University of Nevada
Reno

The Use of Amphoteric Surfactants as Flotation Collectors

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Metallurgical Engineering

by

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ABSTRACT

Amphoteric collectors may be of considerable interest in the area of froth flotation because they combine in the same molecule positive and negative functional groups. Such structure in a collector molecule would indicate that unusual characteristics and interesting results are probable while these substances are in contact with mineral surfaces in aqueous environments.

These surfactants are little known and the technical literature does not appear to contain any pertinent information as to their application to flotation; the present paper is intended to remedy in part this situation.

The flotation response of quartz, alumina, and hematite in amphoteric collector solutions was investigated. Microflotation techniques were applied to the collection of the three pure minerals in $2 \times 10^{-4}$ M solutions of three amphoteric agents with the trade names Deriphat 151, 154, and 160C. The range of collection was from pH 2-11. The electrokinetic properties of the minerals, which have a great effect on flotation behavior, were also studied. Additional tests using combinations of amphoteric surfactants and other cationic and anionic collectors, plus large scale floats, were carried out also.

Results indicate that these amphoteric do indeed provide good collection, especially in the isoelectric range of the surfactants, but that selectivity was very difficult to
obtain. Recovery ranged from 0% to 93.6%, and was considerably higher in acid media than in alkaline. The shape of the recovery curves gave an indication that for certain pH values a high degree of selectivity was possible, but other unknown or untested factors rendered this expectation invalid.

While this presentation is primarily confined to reporting the data obtained and some of the more immediate conclusions, it is apparent that the results, in combination with those of other studies and with further testing of amphoteric surfactants in flotation, promise to provide a basis for a critical evaluation of the application of these collectors.
INTRODUCTION

Research on the flotation and recovery of minerals is of the utmost importance not only from the standpoint of furthering and confirming theories of flotation but also to industrial flotation processes. The insoluble oxides fit into this scheme because they are either the principal constituent of value in an ore, or they make up much of the gangue. The investigations into the flotation of quartz , hematite , and alumina are numerous. Each of these minerals exhibits a specific electrokinetic behavior in pure aqueous and collector media, and this can be utilized in an investigation into their amenability to flotation. Organic ions are adsorbed as counter ions by insoluble oxides mainly because of electrochemical forces existing at the interfaces. Therefore flotation of such minerals without activation should be appreciable when the mineral surface and the collector are oppositely charged. Activation has been used to yield a floatable surface on these minerals . In conventional flotation systems, if an organic compound ionizes to form an anion it should be a collector for basic oxides, which in this case would be alumina and hematite. Positive collector ions are required to collect acidics, such as quartz.

Flotation collectors, even in the most recent technical literature, are divided into three classes: [1] anionic, [2] cationic, and [3] nonionic. Such classification is based upon the behavior and the ability of collectors to ionize in water
solutions. The amphoteric surfactants offer the advantage of having both an anionic and a cationic functional group in the same molecule, and they can exhibit the electrical charge characteristics of both groups at the same time in a specific pH range, termed the isoelectric range. By definition, an amphoteric compound is one which can donate or accept a proton, depending on whether or not such a compound is present in an acid or basic environment. In froth flotation, amphoteric collectors may be employed in aqueous solutions over the range of pH from 2.0 to 12.0 and thus they can show appreciable anionic or cationic properties or alternatively the electrically neutral dipolar form.

Each mineral or solid particle, when submerged in water, exhibits a specific electrical charge. This electrical charge can vary noticeably with the alteration of pH, especially with the insoluble oxides used in this study, since H⁺ and OH⁻ can be considered potential-determining ions for these oxides (3,4,15,21,29-31). The charge also undergoes changes with the addition of activators and depressants, as well as with the adsorption of collecting agents. The correlation between the isoelectric point of amphoteric surfactant solutions in contact with minerals and floatability, as well as the overall change of electrical charges on the oxide surfaces, were all of interest.

While the pH of the solution remains in the isoelectric range, the amphoteric partly resembles a nonionic reagent in properties. However, it should be made very clear that where-
as the net charge on the molecule is essentially zero, the dipolar charges may be very high. Therefore in contact with charged mineral surfaces, there is a tendency for the collector to equalize charges by redistribution. So the adsorption of amphoteric surfactants in the isoelectric range can be much greater than adsorption outside this area. Evidently completely unexpected results using these collectors are thus possible, as is ratified by the data. Insight into all these areas is the object of this thesis.
MINERAL PROPERTIES

Two of the oxides investigated were prepared from natural crystal specimens, while the other was a commercially produced compound. The fundamental occurrences and properties will be outlined below.

Artificial corundum, aluminum oxide, is now being made from bauxite on a large scale. It is widely used as an abrasive and is replacing natural corundum for this purpose. Natural corundum is hexagonal and occurs as large barrel-shaped crystals, ruby, sapphire, and emery. It has a hardness of 9, a specific gravity of 3.9-4.1 and the usual contaminants are iron oxides, chromium, and titanium.

The aluminum oxide that was used in this study was supplied by the J.T. Baker Company. Preparation consisted of screening the material on a 325 mesh Tyler screen; the oversize, which was 100% -65 mesh, was used in the flotation tests; the undersize was employed in the electrokinetic determinations and x-ray analysis. The point of zero charge (PZC) of the alumina was pH 9.0 in distilled, deionized water after one day aging.

Hematite, Fe₂O₃, occurs often as large tabular crystals with a metallic or splendent luster. This variety is usually steel gray or iron black in color, has a hardness of 5.5-6.5, a specific gravity of 4.9-5.3, and a hexagonal crystal structure similar to that of alumina. Hematite is the most important iron ore mineral. It occurs in independent deposits,
sometimes of great extent, as an accessory mineral in many igneous rocks, in cracks and crevices, as an inclusion in many minerals, as a sublimation product in lavas, and sometimes as the result of contact metamorphism.

