Role of Mixed Cationic/Anionic Collector Systems on Hematite Flotation

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Keywords: Hematite; adsorption; mixed collector; flotation; zeta-potential.

Abstract

The adsorption mechanism of mixed cationic alkyl diamine and anionic sulphate/oleate collectors was investigated on hematite through Hallimond flotation studies. The flotation response of hematite independently with cationic and anionic collectors and with mixed cationic/anionic collector systems is assessed. The Hallimond flotation response of hematite as a function of pH and collector concentration was investigated. The study revealed that hematite flotation recovery is maximum at acidic pH with sulphate, neutral pH 6-7 with oleate, and at basic pH about 9.5 with diamine. It is the first time that the hematite flotation results show increased adsorption of cationic collector in the presence of anionic collector apart from its own co-adsorption. The presence of oleate increased the diamine adsorption due to a decrease in the electrostatic head-head repulsion between the adjacent surface ammonium ions and thereby increasing the lateral tail-tail hydrophobic bonds. The increase in oleate concentration beyond diamine concentration leads to the formation of soluble 1:2 diamine-oleate complex or precipitate and the adsorption of these species decreased the flotation since the alkyl groups of these adsorbed species are randomly oriented at the surface.

1. Introduction

Hematite is of significant interest due to its variability in chemical and physico-chemical properties, from one sample to another, which modifies, sometimes significantly, its flotability behaviour [1]. Floatability assessments have been made mainly using highly soluble collectors such as 10 or 12-carbon chain organic molecules [2]. The hematite floatability mechanism using 14-carbon chain collector has been analysed recently [3]. The flotation of hematite using saturated fatty acids with six to 18 carbon atoms in the chain has been investigated [4]. The results show that the values of surface pressure of the surfactants are not always a good indication of their effectiveness as flotation collectors. From the foregoing literature review on the pH range for the amine flotation of hematite it is obvious that discrepancies exist. Classic references cited in many reviews on the flotation of hematite using amines report that hematite only floats above the iep, often quoted as 6.7. Other references give a wide pH range well below the iep of hematite, even as low as 0.8. It would appear that the mechanism(s) of the amine flotation of hematite are still to be elucidated. It is obvious that amine precipitation plays an important role in hematite flotation. Kulkarni and Somasundaran [5] published results for the hematite-oleate system and showed how the solution species, in particular the concentration of oleate acid-soap control the flotation of hematite.

The literature on mixed collector systems in flotation has been reviewed [6]. Increased flotation capacity may also be achieved by addition of non-ionic surfactants to the silicates-amine system. The presence of molecules of non-ionic surfactants (in particular, alcohol) decreases electrostatic repulsion of the like-charged amine cations in the adsorption layer and leads to the formation of hemimicelles on the surface of silicates. This enables the creation of a closely packed adsorption layer and more effective removal of the silicate complex with a general decrease in collector dosage [7-9].

According to our knowledge, the adsorption mechanism of hematite flotation with mixed collector systems has not been studied. However, the reverse cationic flotation of magnetite ore with mixed collectors has been investigated very recently [10]. Thus, the aim of the present work is to understand the adsorption phenomena and the role of mixed collector systems on hematite flotation.

2. Experimental Procedure

2.1. Materials

Pure Hematite mineral was handpicked from Barbil area of Orissa. The chemical analysis of the sample showed that the mineral contained 98% Hematite with 1.01% SiO_2 and 0.35% Al_2O_3. The samples were crushed and ground in an agate mortar. The product was wet sieved to obtain particle size fractions in the range of -150 + 63 μm and -63 μm. A portion of the -63 μm was further ground to obtain -53 μm size fraction. The size fraction, -150 + 63 μm, was employed for Hallimond flotation tests while -53 μm size fraction was used in zeta-potential measurements. The BET specific surface areas for these size fractions of hematite was determined to be 4.6287 and 5.9084 m^2g^{-1} respectively in Micromeritics using Argon gas as adsorbate.

2.2. Reagents

The cationic collector C_{12} amine (Dodecyl amine hydrochloride) with 97% purity was obtained from Lancaster, UK. The anionic collectors of sodium oleate with 99% purity was procured from Loba chemicals, Mumbai and the sodium dodecyl sulphate with 90% purity was procured from Merck, Mumbai. Analar grade HCl and NaOH were used for pH adjustment and de-ionised water (specific conductance, 0.4 - 0.7 $\mu S\ cm^{-1}$) was used in all the experiments.

