

## REFERENCES

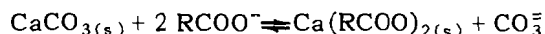
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# THE ROLE OF THE HYDROCARBON CHAIN IN ANIONIC FLOTATION OF CALCITE

by M.C. Fuerstenau and J. D. Miller

*The response of calcite to flotation with saturated fatty acids and alkyl sulfonates of various chain lengths is presented. The amount of collector required for flotation is shown to decrease systematically with increasing carbon content from 8 to 12-carbon atoms per molecule. This systematic flotation response is correlated with the solubilities of the calcium-collector salts, which were established with a nephelometer. The 14-carbon collectors deviate from this systematic behavior, and no flotation is possible with the 16-carbon homologs. As determined by infrared analysis, the mechanism of collector adsorption involves a specific chemical reaction between the collector and the surface. A reaction of the form*



*is suggested. The pH of the system is also shown to be a most important parameter as it controls the carbonate, calcium, and collector ion concentrations in solution and thus controls flotation response.*

**T**he importance of hydrocarbon chain length of collectors was recognized early, and various studies have been made on this aspect of flotation.

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Wilkinson,<sup>1</sup> for example, noted that as the chain length of alkyl xanthates is increased, the amount of collector required for flotation of sphalerite is decreased. The same effect has been shown in the flotation of galena.<sup>2</sup> Similar results were obtained when malachite<sup>3</sup> and calcite<sup>4</sup> were floated with various fatty acids.

DeBruyn<sup>5</sup> has shown that a similar phenomenon occurs when quartz is floated with amines at constant pH. Recently, Fuerstenau, Healy, and Somasundaran<sup>6</sup> correlated this phenomenon with the van der Waals cohesive free energy of association of the hydrocarbon chains.

It seems unlikely, however, that chain association could be involved in the sulfide and carbonate systems with the collector additions employed, especially with the short-chain xanthates. Rather, it would seem that the decrease in collector concentration with increase in chain length noted for flotation is related to the solubility of the metal-collector salt. The purpose of this investigation is to verify this premise and also quantify this phenomenon if possible. Calcite was selected for study with both alkyl sulfonates and saturated fatty acids as collectors.

## EXPERIMENTAL MATERIALS AND METHODS

The collectors used in this investigation ranged from 8 through 14 carbon atoms per molecule. The fatty acids had a reported purity of greater than 99%.

The sodium alkyl sulfonates were provided by the Marathon Oil Co., Littleton, Colorado, and had the

purities reported in Table I. All other reagents used were reagent grade in quality, i.e., n-amyl alcohol as frother and KOH for pH adjustment.

Crystals of Iceland Spar calcite were hand-ground in a porcelain mortar and pestle. The 65x100 mesh sample was then deslimed with conductivity water and dried. The conductivity water was made by passing distilled water through an ion exchange column.

**Flotation Experiments:** Micro-flotation experiments were conducted with the apparatus described previously<sup>7</sup> and with the following procedure.

- 1) the pH of a predetermined amount of water was adjusted to a given value,
- 2) a given amount of collector was added so that the final solution volume was 150 cc,
- 3) two drops of an alcohol solution (20 parts water to one part n-amyl alcohol by volume) were added as frother,
- 4) 3 g of calcite were then added, and the system was conditioned for 3 min,
- 5) the pH was measured (termed flotation pH),
- 6) 30 cc of purified nitrogen were passed through the cell at an average flow of 120 cc per min, and
- 7) a final pH was measured to ensure that no appreciable change in pH occurred during flotation.

When flotation pH values below 9.7 were desired, the pH of the water (step 1) was acidified prior to calcite introduction.

The order of addition of reagents and mineral was found to affect flotation response only when the 14-carbon fatty acid was involved. (See Fig. 8). When the solution was acidified before calcite introduction in this case, a high concentration of  $Ca^{++}$  ion was produced from calcite dissolution which precipitated the collector as calcium carboxylate.

**Solubility Product Determinations:** Solubility products of the calcium-collector compounds were determined with a nephelometer. Collector solution was titrated into a calcium chloride solution, and after each addition the solution was stirred for 10 min, and the intensity of the scattered light was then recorded. From a plot of scattered light intensity as a function of addition of collector, the point of precipitation of

the calcium-collector compound can be detected accurately, and the solubility products can be calculated, utilizing the Debye-Hückel limiting law.

**Adsorption Mechanism Experiments:** The mechanism of collector adsorption on the calcite surface was studied with a Perkin-Elmer 521 infrared spectrophotometer. Only the 12-carbon members of the collectors were studied, and the infrared adsorption spectra for the various samples were determined using a mull technique.

