The Foam Separation of Colloidal Ferric Oxide with an Anionic and a Cationic Surfactant

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Abstract

An experimental investigation is presented of the foam separation of colloidal ferric oxide over the pH range 3 to 12 by using an anionic and a cationic surfactant. A sol containing 1.67 mmole/liter (93 mg/liter) of trivalent iron can be reduced in concentration to 0.09 mmole/liter by 0.17 mmole/liter dodecyl sodium sulfate (anionic) over pH 4.5 to 8; and to 0.18 mmole/liter by 0.17 mmole/liter ethylhexadecyldimethylammonium bromide (cationic) over pH 10 to 12. Soluble iron species produce poorer separations. Between pH 8 and pH 10 the charge of the colloid is reversed from positive to negative, and for an efficient separation a two-step process should be used, first with an anionic surfactant and then with a cationic. The charge of the particulates has little effect on the foam separation of the surfactants although the presence of the particulates has a significant effect, as evidenced by residual surfactant concentrations and collapsed foam volumes.

Introduction

PREVIOUS STUDIES in the Journal of the American Oil Chemists' Society have been concerned with the foam separation behavior of cationic surfactants (1) and with the use of cationic surfactants to remove from aqueous solution such specific anions as orthophosphate, phenolate, and dichromate (2). Similar apparatus and operating conditions may be employed to investigate the foam separation of colloidal particulates. In contrast to froth flotation (3,4), which involves larger-size particles of a crystalline nature which are skimmed off the suspension surface in a froth (with fundamental attention focused on the particles), foam separation (microflotation or colloid flotation) may be carried out with a column of foam rising above the suspension surface. Equal attention is paid to the partly-aggregated particles and to the surfactant. For industrial-scale operation the column of foam could be used for improved stripping and enrichment, and foam volumes (collapsed, as liquid) would be of significance. The split of the surfactant between the foam and bottoms or effluent streams would also be of prime concern.

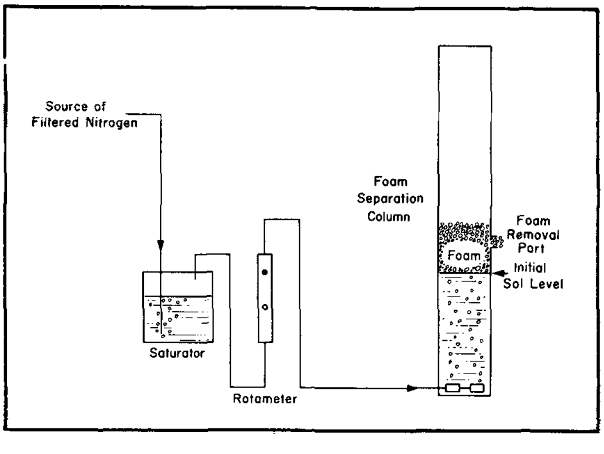


FIG. 1. Schematic diagram of experimental apparatus.

There is much evidence that colloidal ferric oxide, probably stabilized by organic matter, may occur in natural waters (5,6,7), and it has long been a source of difficulty associated with industrial and municipal water supplies. Flotation and foam separation studies have been reported previously (8,9,10,11,12) but have been limited to relatively-narrow pH ranges. Studies on the flotation of precipitated iron (13,14) have included the effects of pH, but the range has also been narrow.

The object of this investigation is to establish the effect of pH over the range 3 to 12 on the foam separation of colloidal ferric oxide. Because the zero point of charge of ferric oxide is about 8.5, both positively-charged and negatively-charged particulates are investigated, and an anionic surfactant and a cationic surfactant are utilized. In addition to residual ferric oxide concentrations, attention is focused on foam quantities and on the foam separation behavior of the surfactants, dodecyl sodium sulfate (DSS) and ethylhexadecyldimethylammonium bromide (EHDA-Br), in the presence of positively- and negatively-charged particles.

