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SYNERGISTIC EFFECT BETWEEN THIOL COLLECTORS IN REACTION WITH SULPHIDE MINERALS

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The study of synergism between potassium ethyl xanthate (Ketx) and sodium diethyl dithiocarbamate (Dtc) in reaction with heazlewoodite (Ni_3S_2) is described. It has been demonstrated that its occurrence can be explored by simple cyclic voltametry and adsorption measurements. Correlation was obtained between flotation recoveries, adsorption isotherms and cyclic voltametry measurements. The maximum synergistic effect between Ketx and Dtc was observed at the ratio of 0.35:0.65.

Key words: Synergistic, Thio collectors, Sulphide minerals.

Introduction

Synergism may be defined as the enhanced effect obtained from the use of a combination of reagents relative to their individual action. In flotation synergistic effects between collectors and frothers have long been recognized implant practice (Taggart 1945), through little attention has been paid to them in laboratory studies. Exceptions to this are, for example, the investigation reported by Glembotskii (1958) on the use of mixtures of collectors of the same type but of differing hydrocarbon chain length or degree of branching, the work of Mingione (1984) on the use of dithiophosphates in conjunction with xanthates and sodium mercaptobenzothiozole in the flotation of platinum group metals and the work of Pomianwski and Pawlikowski-Czubak (1967) who have presented the results of flotation experiments using potassium ethyl xanthate (Ketx) with dodecyltrimethyl ammonium bromide. The study of synergism between xanthate and carbamate and sodium sulphide and carbamate was also carried out by Riaz *et al* (1993 and 1997) on dropping mercury and heazlewoodite electrodes.

The study of such effects between potassium ethyl xanthate (Ketx) and dithiocarbamate (Dtc) in the reaction with heazlewoodite, is described in the present paper. A correlation is obtained in a modified Hallimond tube, adsorption isotherms for the reagents on the mineral surface and simple measurements of cyclic voltametry at controlled potentials.

Experimental

Analytical grade chemicals are used in this investigation. The Ketx was freshly recrystallized for each experiment and distilled water was used through out unless otherwise stated. All experiments were carried out in an electrolyte of 0.1 M sodium tetraborate, the pH of which was adjusted by addition of NaOH or H_2SO_4.

Cyclic voltametric studies were carried out by using the potentiostate Sycopel 7030 together with wave form generator (type WG-01). For current measurements, standard resistance box was used as a counting resistance. Current potential curves were recorded with a Bryan's X-Y recorder (Model No.2500).

A conventional three electrode system consisting of working electrode (Heazlewoodite, surface area 1.87 cm^2), secondary or auxiliary electrode (platinum foil, surface area 0.63 cm^2) was used. Potentials were measured with a saturated calomel reference electrode (SCE). The apparatus was calibrated against standard voltamogram for platinum electrode in contact with deoxygenated 0.1 mol dm^{-3} sodium tetraborate solution. The current potential curves of Ketx and Dtc were obtained separately and for a given total constant concentrations of collectors mixtures on heazlewoodite electrode. The electrode potential was swept anodically starting from the open circuit potential.

Adsorption studies were carried out on ground samples of sulphide packed in a glass column through which the reagent was passed, the technique being similar to that used by Bauer and Caude (1985). The heazlewoodite sample was dry-ground in an agate pestle and mortar. The desired size fraction was stored in jars under vacuum. The surface area of a sample was measured by the conventional BET method, with the use of nitrogen gas and was found to be 0.32 m^2 g^{-1}. For each experiment the column (length 200 mm; internal diameter 6.5 mm; total volume including dead

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space, 150 cm^3) was loaded with 12 g sample of the ground mineral.