The specular hematite that was tested was a highly pure sample from Brazil. The sample was ground and pulverized in an agate mortar and pestle, screened on a 325 mesh screen, and the sizes were separated for individual use. The 100% -65 +325 mesh fraction was saved and used in the flotation study; the -325 mesh material was later investigated to ascertain the purity and the PZC of the hematite specimen. The PZC occurred at pH 6.7 in distilled, deionized water after one day aging time.

Quartz, SiO₂, is extremely common and occurs in many varieties. The crystal structure is hexagonal. It has a hardness of 7, a specific gravity of 2.65, a vitreous luster, and can appear transparent or opaque. Quartz comes in all colors and is classified into three groups as [1] crystalline, [2] cryptocrystalline, and [3] clastic; all the varieties in these groups are too numerous to mention here. The uses for this abundant material are extensive.

Quartz prepared for study was high-grade Brazilian crystals. These were ground and pulverized to a powder in an agate mortar and pestle, screened at 325 mesh, and separated. The oversize was cleaned with hot, dilute hydrochloric acid, and then thoroughly washed with deionized water, dried, and stored in a closed container until the flotation tests were
conducted. The undersize was similarly cleaned and stored; this was eventually used in the x-ray analysis and electrophoretic mobility tests. The PZC of the sample was 2.4 in deionized water with one day aging time.

To insure that the samples of each mineral were pure, further analysis was made by x-ray diffraction. The d spacings determined are shown in Tables I, II, and III along with the standard values. This data confirms that the mineral specimens were very pure and free from major amounts of impurities.

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SURFACE PROPERTIES

The surfaces of quartz, hematite, and alumina have been studied thoroughly and much of what is contained in these investigations is explained below.

Electrokinetic properties are related to the flotation behavior of oxide minerals. The interfacial electrical condition is strongly dependent on pH: $\text{O}^-(\text{surf}) + \text{H}_2\text{O} \rightarrow \text{2OH}^-(\text{soln})$. In the presence of a collector, this interfacial electrical condition is one item that controls floatability.

Basically, the surface charge on a solid in solution plus the counter ions next to the surface for electroneutrality constitute the electrical double layer. Counter ions next to the surface (Stern layer) are strongly held through coulombic, chemical, or van der Waals forces through associations of hydrocarbon chains, whereas the remainder of the counter ions are weakly held by electrical forces and make up the diffuse layer extending out into the liquid. Two electrical potentials are important in the system: [1] the surface or total double layer potential, and [2] the zeta potential which is the potential at the plane of shear between mineral particles and aqueous solution. The ions which give rise to surface charge are called potential-determining ions (PDI's). The PDI's for the minerals in this project can be considered as $\text{H}^+$ and $\text{OH}^-$, since these ions pass through the interface and establish charge. Therefore, surface charge can be controlled by pH regulation. There must be a critical concentration of PDI's in solution for which establishment of equili-
brium between solid and solution does not result in a net transfer of charge in either direction. An electrical double layer will then be absent and the solid surface will show no excess positive or negative charge. This situation at the interface is referred to as the point of zero charge, or PZC. The nature of a reversible interface and the changes that may result in the double layer due to changes in the composition of the solution phase will depend on the location of the PZC.

Quartz is negatively charged in water above about pH 2, due to the unsymmetrical distribution of anions and cations at the interface with the formation of the double layer. The positive charge at low pH is explained by proton uptake by surface OH\textsuperscript{-} groups or surface oxygen sites\textsuperscript{(4)}. Anions predominate at the solid surface and cations form the other part of the double layer in the adjacent solution. The PDI's for quartz, H\textsuperscript{+} and OH\textsuperscript{-}, have a special function at the surface—they participate in the electrolytic reaction that establishes equilibrium at the interface. Adsorption of H\textsuperscript{+} and OH\textsuperscript{-} give rise to an electrical double layer on the quartz surface as follows when quartz is crushed, -Si-O-Si- bonds are broken,\textsuperscript{(3)}

\[
\begin{align*}
\text{Si} & \text{O} \quad \text{Si} \\
\text{Si} & \text{O} \quad \text{Si} \\
\end{align*}
\]

and a polar surface is created:

\[
\begin{align*}
\text{Si} & \quad \text{O} \\
\text{Si} & \quad \text{Si} \\
\end{align*}
\]
When quartz is immersed in water, $\text{H}^+$ ions react with negative oxygen sites and $\text{OH}^-$ ions react with positive $\text{Si}$ sites. The surface charge originates from dissociation of $\text{H}^+$ from this surface silicic acid.

$$
\begin{align*}
\text{Si}^+ + 2\text{OH}^- & \rightarrow \text{Si-OH} + \text{Si-O}^- + 2\text{H}^+ \\
\text{Adsorption} & \rightarrow \text{Dissociation}
\end{align*}
$$

The extent of dissociation is determined by the concentration of $\text{H}^+$ ion in solution. In aqueous environment, quartz should be floatable with a cationic collector above the PZC, it should be difficult to float around the PZC with any regular collector, and it should float below the PZC with addition of an anionic collector. Data has confirmed this. Quartz also responds well to activation.

The establishment of equilibrium between a solid hematite surface and an aqueous solution may be viewed as a two-step process similar to that for quartz: Formation of a surface hydroxide due to surface hydration, followed by dissociation of this hydroxide to yield a positively or negatively charged surface depending on the pH of the solution.

The process may be expressed as follows:

$$
\begin{align*}
\text{O}^=\text{(surf)} + \text{H}_2\text{O} & \rightarrow 2\text{OH}^- \\
\text{Fe}^{+3}\text{(surf)} + 2\text{H}_2\text{O} & \rightarrow \text{Fe(OH)}_2^+\text{(surf)} + 2\text{H}^+
\end{align*}
$$
Fe(OH)\(_\frac{1}{2}\)\(_{\text{surf}}\) + H\(_2\)O $\rightleftharpoons$ Fe(OH)\(_3\)\(_{\text{surf}}\) + H\(^+\)(soln)

Fe(OH)\(_3\)\(_{\text{surf}}\) $\rightleftharpoons$ FeO\(_2\)\(_{\text{surf}}\) + H\(^+\)(soln) + H\(_2\)O

In these reactions Fe(OH)\(_3\)\(_{\text{surf}}\) represents the uncharged surface or rather a surface adsorption site which by adsorbing a proton becomes Fe(OH)\(_\frac{1}{2}\)\(_{\text{surf}}\) or by desorbing a proton becomes FeO\(_2\)\(_{\text{surf}}\). By adding the two reactions we get

Fe(OH)\(_\frac{1}{2}\)\(_{\text{surf}}\) $\rightleftharpoons$ FeO\(_2\)\(_{\text{surf}}\) + 2H\(^+\).