## EXPERIMENTAL RESULTS

**Flotation Experiments:** In the first series of experiments, flotation recovery was studied as a function of collector addition at constant equilibrium pH of 9.7. In the sulfonate system, Fig. 1, it can be noted that as the chain length increases, the addition of collector required for complete flotation decreases. For example, the collector addition necessary for 80% recovery is 20-fold less when a 12-carbon sulfonate is involved as compared with an 8-carbon homolog. Complete flotation could not be obtained

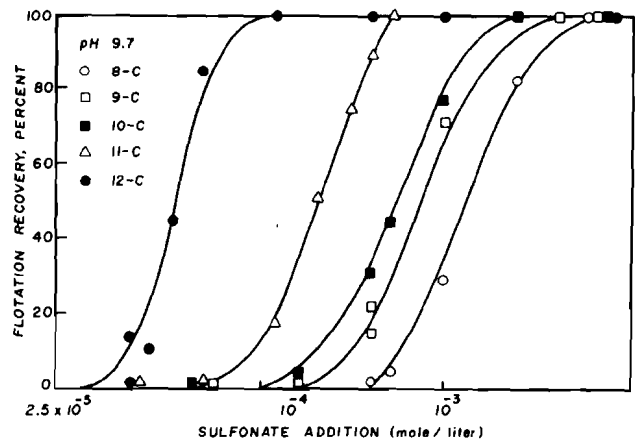


Fig. 1 - Calcite recovery as a function of sulfonate addition for various sulfonates at pH 9.7.

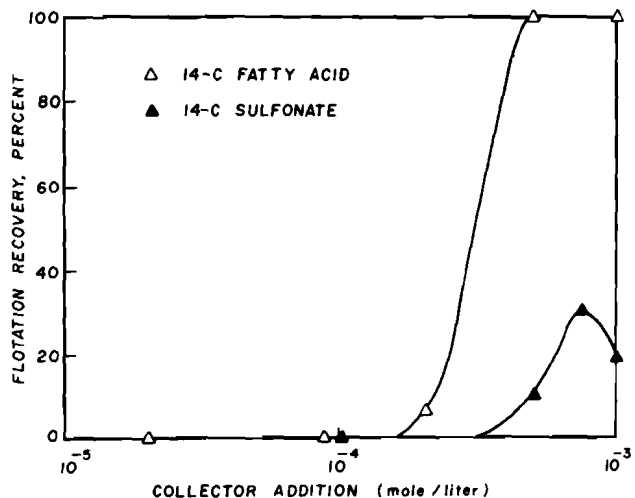


Fig. 2 - Calcite recovery as a function of collector addition for myristic acid and tetradecyl sulfonate at pH 9.7.

Table I. Purity of Sodium Alkyl Sulfonates

Number of Carbon Atoms	Purity, %	
	Infrared Analysis	Carbon Analysis
8	96.4	87.2
9	96.1	84.9
10	99.4	97.0
11	Not measured	90.0
12	99.3	99.7
14	98.0	98.9
16	93.7	96.7

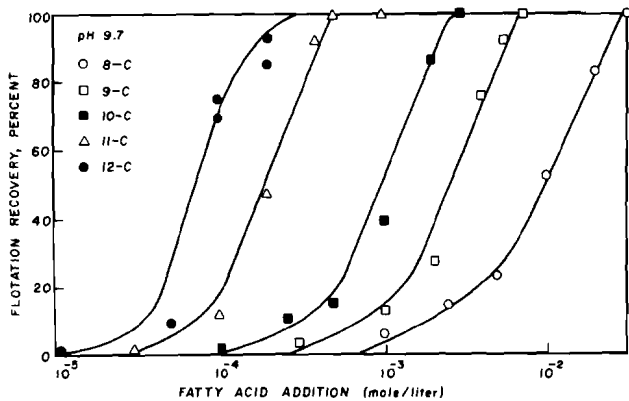


Fig. 3 - Calcite recovery as a function of fatty acid addition for various fatty acids at pH 9.7.

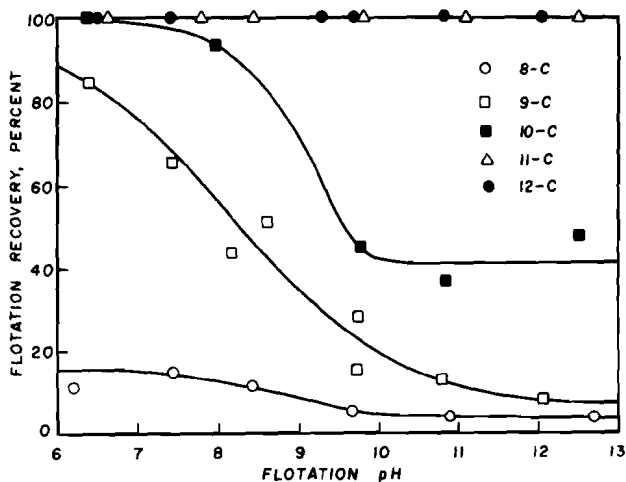


Fig. 4 - Calcite recovery as a function of pH for various sulfonates at a constant collector addition of  $6 \times 10^{-4}$  mole/liter.

with the 14-carbon sulfonate, and no flotation was effected with the 16-carbon member at pH 9.7. See Fig. 2.

The fatty acids behaved in a similar manner, as illustrated in Fig. 3. The addition of fatty acid necessary for 80% recovery for the 8 and 12-carbon members differed by a factor of about 200 in this case.