The following procedure was used for all the adsorption studies. Reservoirs, each with a capacity of 2.5 L were filled with the requisite solutions and thoroughly de-aerated by purging with nitrogen. A clean, reproducible sulphide surface was then prepared on the mineral in the column by washing for 30 min in 0.1 M Na_2S followed by methanol to remove any elemental sulphur that might have formed and subsequently by distilled water to displace the methanol. The column was then sealed off by means of the three way taps at each end and collector solution was pumped through to flush the apparatus up to the column. A sample of the collector solution was then taken for analysis and after starting timer solution was passed through the column at a fixed flow rate of 1.50 cm^3 s^{-1}. Samples of the effluent collector stream were taken for analysis from the end of the column by means of another three way tap located at that point. At the close of the run a further sample of the fresh collector solution was also taken. Analysis was performed with a Perkin-Elmer Lambda 9 ultraviolet/visible-light spectrophotometer. Concentrations were estimated from the intensities of the absorption peaks at 301 nm and 256 nm for Ketx and Dtc respectively.

Flotation tests were performed in a Hallimond tube (height; 150 nm and internal diameter, 35 nm) with a magnetic stirrer, maintaining a constant speed for all the trials. Nitrogen gas was used at a constant flow rate for flotation. A detachable mineral receiver was held in place by a ground glass joint so that by changing receivers as required, the kinetics of flotation could be followed. The 5 g samples of sulphide mineral used for the flotation studies were ground to -200 +100μm.

Results and Discussion

A typical cyclic voltamogram on Ni_3S_2 electrode obtained in 0.1 M borate buffer is given in Fig 1. The wave beginning at a potential of ~-400 mv is most likely related to the formation of oxidation products on the electrode surface.

$$Ni_3S_2 \rightarrow 2Ni^{2+} + 2S^{\circ} + 6e^- \quad \text{.................................} (1)$$

Ni_3S_2 can be oxidised beyond the formation of sulphur to the formation of oxy-sulphur anions, such as $S_2O_4^{2-}$ or $S_2O_3^{2-}$. The most likely oxy-sulphur species to be generated are $S_2O_3^{2-}$ by a reaction:

$$Ni_3S_2 \rightarrow 3Ni^{2+} + S_2O_3^{\ 2-} + 6H^+ + 4e^- \quad \text{................} (2)$$

When an anodic current is flowing, oxidation by both reactions (1) and (2) can take place. The oxidation of Ni_3S_2 to $S_2O_3^{2-}$ is irreversible and to sulphur is reversible. The analysis of the cathodic charges can be used to determine whether oxy-sulphur species are being produced or not. The reaction (1) is essentially reversible. The charge associated with the first anodic peak should be matched by the charge associated with the cathodic peak on reverse scan, provided that the sulphur is the only oxidation product. However, if oxidation proceeds beyond the formation of sulphur, then anodic charge will exceed the cathodic charge. As can be seen from voltamogram (Fig 1), the ratio of anodic and cathodic charges is approximately unity. This suggests that the sulphur is the most probable oxidation product. The second cathodic cur-

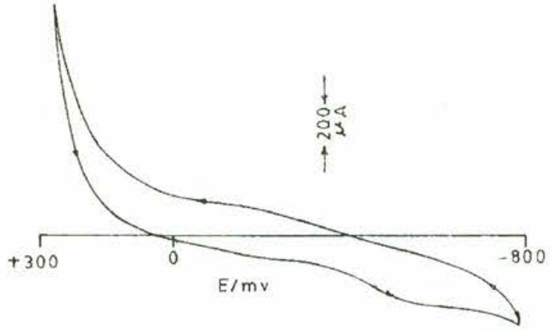

Fig 1. Voltamogram of Ni_3S_2 electrode in 0.1 M borate solution at a potential sweep rate of 30 mvs^{-1}.

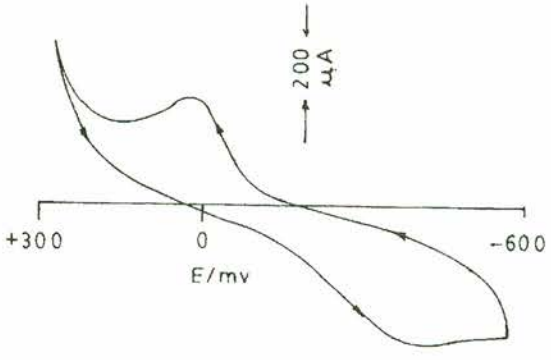

Fig 2. Voltamogram of Ni_3S_2 electrode with the use of Ketx 5 x 10^{-3} M at a potential sweep rate of 30 mvs^{-1}.

