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A Comparative Physicochemical Study of Hematite with Hydroxamic Acid and Sodium Oleate

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ABSTRACT

A comparison of physicochemical properties of hematite ore with octyl hydroxamic acid and sodium oleate collectors has been made in order to describe the mechanism of interactions that control adsorption at the solid/liquid interface and to establish the relative selectivity and specificity. The physicochemical properties studied in this investigation, electrokinetics, adsorption, and microflootation, showed the preferential selectivity of octyl hydroxamic acid over sodium oleate. The results exhibited some differences and similarities in their physicochemical behaviors by which the efficiency of adsorption onto hematite and other oxide surfaces can be qualitatively modulated.

Key Words. Hematite; Octyl hydroxamic acid; Sodium oleate; Microflootation; Electrokinetics; Adsorption cmc

INTRODUCTION

Selection of chemical reagents plays a vital role for any separation process, especially for their selectivity and specificity toward the solid/liquid surface–reagent interaction at solid–liquid and liquid–liquid interfaces (1). Among the chemical reagents used in different mineral processing operations involving solid–solid separation, “collectors” have a special importance for efficient and economic separation. Selective adsorption of reagent at a min-

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eral–water interface is governed by different physical and chemical interactions, either individually or collectively (2). They may be coulombic, of the van der Waal's type, hydrophobic–hydrophobic, hydrophilic–hydrophobic, hydrogen bonding, covalent bonding, coordinate covalent bond, metal–ligand complexation, etc. Chelating types of reagents have been exhaustively tested with the aim of improving their selectivity in separation processes in order to replace conventional reagents (3, 4).

This paper describes the relative selectivity of two collectors, namely octyl hydroxamic acid (HXMA-8) and sodium oleate, on hematite ore as determined by electrokinetic and floatability studies.

EXPERIMENTAL

Materials

A natural hematite procured from Alminrock Indscer, Bangalore (India), was taken for the studies. The sample was 95% pure as per both XRD and laboratory analytical methods. The ore was ground to different size fractions; the +355–234 μm fractions were taken for microflotation tests, and the finer size fractions were taken for electrokinetic and adsorption studies. HXMA-8 was synthesized and characterized by the method used by Pradip (5), and sodium oleate, A.R. Grade, was procured and its purity determined analytically. NaOH and HNO₃ were used as pH modifiers, and NaNO₃ was used as an indifferent electrolyte for the electrokinetic study. Doubly distilled water of <0.1 μS conductivity was used for all experiments.

Methods

Physicochemical Study

The cmc values of the collectors were determined by measurements of their conductivities and surface tensions at different concentrations at room temperature. The effect of pH was also tested. Particle size distribution analysis was done with a Horiba Laser Particle Size Analyser. The specific surface area of the powder sample, which was used for the adsorption study, was determined by a surface area meter (Micromeritus) using the BET adsorption isotherm in a single point method.

Electrokinetic Study

The powder sample was washed with distilled water and air dried before it was used for electrokinetic study. Electrophoretic mobilities were measured with a Zeta Meter 3.0 (Zeta Meter Inc., USA) to determine the pzc and iep shifts at different concentrations of HXMA-8 and sodium oleate.



Adsorption Study

The amount of HXMA-8 adsorbed onto the hematite surface was estimated after a powder sample had been in contact with a HXMA-8 solution for 24 hours in a gyratory shaker. The residual concentration was determined with a UV-VIS spectrophotometer after centrifuging the solution, and the adsorption density was calculated by the solution depletion method.

Microflotation Study

A modified Hallimond tube as designed by Fuerstenau (12) was used for microflotation studies. Samples of approximately 1 g were tested under different reagent conditions. The weight percentage of the sample that floated was considered to be the weight percentage recovered under the specified conditions, and the nonfloating material was classified as "tailings" in the calculations.

RESULTS AND DISCUSSION

Physicochemical Study

Cmc values were determined for octyl hydroxamic acid (HXMA-8) and sodium oleate by surface tension and equivalent conductivity measurements as shown in Fig. 1 which matches values cited in the literature (6, 7). The effect of pHs are not of much significance for the cmc values of both reagents in the intermediate region (pH 5–10), but in the high acidic and alkaline pH ranges there is a slight deviation from their normal behaviors. This effect is due to the low degree of dissociation of HXMA-8 and sodium oleate [their pK_a values are around pH 9.0 (8)].

The average specific surface area for the particles was $6.731 \text{ m}^2/\text{g}$, and the d_{50} passing size was $0.561 \mu\text{m}$. The particles taken for the adsorption experiments exhibited uniform distribution.

