The complex behavior of fatty acids in fluorite flotation

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ABSTRACT: This paper is concerned with the complexities in the flotation behavior of fluorite with fatty acid collectors due to the formation of precipitates and their interaction with mineral surfaces. The system considered in detail in this paper involves palmitic acid as a model carboxylate collector. Several different experimental techniques were used to delineate the behavior of aqueous solutions and precipitates of palmitic acid and calcium palmitate salts and their effect on the wettability and flotation behavior of fluorite.

INTRODUCTION

Chemisorption implies monolayer coverage together with the formation of a chemical bond between the adsorbate and adsorbent. Many, if not most, of the processes termed as "chemisorption" in aqueous mineral systems may be surface reactions that involve chemical exchange of the adsorbate with lattice ions, a reaction that can continue until one of the reactants is consumed or equilibrium is reached. Numerous examples can be found in the flotation literature (Fuerstenau 2005), such as the activation of sulfide minerals with metallic cations where there is an exchange reaction with lattice cations and the sulfidization of oxidized Pb minerals where the exchange reaction takes place between anions. Apparent monolayer coverage in such systems is often observed because of addition of starvation amounts of reagents and short conditioning times.

The flotation of sparingly-soluble salt minerals such as apatite, calcite and fluorite appears to be controlled by chemical interaction with carboxylate collectors. Numerous researchers have conducted infrared spectroscopy studies of oleate collectors on these salt-type minerals and the results generally show the expected metal-carboxylate bond from chemisorption chemical exchange, or chemical reaction. At lower pHs some physical adsorption has been observed. However, with these types of systems, researchers have found that collector uptake generally goes far beyond a monolayer and that virtually a new soap phase may form at the surface, which indeed means that the collection process should be considered as one of surface reaction rather than as one of adsorption. In fact, Kitchener (1984) wrote: "The main problem over soaps is to identify the form of the product, which, in this case, seems very unlikely to conform to the naïve monolayer model. There is no doubt that, given a chance, calcium minerals, for example, would go on reacting with sodium oleate almost indefinitely….. supposed 'adsorption isotherms' for such systems are almost certainly abstraction-by-precipitation curves."

After a detailed study, M.C. Fuerstenau and Elgilanni (1966) considered that a bulk calcium precipitate is necessary for the flotation of Ca-activated quartz with long-chained sulfonate and oleate collectors. Laskowski et al. (1989) presented the results of their detailed study of weak electrolyte collectors, with particular emphasis on the role of amine precipitates on quartz flotation. In 2003, Fa et al. showed that colloidal particles of calcium oleate coagulate onto the surface of fluorite and make it readily flotable.

The objective of this research was to delineate the solution chemistry of a model fatty acid, the interfacial behavior of its precipitates, and their effect on the flotation behavior of fluorite. Although extensive studies were also conducted with myristic acid and oleic acid (which exists as liquid droplets at acid pHs), only the palmitic acid / fluorite system is discussed in this paper.

MATERIALS AN METHODS

The fatty acids used in this work were of 99+% purity, obtained from Fluka and also the Hormel Institute. Supporting inorganic chemicals were all of reagent grade. Triply distilled water was used in all of the experiments. Selected crystals of fluorite (from Rosiclaire, Illinois) were obtained from Wards, NY, and crushed in a porcelain mortar to prepare 75 x 147 and 147 x 300 μm size fractions. These materials were passed dry through a high-gradient magnetic separator to remove the small quantity of weakly magnetic minerals, then deslimed wet, and washed with dilute nitric acid to remove any calcite contaminant. After washing, the sample was dried and stored for later experimentation.

Measurements of pH were carried out with a glass/calomel electrode to an accuracy of 0.05 pH units. Turbidity was measured with a Birtcher Nephelometer and particle size of colloidal materials with a Malvern Zetasizer. Electrophoretic mobility measurements (for determining zeta potentials) were conduced with a Zeta-Meter. The concentrations of metal ions were determined by atomic absorption spectrophotometry and concentrations of organics were measured by carbon analysis using a UIC Coulometer. Flotation experiments were conducted with a 300-ml modified Hallimond tube with a 4-g sample of 147 x 300 μm fluorite. In all experiments a minimum ionic strength of 0.01 M was established with KNO_3, but overridden at high additions of Ca^{2+}. Contact angles were measured with air bubbles on polished specimens inverted in an optical cell, yielding liquid-receding angles.

