

FLOTATION OF QUARTZ AND HEMATITE: ADSORPTION MECHANISM OF MIXED CATIONIC/ANIONIC COLLECTOR SYSTEMS

A Vidyadhar^{1,*}, Neha Kumari² and R P Bhagat³

ABSTRACT

Using pure quartz and hematite minerals, the adsorption mechanism of mixed cationic/anionic reagent schemes was investigated through Hallimond flotation studies. The flotation response of quartz and hematite independently with cationic and anionic collectors as well as with mixed cationic/anionic collector systems is assessed. The flotation response as a function of pH and collector concentration was investigated. The single mineral flotation tests in the presence of anionic collectors, quartz does not respond to flotation, but the C₁₂ amine flotation of quartz was observed to be pH and concentration dependent. It was observed that hematite flotation recovery is maximum at acidic pH with sodium dodecyl sulphate (SDS), neutral pH with oleate, and at basic pH about 9.5 with C₁₂ amine. Flotation results with both quartz and hematite indicate an increased adsorption of cationic collector in the presence of anionic collector apart from its own co-adsorption. The incorporation of oleate in between C₁₂ amine molecules decreases the electrostatic head-head repulsion and thereby increasing the adsorption of C₁₂ amine due to attractive tail-tail hydrophobic bonds, besides forming a closely packed adsorbed layer enhancing the hydrophobicity. The increase in oleate concentration beyond C₁₂ amine concentration leads to the formation of soluble C₁₂ amine-oleate complex / precipitate and the adsorption of these species decreased the flotation since the alkyl chains are in chaotic orientation with a conceivable number of head groups directing towards the solution phase.

Keywords: quartz, hematite, adsorption, mixed collector system, flotation, zeta-potential

INTRODUCTION

The adsorption behavior of mixtures of soluble surfactants at interfaces and their consequent effect on interfacial properties varies significantly over a wide range of relative concentrations. The use of surfactant mixtures can have a synergistic advantage over the use of single surfactant (Scaimehorn, 1986; Holland and Rubingh, 1992; Rao *et al.*, 2011). The literature on mixed collector systems in flotation has been reviewed (Rao and Forssberg, 1997). Although the adsorption of single surfactants at the solid-liquid interface has been studied thoroughly, very few studies exist on the adsorption of mixed surfactant solutions. Increased flotation capacity may also be achieved by the 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 (Vidyadhar *et al.*, 2002, 2003). 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 dodecyl amine report that hematite floats only above the iso-electric point, 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 is still to be elucidated.

1. CSIR - National Metallurgical Laboratory, Jamshedpur - 831 007, India. Email: ari@nmlindia.org

2. CSIR - National Metallurgical Laboratory, Jamshedpur - 831 007, India. Email: neha.binni@gmail.com

3. CSIR - National Metallurgical Laboratory, Jamshedpur - 831 007, India. Email: rpb@nmlindia.org

Thus, the objective of the present investigation is to understand the underlying adsorption mechanism of the mixture of cationic C₁₂ amine and anionic collectors such as Sodium dodecyl sulphate, oleate on pure quartz and hematite minerals.

EXPERIMENTAL TECHNIQUES

Materials

Pure crystalline quartz and Hematite minerals were handpicked from Barbil area of Orissa. The chemical analysis of these samples showed that the quartz purity was more than 99%, and hematite sample contained 68.6% Fe with 1.01% SiO₂, 0.35% Al₂O₃, 0.11% Mn, 0.10% Ti, 0.069% MgO and 0.001%V. The samples were crushed and ground in an agate mortar. The products were wet sieved to obtain particle size fractions in the range of -150 + 63 μ m and -63 μ m. A portion of the -63 μ m was further ground to obtain -53 μ m size fraction. The coarser size fraction, -150 + 63 μ m, was employed for Hallimond flotation tests while the fines (-53 μ m) were used in zeta-potential measurements. The BET specific surface areas for the coarse and fine fractions of quartz were determined to be 0.5868 and 0.5919 m²g⁻¹ and the respective surface areas for hematite size fractions were found to be 4.6287 and 5.9084 m²g⁻¹ in Micromeritics using Argon gas as adsorbate.

Reagents

The cationic collector C₁₂ amine (Dodecyl amine hydrochloride) with 97% purity was obtained from Lancaster, UK. The anionic collector 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-ionized water (specific conductance, 0.4–0.7 μ S cm⁻¹) was used in all the experiments.