Electrokinetic Study

The point of zero charge (pzc) of hematite was determined at around pH 7.5 (Fig. 2), and the iep shifts with different concentrations of HXMA-8 are shown in Fig. 3. At lower concentrations the iep shifts which occur infer the adsorption is due to weak physical forces: coulombic attraction, van der Waal's forces, and hydrophobic–hydrophobic interactions (9). At higher concentrations the chemisorption is typical of iep shifts as is also confirmed by the iep shifts of ferric octyl trihydroxamate $[\text{Fe}(\text{XM})_3]$ precipitate which coincides with the curve at higher concentration (10).



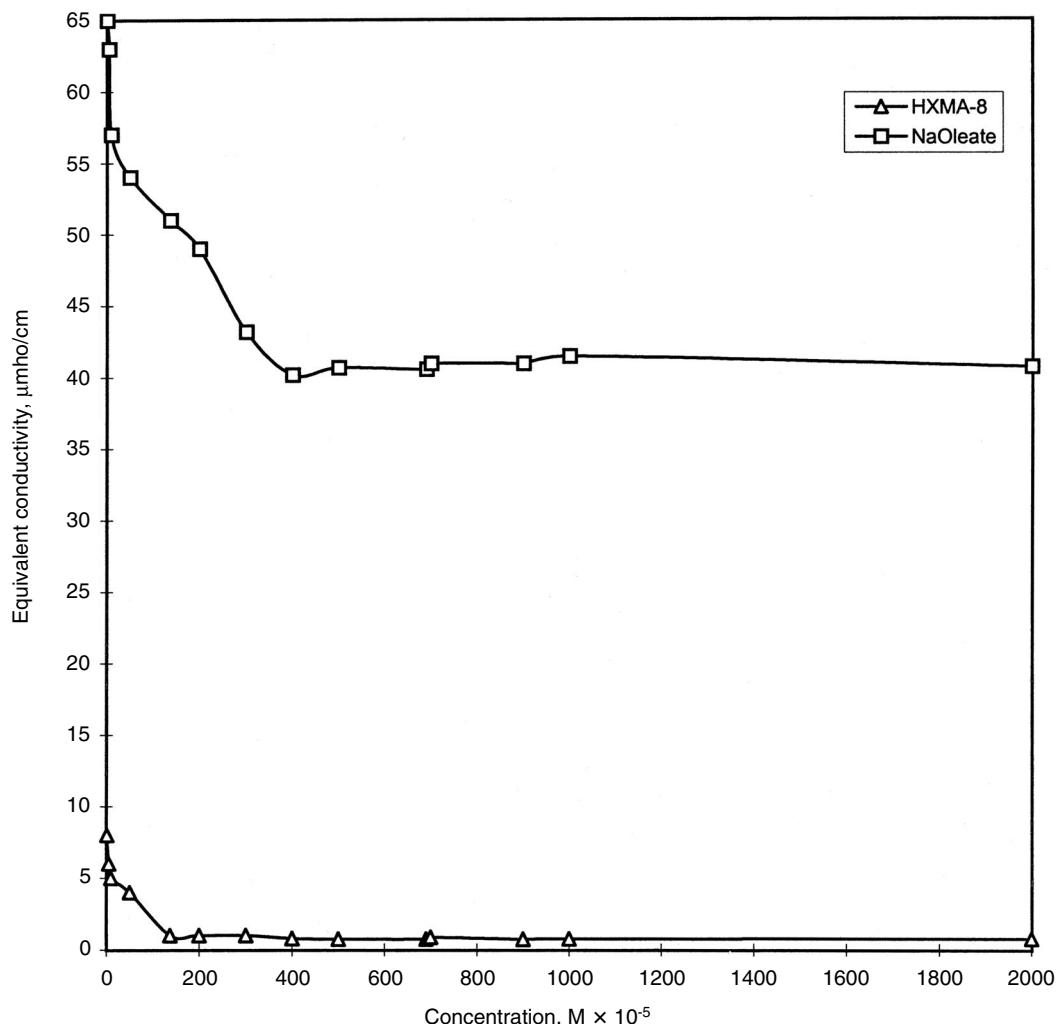


FIG. 1 Critical micellar concentration of HXMA-8 and sodium oleate.