The species Fe(OH)\(_\frac{1}{2}\)(soln) may also be produced, along with such hydrocomplexes as hydrated Fe\(^{+3}\) ion, FeO\(_2\), FeOH\(^+\), Fe\(_2\)O\(_{\frac{4}{2}}\), and as Fe(OH)\(_3\). When equilibrium is established, the concentration of all these species will be fixed. The whole picture of the mechanism of charge origin on an Fe\(_2\)O\(_3\) surface can be depicted as follows:

A negative surface results from desorption of H\(^+\) ions or adsorption of OH\(^-\) ions at the surface. This model also suggests why the metal ion (Fe\(^{+3}\)) plays no active potential-determining role: it is buried under the surface. Only when the protective layer is stripped off at a very acid pH will the concentration of ferric ions in solution become appreciable. The PZC, and hence the pH, would again be expected to control flotation.
Since hematite and alumina are similarly structured, the surface behavior of alumina should also coincide closely with that observed for hematite.

**COLLECTOR PROPERTIES-GENERAL**

It may be asked why amphoteric surfactants were chosen to be studied as flotation collectors. The answer to this must be the answer to: What makes a good flotation collector? Sutherland and Wark and Gaudin shed some light on this question. Collector molecules must consist, at least in part, of hydrocarbons or similar groups. The collector must be adsorbed and render the surface hydrophobic so that air bubbles will attach. But adsorption alone on a mineral does not mean a bubble will adhere. Hydrophobicity will not occur unless the non-polar hydrocarbon is of sufficient length. For the fatty acids the general rule is 12 carbons or more. But the nonionic, non-reactive character of a collector does not give it the means of becoming attached to a solid having an ionic, water-avid surface. The ionic portion of a collector must be sufficiently active to selectively adsorb and displace water from the surface. A collector must have ready dispersibility in water, as by ionization, and should be of moderate to low cost. Any change in the composition of an organic ion that is a collector, such as chain length increase, which causes a decrease in its solubility in water, will increase its effectiveness as a collector. The $pK_a$ value of a collector, or the pH value where ionic and molecular species are equal in number, should be low for anionic collectors and high for cation-
ics. This insures that the collector is ionized over a wide pH range, and thus offers the opportunity for using pH variations to control adsorption. In the amphoteric collectors studied, the functional groups were carboxyls and amines. The $pK_a$ values for these are

$$\text{RCOO}^- + H^+ \leftrightarrow \text{RCOOH} \quad pK_a = 4.7 \ @ 25^\circ C \tag{38}$$

$$\text{RNH}_3^+ \leftrightarrow \text{RNH}_2 + H^+ \quad pK_a = 10.6 \ @ 25^\circ C \tag{39}$$

It is believed that with both these groups in one molecule the $pK_a$ value for the amine group will be lower, rendering it weaker. But the carboxyl should be stronger, which is evident by noting that the isoelectric range, and hence the ionization, extends down near pH 2.

A summary of collection could be stated as follows:

[1] Minerals are made floatable by abstracting hydrocarbon groups from aqueous solution; [2] this removal does not take place unless the hydrocarbon groups are ionic or ionizable, or in some way can form a chemical bond with the mineral; [3] the coating of collector on the minerals is generally far less than a complete monolayer; [4] abstraction of the collector from solution is accompanied by equivalent emission from the mineral of previously adsorbed ions; [5] in the case of oxidizable minerals and agents oxygen plays a significant, yet still unclear, part in the collection mechanism; [6] the abstraction of the collector does not require that it be present in the system in sufficient quantity to saturate the solution; [7] the adsorbed collector is attached from the polar end—whether the collector is vertically or horizontally oriented,
it endows the surface with a hydrocarbon cover; and the partition of collector between solution and mineral favors the mineral very greatly.

Adsorption can be subdivided into three categories: [1] chemisorption, [2] electrostatic adsorption, and [3] physical adsorption. Some of the aspects of these categories will be discussed briefly:

[a] Specific Adsorption—The net effect of combined electrostatic interactions due to the electrical double layer, the chemical affinity of the collector for surface which may be manifested by covalent bonding, and the collector molecules being "squeezed out" of solution by the tremendous affinity of water for itself, will be termed specific adsorption. Higher valence ions tend to be more specifically adsorbed. Amines do not show a chemical affinity for alkaline earth and base metal oxide surfaces, so the electrical double layer would be very important. The opposite is true of the fatty acids.

[b] Hydrocarbon Chain Associations—Interaction starts at a critical concentration; below this value adsorption is principally electrostatic and other ions compete for sites, whereas above this concentration hydrocarbon chains associate and the collector is strongly adsorbed. This type of association has been explained by the hemi-micelle theory of Gaudin and Fuerstenau.

[c] Concentration—Higher concentration of collector gives a wider pH range of recovery, because when it is low
most of the collector ions will be in the diffuse part of the double layer. The object in flotation is to get the ions to the Stern plane, and this can be done by increasing concentration or surface charge. Higher concentration also reduces the effect of competing ions in solution and enhances hydrocarbon chain interactions.

