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Dielectric study of adsorption phenomena of collectors onto fluorite

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Abstract

The chemical adsorption of a complexing collector as the sodium oleate onto fluorite is highlighted by high frequency dielectrical measurements (0.4 – 120 MHz). Physical adsorption of collector acting by electrostatic effect as dodecylamine and dodecylsulfate has no influence on the dielectric properties of mineral pulp. The dielectric method allows to analyze the adsorption phenomena during the monolayer formation.

1. Introduction

Selective flotation of fluorite, which is often associated with other minerals, is extremely complex and requires an accurate analysis of the adsorption phenomena of collectors and depressants. Based on the experimental conditions employed, different interactions such as physisorption, chemisorption and surface precipitation have been reported. In each particular case, the identification of each of these mechanisms is not always easy due to the experimental difficulties related to the very small quantities adsorbed or remaining in solution. Methods such as photoelectron spectroscopy (XPS), atomic force microscopy (AFM), Fourier transform infrared spectrometry (FTIR), and zeta potential measurements [1-17] are currently the most efficient methods to analyze these phenomena. It is thus possible to characterize the surface of the divided solid despite the low concentration of the collectors or depressants used. It should be noted, however, that these techniques require the treatment of the mineral sample and heavy equipment, which is incompatible with the conditions for industrial control in flotation plants.

The present study analyzes the capability of the high frequency dielectrical method for following the adsorption of collector onto fluorite and giving information on the type of bonds between them.

This technique has been proposed to study the nature of the adsorbate/adsorbent bond during the adsorption of the collectors on the surfaces of the conductive minerals and salt-type compounds [18-22]. In general, the dielectric constant ε' is different when the interaction is of chemical type and remains invariant when it is of physical type. The method can also control the behaviour of ion-exchange resins [23,24], the characterization of activated carbon [25], the activation of the zeolites microparticles by the S^{2-} [26] and the monitoring of apatitic cement setting reaction [27].

2. Method and experimental procedure

2.1. *Dielectric method*

The dielectrical characterization of the mineral pulp described previously [27-30] consists in measuring the complex impedance Z^* of a capacitive cell (Fig. 1) filled with the decanted pulp in the frequency range 0.4-120 MHz. For a non-conductive pulp, Z^* values can be transformed in the complex permittivity $\varepsilon^* = \varepsilon' - j\varepsilon''$ where ε' is the dielectric constant and ε'' the permittivity of pulp according to the Hanai physical model [31] and the equation of Bussy [32].

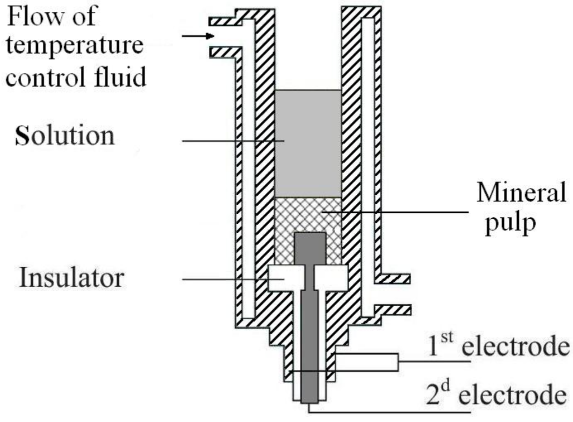

Figure 1: Dielectric cell.

2.2. *Experimental procedure*

Pure fluorite is ground in an agate mortar in the presence of water (particle size range: 40< d <80 µm). Sodium oleate, dodecylsulfate and dodecylamine are of analytical grade. The flotation tests were carried out in a hallimond tube. The density of the pulp was 4% and the volume of the solution was 100ml (4g/100ml). The pulp was continuously stirred, for 2 min with a pH regulator and for 5 min with the collector. The duration of flotation was 2 minutes (air flow rate: 10 l/h).

The dielectrical measurements were conducted at 21°C on the pulp (4g of solid) after decantation in the capacitive cell. The values of Z* were recorded by an HP 4194A impedance/gain-phase analyser (Hewlett–Packard). The experimental device was connected to a computer allowing real-time calculation of the dielectric permittivity ε' and dielectric losses ε". All measurements were repeated three times and led to similar results, giving evidence of the good reproducibility of this technique.