EXPERIMENTAL RESULTS AND DISCUSSION

Aqueous palmitic acid solutions

Palmitic acid (hexadecanoic acid, $C_{15}H_{25}COOH$) has a molecular weight of 256, a melting point of 63C, and a CMC (critical micelle concentration) at 3 mM. Potassium acid palmitate has a molecular weight of 551, melts at 138C and is described as being a white fatty sol. Published data for the solubility products of salts of carboxylates are scattered, contradictory, and far from complete. Through measurement of turbidity versus pH at constant concentration together with titration, speciation of carboxylates was determined. With 4.95 as the pKa of palmitic acid, our results give the solubility of palmitic acid (HPa) as $10^{-7.58}$ M and the solubility product of HPa as $pK_{s,HPa}$ = 12.53. The solubility product of the acid soap ($HKPa_2$) was calculated to be $pK_{s,HKPa2}$ = 19.6. The speciation diagram for palmitic acid in aqueous solutions at different KNO_3 concentrations and pH regulated with KOH is given in Figure 1. At low pH, the acid form dominates, which is practically insoluble and is not taken into further consideration at pHs beyond the pKa.

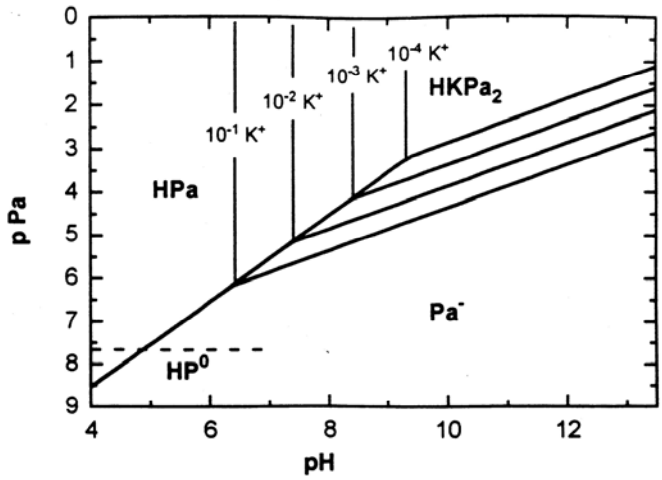

Figure 1. The speciation diagram of palmitic acid showing the major insoluble species and the equilibrium palmitate concentration in solution.

Because of dissolved calcium ions present in pulps containing such minerals as calcite and fluorite, the speciation of palmitic acid in the presence of added calcium was similarly determined by the titration technique. The solubility product for Ca palmitate ($CaPa_2$) was found to be $pK_{s,CaPa2}$ = 17.06. The complete speciation diagram for palmitic acid in calcium solutions is given in Figure 2. The dashed line represents the stability limit of calcium palmitate in the open system. At high pH, the

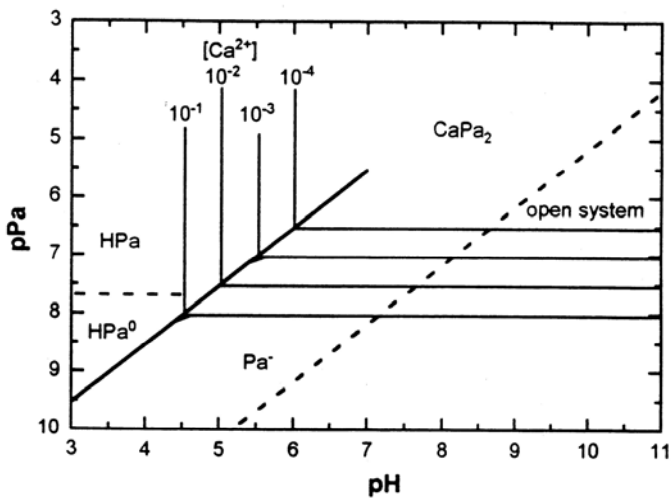

Figure 2. The speciation diagram of palmitic acid at various calcium concentrations,

carbonate concentration increases and eventually precipitates calcium as calcite. The solubility product of calcite is $pK_{s,CaCO_3} = 8.23$ and that of fluorite is given by $pK_{s,CaF_2} = 10.3$.

A wide range of solubility products for palmitic species have been published, but our results match those of DuReitz (1975) and his results are also used palmitic fatty acid species in equilibrium with fluorite in an open system were worked out and the results are presented in Figure 3. Mineral/reagent interactions under flotation conditions generally do not approach equilibrium, but the speciation results given in Figures 1-3 provide a means for interpreting the flotation behavior of fluorite with palmitic acid.