Electrokinetics of hematite-oleate is shown in Fig. 4. There is also evidence of chemisorption from the iep shifts, but this is observed experimentally only at the lower concentrations compared to HXMA-8. The cmc values of both reagents are nearly equal, but the trends in iep shifts at those concentrations do not show any similarities. The structural differences between these two reagents may be the cause of the nonlinearity in the electrokinetic behavior with respect to the concentration. The nonpolar segment in sodium oleate by which the surface interaction is fastened laterally by hydrophobic-hydrophobic interaction results in a monolayer coverage at lower concentration compared to that of HXMA-8 (8). The concentrations where the interaction between surface and reagent begins electrostatically to form a minimum surface



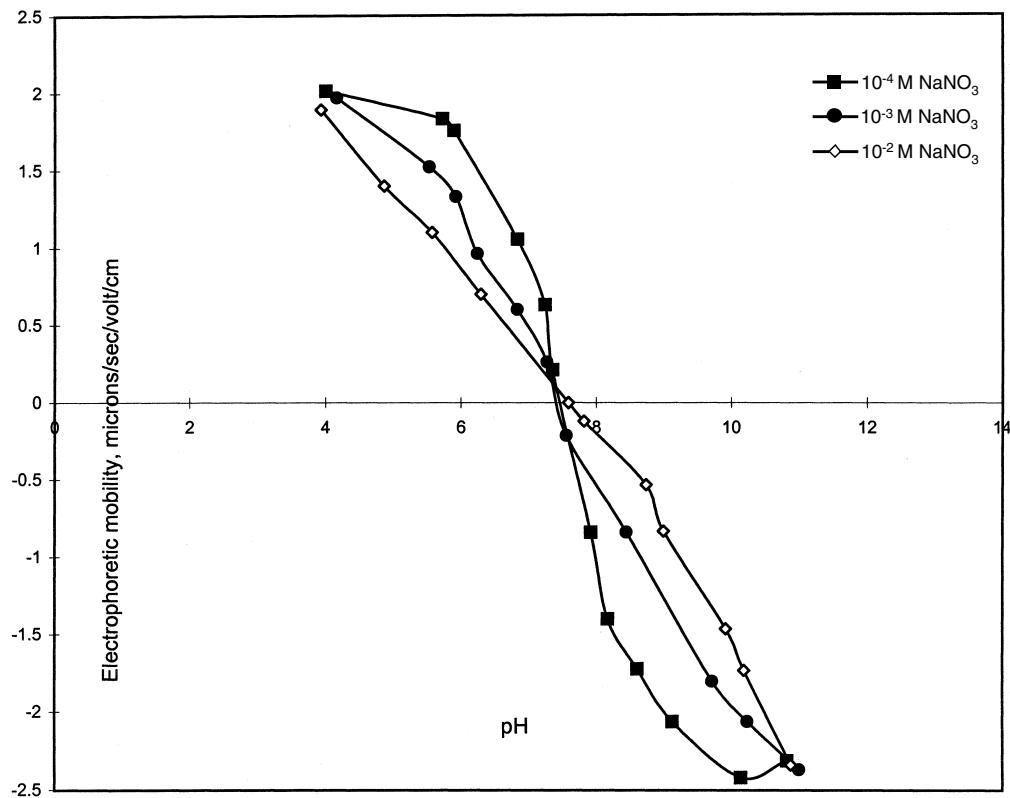


FIG. 2 Point of zero charge (pzc) of hematite (indifferent electrolyte: NaNO_3).