For the determination of the isotherm, fluorite samples (4 g) were mixed with oleate solutions (100 ml) with different initial concentrations at pH 9.5. The stirring time is set at 5 minutes. After the dielectric measurements, the solution is filtered to remove the solid. The amount of oleate adsorbed on the fluorite surface was obtained by the difference between the amount initially introduced and the residual amount.

The residual concentration of collector in the solution was measured with a Beckman UV 5230 spectrophotometer according to the Gregory method [33].

3. Results and discussion

3.1. *Dielectrical characterization of pure fluorite*

The research of optimal conditions for detecting the collector adsorption on a mineral prompts us to examine the effect of frequency and ionic strength.

3.1.1. Effect of frequency

The dielectric constant of the pulp is independent of the frequency in the range 0.4 - 120 MHz while its permittivity decreases when the frequency increases (Table 1).

3.1.2. *Effect of ionic strength*

The previous result showed that it was possible to characterize the mineral pulp by its dielectric constant. It is therefore important to know if the presence of ionic species in solution constitutes an obstacle to the dielectric characterization of the mineral pulp. This leads us to examine the effect of ionic strength on the dielectric response of the mineral/solution system.

To evaluate this effect, sodium nitrate, which is supposed to have no specific interaction with the mineral surface, was added to the washed mineral. The experimental results (Table 1) give evidence that the dielectric constant of the system is substantially independent of the ionic strength for salt concentrations of less than 10^{-1} M. These concentrations are much larger than those of the collector (5.10^{-6} to 10^{-4} M). On the contrary, the permittivity ε" is strongly affected when $NaNO_3$ concentration increases from 10^{-5} to 10^{-1} M.

Table 1: Frequency and ionic strength effect on dielectrical characteristics of fluorite. (T=21°C).

Fluorite + solution	Frequency (MHz)	ε'	ε"
H_2O	5	34.1	7.1
	10	34.2	3.6
	50	34.6	0.6
$NaNO_3$ 10^{-5} M	5	34.5	6.8
	10	34.5	3.4
	50	34.7	0.9
$NaNO_3$ 10^{-4} M	5	34.2	8.4
	10	34.0	4.2
	50	35.2	1.1
$NaNO_3$ 10^{-3} M	5	34.9	20.0
	10	34.6	10.3
	50	34.8	2.6
$NaNO_3$ 10^{-2} M	5	34.6	134
	10	34.5	68.3
	50	34.7	20.2
$NaNO_3$ 10^{-1} M	5	39.1	1110
	10	35.8	555
	50	34.2	113

3.2. *Dielectric characterization of the adsorption of sodium oleate on fluorite*

Sodium oleate is the most extensive-used collectors for calcium-bearing minerals, such as scheelite, fluorite and calcite. Its chemical interaction with the surface has been proven by FTIR spectrometry, zeta potential measurements and flotation tests [34-41].

3.2.1. *Effect of frequency and concentration*

For concentrations lower than 10^{-4} M, dielectric measurements (Fig. 2) show that the dielectric constant is independent of frequency and increases with the collector concentration. These observations indicate that the adsorption of the oleate on the fluorite is clearly demonstrated by the increase of the dielectric constant [19]. Similar results were observed in the adsorption of oleate on barite [22] and salicylaldoxime on malachite [21]. This effect is manifested for very low collector concentrations for which the flotation efficiency is only partial (Fig. 3). The measurements show a clear difference between sodium oleate and sodium nitrate which is devoid of surfactant properties. The detection of the method is therefore sensitive.

