

EFFECT OF CATIONIC AND ANIONIC SURFACTANTS ON ELECTROKINETIC POTENTIALS OF CASSITERITE AND QUARTZ IN PRESENCE OF POLYVALENT CATIONS

By

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تأثير منشطات السطوح الكاتيونية والانيونية على الجهود

الكهروكيميائية للكاستريت والكوارتز في وجود

الكاتيونات عديدة التكافؤ

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تمت دراسة تأثير الألكتروليتات عديدة التكافؤ (كلوريدات الحديد والألومنيوم واللاتانوم والسيريوم والثوريوم) على إمتزاز منشطات السطوح المختلفة (هيدروكلوريد الأمين الأولى وأولييات الصوديوم ودودييسيل كبريتات الصوديوم وأورثوفوسفات الفينيل ثنائي الصوديوم) على الكاستريت والكوارتز باستخدام طريقة الميكروالكتروفوريسز . وكذلك تمت دراسة العلاقة بين الجهد الكهروكيميائي (جهد زيتا) والرقم الهيدروجيني للمحاليل وتم تعيين نقط تلاشي الشحنة للأكاسيد محل الدراسة عند تركيزات ثابتة من كل من الألكتروليتات ومنشطات السطوح .

ونوقشت ميكانيكية إمتزاز هذه المنشطات على سطح كل من الكاستريت والكوارتز في وجود تركيزات ثابتة من الأملاح السابقة .

وتبين نتائج هذه الدراسة أن إضافة هذه المنشطات تؤثر على الجهد زيتا وكذلك على نقط تلاشي الشحنة للأكاسيد في وجود هذه الأملاح .

Key Words: Adsorption, Cassiterite, Electrokinetic potential, Quartz, Surfactant

ABSTRACT

The effect of different polyvalent electrolytes ($FeCl_3$, $AlCl_3$, $LaCl_3$, $CeCl_3$ and $ThCl_4$) on adsorption of different surfactants (primary amine hydrochloride, sodium oleate, sodium dodecyl sulfate and phenyl disodium orthophosphate) on cassiterite and quartz particles was studied using microelectrophoresis technique. The zeta potentials of the oxides and their isoelectric points were determined as a function of pH in presence of constant concentrations of both surfactants and electrolytes. The mechanism of adsorption of surfactants on cassiterite and quartz surfaces modified by salt cations was discussed. In general, the zeta potentials and the isoelectric points (IEPS) of the oxides in presence of the above mentioned salts are considerably changed on addition of different surfactants.

INTRODUCTION

The measurement of the electrokinetic behaviour of colloidal particles is a sensitive method for studying the surface chemistry of solid/liquid interfaces[1-5]. Small changes in the relative amount of chargeable surface groups of the colloidal particles are expected to change their

electrokinetic potentials and/or their isoelectric points. Consequently, in the processing of flotation it is very important to control the electrokinetic behaviour in order to vary the minerals separation[6-10].

Some investigations made in our laboratory[11-13] invited the relation between electrokinetic potential and

flotation properties of minerals. Also, it is well known that the electrokinetic measurements can be used to delineate the adsorption mechanisms of different inorganic salts and surfactants on the minerals[14-16].

Both the mineral surface charge and the extent of electric double layer (EDL) penetration into solution can be strongly influenced by the solution pH and ionic composition. The degree of surfactant adsorption is generally found to be changed with changing salt concentration and composition[17]. These changes may either enhance or reduce the extent of adsorption depending on the nature of the mineral and surfactant involved. Generally, increasing the total amount of salt and increasing the charge number of dissolved cations both act to compress the electric double layer at the mineral surface. In some cases the presence of ions with high charge numbers may enhance adsorption by complex formation with the surfactant if the ion forms part of surface, or by complexing (bridging) between surface and surfactant. The solution pH can also influence surfactant adsorption through its possible influence on surfactant acid-ionization, and on mineral surface group ionization. The influence of electrostatic interactions on adsorption will be surfactant and mineral specific.