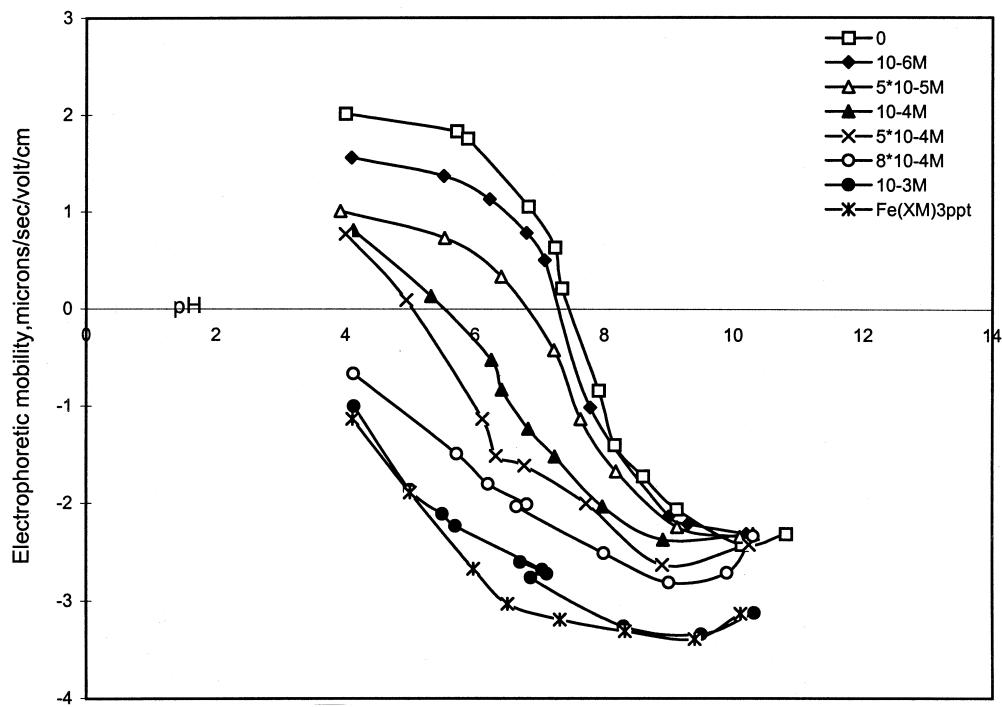


FIG. 3 Electrokinetic behavior of hematite in the presence of HXMA-8 showing iep shifts with respect to the concentration indicating different types of adsorption.



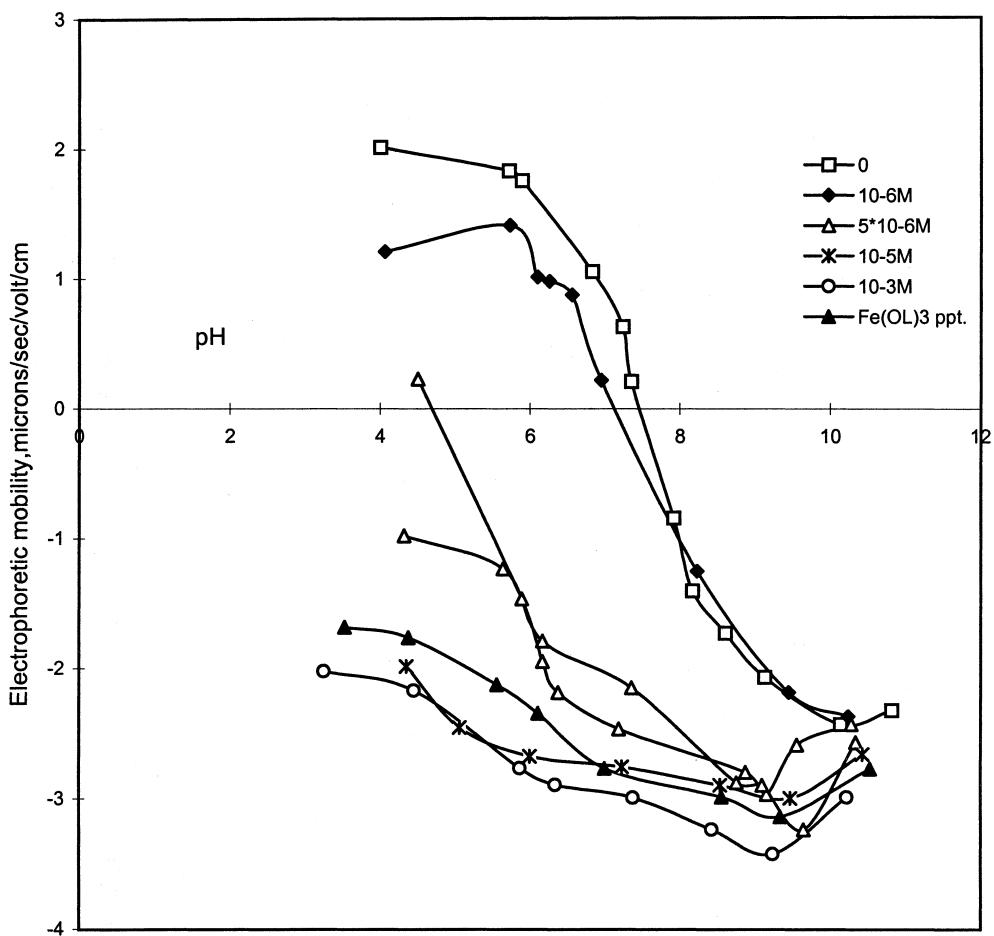


FIG. 4 Electrokinetic behavior of hematite in the presence of sodium oleate showing iep shifts with respect to the concentration indicating different types of adsorption.

coverage (hemimicellar concentration, hmc) so that they can float by attaching air bubbles are different for the two reagents, as can be seen from Figs. 2, 3, and 4. HXMA-8's functional group acts with the surface via a coordinate covalent bond (chemisorption) and at the same time its hydrocarbon segment has the ability to make it hydrophobic at a particular concentration (10). In this context sodium oleate's $-\text{O}-\text{C}=\text{O}$ group interacts chemically with the surface groups and its nonpolar segments interact laterally via hydrophobic-hydrophobic interaction at a lower concentration compared with HXMA-8.