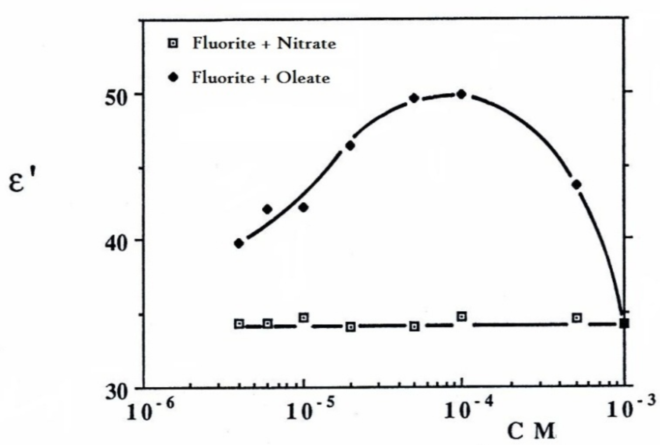

Figure 2: Influence of collector concentrations on dielectric constant of fluorite. (F=5 MHz).

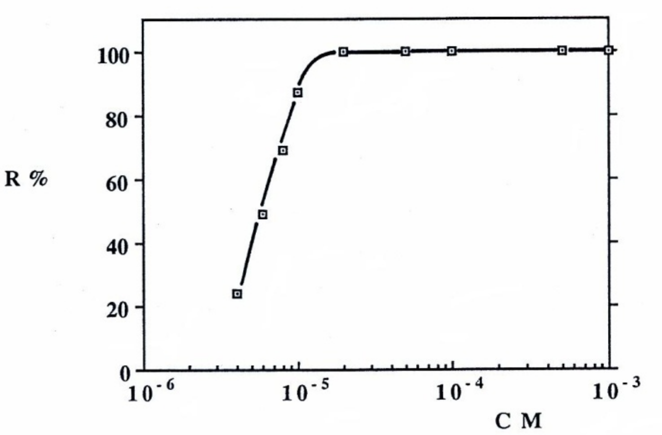

Figure 3: Flotation of fluorite by sodium oleate at natural pH (8.2).

We can note that the relation between the variations of the dielectric parameters and the nature of adsorbate/adsorbent bond appears for concentrations of collector (4.10^{-6} – 2.10^{-5} M) where studies admit that it is a phenomenon of chemisorption by monocoordination of the anion oleate with a cation calcium of surface

[36,42]. Indeed, this area of collector concentration corresponds to the formation of the monolayer. For concentrations greater than 10^{-4} M, we observe a very significant decrease in the value of ε' of the fluorite/oleate system. This phenomenon which is not observed in the case of malachite and barite is discussed by the analysis of the adsorption isotherm.

3.2.2. *Adsorption Isotherm*

The increase in the value of ε' due to the adsorption of the oleate on fluorite prompted us to see if there was a correlation between the dielectric data and the adsorption isotherm of sodium oleate on fluorite at pH = 9,5 (pH value of the stock solution of collector).

The adsorption isotherm (Fig. 4) begins with a linear portion of very low slope for concentrations below 5.8 10^{-5} M and up to an adsorbed amount of 6 µmol/g. Above 5.8 10^{-5} M, we observe a slope rupture and a rapid increase of the adsorbed amount up to 11.9 µmol/g. From 1.2 10^{-4} à 3 10^{-4} M, the adsorbed amount remains constant and then increases rapidly for concentrations greater than 3 10^{-4} M. The aspect of the isotherm is similar to that established by Sivamohan et al. and Rao et al. [39-41].

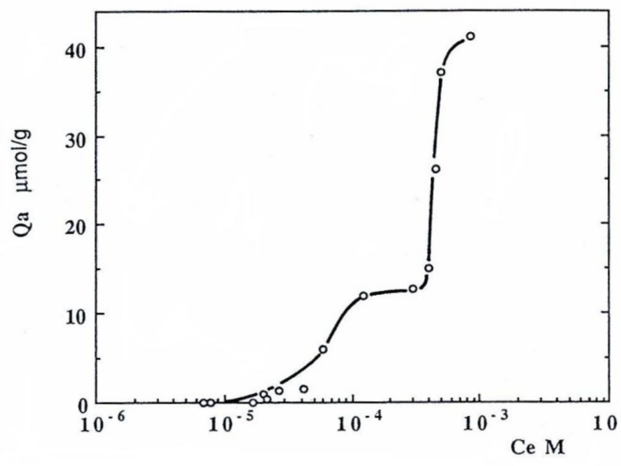

Figure 4: Adsorption isotherm of oleate on the fluorite at pH = 9.5.