Zeta-potential Measurements

The Zeta-potentials were measured using Zeta Probe (Colloidal Dynamics, USA). The mineral suspension was prepared in 10⁻³ M KNO₃ electrolyte solutions, 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.

Hallimond Flotation Tests

The single mineral flotation tests were carried out using Hallimond cell of 100 ml volume. Exactly 1 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 N₂ 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.

RESULTS AND DISCUSSION

Zeta-potential Studies

The zeta-potentials of quartz and hematite as a function of pH are depicted in Figure 1. The quartz iso-electric point (iep) is about pH 2 and for hematite is about 6.7. The zeta-potentials of quartz are negatively charged in the entire pH region, and the negative charge increases with the increase of pH. The hematite acquires positive charge below pH 6.7 and the zeta-potential decreases with the increase of pH.

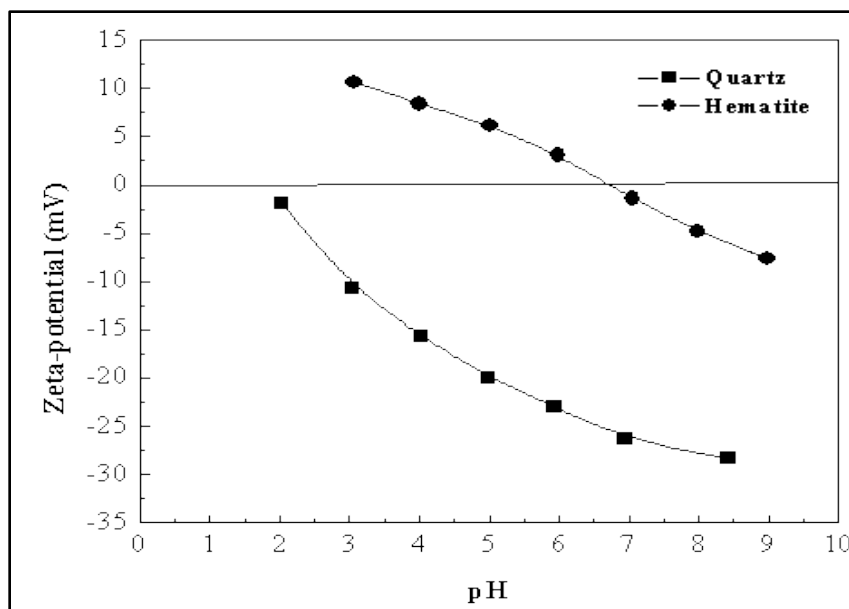


Figure 1. Zeta-potentials of quartz and hematite as a function of pH

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 and the present tests are intended to compare the flotation responses of quartz and hematite with mixed collector systems. The flotation response of quartz and hematite as a function of cationic and anionic collector concentration at pH and the pH values varied from 6.0 to 6.3 are displayed in Figure 2.

The onset hemi-micelle formation for quartz (refer Figure 2A) with C_{12} amine corresponds to about 1×10^{-5} M observed to be precisely the same was presented (Fuerstenau *et al*, 1964; Vidyadhar *et al*, 2002). The flotation recovery of quartz is nearly 90% with 1×10^{-4} M C_{12} amine and above which 100% recovery is attained. However in case of anionic collectors quartz is not floated in the pH range studied and the maximum recovery about 25% is attained even at higher concentration ($\geq 10^{-4}$ M). In general, the flotation recovery of hematite increases with increasing the concentration both in case of cationic as well as anionic collector (refer Figure 2B). At lower level of collector concentration, the recovery of hematite is almost similar and 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 was 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 quartz and hematite as a function of pH with cationic C_{12} amine, anionic oleate and Sodium dodecyl sulphate collectors, is shown in Figure 3. The quartz flotation recoveries are presented at 5×10^{-5} , 1×10^{-4} and 5×10^{-4} M initial C_{12} amine, oleate and sodium dodecyl sulphate concentrations simultaneously (refer Figure 3A). At 5×10^{-5} M C_{12} amine concentration, the rapid rise in quartz recovery begins at about pH 3.5 and above which almost 90% flotation recovery is attained throughout the entire pH region studied. However, with anionic collectors, the flotation response of quartz is not significant throughout the pH range studied even with higher concentrations of oleate and sodium dodecyl sulphate and the maximum recovery of about 45% is attained with sodium dodecyl sulphate at around pH 9.5.