Flotation was possible with the 14-carbon fatty acid, myristic acid, only at high collector additions, i.e.,  $5 \times 10^{-4}$  mole/liter at pH 9.7. See Fig. 2.

Flotation recovery was also studied as function of system pH at constant collector additions. In the sulfonate system, complete flotation was obtained from pH 6 to 12.5 with 11 and 12-carbon homologs with a constant collector addition of  $6 \times 10^{-4}$  mole/liter. With the 9 and 10-carbon sulfonates, flotation response was reduced in basic media. Essentially no recovery was possible at any pH with the 8-carbon sulfonate with this collector addition. See Fig. 4.

It may be noted that the decrease in recovery at higher pH values is a concentration phenomenon. Compare the pH curves of the 12-carbon sulfonate at

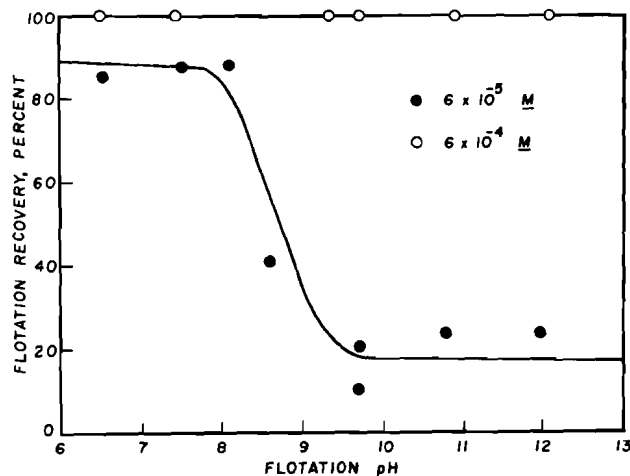


Fig. 5 - Comparison of calcite recovery as a function of pH at two levels of addition of dodecyl sulfonate.

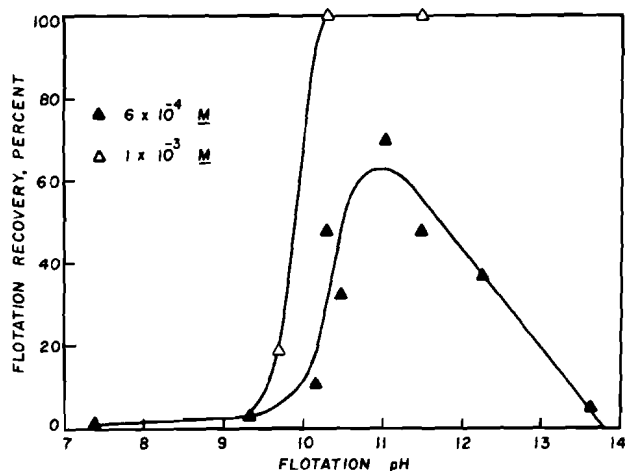


Fig. 6 - Calcite recovery as a function of pH for two levels of addition of tetradecyl sulfonate.

two levels of addition,  $6 \times 10^{-4}$  and  $6 \times 10^{-5}$  mole/liter, in Fig. 5.

The 14-carbon sulfonate behaves differently from the lower homologs, in that flotation could not be effected below pH 10 with an addition of  $6 \times 10^{-4}$  mole/liter (Fig. 6). A precipitate was observed in solution below pH 10, however. A recovery of about 50% was obtained from pH 10.5 to 12, while flotation response decreased at higher values of pH. Complete flotation was obtained when the collector addition was increased to  $10^{-3}$  molar above pH 10.

In the fatty acid system, complete flotation was obtained from pH 6 to 13 with the 11 and 12-carbon fatty acids with an addition of  $1 \times 10^{-3}$  mole/liter. The lower members of the series behaved similarly to the lower member sulfonates, i.e., recovery decreased in basic solution. See Fig. 7. The response of the 14-carbon fatty acid was also similar to that of the 14-carbon sulfonate, in that flotation recovery decreased below pH 9.0 (Fig. 8).

**Solubility Product Determinations:** The solubility products of the calcium salts of the collectors con-

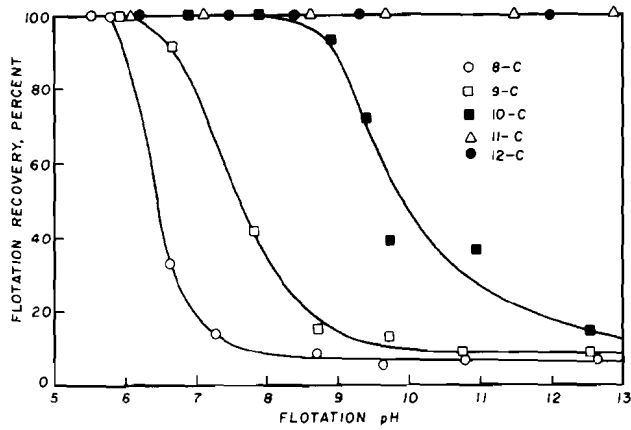


Fig. 7 - Calcite recovery as a function of pH for various fatty acids at a constant collector addition of  $10^{-3}$  mole/liter.