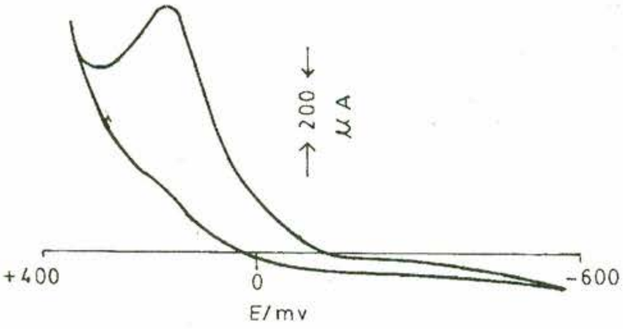

Fig 3. Voltamogram of Ni_3S_2 with the use of Dtc 5 x 10^{-3} M at potential sweep rate of 30 mvs^{-1}.

rent at negative limit of potentials is either the reduction of hydroxides or cathodic dissolution of Ni_3S_2. The voltamograms for Ni_3S_2 electrode in solutions of Ketx and Dtc are given in Fig 2 and 3. The reactions due to the mineral itself were suppressed and only those due to the collectors are observed. The voltamograms are similar to that reported by Hunter (1985) for Ketx addition. He confirmed the oxidation of Ketx addition. He confirmed the oxidation of Ketx to dixanthogen.

The synergistic effects for the oxidation of binary mixtures of Ketx and Dtc are given in voltamograms presented in Figs 4a to 4c. In these, the current potential curves are superimposed for Ketx, Dtc and their mixtures. The effect of Ketx on the course of Dtc voltamograms indicates co-adsorption of both collectors. This results in a significant enhancement of peak current corresponding to Dtc component of the mixture. A comparison of the currents at ~ 200 mv is given in Fig 5. The point of maximum synergistic effect occurs at about 0.35 to 0.65 ratio of the co-adsorbed ions of Ketx and Dtc respectively. The oxidation reaction corresponding to the oxidation of Ketx in mixture is completely inhibited. No explanation can be suggested for the influence of Dtc on this deformation of Ketx wave.

The adsorption isotherms for Ni_3S_2 in 10^{-4}M Ketx and Dtc collectors are shown in Fig 6, where they have been plotted as the fraction of the collector adsorbed as a function of the total volume of collector that has passed through the column up shown in Fig 7, where the fractional adsorptions for each collector, separately and in total are shown as a function of the molar ratio of Ketx and Dtc (10^{-4}M) for a constant volume (120

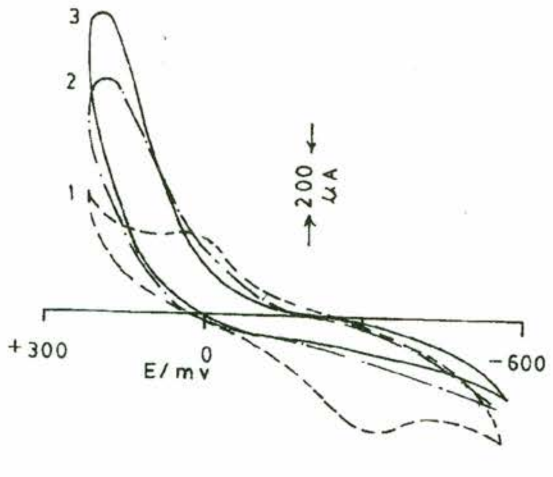

Fig 4a. Super imposed voltamogram of Ni_3S_2 electrode with the use of Ketx, Dtc and their mixtures at constant total concentration (5 x 10^{-3} M) with varying mole ratios; potential sweep rate 30 msv^{-1}.

(1) Ketx, 0.5 x 10^{-3}M; (2) Dtc, 4.5 x 10^{-3}M; (3) Ketx, 0.5 x 10^{-3}M + Dtc, 4.5 x 10^{-3}M.