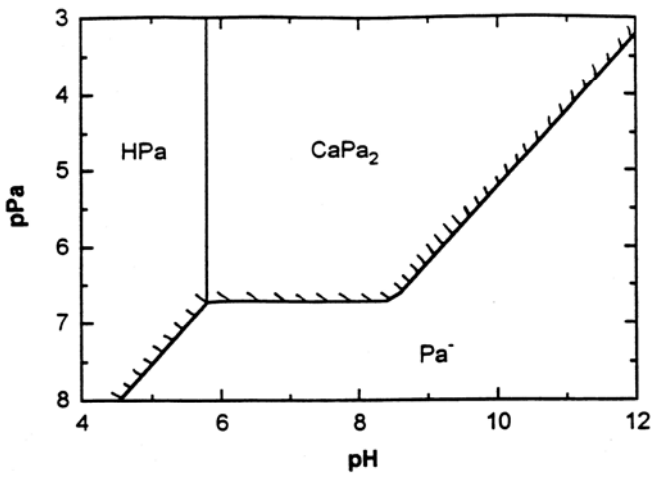

Figure 3. The stability domain of aqueous palmitic species in equilibrium with fluorite in an open system.

Zeta potential of palmitate precipitates

By microelectrophoresis, the zeta potentials (ζ) of palmitic acid particles were evaluated as a function of pH. Stock solutions containing 10^{-3}M palmitate were diluted to 10^{-4}M and the pH dropped to desired values below the precipitation edge. The mobility of the particles was measured after equilibration for 30 minutes for calculation of zeta potentials. Figure 4 presents the ζ potential of palmitic acid as a function of pH. The most likely explanation for the zeta potential of HPa particles becoming increasingly negative as the pH is increased is the adsorption of palmitate ions. In our work, ζ potentials at more acidic pHs were not determined, but Laskowski et al. (1989) found that lauric acid and myristic acid particles become positively charged at pH values between 3 and 3.5. This positive charge must result from the adsorption of hydrogen ions. Because aqueous solutions in equilibrium with fluorite will contain 10^{-4} M Ca^{+2}, the ζ potential of precipitated palmitic species in calcium solutions of different concentrations was determined and the results are also plotted in Figure 4. At low pHs the curves coincide with the palmitic acid base curve, but level off sharply at different pH values that depend on the concentration of calcium. The boundaries between the HPa and $CaPa_2$ stability domains shown on the plots are very close to the point where the zeta

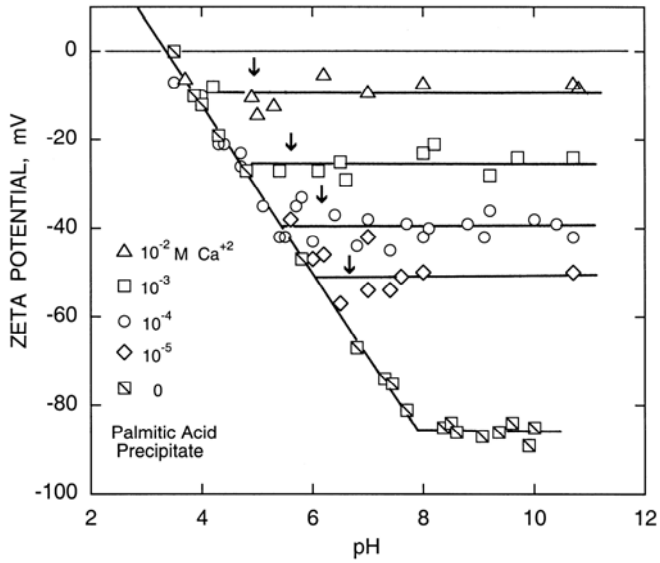

Figure 4. The zeta potential of palmitate species versus pH at different calcium levels. The particles at low pH are palmitic acid and calcium palmitate at higher pH. Arrows designate the HPa/$CaPa_2$ boundaries.

potential of the calcium precipitate deviates from that for palmitic acid. The zeta potential of the acid at the boundary is preserved on the $CaPa_2$ particles throughout the entire pH range. This probably results from the adsorption of palmitate ions being responsible for the negative surface charge on the particles; and after precipitation, their concentration in equilibrium with the calcium salt is fixed by the solubility product.