The flotation results of hematite (refer Figure 3B) clearly indicate that with cationic C_{12} amine collector, the flotation recovery increases with the increase of pH till around pH 9.5 and thereafter, the recovery decreases marginally. A maximum recovery, with C_{12} amine, about 60% is attained at pH 9.5. The flotation recovery with anionic sodium oleate increases with the increase of pH till around 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 and 3, with anionic sodium dodecyl sulphate collector and the recovery decreases considerably with the increase of pH. Maximum flotation

response of hematite is attained with sodium dodecyl sulphate at acidic pH between 2 and 3, with sodium oleate at neutral pH and with diamine at basic pH around 9.5.

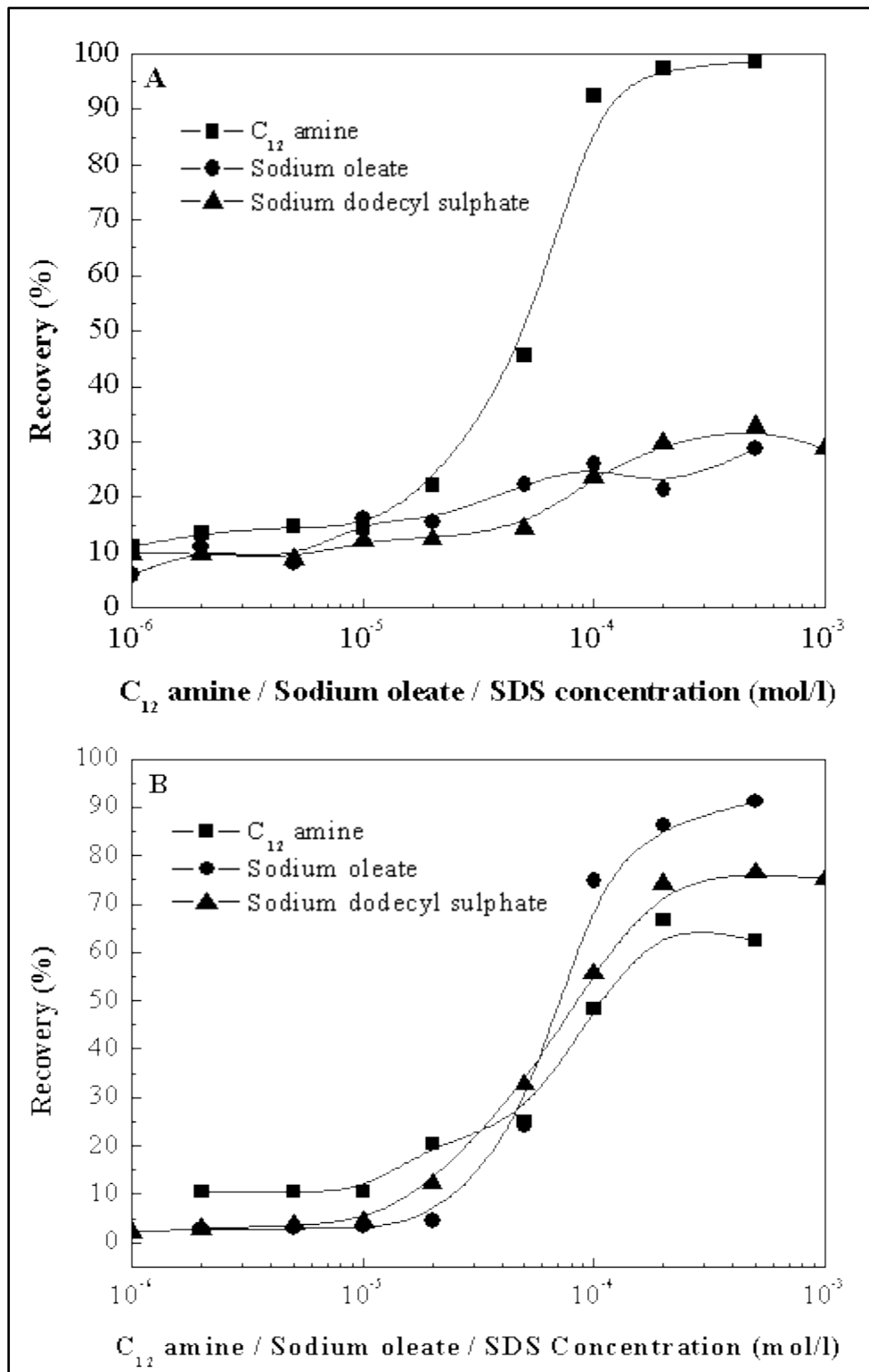


Figure 2. Flotation recovery of quartz (A) and hematite (B) as a function of collector concentration at neutral pH