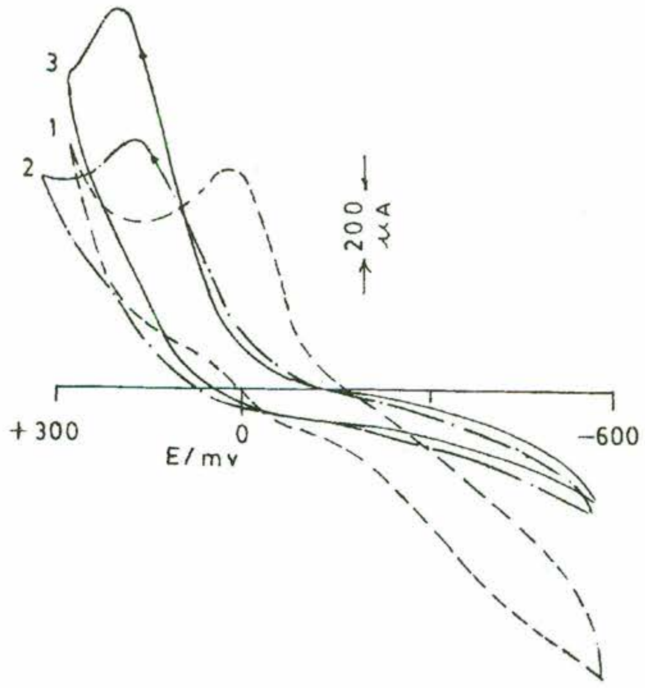

Fig 4b. Super imposed voltamogram of Ni_3S_2 electrode with the use of Ketx, Dtc and their mixtures at constant total concentration (5 x 10^{-3} M) with varying mole ratios; potential sweep rate 30 msv^{-1}.

(1) Ketx, 1.5 x 10^{-3}M; (2) Dtc, 3.5 x 10^{-3}M; (3) Ketx, 1.5 x 10^{-3}M + Dtc 3.5 x 10^{-3}M.

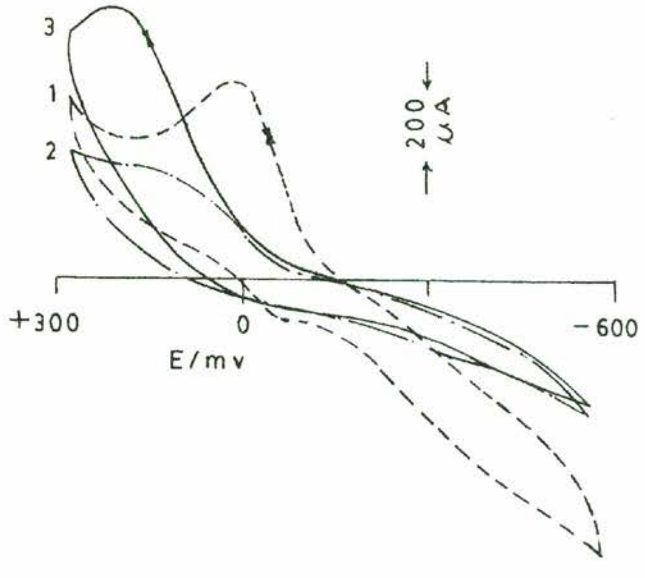

Fig 4c. Super imposed voltamogram of Ni_3S_2 electrode with the use of Ketx, Dtc and their mixtures at constant total concentration (5 x 10^{-3} M) with varying mole ratios; potential sweep rate 30 msv^{-1}.

(1)Ketx, 2.5 x 10^{-3}M; (2) Dtc, 2.5 x 10^{-3}M; (3) Ketx, 2.5 x 10^{-3}M + Dtc, 2.5 x 10^{-3}M.