Effect of the palmitic acid on the zeta potential of fluorite

The zeta potential of fluorite as a function of pH in the presence of 0.1 mM added calcium nitrate was evaluated by electrophoresis. The results given in Figure 5 show that the zeta potential reverses sign at pH 10.7, in agreement with the earlier findings of Miller and Hiskey (1972). Over a wide pH range, the addition of 10^{-5} M palmitate has a pronounced effect on ζ, as can be seen by the results also given in Figure 5. At about pH 3, the zeta potential begins to deviate markedly from the curve without added palmitate, reversing sign at about pH 4 and reaching

a minimum at about pH 6, which represents conditions where calcium palmitate forms. As the pH is raised further, ζ becomes less negative, reverses sign again at pH 8.7, and rejoins the curve for curve for fluorite at about pH 9.5. Fuerstenau and Shibata (1999) discussed how the shift in the zeta potential (Δζ) by the addition of a surface-active reagent represents the specific free energy of adsorption. When Δζ is zero (where the curves coincide), there is no specific adsorption. Thus, the flotation of a mineral should occur over the pH region where the curve with the added surfactant deviates from that without the collector.

In standard chemisorption systems, the curves with and without the specifically adsorbing reagent always come together again after the adsorbent reverses its surface charge. For example, if an anionic collector is specifically, then the two curves join again after the mineral surface has become quite highly negatively charged as the pH is raised. In the present case, the two curves come together when the mineral surface is still positively charged. This suggests that palmitate/fluorite interaction is that of

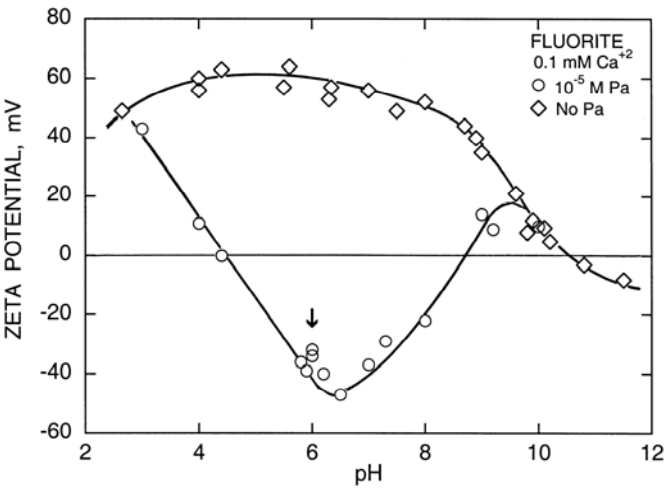

Figure 5. The zeta potential of fluorite in aqueous solutions containing 0.1 mM calcium with and without palmitate as a function of pH.

heterocoagulation of the charged palmitic acid and calcium palmitate particles with fluorite, rather than adsorption, or that $CaPa_2$ is less stable than Pa^- ions.

Palmitate adsorption on fluorite

Since the adsorption of a collector on the surface of a mineral is generally considered to be a prerequisite for flotation, it is instructive to measure the quantity of collector adsorbed. For this purpose, fluorite samples of known surface area were added to 0.5 mM oleic acid and 0.5 mM palmitic acid solutions at pH 6 for two minutes and then decanted. The residual collector concentration was then analyzed by carbon analysis. With oleate as the collector, the adsorption isotherm exhibited a plateau at roughly bilayer coverage, in agreement with the results of others (Marinakis & Shergold 1985, Bahr et al. 1968). For the adsorption of palmitic species on fluorite, the uptake was much greater than in the case of oleate. A linear plot of the uptake of palmitate species as a function of the residual concentration of palmitate was found to be a straight line (Bunge 1993), which can be expressed simply as $\Gamma = 4.4 \times 10^5$ C where Γ is the adsorption density in $\mu mol/m^2$ and C is the residual solution concentration in mol per liter. For example, at a residual concentration of 0.4 mM, the uptake of palmitate species is equivalent to about 10 monolayers. Since the concentration of calcium ions in solution would be low when the dry mineral sample was added to the solution, the large uptake of collector appears to be the heterocoagulation of negatively charged palmitic acid particles onto the positively charged fluorite surface during the short time for reaction. This is in general agreement with the foregoing results of zeta potential measurements.

Palmitate species and contact angles on fluorite

The captive bubble method was used to determine the effect of pH at constant palmitate concentration (5×10^{-7} M) at various Ca^{+2} concentrations on the contact angle on polished sections of fluorite. Air bubbles were placed on an inverted mineral specimen and the receding angle measured with a goniometer. In each case, before making a measurement, the solution containing the nominal concentration of Ca was first equilibrated for 10 min with the palmitate at the desired pH. As can be seen from the plots given in Figure 6, contact angles when palmitate is present are appreciable between about pH 3 and 10. One series of experiments was conducted without added calcium ions, yielding the largest contact angle on fluorite (at about pH 7). When additional calcium is present, the contact angle-versus-pH curves given in Figure 6 clearly exhibit two distinct peaks. In that figure, arrows mark the precipitation edge of calcium palmitate in 1 mM and 10 mM Ca solutions.