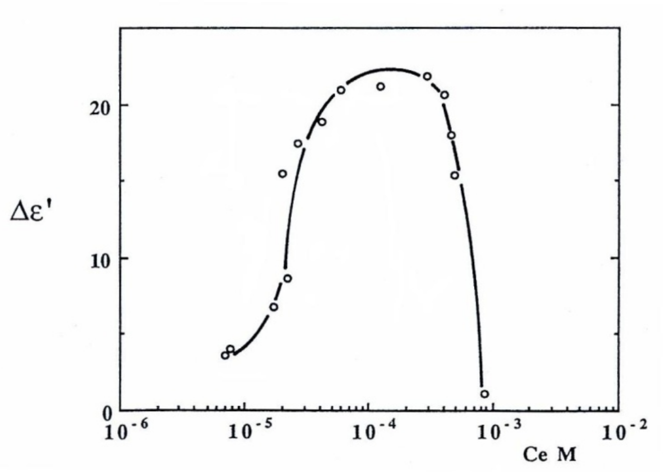

Figure 5: Evolution of Δε' as a function of the residual concentration. (F = 5 MHz).

The evolution of Δε' ($\varepsilon'_{\text{fluorite+collector}}$ - $\varepsilon'_{\text{fluorite +water}}$) as a function of the residual concentration is represented by Figure 5. For concentrations less than or equal to 5.8 10^{-5} M, the Δε' values increase from 5 to 20 units. This variation of the dielectric constant remains constant between 5.8 10^{-5} and 3 10^{-4} M, and then drops sharply for concentrations greater than 3 10^{-4} M. The superposition of these two curves leads us to distinguish four regions (Fig. 6):

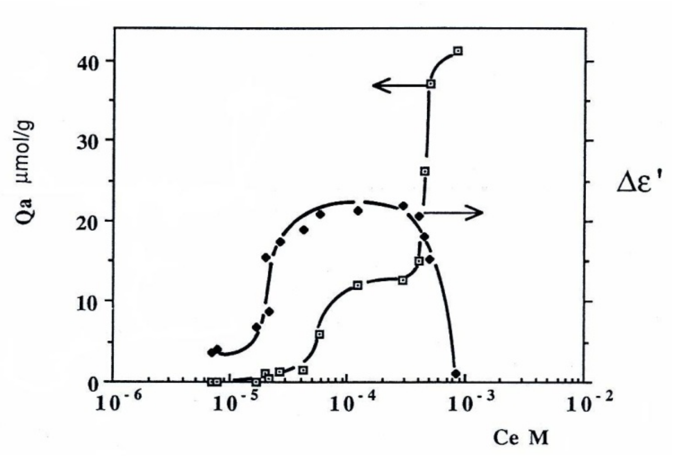

Figure 6: Evolution of Δε' and the quantity adsorbed as a function of the residual concentration. (F= 5 MHz).

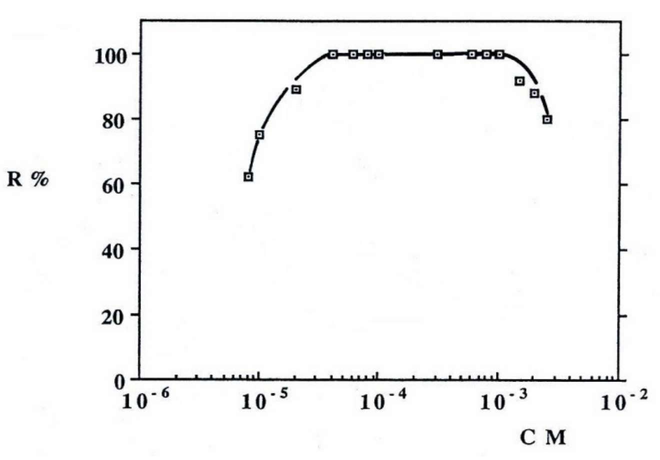

Figure 7: Flotation recovery of fluorite by oleate at pH = 9.5.