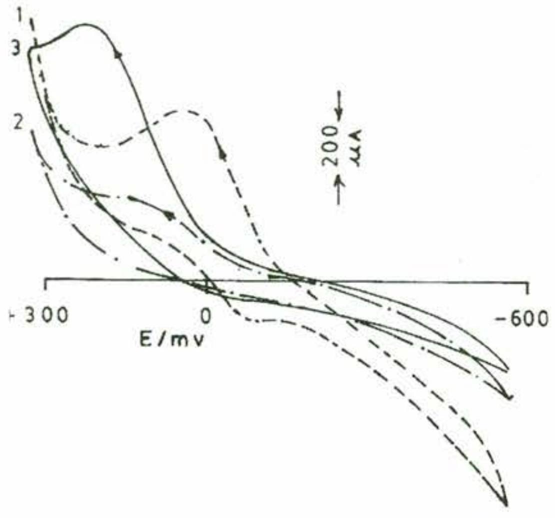

Fig 4d. Super imposed voltamogram of Ni_3S_2 electrode with the use of Ketx, Dtc and their mixtures at constant total concentration (5×10^{-3} M) with varying mole ratios; potential sweep rate 30 msv^{-1}.

(1) Ketx, 3.5×10^{-3}M; (2) Dtc, 1.5×10^{-3}M; (3) Ketx, 3.5×10^{-3}M + Dtc, 1.5×10^{-3}M.

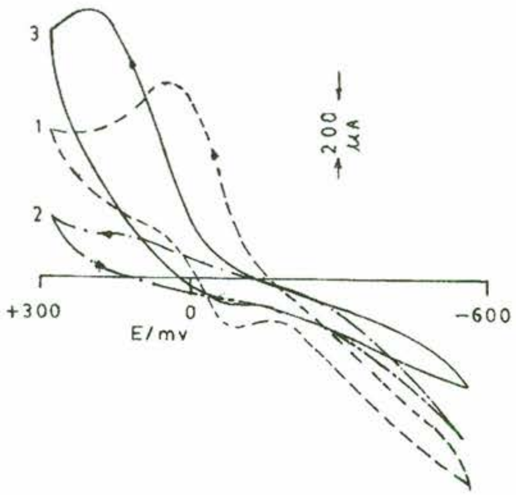

Fig 4e. Super imposed voltamogram of Ni_3S_2 electrode with the use of Ketx, Dtc and their mixtures at constant total concentration (5×10^{-3} M) with varying mole ratios; potential sweep rate 30 msv^{-1}.

(1) Ketx, 4.5×10^{-3}M; (2) Dtc, 0.5×10^{-3}M; (3) Ketx, 4.5×10^{-3}M + 0.5×10^{-3}M.

ml) of collector. It is apparent that the adsorption of each collector is enhanced by the presence of the other and that the total synergistic effect reaches a maximum at a Ketx: Dtc molar ratio of about 0.35 : 0.65.

Flotation recoveries obtained with Ketx and Dtc separately at a concentration of 5×10^{-4} M are given as a function of time in Fig 8. Recoveries after 10 and 20 min for the mixed collectors are shown as a function of the molar ratio Ketx: Dtc in Fig 9, where the synergistic effect is clearly evident; Fig 10, flotation recoveries for 20 min are plotted as a function of pH for Ketx and Dtc separately and for a mixture at a molar ratio of 1:2 and the same total concentrations. It is apparent that the synergistic effect extends over the whole pH range where significant flotation is observed.

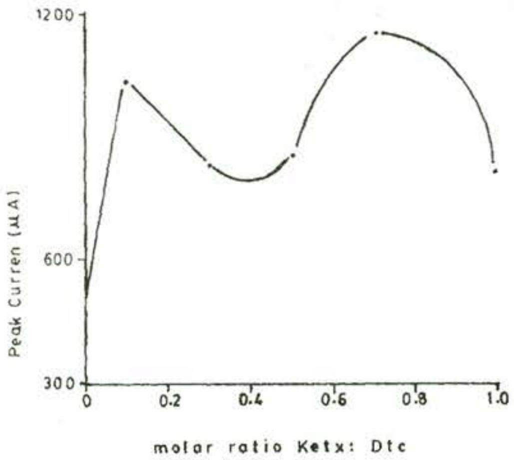

Fig 5. Anodic current corresponding to Ketx and Dtc and their mixtures at constant total concentration 5×10^{-3} M as a function of their molar ratio.