Experimental Section

The ferric oxide sol was prepared by the hydrolysis of ferric chloride in vigorously-boiling, distilled water (15). Two hundred ml of a 10-g/liter ferric chloride solution were allowed to fall drop-wise from a burette into 2,500 ml of boiling, distilled water; the final volume of about 2,300 ml (after cooling) was diluted to 2,500 ml to yield a sol containing 5.23 mmole/liter (292 mg/liter) trivalent iron, Fe^{3+}, as measured by the standard phenanthroline method (16). The sol was not dialyzed but remained quite stable. Dilutions were made for the foaming experiments: each initial sol of 2,000-ml volume contained 1.67 mmole/liter trivalent iron with the pH adjusted from 2.4 to the required initial value (from 3.0 to 12.15) with 2.5 normal sodium hydroxide; surfactant was added and was contacted with the sol (with hand mixing) for 5 min just before the initiation of each experiment. The surfactants were dodecyl sodium sulfate (DSS), anionic, in concentrations of 0.069 mmole/liter (20 mg/liter) or 0.17 mmole/liter (50 mg/liter); or ethylhexadecyldimethylammonium bromide (EHDA-Br), cationic, in concentrations of 0.069 mmole/liter (26 mg/liter) or 0.17 mmole/liter (65.5) mg/liter. The addition of either surfactant did not affect the pH of any initial sol.

The 2,000 ml of initial sol were then added to the foaming column shown in Figure 1. The column was made of Pyrex and was 82 cm in height and 9.7 cm in diameter. Nitrogen gas, saturated with water and metered with a calibrated rotameter, was dispersed through twin, sintered glass diffusers of 50-micron porosity at a rate of 3,200 ml/min (at one atmosphere and 25C). Each experiment was carried out for 5 min with foam collected continuously from a port located 7.0 cm above the initial sol level. Temperature was maintained at 25C throughout each experiment. After each experiment was terminated, the residual sol volume and pH were measured, the residual concentration of DSS or of EHDA-Br was determined by a two-phase titration technique by using methyl orange as the indicator (17), and the residual concentration of ferric iron was determined by the standard phenanthroline method (16).

Electron micrographs were taken of the sol at pH 5.8 and at pH 10.8; no surfactant was added. Individual particles of 150 Å diameter could be detected. There was some evidence of agglomeration at pH 10.8, with dimensions of about 5,000 Å. At pH 5.8, irregularly-shaped, loosely-packed agglomerates of dimensions from 20,000 to 40,000 Å were detected.

Results and Discussion

For each experiment the following material balances can be written:

$$V_i = V_f + V_r \qquad (1)$$

$$x'_i V_i = x'_f V_f + x'_r V_r \qquad (2)$$

$$z'_i V_i = z'_i V_f + z_r V_r \qquad (3)$$

V_i, V_f, and V_r are the volumes in liters of initial sol, collapsed foam, and residual sol respectively. The concentration of surfactant is designated by x′, mmole/liter, and that of ferric oxide as trivalent iron is designated by z′, mmole/liter. The subscripts refer to the initial sol (i), the collapsed foam (f), and the residual sol (r) respectively. V_i was held constant at 2.0 liters, and z'_i was maintained at 1.67 mmole/liter.

Results of the first series of experiments are presented in Figure 2. The residual ferric oxide concentration (as trivalent iron) was related to pH for two initial concentrations of dodecyl sodium sulfate. The high residuals at pH <4 were produced by some of the iron remaining in solution as $[Fe(H_2O)_6]^{3+}$, $[Fe(H_2O)_5(OH)]^{2+}$, and $[Fe(H_2O)_4(OH)_2]^{+}$. Soluble iron is more difficult to foam-separate than particulate (colloidal iron) and, in addition, requires more DSS per mole of iron removed. Above pH 4 little soluble iron would remain. Similar results had been reported (10) although the effects were less pronounced because of longer foaming times and lower residual concentrations. Studying the foam separation of soluble iron and of precipitated iron (not colloidal ferric oxide), Rubin (14) found that a sharp decrease in the residual ferric iron concentrations occurred around pH 3. This corresponded to the solubility behavior of iron and also indicated the more efficient foam separation of particulate than of soluble species. Over the pH range 4 to 8 in the present study the residual concentrations are low; the small variations may have been produced by interconversion among the hydrolyzed colloidal species, represented as Fe_2O_3, FeOOH, and $Fe(OH)_3$, which, if all other conditions are held constant, should be foam-separated to slightly different extents. In addition, it is possible to consider colloidal ferric oxide as a polymer (7), particularly at the lower pH values 3 to 5. The dimer would have the formula $[Fe_2(H_2O)_8(OH)_2]^{4+}$; the trimer $[Fe_3(H_2O)_5(OH)_4]^{5+}$; etc. These polymerized forms would require more DSS per mole iron removed and could also have produced the high residuals below pH 4 and some of the variations above pH 4. This would also explain the greater improvement in the separation achieved with 0.17 mmole/liter versus 0.069 mmole/liter DSS below pH 4 (vertical difference between the curves) compared with that achieved above pH 4.