An attempt is made here to study the effect of ferric, aluminium, lanthanum, cerium and thorium ions on the surface properties of cassiterite and quartz through zeta potential measurements. The experiments were conducted in solutions of these ions, in order to identify their effect on the adsorption of primary amine hydrochloride, sodium

oleate, sodium dodecyl sulphate and phenyl disodium orthophosphate on cassiterite and quartz.

EXPERIMENTAL

Minerals

Natural high grade cassiterite and quartz minerals were used. Mineral specimens were ground in an agate mortar, followed by elutriating to obtain the -5 mm fraction. The two oxides samples were then cleaned with a hot concentrated HCl solution for 4 h to remove iron contaminants, the two suspensions (at pH << 2.0) were cooled and the supernatant liquid removed. The two samples were rinsed with distilled water until no chloride ions were detected. Both samples were dried at 110 °C and stored in glass bottles. For the electrophoresis experiments, both samples were immersed in doubly distilled water for about 24 hour prior to experiments.

Chemical analysis showed that cassiterite sample contains 96.44% SnO₂, 1.40% SiO₂, 1.2% TiO₂, 0.55% CaO and 0.34% Fe, whilst, quartz sample contains 99.30% SiO₂, 0.24% total Fe, 0.22% Al₂O₃, 0.12% CaO and 0.08% MgO.

Reagents

All inorganic chemicals [FeCl₃. 6H₂O, AlCl₃. 6H₂O, LaCl₃. 7H₂O, CeCl₃. 7H₂O and ThCl₄ (solution 56%)] were analytical reagent grade or better. The cationic and anionic surfactants used in this study were listed in Table 1. The surfactant reagents were obtained as commercial products and were used as received without purification.

Table 1
Surfactants used in the electrophoretic measurements

Reagent	Abbreviation used	Commercial name and manufacturer	Comments
Primary amines hydrochloride	ANP	Russian cationic surface active agent, Russian	83% active ingredient, cationic, single hydrocarbon chain, liquid
Sodium oleate	NaOI	Sodium oleate, BDH Chemicals, Poole, England	98% active ingredient, anionic, single hydrocarbon chain, liquid
Sodium dodecyl sulfate	SDS	Sodium dodecyl sulfate, MERK-Schuchardt, Germany.	90% active ingredient, anionic, single hydrocarbon chain, powder
Phenyl disodium orthophosphate	PDSP	Phenyl phosphate disodium salt dihydrate, BDH chemicals, Poole, England	98% active ingredient, anionic, powder.

Method and Procedure

The microelectrophoresis technique was used for electrokinetic measurements of cassiterite and quartz particles as a function of pH using Rank Brothers Microelectrophoresis Apparatus Mark II (Rank Brothers, Cambridge, UK) with a rectangular glass cell.

Microelectrophoresis experiments were performed after addition of 1 ml of 2.0 g l⁻¹ suspension of the oxide particles to 60 ml of doubly distilled water in a 100 cm³ volumetric flask. After addition of the salt solution, the suspension was stirred for 5 min., followed by a portion of the desired surfactant was added, the pH was adjusted using

analytical reagent grade NaOH and HCl and then the volume was made up to 100 ml. The suspension was conditioned at constant temperature ($\sim 25^\circ\text{C}$) for at least 3 h at the desired pH to equilibrate the oxide/liquid suspensions. The pH was measured immediately before the samples were injected into the electrophoretic cell using a Fisher Accumet Model 825 MP pH meter (accuracy ± 0.001 pH). Usually about 20 particles were timed in each direction at each stationary level to obtain an average mobility value which was then converted to zeta potential using the following equation:

$$\zeta = 14.3 v/E \text{ mV at } 25^\circ\text{C}$$

where v represents the mobility of the particles, microns/s, and the electric field strength $V \text{ cm}^{-1}$. No corrections were made for a retardation ion effect [14]. Doubly distilled water ($\text{pH} = 7.093$) was used in all experiments.