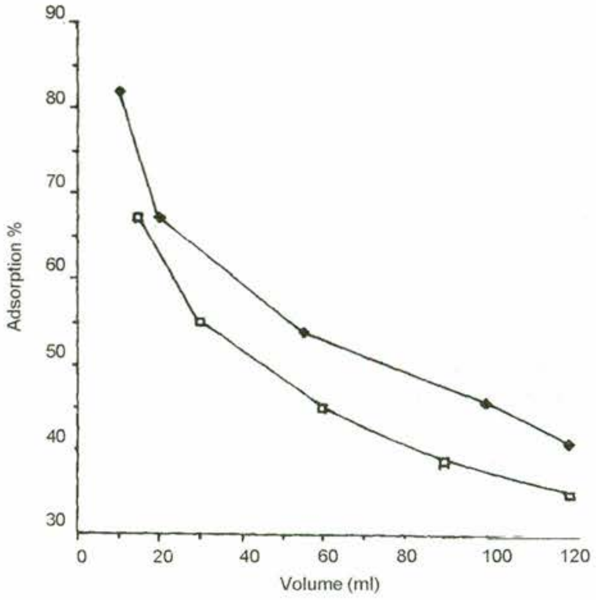

Fig 6. Percentage adsorbtion of Ketx and Dtc collectors on Ni_3S_2 as function of volume passed.

Upper curve, Dtc; lower curve, Ketx.

Conclusion

It is evident from these experiments that synergism between collectors is an important factor in the selection of reagents in flotation. It has been demonstrated that, its occurence can

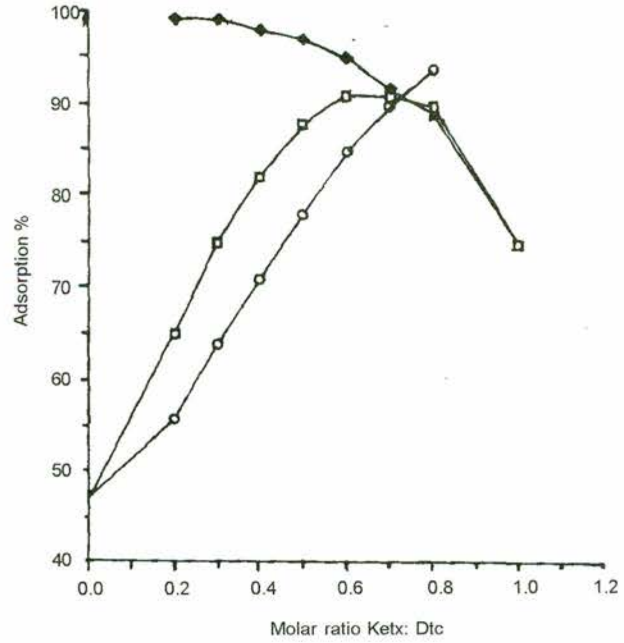

Fig 7. Percentage adsorption of Ketx and Dtc and Ni_3S_2 from 10^{-4} M solution of mixed collectors as finction of their molar ratio. vol. passed = 120 ml.

Upper curve, Total Ketx plus Dtc; Lower curve, Ketx; Middle curve, Dtc.

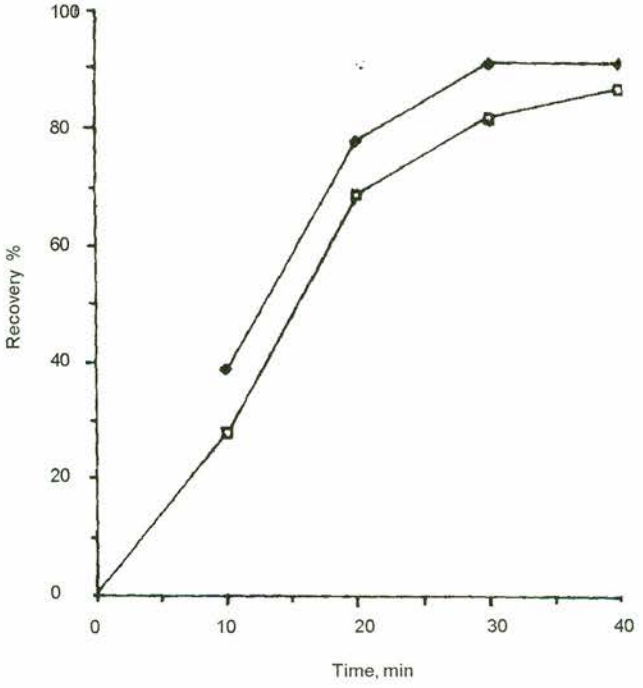

Fig 8. Cummulative percentage recoveries as function of time for flotation of Ni_3S_2 with use of $5x10^{-4}$ M, Ketx and Dtc separately.