Region 1: For concentrations less than to 5.8 10^{-5} M, the oleate reacts with the calcium of the surface by monocoordination to form a compact and well-organized monolayer adsorbed on the fluorite. At this progressive filling of the monolayer corresponds an increase in the dielectric constant. It is assumed that this monocoordination is not carried out according to an electrostatic process as suggested by Sivamohan et al. [39] and Rao et al. [40,41], but by a chemical process involving solid coordination by charge transfer.

Region 2: From 5.8 10^{-5} to 1.2 10^{-4} M, the adsorbed amount increases rapidly with the concentration. Cases [43] and Sivamohan et al. [39] admit that this region corresponds to the formation of the second layer. It can be noted that this additional adsorption does not entail a variation of ε '. The nature of bond between collector and surface is not of the same type as existing in region 1. It is a collector/collector bond via lipophilic groups [44].

Region 3: Between 1.2 10^{-4} and 3 10^{-4} M, we observe a simultaneous stabilization of the quantity of adsorbed collector and of the dielectric constant. This is the end of the formation of the second layer.

Region 4: When the collector concentration is greater than 3. 10^{-4} M, the adsorption isotherm reveals the three-dimensional condensation. We observe a sudden increase in adsorption. This phenomenon corresponds to the precipitation of insoluble calcium oleate on the fluorite surface. This results in a significant decrease in the dielectric constant indicating a decrease in the polarity of the system.

If the isotherm is compared with the flotation recovery curve at pH = 9.5 (Fig. 7), we can note that 100% of the fluorite is recovered for residual collector concentrations of less than 5.8 10^{-5} M. This value corresponds to the end of filling of the monolayer. For the high residual concentrations, the decrease of recovery corresponds to a concentration of 10^{-3} M, which remains higher than that of the three-dimensional condensation.

3.2.3. *Effect of pH*

The flotation yields and dielectric constants of the fluorite pulps in the presence of oleate were measured between pH=2 and pH=12. The collector concentration was set to 2.10^{-5} M. The results are presented in Figure 8 and Figure 9. The fixing of the collector is translated between pH = 2 and pH = 10 by an increase in the dielectric constant. This new value of ε' remains practically constant in this pH range. The values of ε' are lower for pH greater than 10 and correspond to a decrease in flotation yields. In the pH range between 2 and 5, the adsorption of the collector is demonstrated even if the flotation is not complete. It can thus be seen that the dielectric detection of the adsorption of a collector may sometimes be more sensitive than the measurement of flotation recovery. The increase of ε' would result from a chemical interaction by monocoordination between oleic acid and surface calcium.

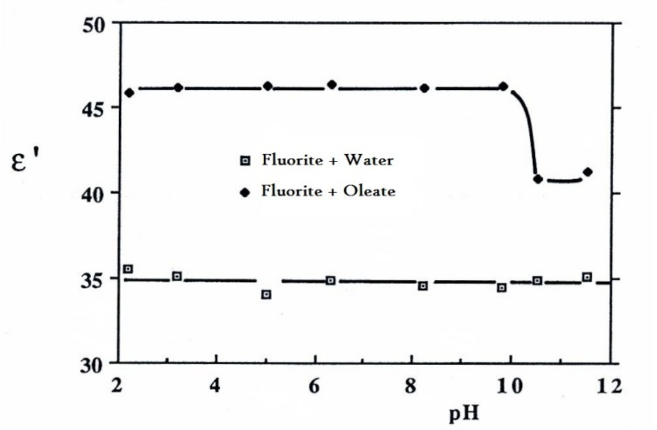

Figure 8: Effect of pH on the dielectric constant of fluorite/oleate system. ([oleate]=2. 10^{-5} M, F = 5 MHz).