Microflootation Study

The microflootation results for hematite with oleate and hydroxamic acid exhibit conditioning periods of 5 and 15 minutes, respectively, for identical max-



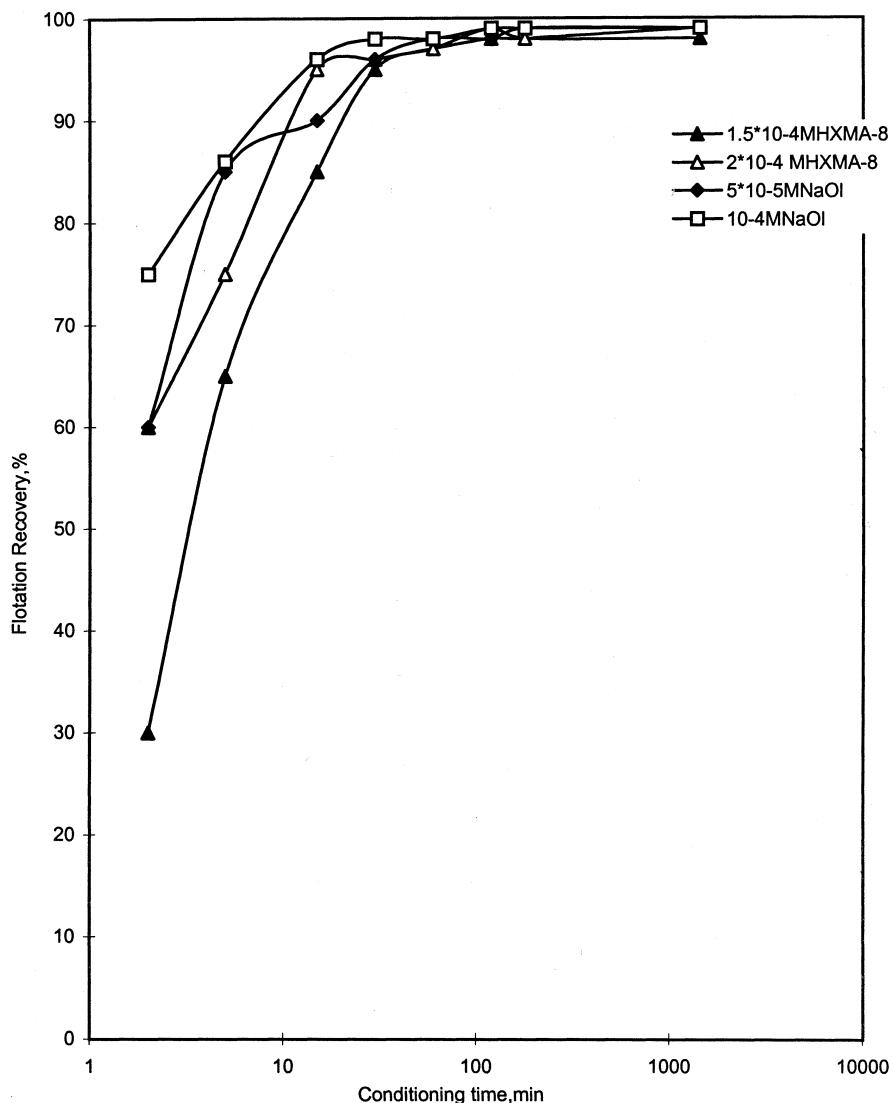


FIG. 5 Effect of conditioning time on microflotation recovery at different concentrations (pH 9.0).

imum recovery (Fig. 5). The minimum concentrations required to achieve maximum recovery at their respective optimum conditioning times are 10^{-5} M for sodium oleate and 3×10^{-4} M for HXMA-8 with a tenfold time difference (Fig. 6). Figures 7 and 8 show that maximum recovery is obtained around pH 9.0 (11). This is due pK_a values of both reagents around pH 9.0 where there is a maximum availability of the reagent. This infers that maximum flotation recovery can be achieved at the pK_a (pH) of the reagent but not at the point of zero charge of the oxide mineral (9).