Upper curve, Dtc; Lower curve, Ketx.

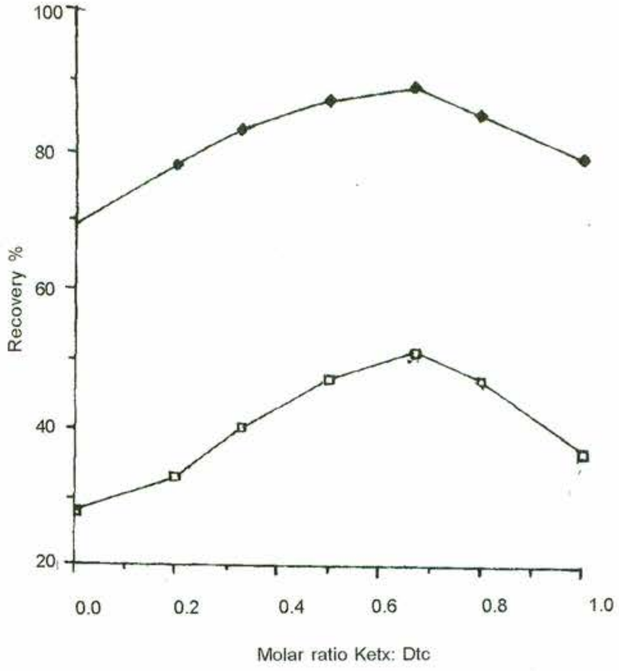

Fig 9. Recovery as a function of molar ratio of Ketx to Dtc at constant total concentration of collector $5x10^{-4}$ M and for given flotation times.

Lower curve, 10 min; Upper curve 20 min.

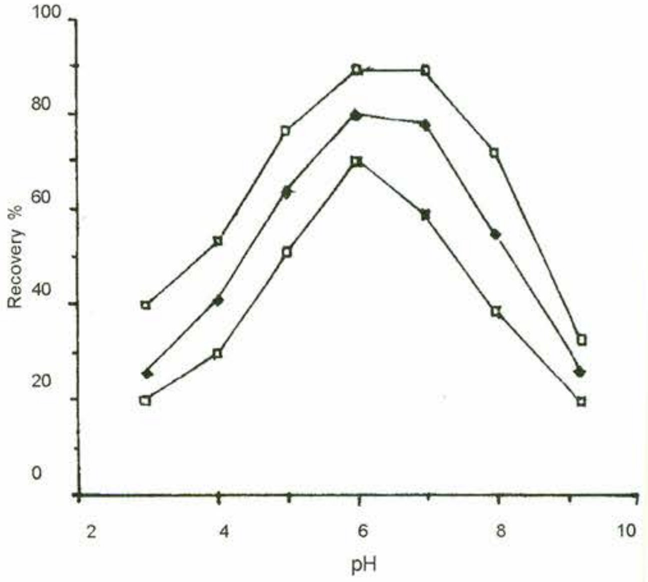

Fig 10. Recovery as function of pH for flotation of Ni_3S_2 with Ketx, Dtc and 0.35 : 0.65 molar ratio mixture at constant total concentration of collector ($5+ 10^{-4}$ M).

Flotation time, 20 min; Upper curve, mixed collectors; Middle curve, Dtc; Lower curve, Ketx.

readily be explored by quite simple cyclic voltametry and adsorption measurements, which can be related to the recoveries obtained in flotation.

By applying these methods to other combinations of collectors and other mineral species, it could be possible to obtain the full understanding of the factors that control synergism, both in general terms and in particular systems. The methods may also be developed into a useful industrial tool for the improvement of plant performance. It is hoped that this aspect of the work would be developed further.

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