[d] Frothers—Froth stability has a great influence on flotation rate. The action of frothers is to adsorb at the gas/liquid interface and create a stable froth. The theory has been presented that states there must be a frother-collector interaction for good adsorption and flotation to occur. In this investigation using a collector that has a carboxyl group in it, the interaction will not occur since the collector is the frother, and an effective one. There is the problem of froth control and froth breakdown, however, that could limit these collectors in their use. Another problem with collectors that are also frothers is that a substantial amount of collector may act as a frother, thus limiting the collector that could be adsorbed.

[e] Orientation—Some researchers believe that adsorption occurs in a vertically oriented monolayer, while others favor the horizontal position. Energetically it would appear easier for the chain to take up a position close to the surface, since it is repellent to the aqueous phase and does not fit well into the hydrogen-bonded water structure. Vertical orientation with a high degree of perturbation seems
improbable. In a horizontal position the collector would displace water from the surface, render it hydrophobic, and would provide a solid basis for a good contact angle needed for flotation.

COLLECTOR PROPERTIES-AMPHOTERIC

Surface-active agents derive the bulk of their physical and performance characteristics from their electrochemical nature. The properties of amphoteric surfactants are to an even greater extent dependent on electrochemical factors than are surfactants in general. Not only does the ionic environment exert a marked force on the measurable properties, but pH actually determines the type of property (anionic, cationic, or both) to be manifested. Performance and electrical properties cannot be separated. Performance properties are merely measurable manifestations of much more complex electrochemical forces.

There are two keys to the performance of an amphoteric surfactant: pH and chain length of the fatty portion. The pH of the formulation determines the solubility, viscosity, and ionic character. These two factors cause considerable overlapping of functionality and application.

The amphoteric collectors that can be synthesized at the present time may be classified according to their acidic functional group or groups which they contain as follows:

[1] amino or imino carboxylic acids and their salts
[2] amino or imino sulfonic acids and their salts
[3] amino or imino acid sulfates and their salts

The chemical composition of amphoteric collectors may be broadly represented as $R_1X_1R_2X_2$, where $R_1$ is a long alkyl chain with usually 8 to 18 carbon atoms, $R_2$ is one or more alkyl, aryl, or cyclic chains usually of shorter length, $X_1$ is one or more cationic functional groups, and $X_2$ is one or more anionic functional groups.

Theoretically, it is possible to place in the molecule of the amphoteric collector any of the existing types of anionic and cationic functional groups. Consequently the number of amphoteric collectors possible is virtually unlimited; in actual practice, however, it is restricted by the availability of suitable intermediates and by price.

The most common type available, and the type used in this study, are those based on one or two carboxyl and an amine group: $R_1NHR_2COOH$ and $R-NH\frac{R_2COOH}{R_2COOH}$

The effect of the cationic group, $NH_2$, a base, is accentuated most in acid media, and the carboxyl, $COOH$, an acid, in basic aqueous surroundings. The unshared electron pair on the nitrogen is capable of accepting a proton from acid solution by formation of a coordinate covalent bond. This proton imparts a positive charge to the molecule:
The reverse phenomenon occurs in alkaline solution. At some solution pH when just the right amount of acid or base is added, an isoelectric point will be reached where the basic and acid radicals of the amphoteric molecule balance each other and where the net charge on the collector is zero. At this point a "Zwitterion" is obtained: \( R_1NH_2^+R_2COO^- \). This ion is both positive and negative at the same time. Such a condition is common to all amphoteric surfactants but may vary from very acidic to quite strongly basic. The isoelectric point is dependent on the relative strength of the functional radicals. When the isoelectric point is on the acid side this indicates that the net acid strength of the functional group is greater than the basic strength. The amphoterism may be represented as follows:

\[
R_1^+NH_2CH_2CH_2COOH \rightleftharpoons R_1^+NH_2CH_2CH_2COO^- \rightleftharpoons R_1NHCH_2CH_2COO^-
\]

In its isoelectric range the collector exhibits special behavior, viz., minimum solubility in water, minimum foaming, minimum wetting, etc. These special properties may be attributed to the internally compensated, or self-neutralized, "Zwitterion" ring that theoretically forms in the isoelectric pH range:

The surfactants used in this investigation were made by General Mills with the trade name Deriphats. They are summarized in Table IV.
**TABLE IV**

Deriphat Amphoteric Surfactants

<table>
<thead>
<tr>
<th>NAME</th>
<th>CHEMICAL FORMULA</th>
<th>ISOELECTRIC RANGE*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deriphat 151</td>
<td>( \text{Sodium N-coco} ) ( \text{RNHCH}_2\text{CH}_2\text{COONa} )</td>
<td>pH 2.1-4.2</td>
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<tr>
<td></td>
<td>beta-aminopropionate</td>
<td></td>
</tr>
<tr>
<td>Deriphat 154</td>
<td>( \text{Disodium N-tal-} ) ( \text{RN(CH}_2\text{CH}_2\text{COONa)}_2 )</td>
<td>pH 1.3-4.7</td>
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<tr>
<td></td>
<td>low beta-iminodipropionate</td>
<td></td>
</tr>
<tr>
<td>Deriphat 160C</td>
<td>( \text{Partial Sodium} ) ( \text{RNCH}_2\text{CH}_2\text{COOH} )</td>
<td>pH 1.7-3.5</td>
</tr>
<tr>
<td></td>
<td>Salt of N-lauryl beta-iminodipropionic acid</td>
<td></td>
</tr>
</tbody>
</table>

* 25% solids in 3.7% HCl

Note: It should be mentioned that Deriphats 151 and 154 are mixtures of different hydrocarbon chains. Therefore when making up the standard \(10^{-4}\) M collector solutions the molecular weight based on the mixture had to be considered.