2.3. Zeta-potential Measurements

The Zeta-potentials were measured using Zeta Probe (Colloidal Dynamics, USA). The mineral suspension was prepared in 10^{-3} M KNO_3 electrolyte solutions and conditioned for 15 minutes at room temperature (28°C). The solid content of the suspension was maintained at 2 wt%. The pH of the slurry was varied using acid / alkali (0.2 M HCl / 0.2 M NaOH) solutions prepared from analytical-grade reagents.

2.4. Hallimond Flotation Tests

The single mineral flotation tests were carried out using Hallimond cell of 100 ml volume. Exactly 1.0 g of the mineral sample was conditioned first in predetermined concentration of reagent solution for 5 min and the suspension was transferred to the flotation cell. The flotation was conducted for 1 min at N_2 gas flow rate of 75 cc min^{-1}. When the tests were performed in mixed collectors, the mineral was conditioned in a solution containing both the reagents at specified concentration ratio.

3. Results and discussion

3.1. Zeta-potential Studies

The zeta-potentials of hematite as a function of pH are depicted in Fig. 1. The iso-electric point (iep) for hematite is observed at about 6.7. The hematite acquires positive charge below pH 6.7 and the zeta-potential decreases with the increase of pH with a charge reversal occurring at pH 6.7.

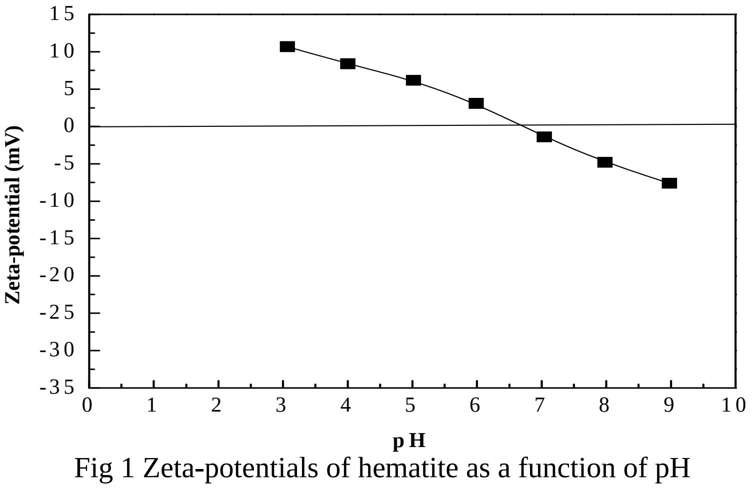

Fig 1 Zeta-potentials of hematite as a function of pH

3.2. Hallimond flotation studies

Although the objective of the study is to delineate the underlying mechanism of mixed cationic/anionic collectors in preferential flotation, the flotation response of the minerals independently with cationic and anionic collectors is first assessed. The flotation results of hematite as a function of collector concentration at pH 6–7 are depicted in Fig. 2. Numerous microflotation studies of hematite have been made using various cationic and anionic collectors, and the present tests are intended to compare the flotation responses of hematite with dodecyl amine, sodium oleate and sodium dodecyl sulphate.

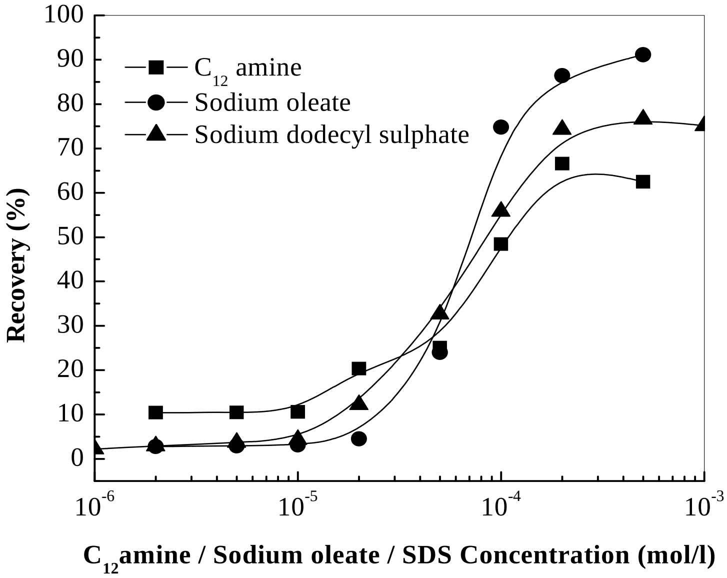

Fig 2: Flotation recovery of hematite as a function of collector concentration at pH 6–7