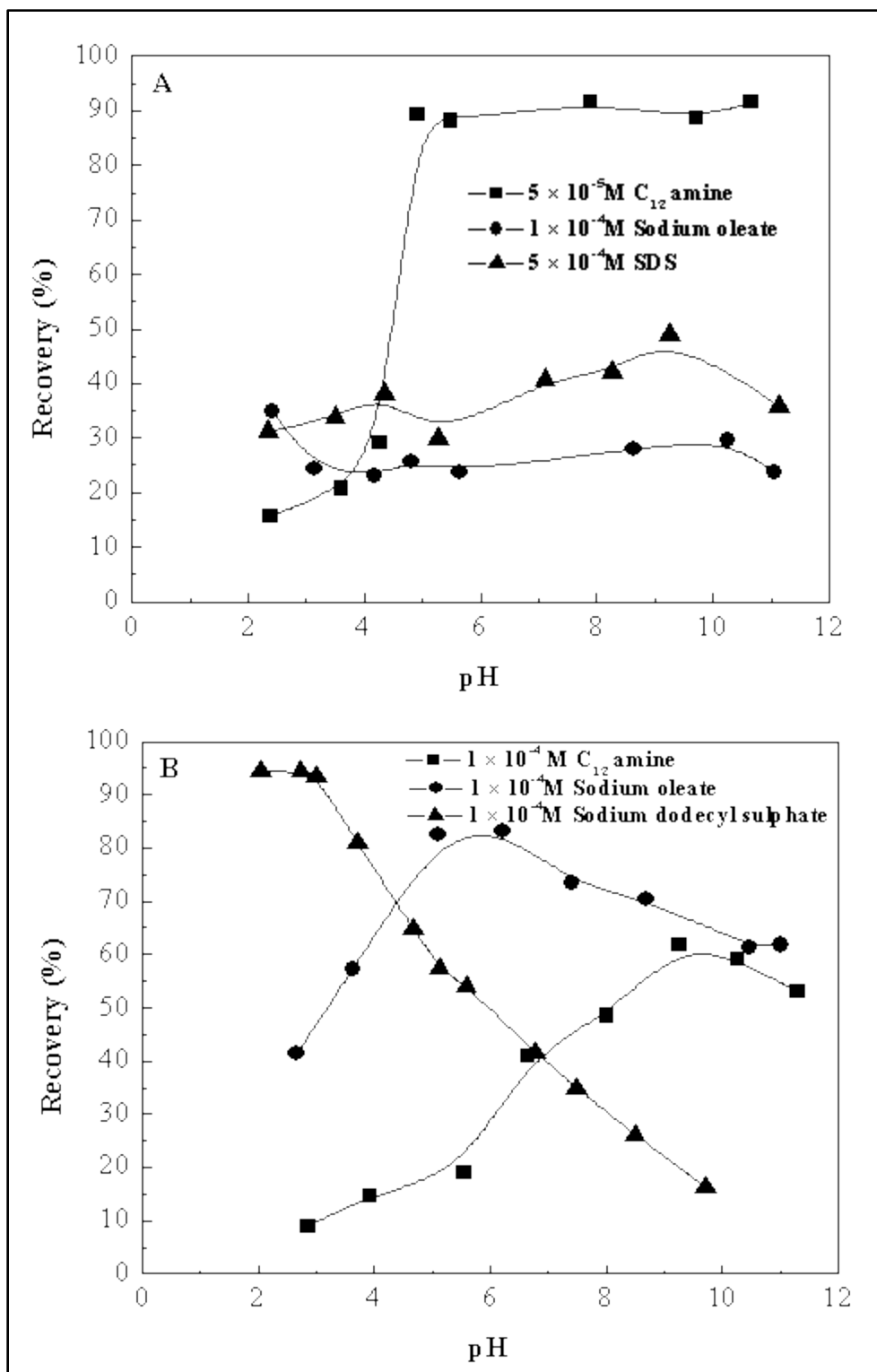


Figure 3. Flotation recovery of quartz (A) and hematite (B) as a function of pH at fixed collector concentration (Fig 3B - Vidyadhar *et al*, 2012)

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 and the behavior of surfactant mixtures in solution, at the liquid/gas and liquid/solid interfaces. 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 sincere 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.