Deriphat 151 (coco) \(\text{C}_8-3\%, \text{C}_{10}-5\%, \text{C}_{12}-50\%, \text{C}_{14}-23\%, \text{C}_{16}-11\%, \text{C}_{18}-8\%\)

Deriphat 154 (tallow) \(\text{C}_8-\text{C}_{12}-0.5\%, \text{C}_{14}-2.5\%, \text{C}_{16}-28\%, \text{C}_{18}-68\%\)

Deriphat 160C \(\text{C}_{12}-98-100\%\)

These reagents have many interesting properties and uses which do not apply here, but may be found in the literature.
EXPERIMENTAL

REAGENTS
The minerals and collectors have been previously described. The reagents used to prepare samples, clean the apparatus used, and adjust pH, namely HCL and NaOH, were of standard reagent grade. In the flotation study, using a combination of amphoteric and standard anionic or cationic collectors, pure dodecylamine hydrochloride and sodium dodecyl sulfate (Sargent) solutions of $10^{-3}$ M were prepared. No frother was employed in any of the microflotation tests. In the larger scale bench flotation tests pine oil was used as a frother. Distilled, deionized water was used at all times.

X-RAY DIFFRACTION
A North American Phillips X-Ray Diffractometer was utilized to yield an accurate analysis of the minerals. Samples of -325 mesh size were put into powder sample holders, and then placed on the machine. Machine settings were as follows:
Scanning Speed: 1 degree 2θ per minute
Divergence and Scatter Slits: 1 degree
Receiving Slit: 0.006 inch
Tube: Copper x-ray
Filter: Nickel
Voltage: 40 kilovolts
Amperage: 15 milliamps
Graphical patterns were taken off at the end of the run, read, and interpreted.
ELECTROPHORETIC MOBILITY

A Zeta-Meter was used to measure the surface charge on the minerals in deionized water and in the amphoteric surfactant solutions. Preparation of the samples was described before. One day before the measurements were taken, the powdered minerals were placed in the particular media to build up a double layer on the particles.

To a clean beaker containing the suspending fluid, either water or $2 \times 10^{-4}$ M collector solutions, HCl or NaOH was added to obtain the desired initial pH. To this a few drops of a fine suspension of the mineral in water or $2 \times 10^{-4}$ M surfactant solution was put into the beaker and stirred. This suspension was placed in the Riddick Plexiglas Cell and measurements were taken at 100 volts DC. The final pH of the suspension was recorded. Data collected included initial pH, direction of particle travel, elapsed time for one distinct particle to traverse one full division or a fraction thereof across the calibrated eyepiece, and the final pH. From this information the PZC could be located. More detailed operating instructions for the Zeta-Meter are available (44).

After each measurement the cell was cleaned with dilute HCl and deionized water, and dried prior to the next test at the next pH. The average travel time determined the electrophoretic mobility, and the PZC was then found by making a graphical plot of the electrophoretic mobility vs. pH.
There was some question as to whether or not a different PZC would be found for particles that were not left in solution for one day aging time. Hence a separate set of measurements were taken for particles placed in suspension immediately before measurement. No difference was found in PZC values.

**MICRO-FLOTATION**

The apparatus used in this investigation was identical to that described by Fuerstenau, except that Ascarite and a manometer were not utilized. The experimental procedure involved the following:

1. The amount of mineral to be floated, either two or three grams, was weighed out.
2. The 50 ml inverted burette was filled with nitrogen.
3. 20 ml of $10^{-3}$ M collector solution was added to 80 ml of pure water, yielding a concentration of $2 \times 10^{-4}$ M; for combinations of collectors 10 ml of each was used.
4. Collector solution and mineral were added to the cell.
5. Magnetic stirrer was turned on, and the suspension was conditioned for three minutes.
6. The pH was adjusted to the flotation pH with HCl or NaOH.
7. 50 ml of nitrogen was passed through the porous bottom of the flotation cell at an average rate of 200 ml/min, and the froth was collected in 50 ml beakers.
8. The final pH was measured, and the contents of the cell were emptied into a beaker.
9. The concentrate and tails were observed, dried, and sub-
sequently weighed to determine recovery.

The pH range tested was usually from 2.0 to 11.0 in increments of one pH unit. For floats of more than one mineral, a weight of three grams for three minerals or two grams for two minerals was used. Concentrates were dried and then analyzed for constituent percentage on an atomic absorption spectrophotometer.

For each series of tests (one mineral collected over the pH range) fresh collector solution was prepared. Temperature variation could affect flotation, so the temperature in the area each day was noted; it was fairly constant at 23 $\pm$ 0.5°C.

**Bench Scale Tests**

A Denver laboratory flotation machine was used for all the experiments. A limited number of floats were conducted merely to see what the larger volume did to recovery.

A 250 gram sample of the mineral was charged to the cell and made up to 12% solids. Collector was added to a concentration of 1.0 lb/ton, and the pH was adjusted to the desired value. The pulp was then conditioned for five minutes at 1600 rpm. A drop of pine oil was added in some tests, while in others the collector acted as the frother. The air was then turned on and the mineral was collected, dried, and weighed to determine recovery.
RESULTS

MICRO-FLOTATION

Results of the micro-flotation tests using single amphoteric collectors and single pure minerals are in Figures 1, 2, and 3, and tabulated in Table V. To become familiar with the equipment and micro-flotation procedure, and to set some guidelines for reagent additions, it was necessary to run several initial experiments. This helped to insure accurate and reproducible results.

In Figure 4 and Table VI is presented the results of the flotation tests on quartz using a combination of amphoteric surfactants and conventional collectors.

SELECTIVE FLOTATION

Utilizing the data from the Flotation Recovery vs. pH curves, float tests to investigate selectivity of the amphoteric surfactants were run. Recovery was determined at pH values where one mineral should have floated preferentially to one or two others in the same system. Data obtained is set forth in Table VII, including ideal and actual recovery. Tests conducted were as follows:

[1] Float alumina from hematite and quartz at pH 2 using Deriphat 151; raise pH to 7 and float the hematite.
Float hematite from quartz at pH 7 using Deriphat 154.
Float hematite from alumina at pH 8.5 using Deriphat 154.
Float alumina from quartz at pH 2 using Deriphat 160C.
Float alumina from hematite at pH 2 using Deriphat 160C.
Float hematite from quartz at pH 5 using Deriphat 160C.

