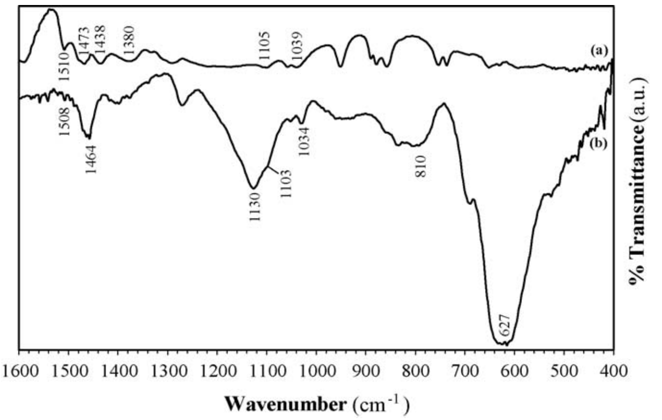

Fig. 4. DRIFTS spectra between 1600 cm^{-1} and 400 $cm^{-1}$for (a) Tiron and (b) Tiron-modified Cu_2O.

Addition of dispersant in all concentrations tested decreased the viscosity value, the minimum being attained for 0.7 wt.% Tiron (5.4 Pa s). This dramatic viscosity decrease indicates that the organic surface coating is overcome, allowing Tiron's adsorption at the powders surface and accomplishment of its role as a dispersant.

The superimposed curve in Fig. 3 refers to Tiron's adsorption behaviour upon Cu_2O particles surface sites as determined by UV–vis (additional suspensions with 1.0 wt.% and 1.2 wt.% Tiron were prepared). For 0.1 wt.% added Tiron, roughly 50% of the added dispersant molecules are adsorbed, corresponding to an adsorbed amount of 1.9×10^{-6} mol/m^2. Higher additions lead to increased adsorption, until an adsorption dwell around 5.6×10^{-6} mol/m^2 is attained for 0.5 wt.% added dispersant and beyond, indicating that powder particles' surface is saturated in dispersant. The shape of the curve is typical of Langmuir physisorption isotherms, in which the dwell corresponds to the monolayer capacity. Surface coverage by the dispersant is limited mainly by the size and rigidity of the benzenic ring and mutual repulsions between adsorbed-dispersant molecules [26].

The Tiron–Cu_2O interaction mechanism at the natural suspensions pH was assessed through DRIFTS results from as-received Cu_2O (Fig. 2), as-received Tiron and Tiron-modified Cu_2O analysis. After surface modification with dispersant, the most meaningful differences between spectra appear bellow approximately 1600 cm^{-1} (Fig. 4). Nevertheless, it must be mentioned that above 1600 cm^{-1} the Tiron-modified Cu_2O spectra also shows bands at 2964 cm^{-1}, 2929 $cm^{-1}$and 2868 cm^{-1} assigned, respectively, to the C–H asymmetric stretch (CH_3), C–H asymmetric stretch (CH_2) and C–H symmetric stretch (CH_3) of the polymeric coating. That is, at the most stable suspension Tiron concentration tested, the dispersant amount apparently is not enough to completely remove the protective coating, although it decreases the viscosity of the suspension and allows colloidal processing. Band assignment is displayed in Table 2. Bands appearing at 1510 cm^{-1}, 1473 cm^{-1} and 1438 cm^{-1} in as-received Tiron spectrum were assigned to the C=C benzene ring characteristic vibrations [27–29]. Comparatively, in the Cu_2O + Tiron spectrum, the 1473 cm^{-1} band shows increased intensity and shifts to higher vibration energy, indicative that dispersant immobilization upon Cu_2O occurs by chelate ring formation [27]. The band at 1380 cm^{-1}, corresponding to the O–H in plane bending vibration, disappears, strongly suggesting coordination of the two oxygen atoms in the Tiron molecule to a copper ion, with removal of the OH groups [29]. Also, the Tiron bands at 1105 cm^{-1} (SO_3^- stretching, appearing as a shoulder in the Cu(I)–O stretching vibration band) and 1039 cm^{-1} (symmetric stretching frequency of the $NaSO_3$ group) remain practically unchanged, signifying that the sulfate group was not particularly involved in the immobilization of dispersant's molecules on the powders surface [27].