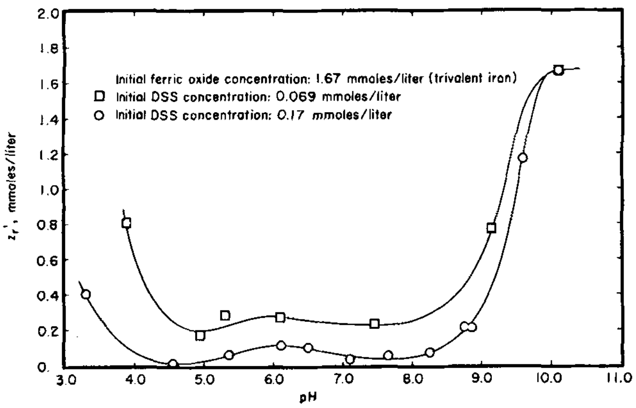
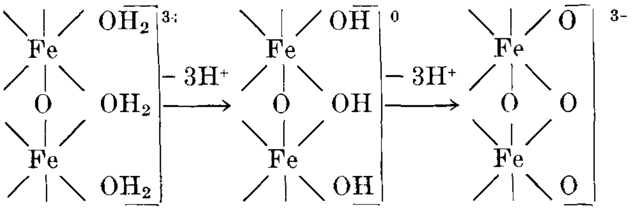


FIG. 2. Effect of pH on residual ferric oxide (trivalent iron) concentrations for two initial concentrations of an anionic surfactant.

Over the pH range 8–10 the ferric oxide residuals increase sharply, rising to values of 1.67 mmole/liter at pH 10.1, corresponding to no separation. Over this range the charge of the colloid is reversed from positive to negative: the positive charge is produced by the adsorption of hydrogen ions at and in the particulate ferric oxide surface; the negative charge is produced by the desorption of hydrogen ions (or the adsorption of hydroxyl ions). Thus, as the pH is raised over this range, an interconversion of species occurs (18,19).



Because a preliminary, electrostatic adsorption step is required before ferric oxide can be foam-separated with an anionic surfactant, the colloid must carry a positive charge. The zero points of charge of ferric oxide sols have been determined by micro-electrophoresis techniques and have been reported to occur at pH = 8.3 (20) and at pH = 8.6 (21). The somewhat higher value (9–9.5) that would be indicated by Figure 2 was produced because the colloid was nondialyzed and/or because there were variations in ionic strength compared with those employed for the microelectrophoresis experiments.

The effect of charge reversal of the colloid on foam separation is shown further by results presented in Figure 3. The residual ferric oxide concentration (as trivalent iron) was related to pH for two initial concentrations of ethylhexadecyldimethylammonium bromide, a cationic surfactant. The molar surfactant concentrations are the same as those utilized for DSS in the first series of experiments. With the cationic surfactant no separation is achieved until the pH is elevated to 9.5; then a rapid drop occurs in the residuals; the residual ferric oxide concentrations remain relatively constant (for $x'_i = 0.17$ mmole/liter) over

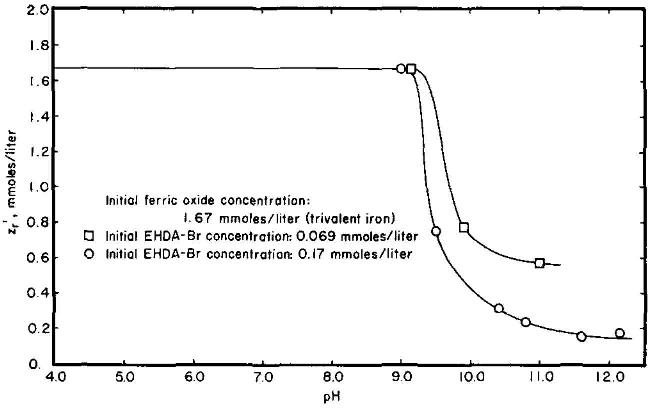


FIG. 3. Effect of pH on residual ferric oxide (trivalent iron) concentrations for two initial concentrations of a cationic surfactant.

the pH range 10.5 to 12. It may be noted, in comparing Figures 2 and 3 at $x'_i = 0.17$ mmole/liter, that the ferric oxide residuals with DSS and the positively-charged colloid are consistently lower than those with EHDA-Br and the negatively-charged colloid. This was produced by solubilization of some of the colloid as $Fe(OH)_4^-$ and FeO_2^- above pH 10; the soluble iron was more difficult to foam-separate. This may have also had some effect on the somewhat higher pH corresponding to the zero point of charge that would be predicted from Figure 3 if compared with Figure 2.