**BENCH SCALE FLOTATION**

These flotation tests were conducted simply to observe the differences between response to amphoteric surfactants on large and small scale. The results are certainly not conclusive or very valuable at this stage, but they do offer some insight into what occurs as flotation dimensions are scaled up. Table VIII contains this data.

**ELECTROPHORETIC MOBILITY**

Graphical representations of the results of the electrophoretic mobility measurements of the pure minerals in water and in $2 \times 10^{-4}$ M amphoteric collector solutions are shown in Figures 5, 6, 7, and 8. This data is indispensible to an interpretation of what is happening in the flotation systems.
FIGURE 1
DERIPHAT 151
FLotation RECOVERY VS. pH

% RECOVERY

pH

0  2  4  6  8  10  12

- Isoelectric Range

- quartz
- alumina
- hematite
FIGURE 2
DERIPHAT 154

FLOTATION RECOVERY VS. pH

Isoelectric Range

- quartz
- alumina
- hematite

% RECOVERY

pH

0 2 4 6 8 10 12
FIGURE 3
DERIPHAT 160C

FLOTATION RECOVERY VS. pH

% RECOVERY

pH

Isoelectric Range

- quartz
- alumina
- hematite
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<th>WEIGHT, GRAMS</th>
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<th>$pH_f$</th>
<th>FLOATED, GRAMS</th>
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D-151 = Deriphat
D-154 = Deriphat 154
D-160C = Deriphat 160C
FIGURE 4
QUARTZ

FLOTATION RECOVERY VS. pH

% RECOVERY

pH

100
80
60
40
20
0

DERIPHAT 151
+ C12H25SO4Na

DERIPHAT 154
+ C12H25NH3Cl

DERIPHAT 154
+ C12H25SO4Na

DERIPHAT 151
+ C12H25NH3Cl

DERIPHAT 16OC
+ C12H25NH3Cl
### TABLE VI
Quartz Flotation With Collector Combinations

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NaDSO<sub>4</sub> = Sodium Dodecyl Sulfate

DDAHCl = Dodecylamine Hydrochloride
### TABLE VII

Selective Flotation

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### Recovery, Percent

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<td>4 min</td>
<td>5 min</td>
<td>5 min</td>
</tr>
<tr>
<td>Flotation Time</td>
<td>10 min</td>
<td>5 min</td>
<td>6.5 min</td>
<td>12.5 min</td>
</tr>
<tr>
<td>Frother</td>
<td>Pine Oil</td>
<td>none</td>
<td>none</td>
<td>Pine Oil</td>
</tr>
<tr>
<td>Machine Speed</td>
<td>1600 rpm</td>
<td>1600 rpm</td>
<td>1600 rpm</td>
<td>1650 rpm</td>
</tr>
<tr>
<td>Weight Floated</td>
<td>76.8 g</td>
<td>240.2 g</td>
<td>249.3 g</td>
<td>211.7 g</td>
</tr>
<tr>
<td>Recovery</td>
<td>30.9%</td>
<td>97.0%</td>
<td>99.2%</td>
<td>85.9%</td>
</tr>
</tbody>
</table>
FIGURE 5

ELECTROPHORETIC MOBILITY VS. pH

1 DAY AGE IN WATER

- ELECTROPHORETIC MOBILITY VS. pH
- 0 2 4 6 8 10 12
- pH

- quartz (2.4)
- alumina (9.0)
- hematite (6.7)
FIGURE 6

ELECTROPHORETIC MOBILITY VS. pH

QUARTZ

0.1 DAY AGE IN SURFACTANT

![Graph showing electrophoretic mobility vs. pH for different surfactants.](image)
FIGURE 7

ELECTROPHORETIC MOBILITY VS. pH

ALUMINA

0.1 DAY AGE IN SURFACTANT
FIGURE 8

ELECTROPHORETIC MOBILITY VS. pH

HEMATITE

0.1 DAY AGE IN SURFACTANT

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The diagram shows the electrophoretic mobility vs. pH for hematite samples aged for 0.1 day in surfactants. The data points indicate the mobility changes at different pH values, with Deriphat 151, Deriphat 154, and Deriphat 160C showing distinct trends. The graph is essential for understanding the stability and behavior of hematite under varying pH conditions.
DISCUSSION OF RESULTS

This series of experiments yielded some surprising and interesting results. As can be seen from the graphs of recovery and flotation pH, there are appreciable differences between the floatabilities of the minerals in aqueous amphoteric surfactant media. These differences generally are particularly striking in the pH range outside the approximate isoelectric range of the collector. Peak flotation response occurs near or in the isoelectric range, and always below pH 7. The isoelectric range of these collectors is below pH 5, and this in conjunction with the $pK_a$ values of these functional groups, indicates that the basic group is slightly stronger than the acidic group. This fact combined with the electrokinetic behavior of these minerals in collector solutions appears to be concretely correlated with the observed peak recovery near the isoelectric range.

Quartz is known to be a poorly-floated mineral near its PZC in water. The quartz sample employed in these tests had a PZC of 2.4 in water, and a PZC of 4.4, 3.8, and 3.5 in 2 X $10^{-4}$ M solutions of Deriphats 151, 154, and 160C respectively. Results indicate that quartz floated best in the range pH 4.6-5.2 using Deriphat 151, in the range pH 3.5-4.2 using Deriphat 154, and in the range pH 3.5-4.2 using Deriphat 160C. Above pH 7, where quartz floats well with conventional cationic collectors, or anionic collectors with multivalent metal cation activation, recovery was very poor. Collector ability to
float quartz seemed to be in the order Deriphat 151 > Deriphat 154 > Deriphat 160C.

Alumina had a PZC of 9.0 in water; in Deriphats 151, 154, and 160C alumina had PZC's of 4.2, 3.7, and 3.4 respectively. Maximum recovery was obtained in the range pH 2.1-5.0 when Deriphat 151 was used, in the range pH 2.0-7.0 using Deriphat 154, and in the range pH 2.3-5.0 when the collector was Deriphat 160C. Alumina floats well with an anionic collector below pH 9 and with a cationic collector above pH 9. Using amphoteric surfactants, there was not a significant decrease in recovery until a flotation pH of 9 was reached.