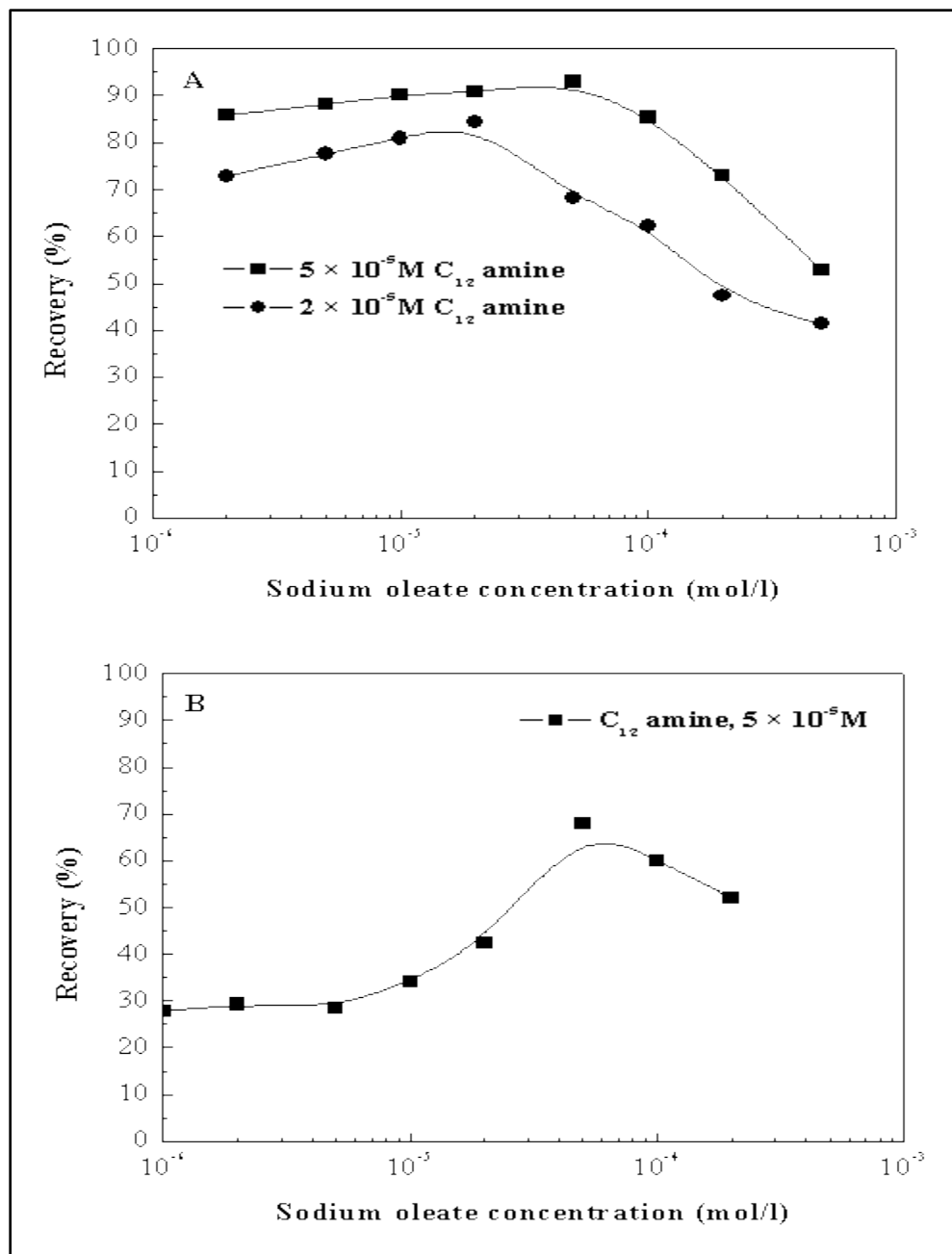


Figure 4. Flotation recovery of quartz (A) and hematite (B) as a function of Sodium oleate concentration in the presence of different amine concentration at neutral pH