The onset of hemi-micelle formation for both C_{12} amine and sodium dodecyl sulphate corresponds to about 1×10^{-5} M and 2×10^{-5} M for sodium oleate. In general, the recovery of hematite increases with an increase in the concentration of both cationic as well as anionic collectors. At lower level of collector concentration (1×10^{-5} M to 1×10^{-6} M), the recovery of hematite is almost similar for both and the recovery is enhanced with the increase of collector concentration. The results show that the flotation recovery of hematite is about 75% at 1×10^{-4} M sodium oleate while at the same concentration the recovery is about 40–50% for C_{12} amine and sodium dodecyl sulphate. The maximum flotation recovery of 90% is attained at 5×10^{-4} M sodium oleate concentration.

The flotation response of hematite as a function of pH at fixed cationic and anionic collector concentration is shown in Fig. 3. The results clearly indicate that with cationic diamine collector the flotation recovery increases with the increase of pH till around pH 9.5 and thereafter, the recovery decreases marginally. The maximum recovery of about 60% is attained at pH 9.5 with diamine. The flotation recovery with anionic sodium oleate increases with the increase of pH till around pH 6.0 and thereafter, the recovery decreases. The maximum flotation recovery of 80% is attained at pH 6.0 with sodium oleate. These results show that maximum flotation recovery of about 95% is attained at highly acidic pH between 2–3, with anionic sodium dodecyl sulphate collector and the recovery decreases considerably with the increase of pH. The maximum flotation response of hematite is attained with sodium dodecyl sulphate at acidic pH between 2–3, with sodium oleate at neutral pH 6–7 and with diamine at basic pH around 9.5.

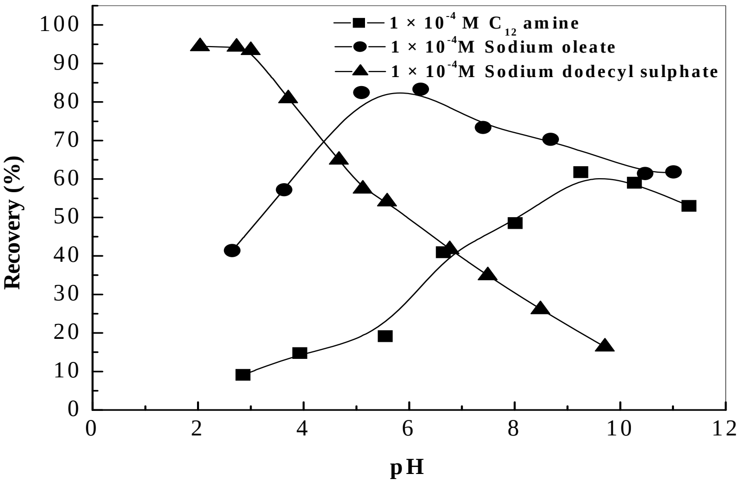

Fig 3 Flotation recovery of hematite as a function of pH at fixed collector concentration

Since the maximum flotation response of hematite is attained with diamine at pH 9.5, the effect of collector concentration was studied at this pH and flotation results are shown in Fig. 4. The enhanced flotation recovery is observed at pH 9.5 (Fig. 4) when compared with the flotation results at neutral pH 6–7 (Fig. 2). The results indicate that the flotation recovery increases with the increase of diamine concentration (> 2×10^{-5} M).

The understanding of the mechanism of adsorption of the dissimilar surfactant mixtures can provide guidance for the manipulation of surface properties. In processes such as detergency, enhanced oil recovery, surface wetting modification, emulsification, foaming control, etc., the differently structured mixed surfactants showed better properties than the individual components. The behaviour of surfactant mixtures in solution at the liquid/gas and liquid/solid interfaces has received increased attention [11, 12]. Even though the use of surfactant mixtures as collectors for increasing the recovery and selectivity during flotation has been reported from time to time, no serious effort has been made to understand the adsorption mechanism of differently structured collector mixture at the solid/liquid interface and their effect on flotation performance.