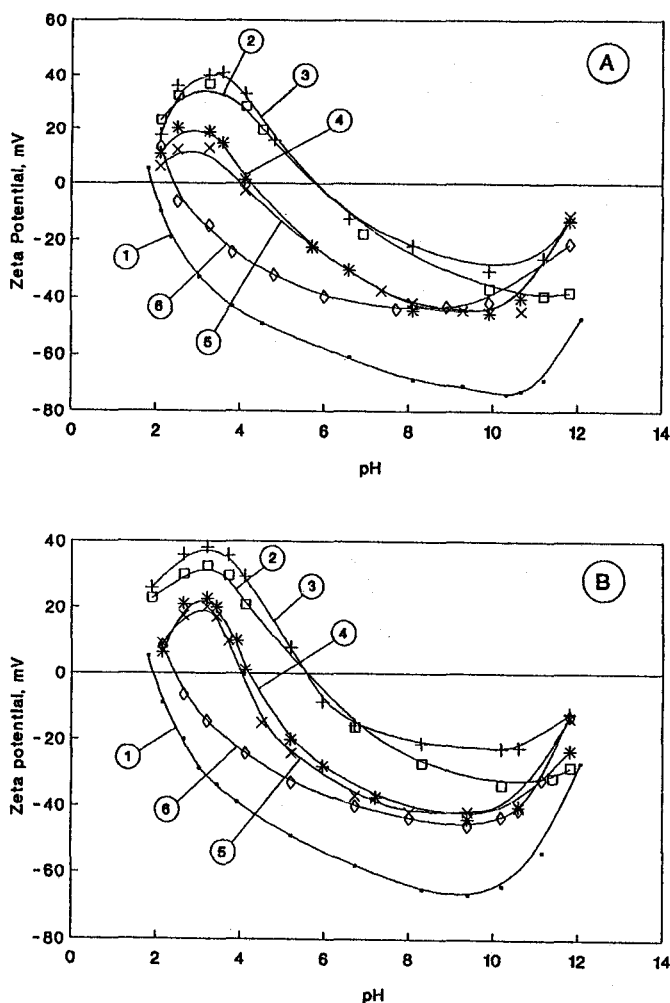


Fig. 1 Zeta potentials of cassiterite (A) and quartz (B) as a function of pH: (1) without reagents; (2) with $100 \text{ mg l}^{-1} \text{ FeCl}_3$; (3) with $100 \text{ mg l}^{-1} \text{ FeCl}_3$ and $10 \text{ mg l}^{-1} \text{ ANP}$; (4) with $100 \text{ mg l}^{-1} \text{ FeCl}_3$ and $10 \text{ mg l}^{-1} \text{ NaOI}$; (5) with $100 \text{ mg l}^{-1} \text{ PDSP}$; and (6) with $100 \text{ mg l}^{-1} \text{ FeCl}_3$ and $10 \text{ mg l}^{-1} \text{ SDS}$.

RESULTS

The surface charges of cassiterite and quartz with or without additives (salt and cationic and anionic surfactants) were inferred from the zeta potential properties.

Figure 1 to 5 illustrate the zeta potentials of cassiterite and quartz as a function of pH in presence or in absence of different reagents.

The surfaces of cassiterite and quartz without reagents (curve 1) are negatively charged at $\text{pH} > 2.0$. The plots show a striking effects of salts on the zeta potentials of the two oxides (curve 2), the negative values of zeta potentials either decreases or becoming positive in the pH range examined, and the curves intersect the pH axis defining a new created IEPs (Table 2). The changes in the zeta potentials in the pH range noted is due to adsorption of $\text{M}_q(\text{OH})_q^{(nq-p)+}$ species on the surface of the two oxides, where n is the cation charge number.