The flotation response of quartz and hematite with increasing sodium oleate concentration in the presence of different amine concentration at neutral pH and pH values are varied from 6.0 to 6.3, is presented in Figure 4. The flotation results of quartz with increasing sodium oleate concentration at 2×10^{-5} and 5×10^{-5} M initial C_{12} amine

concentrations is presented in Figure 4A. Similarly, the flotation response of hematite as a function of sodium oleate concentration in the presence of 5×10^{-5} M C_{12} amine at neutral pH is shown in Figure 4B. In general, the recovery of quartz and hematite increases with increasing concentration of sodium oleate. The results clearly indicate that the presence of anionic sodium oleate enhanced the flotation recovery until the oleate concentration equals that of the C_{12} amine concentration and above which, decrease in the recovery is observed.

The increase in the flotation recovery is obviously due to the adsorption of C_{12} amine caused by the presence of oleate. This can be realized 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. The results show that the increased adsorption of cationic collector in the presence of anionic collector apart from its own co-adsorption (Vidyadhar *et al*, 2012). When the anionic collector concentration exceeds the C_{12} amine concentration, it is reasonable to suggest that the C_{12} amine forms soluble 1:2 complex with oleate / 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 C_{12} amine is available for adsorption or the surface is already saturated with the mono-layer formation, the increase in oleate concentration causes the adsorption of oleate in reverse orientation imparting hydrophilicity resulting in the decrease in flotation.

CONCLUSIONS

The iso-electric points of quartz and hematite are observed at pH 2.0 and 6.7 respectively. Quartz does not respond to flotation with anionic collectors, but with C_{12} amine it was observed to be pH and concentration dependent. Hematite flotation recovery is maximum at acidic pH between 2 and 3 with sodium dodecyl sulphate, neutral pH with oleate, and at basic pH about 9.5 with C_{12} amine. It was shown from flotation results of both quartz and hematite, an increased adsorption of cationic collector in the presence of anionic collector. The presence of oleate increases the adsorption of C_{12} amine apart from its co-adsorption, due to a decrease in the adjacent surface alkyl ammonium electrostatic head-head repulsion and thereby increasing the hydrophobic tail-tail bonds. The increase in oleate concentration beyond C_{12} amine concentration, it should be suggested that C_{12} amine forms soluble 1:2 complex / precipitate and the adsorption of these species decreases the flotation since the alkyl chains are in chaotical orientation with a conceivable number of head groups directing towards the solution phase.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support from the Department of Science & Technology (DST) under Integrated Long Term Programme (ILTP) with Russian Academy of Sciences (RAS), Russia.

REFERENCES

- Fuerstenau, D W, Healy, T W, Somasundaran, P, 1964. The role of hydrocarbon chain of alkyl collectors in flotation, Trans. SME/AIME, 229: 321-325.
- Hanumantha Rao, K, Dwari, R K, Lu, S, Vilinska, A, Somasundaran, S, 2011. Mixed anionic/non-ionic collectors in phosphate gangue flotation from magnetic fines, The Open Mineral Processing Journal, 4: 14-24.
- Hanumantha Rao, K, Forssberg, K S E, 1997. Mixed collector systems in flotation, International Journal of Mineral Processing, 51: 67-79.
- Holland, P M, Rubingh, D N, 1992. Mixed Surfactant Systems. ACS Symposium Series 501, 1992, (American Chemical Society: Washington, DC).
- Scamehorn, J F, 1986. Phenomena in Mixed Surfactant Systems. ACS Symposium Series 311, (American Chemical Society: Washington, DC).
- Vidyadhar, A, Hanumantha Rao, K, Chernyshova, I V, Pradip, Forssberg, K S E, 2002. Mechanisms of amine-quartz interaction in the absence and presence of alcohols studied by spectroscopic methods, Journal of Colloid and Interface Science, 256: 59-72.

- Vidyadhar, A, Hanumantha Rao, K, Chernyshova, I V, 2003. Mechanisms of amine-feldspar interaction in the absence and presence of alcohols studied by spectroscopic methods. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 214: 127-142.
- Vidyadhar, A, Kumari Neha, Bhagat, R P, 2012. Adsorption mechanism of mixed collector systems on hematite flotation, *Minerals Engineering*, 26: 102-104.