In the pH range 8 to 10 it appears likely that ferric oxide could be foam separated efficiently only by means of a two-step process, first utilizing an anionic surfactant and then a cationic surfactant. As noted in the experimental section, the pH of each initial sol was not affected by the addition of surfactant. The pHs of the residual sols (after foaming) were approximately the same as the initial sols except in the range 5–7, in which the pH of the residual sol was greater than that of the initial sol due to CO_2 degasification. The increase was from 0.5 to 1.0 pH unit.

For the efficient foam separation of colloidal ferric oxide, in addition to obtaining low residual concentrations of iron, it is mandatory to obtain small quantities of foam rich in iron (and in surfactant) and low residual concentrations of surfactant. In the first series of experiments, with DSS, above pH 4.5 there was little variation in collapsed foam volumes, V_f, with pH. At $x'_i = 0.069$ mmole/liter, V_f ranged randomly from 0.25 to 0.46 liter ($V_i = 2.0$ liter); and at $x'_i = 0.17$ mmole/liter, from 0.56 to 0.72 liter. Below pH 4.5 foam volumes were much lower. The sharp increase in V_f over the range 4 to 5 had been reported previously (10) and was probably produced by polymerization of the complexed iron. The residual surfactant concentrations in the present study were also quite insensitive to pH above pH 5; x'_r varied from 0.023 to 0.042 mmole/liter at $x'_i = 0.069$, and from 0.071 to 0.11 at $x'_i = 0.17$. Below pH 5 the values were lower, again indicating the removal of more surfactant per mole iron by the higher-charged complex ions or polymers.

In the second series of experiments, with EHDA-Br, V_f and x'_r remained rather constant over the entire pH range. At $x'_i = 0.069$ mmole/liter, V_f ranged from 0.32 to 0.36 liter ($V_i = 2.0$ liter) and x'_r from 0.015 to 0.017 mmole/liter; at $x'_i = 0.17$ mmole/liter, V_f ranged from 0.45 to 0.67 and x'_r from 0.045 to 0.059 in a random manner.

TABLE I

Foam Separation Parameters

x'_i, mmole/liter	$\frac{z'_f V_f}{z'_i V_i}$	$\frac{z'_f V_f}{x'_i V_i}$	$\frac{z'_f}{z'_r}$	$\frac{x'_f}{x'_r}$
Ferric oxide-dodecyl sodium sulfate pH = 6.1				
0.17	0.95	9.3	47	5.5
0.069	0.88	21.2	27	5.6
Ferric oxide-ethylhexadecyldimethylammonium bromide pH = 10.8				
0.17	0.91	9.0	23	11
0.069	0.71	17.2	13	24

Over the pH range 8 to 10 there were virtually no changes in collapsed foam volumes or residual surfactant concentrations, indicating that the reversal of change of the colloidal particulates had virtually no effect on the foam separation of DSS or of EHDA-Br. This is in contrast to the behavior observed with negatively-charged stannic oxide sols (22), which produced increased collapsed foam volumes with a cationic surfactant and decreased collapsed foam volumes with an anionic surfactant. In the present study the presence of ferric oxide particulates (compared with aqueous solutions of the pure surfactants) produced increased collapsed foam volumes and decreased residual surfactant concentrations with both surfactants, regardless of the charge of the particulates.

A final comparison can be made, with positively-charged ferric oxide and DSS (at pH 6.1) versus negatively-charged ferric oxide and EHDA-Br (at pH 10.8). Table I presents results in terms of the removal ratios, $z'_f V_f / z'_i V_i$, mmole trivalent iron foam separated per mmole in the initial sol, of the surfactant utilization efficiency, $z'_f V_f / x'_i V_i$, mmole trivalent iron foam separated per mmole surfactant in the initial sol, and of the trivalent iron and surfactant enrichment ratios, the ratios of the foam concentrations to the residual concentrations. Better removals were achieved with DSS, particularly when making the comparison at $x'_i = 0.069$ mmole/liter. This was probably produced by soluble iron species at the high pH. For each surfactant $z'_f V_f / x'_i V_i$ decreased as the initial concentration of surfactant was increased. This was brought about mainly by the decreased value of $z'_i V_i / x'_i V_i$ but may have been influenced by the partial redispersion of the colloid (build-up of a second adsorbed layer of surfactant ions on the particle surface) at the high value of x'_i. For both surfactants the iron enrichment ratio decreased with initial surfactant concentration, but the surfactant enrichment ratio decreased with initial surfactant concentration.

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