As the pH is increased above 3, the contact angle increases, reaching a maximum just before the pH of the $CaPa_2$ precipitation edge. The increase in the contact angle must result from the coating of HPa on

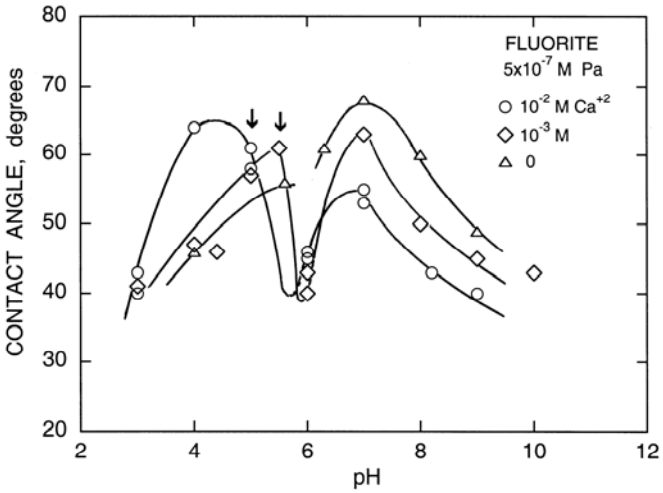

Figure 6. The effect of pH on the contact angle on fluorite in 5x10^{-7} M palmitate solutions with and without added calcium ions. The arrows indicate the boundary of the HPa/$CaPa_2$ stability regions.

the surface through adsorption of palmitate ions and heterocoagulation of the HPa particles onto the surface. The sharp decrease in the contact angle at about pH 6 appears to be related with the transformation of HPa to $CaPa_2$. The particles of $CaPa_2$ that form apparently do not remain attached to the inverted fluorite surface. As the pH is raised, palmitate ions must chemisorb onto the mineral and react to form a surface precipitate. At high pH, about pH 10, as the fluorite surface itself becomes less positively charged, palmitate uptake ceases and the apatite again becomes hydrophilic, as shown by the contact angle decrease. The double peaks that can be seen in the contact angle behavior is similar to that often observed for the oleate flotation of oxide minerals (M.C. Fuerstenau and Palmer 1976), which they interpreted as resulting from physical adsorption at low pH and chemisorption at high pH.

Flotation of fluorite with palmitate collector

In order to establish the collector concentration appropriate for further experimentation, the effect of collector addition on flotation recovery at pH 4, 7, and 9 was determined. In general, very low amounts of palmitate are sufficient for complete flotation of fluorite. At pH 7, full recovery of fluorite was obtained with 5 x 10^{-7} M palmitate, so all subsequent flotation tests were carried out with this collector addition [the same as was used for the contact angle studies]. The main emphasis of the flotation studies was to investigate the effect of added calcium ions and pH on the flotation behavior of fluorite.

In the first set of experiments, the fluorite sample was equilibrated with a solution at the selected concentration of calcium nitrate for 10 min under moderate stirring. Except for the highest addition of Ca^{+2}, all experiments were conducted at an ionic strength of 0.01 M through KNO_3 addition. After the appropriate amount of collector was added slowly from a 0.l mM stock solution (pH 11) maintaining the desired pH, the slurry was stirred for another 10 min, before being transferred to the Hallimond tube and floated for 5 min with nitrogen. Figure 7 presents the curves showing the recovery of fluorite as a function of pH at four levels of calcium nitrate additions. This figure shows that with this procedure, added Ca has little effect on flotation recovery in slightly acidic systems whereas there is a pronounced effect at higher pHs. At lower Ca additions, the overall pH range at which full flotation takes place is much wider, namely to about pH 8 to 9 with 1 mM Ca and pH 9 to 10 with 0.l mM Ca. With 0.01 M and 0.1 M Ca additions, flotation is a maximum at the HPa/$CaPa_2$ boundary and begins to decrease as the pH is increased above the boundary value, probably because of collector precipitation as Ca Pa_2.