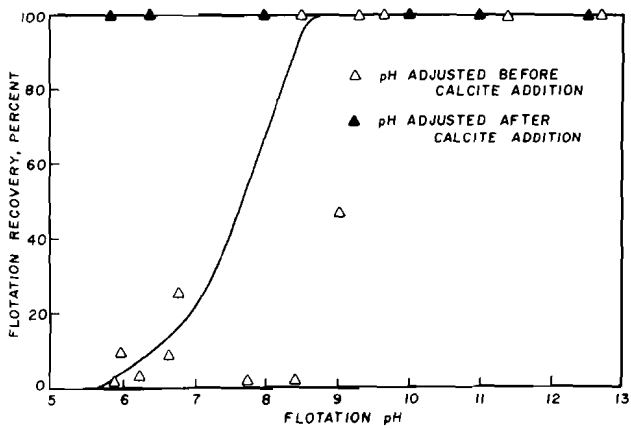


Fig. 8 - Comparison of results obtained in calcite recovery versus pH for two different orders of reagent addition; myristic acid,  $10^{-3}$  mole/liter.

Table II. Solubility Products of Calcium-Collector Salts at 23°C.

Number of Carbon Atoms	$K_{sp}$ Calcium Sulfonate		$K_{sp}$ Calcium Carboxylate	
	Experimental	Reported*	Experimental	Reported*
8	$6.2 \times 10^{-9}$		$2.7 \times 10^{-7}$	$1.4 \times 10^{-6}$
9	$7.5 \times 10^{-9}$		$8.0 \times 10^{-9}$	$1.2 \times 10^{-7}$
10	$8.5 \times 10^{-9}$	$1.1 \times 10^{-7}$	$3.8 \times 10^{-10}$	
11	$2.8 \times 10^{-9}$		$2.2 \times 10^{-11}$	
12	$4.7 \times 10^{-11}$	$3.4 \times 10^{-11}$	$8.0 \times 10^{-13}$	
14	$2.9 \times 10^{-14}$	$6.1 \times 10^{-14}$	$1.0 \times 10^{-15}$	
16	$1.6 \times 10^{-16}$	$2.4 \times 10^{-15}$		$1.6 \times 10^{-16}$
18		$3.6 \times 10^{-15}$		$4.0 \times 10^{-18}$

\*The reported solubility products were calculated from solubilities given by Reed and Tartar,<sup>8</sup> Seidell,<sup>9</sup> and DuRietz.<sup>10</sup>

sidered in this investigation were determined with a nephelometer and are listed in Table II. The calcium carboxylates behaved as would be expected, i.e., the solubility product decreased as the chain length was increased. However, the calcium sulfonates did not behave as expected. Their solubility products remained essentially constant for the lower members

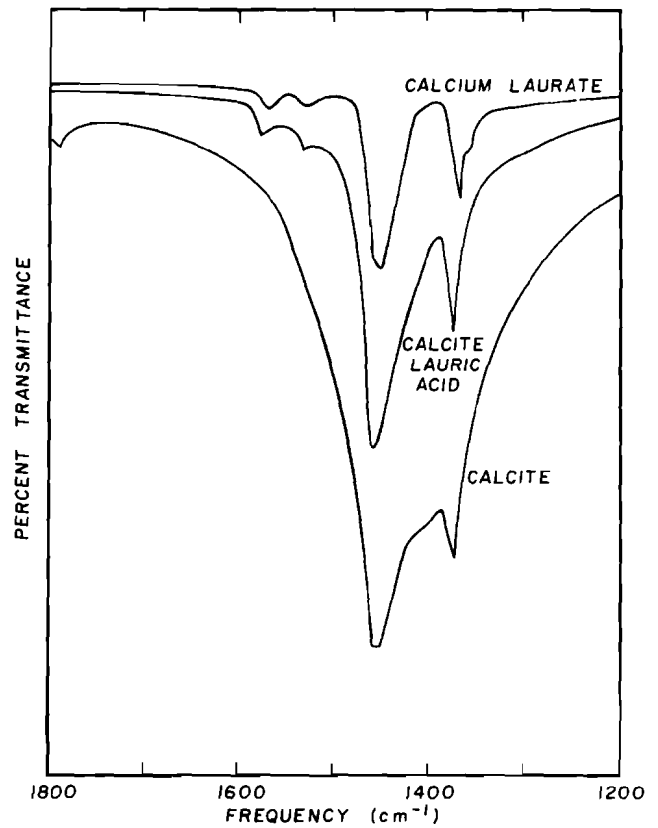


Fig. 9 - Infrared spectra calcite, calcite-lauric acid, and calcium laurate at pH 9.0.