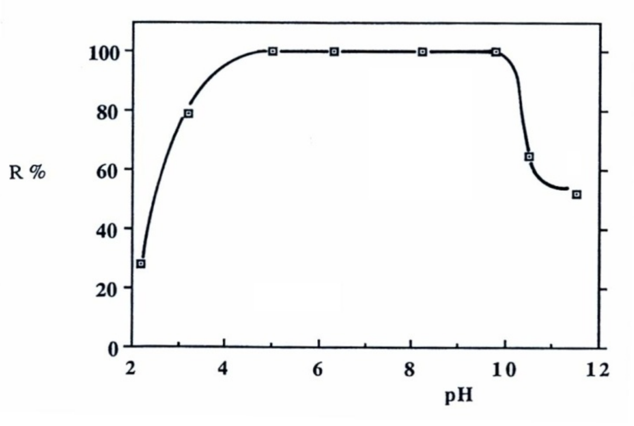

Figure 9: Effect of pH on the flotation recovery of fluorite by oleate 2. 10^{-5} M.

3.3. *Dielectrical behaviour of fluorite in the presence of dodecylsufate and dodecylamine*

These two collectors are widely used in flotation of non-sulphurous minerals and most often act by electrostatic effect [45-52]. Unlike oleate, these reagents do not give precipitation when in dilute solution (concentration less than 5. 10^{-3} M). At higher concentrations, calcium-engaging micellization phenomena may occur. It can thus be assumed that the adsorbate/adsorbent interaction is not directly specific to calcium, but rather depends on the electrical charges appearing at the solid/solution interface which are opposite to that of the collector.

For the dielectric analysis of the adsorption of dodecylsulfate ($DDSO_4$) and dodecylamine (DDA) on fluorite pulps, the pH values were fixed respectively at 5 and 9. The results are presented in Table 2. The maximum flotation is observed for $DDSO_4$ at 5.10^{-5} M and for DDA at 7.10^{-5} M.

For concentrations below 10^{-4} M, the adsorption of these two collectors does not cause any variation of the dielectric constant. The presence of ion pairs at the interface between the collector and the mineral surface that do not participate in the phenomena of dielectric polarization explains the constant of the parameter. These observations confirm the absence of specific chemical interactions between the collector and the mineral. Similar results have been obtained in the case of the flotation of malachite with dodecylsulphate [21] and the flotation of barite with the Dodecylamine [22].
At high concentrations (10^{-3} M), the $DDSO_4$ is able to precipitate Ca^{2+} ions, and probably the small increase in ε' corresponds to adsorption of a precipitated species in solution, which would lead to an increase in polarity of system. The same phenomenon was reported by Shergold [51] in the $CaF_2/DDSO_4$ system study by infrared. The author does not exclude the possibility of precipitation of $Ca(DDSO_4)_2$ and the adhesion of this compound to the surface of the mineral by physical interaction.

Table 2 : Dielectrical characteristics of the fluorite pulp in the presence of dodecylsulfate (pH=5) and dodecylamine (pH=9). Frequency and concentration effect.

Fluorite + solution	Concentration (M)	F (MHz)	ε'	Recovery %
H_2O pH = 5	-----	2 5 10	35.5 34.9 34.3	< 10
Dodecylsulfate pH = 5	2. 10^{-5}	2 5 10	36.2 36.7 36.7	89
	10^{-4}	2 5 10	37.0 36.2 36.9	100
	10^{-3}	2 5 10	47.6 46.8 45.3	100
H_2O PH = 9	----	2 5 10	35.9 35.4 35.4	< 10
Dodecylamine pH = 9	2. 10^{-5}	2 5 10	36.2 35.6 35.4	65
	10^{-4}	2 5 10	37.4 36.7 36.6	100
	10^{-3}	2 5 10	37.2 36.6 36.3	100

Conclusion

The analysis of the adsorption phenomena by the high-frequency dielectric measurements applied to the fluorite pulp confirms the interest of the method to characterize the solid/solution interface. Its "in situ" character constitutes the originality of the method which has the advantage of a direct characterization of the interface. It is clear that the adsorption of complexing collector (sodium oleate) on fluorite results in a significant increase in the dielectric permittivity of the mineral pulp. On the contrary, the adsorption of collectors by electrostatic interaction (dodecylamine and dodecylsulfate) has no effect on the dielectrical characteristics. The sensitivity of the technique makes it possible to establish a relationship between the dielectric measurements and the adsorption isotherm by analyzing the phenomena in a non-invasive manner at the level of the monolayer.

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