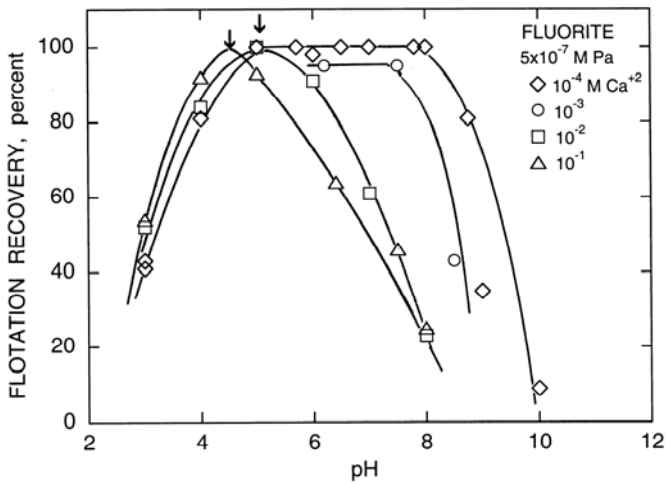

Figure 7. Flotation of fluorite with palmitate collector at various calcium concentrations. The arrows give the HPa / $CaPa_2$ boundary.

During the course of flotation experimentation, it was observed that the recovery depended somewhat on the procedure and speed employed when adding the collector because of competition between both the fluorite surface and bulk Ca^{2+} for the palmitate ions being added. To separate these two effects the flotation procedure was modified such that after equilibration of the mineral in the calcium solution, the slurry was left to settle for 30 sec and the solution cautiously decanted. The collector was then

added to this clear solution, equilibrated for 10 min and reunited with the fluorite sample.

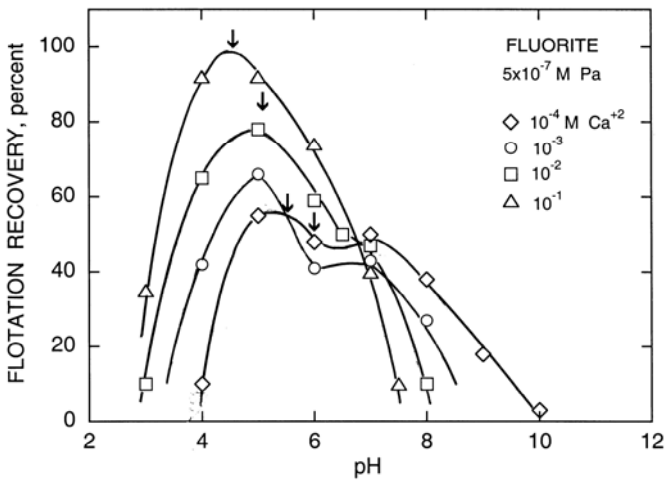

Figure 8. Flotation of fluorite with palmitate in systems different levels of excess calcium ion additions. Here the collector is first reacted with the Ca ion solutions before being contacted with the mineral at the various pHs.

After 10 min of additional equilibration, flotation was conducted. In effect, flotation was carried out in a system containing fresh calcium palmitate. The results of these experiments are presented in Figure 8, which shows behavior that differs considerably from that observed in Figure 7.

Under these conditions where the collector is effectively added as calcium palmitate, flotation is best under slightly acidic pH conditions where palmitic acid is the stable species. As Figure 7 shows, at low pH the added calcium ions enhance flotation. This is probably the result of calcium ions enhancing the heterocoagulation of HPa particles with the surface of the fluorite particles. Ca^{+2} may function as an activator or may raise the zeta potential of fluorite, increasing the tendency for HPa heterocoagulation. The optimum flotation in each case occurs at or just before the boundary for the HPa / $CaPa_2$ transformation, as shown by the arrows for each condition. As the pH is raised above this value, flotation decreases. At higher Ca additions, the precipitation of $CaPa_2$ reduces the concentration of palmitate in solution below that necessary for adsorption. There is a slight resemblance here to the dip in contact angles shown in Figure 6.

SUMMARY

The complex solution chemistry of weak electrolyte collectors, surface reactions, the formation of precipitates, and heterocoagulation phenomena all have a pronounced effect on the flotation of fluorite with palmitic acid as a model fatty acid. Stability domains of palmitic acid and palmitate precipitates were determined as a function of pH and calcium ion concentration. In slightly acidic pHs, fluorite floats readily with palmitic acid as collector. The boundary between the region for palmitic acid and calcium palmitate formation has an influence on the flotation and wetting behavior of fluorite. When calcium palmitate precipitates at the surface, flotation is not affected significantly but if the precipitate forms out in the bulk solution, then flotation is depressed.

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