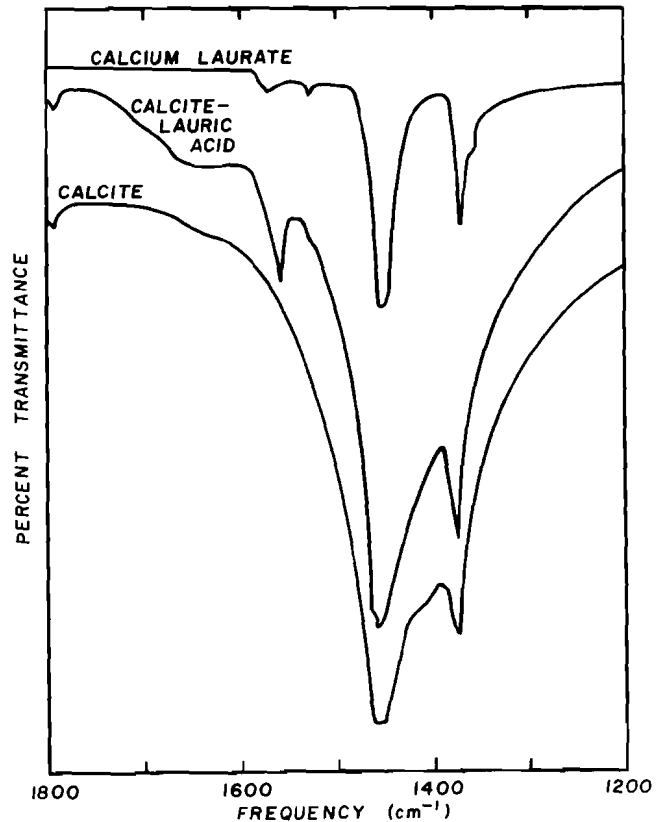


Fig. 10 - Infrared spectra for calcite, calcite-lauric acid, and calcium laurate at pH 12.5.

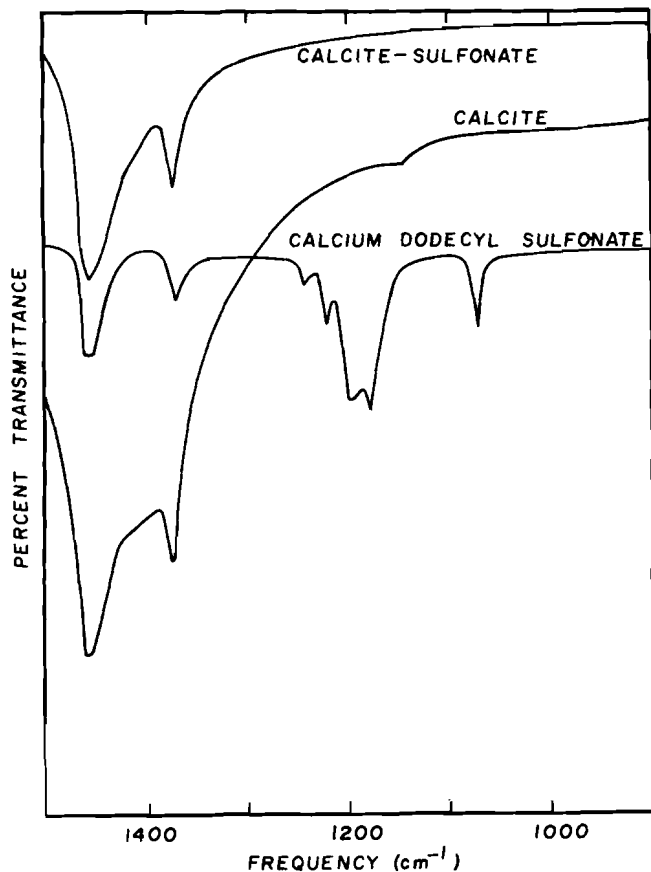


Fig. 11 - Infrared spectra of calcite, calcite-sodium dodecyl sulfonate, and calcium dodecyl sulfonate at pH 9.0.

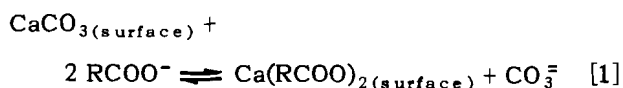
of the homologs, i.e., for the 8, 9, and 10-carbon sulfonates, while the higher members exhibited a definite incremental change per CH<sub>2</sub> group added.

**Adsorption Mechanism Experiments:** The spectra of calcium laurate, calcite alone, and calcite which had been conditioned with 10<sup>-3</sup> mole/liter lauric acid were determined at pH 9.0, shown in Fig. 9, and at pH 12.5, shown in Fig. 10. The characteristic frequencies of calcium laurate were then determined from the spectra. They are 1530 cm<sup>-1</sup> and 1570 cm<sup>-1</sup>.

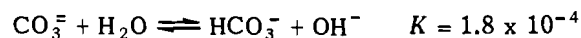
Infrared absorption experiments were also conducted with the 12-carbon sulfonate in the same manner at pH 9.0. See Fig. 11. Characteristic frequencies of calcium dodecyl sulfonate are 1075 cm<sup>-1</sup>, 1180 cm<sup>-1</sup>, 1200 cm<sup>-1</sup>, and 1220 cm<sup>-1</sup>.