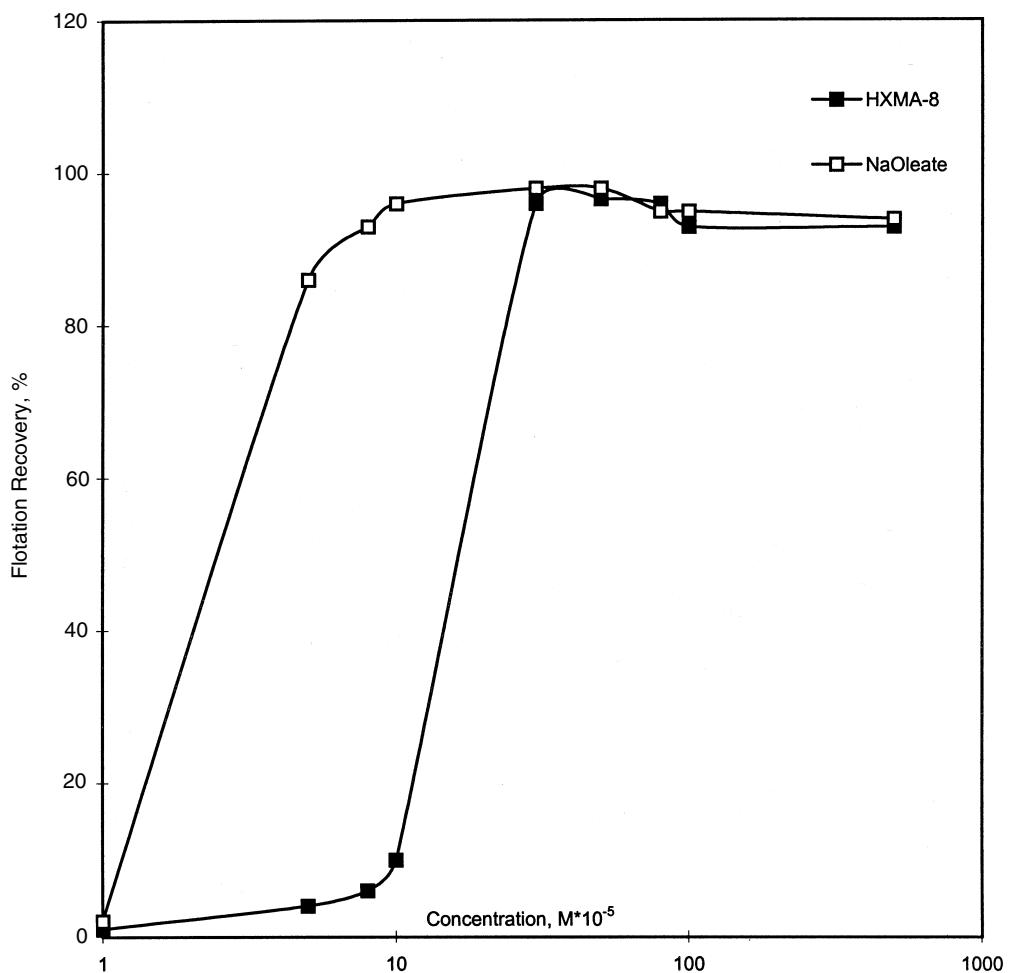


FIG. 6 Effect of concentration of HXMA-8 and sodium oleate on microflotation recovery of hematite (pH 9.0).

Adsorption Studies

Figures 9 and 10 are adsorption isotherms of HXMA-8 on hematite (Langmuir type). Figure 9 shows that adsorption starts increasing from pH 7.0 to pH 9.0, remains steady up to pH 10, and then declines suddenly due to the high degree of association of hydrocarbon segments with each other in the solution because they are unable to configurate themselves onto the surface due to their bulky structure. Figure 10 shows the amount of HXMA-8 adsorbed at different concentrations. Monolayer coverage occurs at $10^{-4} M$, which is 1/100th of the cmc of HXMA-8 (experimentally determined). The microflotation recovery results here are comparable with the results of adsorption density at a similar HXMA-8 concentration.