Table 2
Band assignment for Tiron and Tiron-modified Cu_2O.

Band position (cm^{-1})		Band assignment
Tiron	Tiron + Cu_2O	
1510	1508	C=C ring stretching
1473	1464	C=C ring stretching
1438		C=C ring stretching
1380		O–H in-plane bending
	1130	Cu(I)–O stretching (Cu_2O)
1105	1103	SO_3^- stretching
1039	1034	$NaSO_3$ symmetric stretching
	810	Cu(I)–O stretching (Cu_2O)
	627	Cu(I)–O stretching (Cu_2O)

The described behaviour strongly suggests that immobilization of Tiron molecules upon Cu_2O powders surface at the suspensions natural pH takes place mainly by inner-sphere complexation. The ligand exchange theory [20,29–31] postulates that in addition to the protonation–deprotonation reactions between water molecules and surface metal ions, surface charge also develops through other ligand exchange reactions. The main contribution to surface charge and surface charge change is accountable to added surface active agents, corresponding to preferential adsorption of specific ions from solution with formation of outer- and/or inner-sphere surface complexes [15,32,33]. When a direct chemical bond is established between the adsorbing anion and the metal ion, through the exchange of surface bound water molecules or OH– ions for the adsorbing ligand (the complexing species), and inner-sphere surface complexation takes place, with formation of chelate ring. The ligand exchange reaction described for dispersion of Al_2O_3 [10,29,33] and TiO_2 [13] suspensions by 4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt considers that the two alcohol groups on the dissociated organic molecule exchange ligands with the hydroxyl sites at the powder surface, forming an inner-sphere complex between the two species. The same model is suggested here for Tiron's adsorption upon Cu_2O surface.

3.3. Electrophoretic characterisation

Fig. 5 renders zeta potential curves for as-received and 4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt dispersed Cu_2O aqueous suspensions. Natural pH for as-received Cu_2O suspensions after overnight hydration is 7.35. At this pH value the zeta potential is approximately −8 mV. The repulsive potential continually increases for more basic pH values and a value of −32 mV is reached at pH 10. In the pH range between 7.35 and 5.87 the repulsive potential absolute value continually decreases to approximately −2 mV, at pH 5.87. Below pH 5.87 it was not possible to stabilize the suspension's pH value or to measure zeta potential values. Cu_2O solubility in acid medium degrades suspension properties at such pH values [5,34] making its use impractical. In fact, Cu_2O is soluble in hydrochloric acid, forming CuCl salt (attested by the formation of blue-green crystals on the container walls at the lower pH value), which dissolves back into solution in the presence of excess HCl [35].

The attained curve shows no isoelectric point (IEP): zeta potential values are always negative in the pH range tested, *i.e.* ionisation of Cu_2O surface hydroxyl groups is predominantly negative ($Cu–O^-$). Although no reference to the IEP of Cu_2O could be found in the literature, these results must be regarded with some caution, because Cu_2O is soluble in acid media. At ambient temperature, its degree of solubility decreases with increasing pH, attaining a broad minimum between pH 8.5 and 10 [34]. Hence, at the natural suspensions' pH range, there will be a concentration of copper in solution. Under these conditions, the ionic strength increases and consequently the zeta potential value is expected to decrease, even if the surface charge remains unchanged. Additionally, Tiron-modified Cu_2O DRIFTS results suggest that the protective surface coating is not completely removed by Tiron, possibly hindering true surface behaviour. Zeta potential absolute values are higher for pH values above 8.6, corresponding to the minimum solubility pH range [35] and, consequently, where variations on pH value have little effect on the concentration of copper brought into solution.