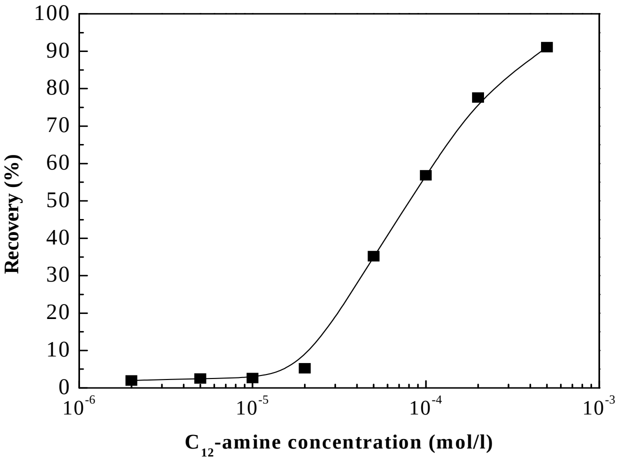

Fig 4 Flotation recovery of hematite as a function of amine concentration at pH 9.5

The flotation results of hematite as a function of sodium oleate concentration in presence of 5×10^{-5} M C_{12} amine at natural pH 6–7 is shown in Fig. 5. In general, the recovery of hematite increases with increasing concentration of sodium oleate. The presence of anionic oleate enhanced the flotation recovery until the oleate concentration equals that of the diamine concentration and above which, steep decrease in the recovery is observed. The increase in the flotation recovery is obviously due to the adsorption of diamine caused by the presence of oleate. This can be realised by the incorporation of oleate in between two adjacent surface amine head groups, thereby, screening out their electrostatic repulsion, which increases the attraction of tail-tail lateral bonds inducing further adsorption of alkyl ammonium ions. It is the first time that the hematite flotation results show that the increased adsorption of cationic collector in the presence of anionic collector apart from its own co-adsorption.

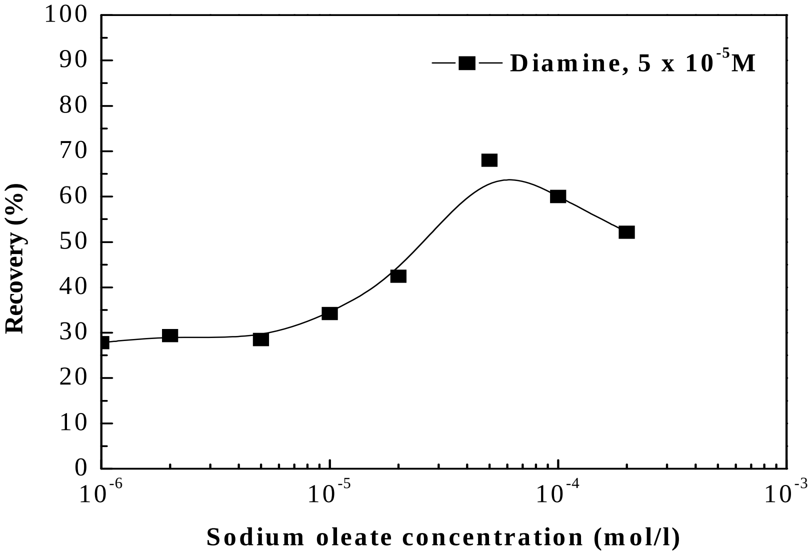

Fig 5 Flotation recovery of hematite as a function of sodium oleate concentration in presence of 5×10^{-5} M C_{12} amine at pH 6–7

When the anionic collector concentration exceeds the diamine concentration, it is reasonable to suggest that the diamine forms soluble 1:2 complex with oleate or precipitate causes the flotation recovery to decrease, since the alkyl groups of these adsorbed species are randomly oriented at the surface. Alternatively, if no further diamine is available for adsorption or the surface is already saturated with mono-layer formation, the increase in oleate concentration causes the adsorption of oleate in reverse orientation imparting hydrophilicity and resulting in the decrease in flotation.

4. Conclusions

The iso-electric point of hematite was found out to be 6.7. Sodium oleate has stronger influence on flotation response of hematite compared to that of diamine and sulphate. Maximum hematite flotation recovery is obtained at acidic pH with sulphate, neutral pH 6–7 with oleate and at basic pH about 9.5 with diamine. It is the first time that the hematite flotation results show an increased adsorption of cationic collector in the presence of anionic collector apart from its own co-adsorption. When the anionic collector concentration exceeds the diamine concentration, it is reasonable to suggest that the diamine forms soluble 1:2 complex with oleate or precipitate causes the flotation recovery to decrease, since the alkyl groups of these adsorbed species are randomly oriented at the surface. The intrusion of oleate in between adjacent surface alkyl ammonium ions decreases the electrostatic head-head repulsion and thereby increases the diamine adsorption by increasing the hydrophobic tail-tail bonds.

5. References

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