Hematite has a rather neutral PZC in water at pH 6.7, and usually shows a flotation behavior similar to that of alumina. But as seen with both quartz and alumina in amphoteric systems, hematite floats best near its PZC in amphoteric collector solution. PZC values of 4.2, 3.8, and 3.2 were found for hematite in 2 X 10^-4 M solutions of Deriphats 151, 154, and 160C respectively. Maximum flotation response using Deriphat 151 was from pH 4.9-7.0, from pH 6.0-7.0 using Deriphat 154, and from pH 4.3-5.3 using Deriphat 160C. Above pH 9 flotation was generally very poor. Reasons for poor recovery in the higher pH range will be detailed later for all the minerals and collectors. For both alumina and hematite, collector ability to float these minerals seemed to be in the order Deriphat 151 > Deriphat 160C > Deriphat 154. This ordering is based on the interpretation of the recovery curves.
The recovery curves obtained were generally very smooth (some points had to be confirmed by rerunning identical tests), which seems to indicate that the technique of collecting data points was reliable and accurate. Deriphat 160C seemed to be a weaker collector than the other two, in general, and this can probably be attributed to the fact that only one of the carboxyl groups in di-carboxylic Deriphats can form the insoluble "Zwitterion", whereas the other collectors can theoretically be completely "Zwitterionic" in the isoelectric range (43).

Initially tests were conducted with a collector concentration of $10^{-4}$ M, and although these tests provided adequate data, the froth was insufficient. For this reason it was decided to use double this concentration, or $2 \times 10^{-4}$ M. All the amphoteric collectors were very good frothers and yielded a stable froth at any concentration, but a more voluminous froth resulted with a concentration of $2 \times 10^{-4}$ M.

The character of the froth was one of the most striking phenomena encountered. If a good frother such as amyl alcohol was used in the tests, it seemed to offer too much competition to the collector; hence no froth would form and nothing would float. The froth produced with amphoteric surfactants alone would present a problem of major proportions if these were ever employed in industrial flotation operations, since the froth is so tough and long-lasting that it can be broken down only by drying. It was observed that better froth was
produced in all the tests at higher pH values, and this can be attributed to the carboxyl group which is ionized in this range. Carboxylics are powerful frothers, which makes it difficult to control frothing independently of collector action. In the isoelectric range where frothing power is at a minimum, a decrease in froth was not observed.

There existed some question as to whether or not micelles were present in the flotation systems. Micelles tend to be hydrophilic, so that collector ions are not available for adsorption; hence recovery drops. Surfactants form micelles above their critical micelle concentration (CMC). A study was proposed in which the CMC of the amphoteric surfactants would be determined. But a search of the literature rendered this unnecessary. The CMC of N-dodecyl-beta-aminopropionic acid in 0.1 M NaCl solution lies at 0.3-3.5 X 10^{-3} M in the range pH 2.3-11.0, and the CMC values of N-dodecyl-beta-iminopropionic acid in 0.1 M NaCl solution were found to be 0.7-1.8 X 10^{-3} M in the range pH 4.8-11.0. These amphoteric surfactants are almost identical to the Deriphats used in this investigation. This information, plus the fact that in solutions containing added inorganic salts whose ions are counter ions for the micelles, such as NaCl, the CMC is lowered, almost insures that at the concentration used, 2 X 10^{-4} M, micelles were not present.

As is evident from a look at the recovery curves, collection is generally very poor above pH 8-9. Some reasons for
this may be: [1] the collectors which operate in this range may be weakly attached, and violent agitation in the flotation cell by the stirring bar may cause a severance of this attachment; [2] at high pH values, hydroxides formed by the hydration of the oxide may coat the mineral particles and prevent adsorption of the collector; [3] micelles tend to form at lower concentrations than normally required, provided the solution is very alkaline; [4] at high pH values there is a more voluminous froth, which means that some of the collector that would normally be adsorbed on the mineral is acting as a frother.

The two conventional collectors used in the combination tests, sodium dodecyl sulfate and dodecylamine hydrochloride, acted as expected. Collection with the cationic collector, DDAHCl, was tremendous above the PZC value of quartz. With NaDSO₄, an anionic collector, there was little froth and very poor flotation, even below the PZC. Tests with this combination were discontinued. The effect of the amphoteric collectors was hardly noticed; both collectors appeared to mask the action of the amphotericics and act as normal anionic or cationic collectors. The reason this happens probably lies in an interaction between the two types of collectors. If an anionic collector is put into solution with an amphoteric surfactant that can ionize to two different polarities, electrostatic attraction between the negative end of the anionic collector molecule and the positive end of the amphoteric molecule is likely to result. This would leave in solution the negative end of the amphoteric molecule, which would act as
the original anionic collector would have acted. The opposite would probably hold for a cationic collector added to an amphoteric surfactant system. Research has shown that molecules do interact like this\(^{(40)}\), sometimes even giving a very noticeable precipitate.

Results from the selective flotations were unexpected and did not conform with the floatability curves. In tests of this nature there is always the chance of one mineral activating another. A glass float cell was used, which has less tendency to provide activation than a metallic cell. And since iron would be the most likely offender in the systems, an iron depressant solution was prepared to be used if necessary. But tests were attempted without depressant to see if the iron would activate either of the other minerals. It did not, as the results indicate, and recovery was so poor anyway that the depressant was not used. The initial selectivity float had all three minerals in the system, and after the first float the pH was raised and a second product was collected. All the other tests had only two minerals present. All results were poor, which points out the need for much more data on amphoteric collector selectivity.

All the systems used consisted of collector plus pure mineral, which is not encountered in commercial flotation. If these surfactants are ever applied to industrial flotation, they will be required to preferentially float one mineral from several others; therefore the key to success is selectivity in
bulk systems. Much of the further study must be channeled in this direction.