Addition of 0.7 wt.% Tiron into suspension (*i.e.* the concentration corresponding to the most stable suspension tested) allowed electrophoretic measurements further into the acid region, confirming that surfactant's adsorption involves formation of a complex between negatively charged surface sites and the adsorbing species, decreasing the solubility of the oxide. Nevertheless, no IEP was also found in this case. Adsorption of the anionic dispersant species caused a downshift of 8–25 mV of the whole electrophoresis curve, increasing the absolute values of zeta potential and therefore of the repulsive forces between the dispersed particles. A colloidal stabilization dwell is attained at pH 9. At pH values bellow Tiron's pK_{a_3}, the dispersant is present mainly in the undissociated form and as-received powders surface charge is relatively low. Thus, OH neutral surface groups are available for ligand exchange with Tiron and grafting takes place through the alcohol groups. The formed complex has a negative net charge. This, together with the negative charge of the ionised sulfonate groups on Tiron molecule, further contributes to develop a negative charge of high magnitude and to increase the repulsive potential between particles. As the pH value increases, as-received oxide particles develop a more negative surface charge and Tiron predominantly displays the $C_6H_3O_8S_2^{3-}$ species. In as much, electrostatic repulsion between those negative charges arises and adsorption tends to decrease: additional adsorption experiments at pH 9 confirmed that an approximate amount of 3.3×10^{-6} mol/m^2 is adsorbed, in comparison to the 5.6×10^{-6} mol/m^2 adsorbed at the natural pH (6.65 for 0.7 wt.% Tiron suspensions).

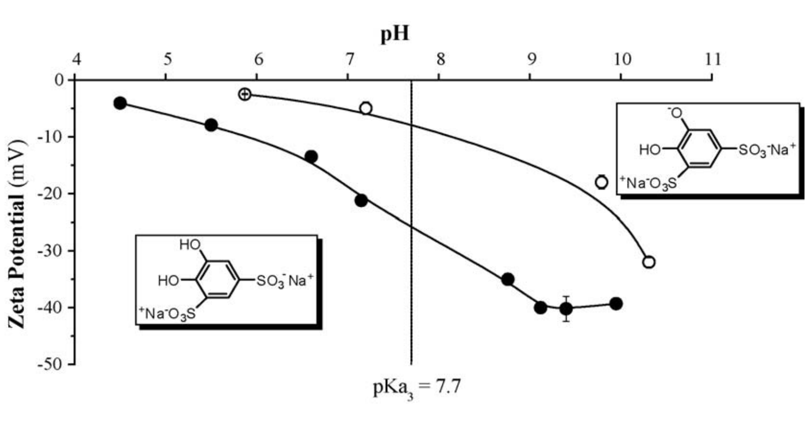

Fig. 5. Zeta potential vs. pH curves for Cu_2O suspensions (○: as-received Cu_2O suspension; ●: 0.7 wt.% Tiron suspension). Predominant dispersant species in each pH range are shown.

4. Summary

The present work contributes to the general knowledge on Cu_2O dispersion behaviour in water and to the development of dispersion methods for cuprous oxide processing. As general conclusions it may be stated that (i) Cu_2O powders are feasible of aqueous processing, which offers environmental and economic benefits; (ii) addition of 4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt (Tiron), a well known and very efficient commercial dispersant, allows manipulation of interparticle forces between Cu_2O particles in aqueous suspension, rendering successfully stabilized suspensions; (iii) dispersant's effectiveness upon Cu_2O commercial powders, protected by a polymeric surface coating, seems to depend on the coating composition and its interaction with the dispersant.

As-received Cu_2O suspensions with maximum solid loading present high viscosity value (152.5 ± 7.3 Pa s) and low colloidal stability, with particles' surface charge continually decreasing with pH increase in all tested pH range (5.7–10.5). Zeta potential curve for as-received Cu_2O particles in aqueous medium shows no IEP, with negative particles' surface charge in all the pH range tested. The 4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt molecule was found to be a highly efficient dispersant for this system, altering Cu_2O surface charge properties and providing colloidal stability in the pH range above 9. Addition of 0.7 wt.% dispersant resulted in the most stable suspension, with the lowest viscosity value, among the tested concentrations. Electrophoresis curves for 0.7 wt.% dispersant suspensions are shifted into the acid range when compared with curves for as-received powders, confirming Tiron's strong electrostatic action upon Cu_2O and rendering a high state of dispersion at the suspensions natural pH.

FTIR results suggest that the dispersing effect of 4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt upon cuprous oxide at the natural pH value is determined by its ability to adsorb by inner-sphere complexation, through the alcohol groups, on hydroxyl sites at the oxide powder surface. Speciation of hydroxyl surface groups at the metallic oxide powder surface and its specific interactions with dispersant molecules leads to adsorption by chelate ring formation.

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