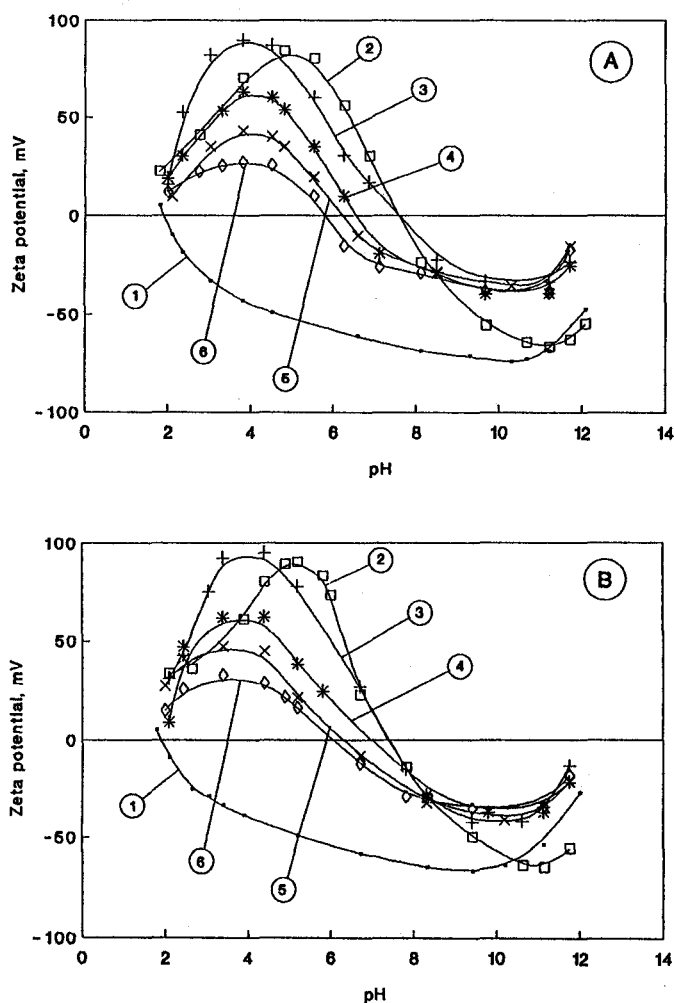


Fig. 2 Zeta potentials of cassiterite (A) and quartz (B) as a function of pH: (1) without reagents; (2) with $100 \text{ mg l}^{-1} \text{ AlCl}_3$; (3) with $100 \text{ mg l}^{-1} \text{ ANP}$; (4) with $100 \text{ mg l}^{-1} \text{ AlCl}_3$ and $10 \text{ mg l}^{-1} \text{ NaOI}$; (5) with $100 \text{ mg l}^{-1} \text{ AlCl}_3$ and $10 \text{ mg l}^{-1} \text{ PDSP}$; and (6) with $100 \text{ mg l}^{-1} \text{ AlCl}_3$ and $10 \text{ mg l}^{-1} \text{ AlCl}_3$ and $10 \text{ mg l}^{-1} \text{ SDS}$.

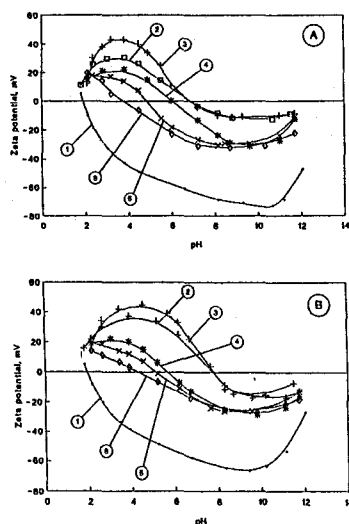


Fig. 3 Zeta potentials of cassiterite (A) and quartz (B) as a function of pH: (1) without reagents; (2) with 500 mg l⁻¹ LaCl₃ and 10 mg l⁻¹ ANP; (4) with 500 mg l⁻¹ LaCl₃ and 10 mg l⁻¹ NaOI; (5) with 500 mg l⁻¹ LaCl₃ and 10 mg l⁻¹ PDSP; and (6) with 500 mg l⁻¹ LaCl₃ and 10 mg l⁻¹ SDS