Along this same line, bench scale flotation response was very encouraging. Recovery was usually very high, the froth was tenacious and loaded with mineral, and most of the flotation occurred within one minute after the air was introduced. Pine oil seemed to destroy the collector-mineral attachment in one case but did not in another. Natural pH and starvation amounts of collector worked best. One test was tried above pH 9 to observe whether or not recovery dropped off as in the micro-flotation tests; only 30% recovery resulted. Selectivity floats were not conducted at this level.

Amphoteric surfactants can, by careful pH control, be made to simulate the properties of anionic, cationic, and nonionic collectors. Such conditions are impossible to attain otherwise, even by the employment of mixtures of collectors, as these are normally incompatible. Furthermore, the activity cannot be transferred from one functional group to another or reversed; major cost is also involved. Amphoteric collector flexibility is the reason these surfactants could be extremely valuable in the flotation operations in the mineral industry.
PROPOSED FLOTATION MECHANISM

From the electrophoretic mobility measurements and flotation results, it is proposed that the mechanism of adsorption and flotation in this study is directly related to the electrokinetic behavior of the minerals in amphoteric surfactant solution. To support this several points must be emphatically made clear. The collector must be adsorbed before flotation will occur. These collectors are surfactants, which by definition means that they are surface active. Surface active behavior of a collector may be explained by the combined effects of electrostatic interaction, chemical affinity of the collector for the surface atoms, and hydrocarbon chain "squeezing-out" associations . An electrical double layer phenomenon would be the usual answer as to why a mineral had collector adsorbed on it and was eventually floated. But in this case the minerals had an anhydrous surface fresh from the grinding operation, consisting of approximately equal numbers of positive and negative sites. This idea is supported by the literature . The minerals were added directly to the flotation collector solutions and had no time to build up an electrical double layer with water.

The pH of the water used was 6.8, and the pH of $2 \times 10^{-4}$ M solutions of the amphoteric surfactants utilized were: Deriphat 151-pH 7.0; Deriphat 154-pH 8.5; Deriphat 160C-pH 6.6. These values are indicative that the collectors were in a predominantly anionic form, but still with plenty of cations
present. When contact was made with the mineral surface that had many positive and negative sites, the collector adsorbed. Supporting evidence for this strong adsorption is the immediate change in mineral PZC's, which held for at least one day. Flotation occurred directly after addition of mineral and collector and conditioning, so this one day aging time matters only to the electrophoretic mobility data. Nothing in the system could have caused the PZC's to shift to a constant value for each collector except adsorption of that collector. If a mineral in surfactant solution indicates a positive or negative surface, it most likely is due to collector adsorption on the surface.

Complete collector coverage on a mineral surface is not a necessary prerequisite for good collection. Just as a mineral surface is not completely covered with positive or negative sites, so an amphoteric collector, though primarily anionic, will still have many positive ions available for adsorption to the negative sites of a fresh, anhydrous surface. If the pH of the solution is then lowered, more cations will become available until the "Zwitterion" ring is formed in the isoelectric range. Thus it seems apparent that by changing pH the ionic character of an adsorbed amphoteric surfactant may be regulated. At lower pH values a positive adsorbed surface will form.

The presence of a positive charge on a solid should not be regarded as evidence that it has adsorbed only positive ions, but rather that it has adsorbed more positive ions than negative ions.
To reiterate, as soon as collector and mineral are in contact, the collector adsorbs. While the pH of the solution remains in the isoelectric range, the net charge on the molecule is essentially zero; but the individual charges may be very high. Therefore in contact with charged mineral surfaces, there is a tendency for the collector to equalize charges by redistribution. So the adsorption of amphoteric surfactants in the isoelectric range can be very great, which will probably result in excellent flotation and recovery of mineral. Also in this range there are two functional groups available for strong attachment; the amine part of the molecule should have an electrostatic affinity for the negative oxygen site of the oxide, and the oxygen of the carboxyl should have a chemical affinity for the mineral surface cations. The isoelectric range is the range of minimum solubility, and as these collectors approach this range they would naturally attempt to remove themselves from the solution by any means possible. One method may be attachment to a mineral surface, which may result in flotation of the mineral. All these explanations contribute to the fact that peak flotation recovery occurs in or very near the isoelectric range of the collectors. And it must be remembered that while all the collector-mineral attachments are achieved and held, the hydrocarbon chain of the collector is extended out into the solution to pick up a bubble when one is introduced to the system.
CONCLUSIONS

[1] Quartz, alumina, and hematite respond well to flotation with the amphoteric surfactants Deriphat 151, Deriphat 154, and Deriphat 160C.

[2] The amphoteric surfactants also act as suitable frothers.

[3] The electrokinetic behavior of the minerals in collector solutions, marked by an immediate shift of the mineral PZC's, determined the floatability areas in the approximate range pH 2-11.

[4] All minerals investigated floated best in the vicinity of the isoelectric range of the collector used, and worst above pH 8-9.

[5] Other collectors combined with the amphoteric collectors seem to act as they normally would in conventional systems.


[7] Flotation of individual minerals on a larger scale than micro-flotation yields excellent recovery results.
RECOMMENDATIONS FOR FUTURE RESEARCH

The following areas are suggested as needing further investigation:
[1] Selective flotation experiments should be attempted on a larger scale.
[2] More combinations of collectors with amphoteric surfactants, collecting power on a larger assortment of mineral varieties, and molecular interactions of collectors should be studied.
[3] Flotation response of many minerals to many amphoteric surfactants should be tested.
[4] Infrared studies of the type of adsorption involved with these collectors would provide a solid basis for explanation of flotation behavior.
[5] A collector concentration vs pH diagram would indicate the most favorable bubble-attachment regions.
[7] It would be helpful to know how recovery varies with mineral particle size.
[8] More work should be directed to electrokinetic behavior of minerals in amphoteric surfactants.
[9] Determination of contact angles would furnish much vital data.
[10] If the minerals were stored under water until floated, results would surely be different and should further confirm or successfully refute the proposed mechanism.