## DISCUSSION OF RESULTS

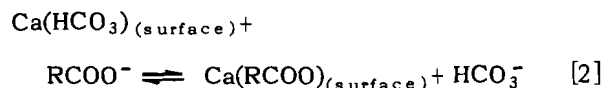
Infrared absorption experiments revealed the presence of surface calcium laurate on calcite at pH 9.0. This observation was anticipated in view of the previous work by Peck.<sup>11</sup> As a result, proposed mechanisms of adsorption may be written, and when carboxylates are involved



Or in view of the equilibrium constant for the hydrolysis of carbonate,<sup>12</sup>



it might be expected that the surface carbonate has hydrolyzed to bicarbonate, say below pH 10. If this has happened, then the following reaction can be proposed



The mass action expression for the reaction in Eq. 1 is as follows

$$\frac{(\text{aCO}_3^{2-}) (\text{aCa}(\text{RCOO})_{2(\text{s})})}{(\text{aRCOO}^-)^2 (\text{aCaCO}_{3(\text{s})})} = K_{\text{adsorption}} \quad [3]$$

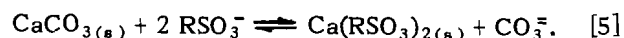
Assuming that the activity of the solid surface species is unity, that the activity coefficients of the aqueous species are unity, and that the activity of carbonate is the same at pH 9.7 for all of the flotation systems in Fig. 3, Eq. 3 becomes

$$\frac{1}{(\text{RCOO}^-)^2} = K'_{\text{adsorption}} \quad [4]$$

If Eq. 1 describes the mechanism of adsorption involved, then from Eq. 4, a linear relationship should be present between the negative logarithm of the square of the collector concentration at which a given recovery is obtained (say 80%) and the number of carbon atoms in the collector molecule.\* Further, if this is the mechanism involved, this relationship should parallel a similar plot of pK of the solubility product of the calcium carboxylate as a function of the carbon content of the collector. Plots of these types are shown in Fig. 12, and it can be noted that a good correlation between these two relationships is present.

If the reaction proposed in Eq. 2 describes the mechanism of collector adsorption, then a plot of the negative logarithm of the collector concentration at which 80% recovery is obtained should parallel the pK vs carbon content plot. The slope of this relationship is far different from the other two slopes, which suggests that collector ions are replacing surface carbonate rather than surface bicarbonate ions.

In view of the stability of the various calcium sulfonates, it would be expected that a similar mechanism of collector adsorption will occur in these systems, that is



\*Assuming that only a minor amount of the added collector has adsorbed on the surface, the equilibrium concentration will be equal to the collector addition.

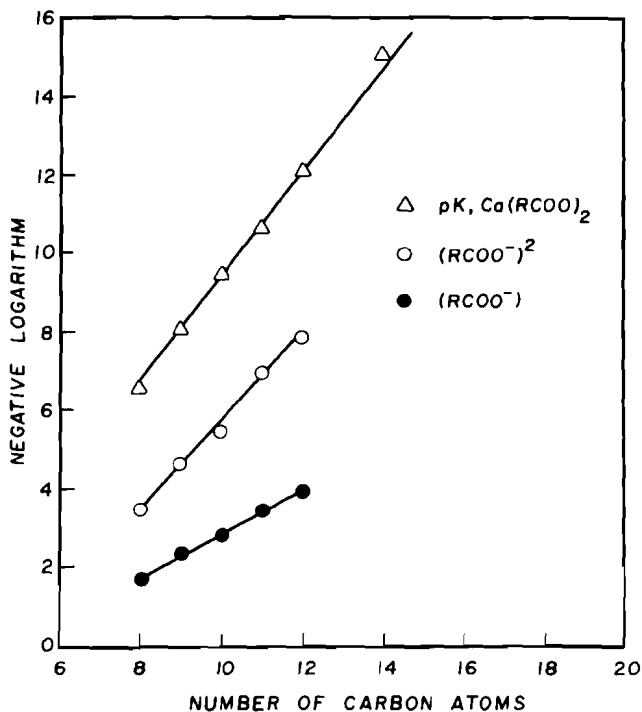


Fig. 12 - Correlation of flotation data with solubility product data for saturated fatty acids.

With reference to Fig. 13, a parallelism can be seen between the plot of the pK of the calcium sulfonate as a function of chain length and the plot of the negative logarithm of the square of the collector concentration at which 80% recovery was obtained. Below 10 CH<sub>2</sub> groups in the chain, an anomaly can be noted, in that a linear relation should be present between the pK of any metal-collector salt and carbon content of the chain. The reason for the abnormal behavior below C<sub>10</sub> is not clear; however, the purity of the C<sub>8</sub> and C<sub>9</sub> sulfonates, as determined by carbon analysis, is not as high as the others involved. Since the principal contaminant of these sulfonates is sodium sulfate, perhaps the sulfate contribution is responsible for this anomalous behavior. At the concentrations involved, though, it is unlikely that this amount of sulfate could have such a profound effect.

The presence of surface calcium sulfonate could not be detected with infrared absorption techniques. Our experience has been in this system and others that adsorbed sulfonate is very difficult to detect with such techniques. In view of the similarity between the plots of pK and the square of the collector concentration in Figs. 12 and 13, it seems logical to assume that sulfonate is chemisorbing on the calcite surface.