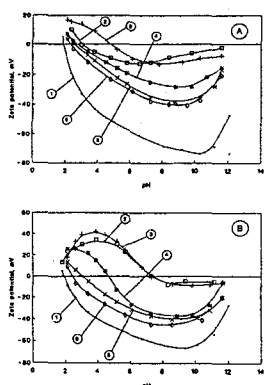


Fig. 4 Zeta potentials of cassiterite (A) and quartz (B) as a function of pH: (1) without reagents; (2) with 500 mg l⁻¹ CeCl₃; (3) with 500 mg l⁻¹ CeCl₃ and 10 mg l⁻¹ ANP; (4) with 500 mg l⁻¹ CeCl₃ and 10 mg l⁻¹ NaOI; (5) with 500 mg l⁻¹ CeCl₃ and 10 mg l⁻¹ PDSP; and (6) with 500 mg l⁻¹ CeCl₃ and 10 mg l⁻¹ SDS.

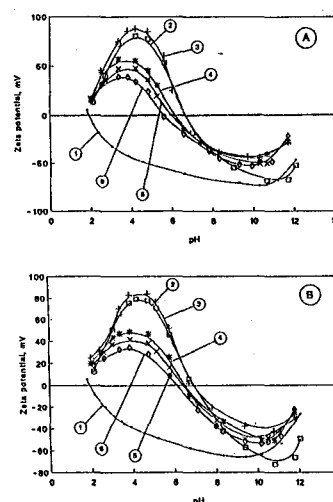


Fig. 5 Zeta potentials of cassiterite (A) and quartz (B) as a function of pH: (1) without reagents; (2) with 100 mg l⁻¹ ThCl₄ and 10 mg l⁻¹ ANP; (4) with 100 mg l⁻¹ ThCl₄ and 10 mg l⁻¹ NaOI; (5) with 100 mg l⁻¹ ThCl₄ and 10 mg l⁻¹ PDSP; and (6) with 100 mg l⁻¹ ThCl₄ and 10 mg l⁻¹ SDS.

The effect of ANP, NaOI, PDSP and SDS (10 mg l⁻¹) additions on the zeta potentials of the two oxides modified by the above mentioned salts is also illustrated in Figs. 1 to 5 (curves 3,4, 5 and 6). The zeta potentials were more positive for the oxides treated with ANP (curves 3), while, the zeta potentials were more negative for those treated with NaOI, PDSP and SDS (curves 4,5 and 6) in relation to untreated oxides (curve 2), indicating the adsorption of R-NH₃⁺ cations or OI⁻, PDP²⁻ and DS⁻ anions over the pH range studied.

DISCUSSION

The zeta potential-pH curves for cassiterite and quartz in the presence of different salts (FeCl₃, AlCl₃, LaCl₃, CeCl₃ and ThCl₄) show that the surface charge of the oxides is strongly affected by all these salts. The positive zeta potential in the pH range noted due to a consequence of the adsorption on the surfaces of the two oxides not only of the free cations but also of their positive hydroxy complexes decreases and consequently the surface charge of the two oxides remains negative in the presence of these salts.