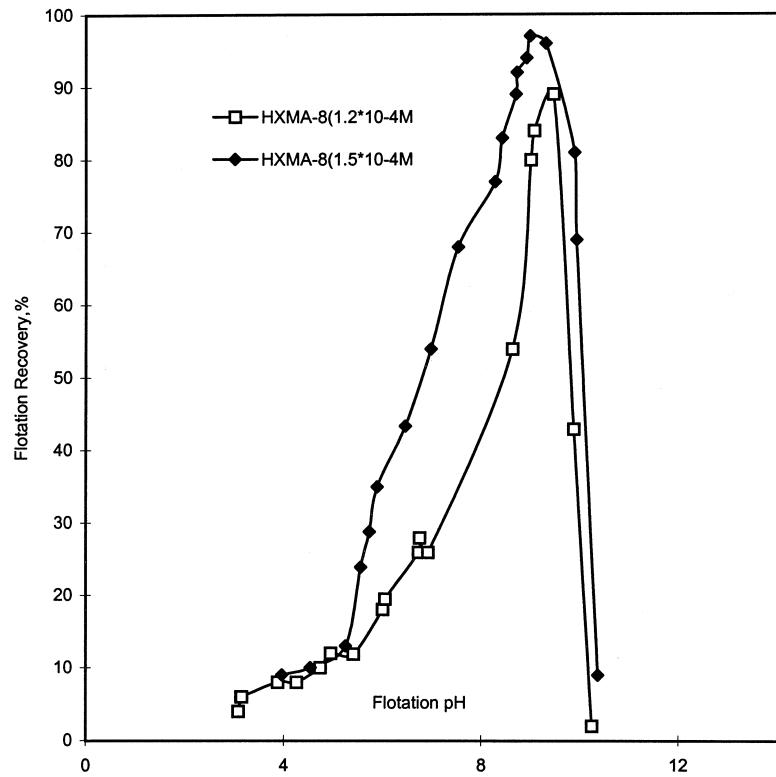


FIG. 7 Effect of pH on microflotation recovery of HXMA-8.

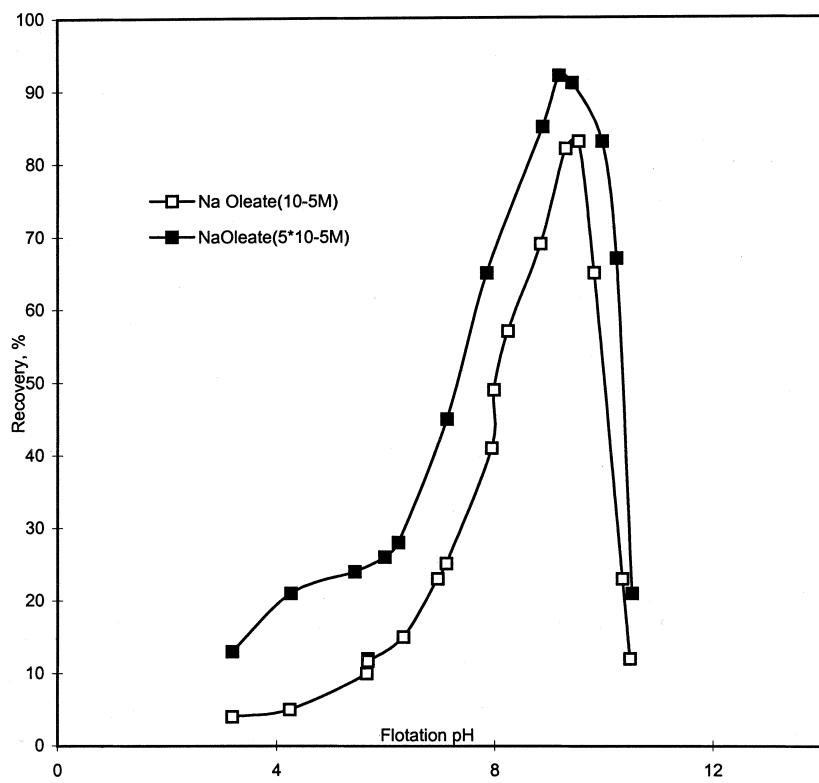


FIG. 8 Effect of pH on microflotation recovery of sodium oleate.