System depression at higher values of pH with the shorter-chained homologs of sulfonate and carboxylate can probably be attributed to the increased carbonate concentration present under these conditions. Fig. 14 shows a plot of the activity of the various carbonate and calcium species as a function

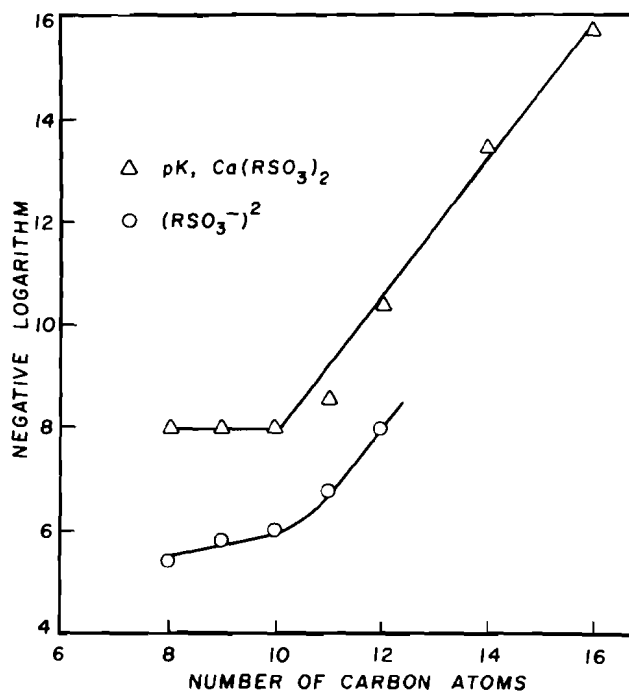
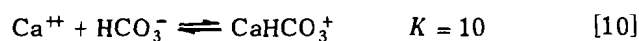
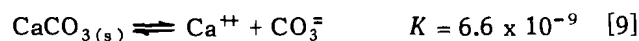


Fig. 13 - Correlation of flotation data with solubility product data for alkyl sulfonates.

of pH in a solution saturated with calcite and open to the atmosphere. This figure was constructed from the equilibria presented in Ref. 12. Note that an electrical balance in solution is not shown in this figure. This balance naturally is maintained with Na<sup>+</sup> and Cl<sup>-</sup> obtained from either HCl or NaOH used for pH adjustment.



It can be seen that at equilibrium, extremely high carbonate activities are present in basic media, whereas extremely high calcium activities are present around neutral pH. If the reactions described by Eqs. 1 and 5 are controlling adsorption, then it is to be expected that at some value of pH (or some carbonate concentration) adsorption of collector will not occur. In view of the high carbonate concentration at high pH, it is surprising that flotation was possible with both the 11 and 12-carbon sulfonates and carboxylates at high values of pH. This fact suggests that equilibrium is not attained very rapidly at higher values of pH, or, in other words, that the carbonate concentration is not as high as equilibrium dictates. To establish whether this premise is correct, one

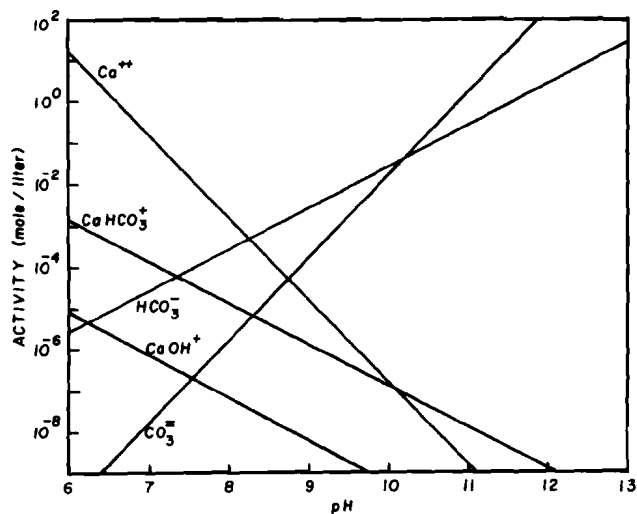


Fig. 14 — Activity of various aqueous species present in a saturated solution of calcite open to the atmosphere.

mole/liter sodium carbonate was added to water, and a flotation pH of 11.8 was used. No flotation was effected under these conditions with  $1 \times 10^{-3}$  mole/liter lauric acid. With reference to Fig. 7, it can be seen that complete flotation was obtained when calcite was conditioned for 3 min at this pH and floated with the same collector addition. These facts tend to corroborate the suggested mechanism of collector adsorption proposed with Eqs. 1 and 5.

An alternative explanation for the system depression observed at higher values of pH can be offered. That is, carbonate and calcium ions are both potential determining for calcite and, as the pH is increased, the carbonate concentration is correspondingly increased. Further, as the bulk concentration of a potential determining ion is increased, the adsorption of this ion on the surface is also increased. At some particular carbonate concentration, it is likely that the surface will be so negatively charged, that the decrease in free energy experienced by the system due to  $\text{Ca}(\text{RCOO})_2$  formation at the surface, is not sufficient to overcome the electrostatic repulsion between the surface and collector ion. The work of Sun,<sup>13</sup> however, suggests that this phenomenon is probably not responsible for depression at higher values of pH, in that he found almost no change in the magnitude of the zeta potential of calcite for additions of sodium carbonate ranging from 0 to 2.3 gpl.