Table 2
IEBS of cassiterite and quartz in presence of salt and surfactant

Surfactants	Salts	-	ANP	NaOI	PDSP	SDS
FeCl ₃	SnO ₂	5.8	5.8	4.4	4.1	2.5
	SiO ₂	5.7	5.7	4.3	4.1	2.6
AlCl ₃	SnO ₂	7.5	7.5	6.7	6.3	5.8
	SiO ₂	7.5	7.5	7.1	6.5	6.0
LaCl ₃	SnO ₂	7.0	7.0	6.1	5.0	3.8
	SiO ₂	7.8	7.8	5.7	5.2	4.3
CeCl ₃	SnO ₂	3.3	5.0	3.0	2.8	2.5
	SiO ₂	7.6	7.6	4.8	3.2	2.4
ThCl ₄	SnO ₂	6.8	6.8	6.3	6.1	5.7
	SiO ₂	7.0	7.0	6.6	6.5	6.3

It can be seen that Fe^{3+} , Al^{3+} , La^{3+} , Ce^{3+} and Th^{4+} ions are dominant only in strong acidic solution. With increasing pH hydrolysis of the cations becomes significant, and the positive hydroxy complexes (e.g. $\text{Fe}(\text{OH})_2^+$, $\text{Fe}(\text{OH})_2^{2+}$, $\text{Fe}_2(\text{OH})_4^{4+}$ and $\text{Fe}_3(\text{OH})_4^{5+}$) are the predominant species (distribution diagram)[18-22]. Negative hydroxy complexes predominate in the solution at high pH values. At high pH, particles regain their negative charge due to competitive adsorption of other species (such as $\text{Fe}(\text{OH})_4^-$).

Primary amines which pertain to the group of important flotation cationic collectors are weak electrolytes and their ionization is pH dependent. Their adsorption onto minerals from aqueous solutions is of great importance for understanding the surface chemistry of cationic flotation[8,9,23,24].

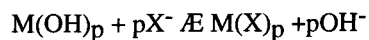
As the solution chemistry of primary amine hydrochloride is strongly pH dependent, the concentration of various species such as aminium ions, R-NH_3^+ , neutral primary amine molecules, $\text{R-NH}_2(\text{aq})$ and precipitated primary amine, $\text{R-NH}_2(\text{s})$, is given by the hydrolysis equilibria[25].

Our electrokinetic measurements (Figs 1 to 5) reveal that adsorption of ANP cations (R-NH_3^+) on cassiterite and quartz surfaces modified by salts occurred through the tested pH range (curve 3), leading to an increase in the positive charge of the two oxide surfaces compared to that in presence of salt only (curve 2).

The mechanism of ANP adsorption on the two surfaces modified by salt cations is an intensive adsorption of R-NH_3^+ that takes place in acidic and neutral media. In alkaline media, the amine collector is found in its molecular form. By calculation, considerable amounts of amine molecules in water solution appear only at pH 9.0, but as in case of oleate[23], it could be suggested that the existence of amine collector in molecular and ionic forms in presence of metal hydroxide, $\text{M}(\text{OH})_p$, is shifted to more acidic region. This may be due to bonding of amine ions with OH^- ions. On increasing the pH of the solution (>8.0), displacement of collector ions by OH^- ions occurs.

Several investigations[26-28] indicate that anionic surfactants are unable to collect the minerals unless metallic cations are present, thus the influence of some cations (Fe^{3+} , Al^{3+} , La^{3+} , Ce^{3+} and Th^{4+}) on the adsorption of the anionic surfactants (NaOI, PDSP and SDS) on cassiterite and quartz was examined as shown in in Figs 1 to 5 (curves 4,5 and 6). The decrease in the zeta potential is due to the strong adsorption of surfactants anions (X^-). At pH less than that of metal hydroxide formation, adsorption of X^- ions from the solution on metal (as metal ion form or hydroxo-metal ion complex, $\text{M}_q(\text{OH})_p^{(nq-p)+}$) surface sites was possible, leads to a decrease in the positive charge of the oxide surface (curves 2, 4, 5 and 6). Based on the zeta potential data, the mechanism of X^- adsorption on cassiterite and quartz surfaces, modified by a salt in an alkaline medium, can be measured, viz. the exchange reaction

between $\text{M}(\text{OH})_p$ from the surface and X^- from the solution forming $\text{M}(\text{X})_3$ [29,30]:



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