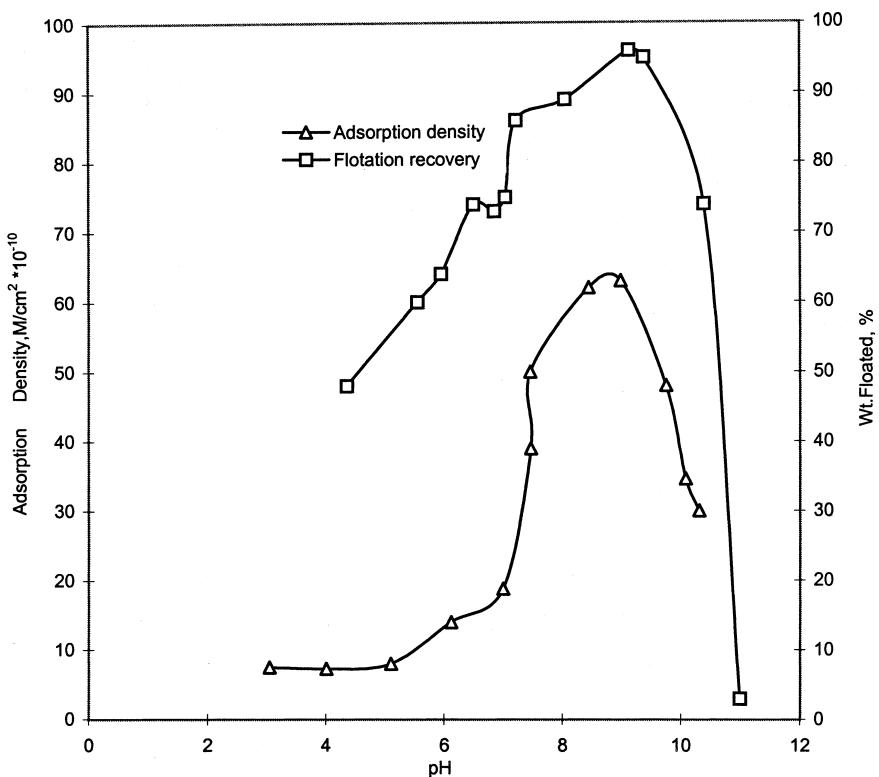


FIG. 9 Comparison of adsorption density and microflotation recovery at different pH values (concentration: 2.0×10^{-4} M HXMA-8).

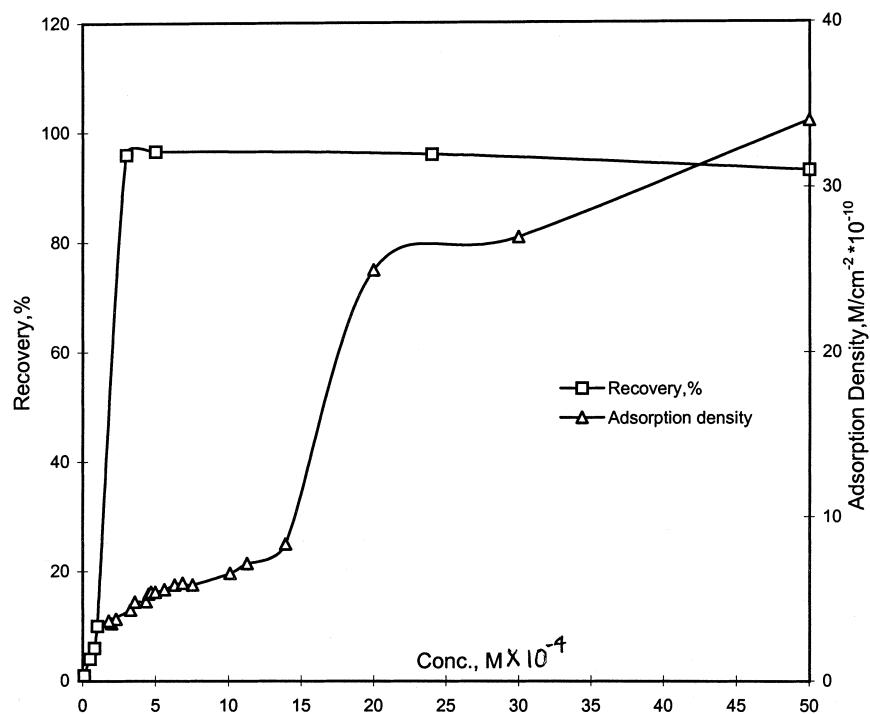


FIG. 10 Comparison of adsorption density and microflotation recovery at different concentrations of HXMA-8 (pH 9.0 ± 0.1).



CONCLUSIONS

The cmc of sodium oleate is around two times that of octyl hydroxamic acid (HXMA-8), but the maximum recovery is achieved at the concentration difference of 100 times. This is due to the better degree of hydrophobicity of sodium oleate whereas the selectivity and specificity cannot be acquired simultaneously. The selectivity of a collector is affected by its nonpolar segment. Essentially, there is no difference in the conditioning time and pH of flotation of sodium oleate and HXMA-8. A monolayer coverage of HXMA-8 occurs at a concentration which is 100 times that of its cmc. Adsorption results show parallel functionality with flotation recovery with respect to different concentrations of HXMA-8.

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