To gain further insight into the mechanism of collector adsorption at high pH, the infrared spectra of various components of the system were examined at pH 9.0 and 12.5 to determine if the mechanism of collector adsorption was different at high hydroxyl concentrations. By comparing Fig. 9 (system at pH 9.0) with Fig. 10 (system at pH 12.5), it can be seen that the spectrum of calcite is the same at both values of pH as is that of calcium laurate. However, when the spectrum of calcite conditioned with lauric

acid is examined, it can be noted that the calcite condition at pH 12.5 exhibits only one characteristic frequency which is shifted to  $1599 \text{ cm}^{-1}$ , while the calcite-lauric acid at pH 9.0 has both characteristic frequencies of calcium laurate at  $1577 \text{ cm}^{-1}$  and  $1535 \text{ cm}^{-1}$ . These facts indicate that the two surface calcium laurates are different. One possibility is that some of the surface calcium ions have hydrolyzed. In aqueous media, for example, some of the calcium ions will have hydrolyzed to  $\text{CaOH}^+$  at higher values of pH. This fact can be seen from Eq. 12. If this same phenomenon occurs at the surface, a somewhat different compound may be formed, e.g., calcium hydroxy laurate, which might account for a frequency shift and the elimination of one characteristic frequency. However, no differences were noted in the spectra of calcium laurate precipitated at pH 9.0 and that precipitated at pH 12.5. Consequently, the formation of a surface calcium hydroxy laurate is somewhat in question, and the differences in spectra at pH 9 and 12.5 may be due to some other phenomena.

The experimental results obtained with the 14-carbon sulfonate and carboxylate also suggest that adsorption of longer-chained collectors may be different from that involved with shorter-chained collectors at higher values of pH. With reference to Fig. 2, it can be noted that complete flotation was obtained with an addition of  $7.5 \times 10^{-4}$  molar of the 14-carbon fatty acid at pH 9.7, while a maximal recovery of about 30% was obtained with the 14-carbon sulfonate.

The depression observed below about pH 10 can probably be attributed to the precipitation of the collector as the calcium salt. The calcium concentration will be reasonably high at lower values of pH (Fig. 14), and precipitates were observed under these conditions.

Good flotation was achieved with both the 14-carbon sulfonate and carboxylate above pH 10 (Figs. 6 and 8), and the recovery curves look similar to those obtained in calcium activation of quartz.<sup>14</sup> In the activation systems it has been postulated that the collector is either a precipitate or an aqueous complex of calcium hydroxy sulfonate, for example, that is functioning as the collector. The possibility of a similar mechanism occurring in the calcite systems at higher values of pH with the longer-chained homologs should not be overlooked.

No flotation was possible with either the 16-carbon alkyl sulfonate or 16-carbon saturated carboxylate. In both of these cases, sufficient amounts of collector could not be dissolved for flotation to be effected.

#### ACKNOWLEDGMENTS

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# THE DEVELOPMENT OF FORMULA FOR DIRECT DETERMINATION OF FREE SETTLING VELOCITY OF ANY SIZE PARTICLE

by Vernon F. Swanson

An equation has been developed which will permit the direct determination of free settling velocity of any sized particle encountered in mineral beneficiation. The equation is based on Newton's Law with the friction factor defined as a function of the laminar boundary layer.

Development of the equation is described first from an empirical trial-and-error approach. Examples are given of actual settling data from the literature versus calculated data to prove the validity of the new equation.

**N**ewton's law of resistance of a fluid to flow around a sphere is expressed in Eq. 1.

$$R = \frac{\rho_L V^2}{2} \times \frac{\pi d^2}{4} \times f_D \quad [1]$$

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Free settling velocities can be determined by setting Eq. 1 equal to the gravitational force on a particle and solving for  $V$ .

$$\frac{\rho_L V^2}{2} \times \frac{\pi d^2}{4} \times f_D = g \frac{\pi}{6} d^3 (\rho_S - \rho_L) \quad [2-a]$$

$$V = \sqrt{\frac{4gd(\rho_S - \rho_L)}{3\rho_L f_D}} \quad [2-b]$$

Experience has shown that when the solids are greater than 1 mm in diam, or when Reynold's number for the system is greater than 800-1000, the friction factor term,  $f_D$ , essentially becomes a constant, and Eq. 2-b becomes Newton's equation for free-settling and is applicable under the conditions stated.

Another special condition exists for particles smaller than 0.05 mm or when Reynold's number for the system is less than three. In this case  $f_D = 24/N_R$  or  $24\mu / \rho_L dV_\infty$ .

Eq. 2-b can then be rewritten as

$$V = \frac{gd^2(\rho_S - \rho_L)}{18\mu} \quad [3]$$