

## ELECTROCAPILLARY AND FLOTATION STUDIES USING POTASSIUM ETHYLXANTHATE, DITHIOPHOSPHATE COLLECTORS AND THEIR MIXTURE.

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The surface tension measurements were carried out on dropping mercury electrode (dme) in 0.1 M sodium tetraborate buffer solution, with potassium ethylxanthate (KETx) and dithiophosphate (Dtp) added separately or in combination under comparable conditions. The electrocapillary curves determined as function of potential indicating reduction in surface tension by the addition of KETx and Dtp. Synergistic behaviour was also studied by comparing the decrease in surface tension of individual collectors with that of their mixtures at various mole ratios and potentials. Flotation studies were also conducted on heazlewoodite ( $\text{Ni}_3\text{S}_2$ ) with these collectors separately and in combination to study the synergistic effect.

**Keywords:** Electrocapillary, Flotation, Collectors

### Introduction

Synergism may be defined as the enhanced effect obtained from the use of a combinations of reagents relative to their individual action. In flotation, synergistic effect between collectors and frothers have long been recognized in plant practices (Taggart 1945), though little attention have been paid to these in laboratory studies. Exception to this area, for example, the investigation reported by Glembotskii (1958) on the use of mixtures of collectors of same type but of different hydrocarbon chain length or degree of branching. The work of Mingion (1984) on the use of dithiophosphates in conjunction with xanthates and sodium mercaptobenzothiozole in the flotation of platinum group metals, and the work of Pomianowski and Powlikowski - Czubak (1967), who have presented the results the tensammetric measurements on mercury and of flotation using KETx with dodecyltrimethyl ammonium bromide. The study of synergism between xanthate and carbamate, sodium sulphide and carbamate was also carried out (Critchely and Riaz 1991; Riaz and Critchley 1993; Riaz *et al* 1997; Riaz *et al* 2001) on dropping mercury electrodes and other metal electrodes. The study of such effects between KETx and dithiophosphate (Dtp) in reaction with mercury electrode and flotation studies of heazlewoodite ( $\text{Ni}_3\text{S}_2$ ) synergised and supplied by Johnson Matthey Research, Ltd. is described in the present contribution. Correlation was obtained between flotation recoveries obtained in a modified Hallimond tube and simple measurements of surface tension carried out on a dropping mercury electrode at controlled potentials (in electrocapillary phenomenon).

### Experimental

**Reagents.** All the chemicals used in the investigation were of analytical grade. The KETx and Dtp were freshly recrystallized for each experiment, single distilled water being used through out. Unless otherwise stated, all experiments were carried out in an electrolyte of 0.1M sodium tetraborate which gives a constant pH of 9.2. The pH was adjusted as necessary by addition of NaOH or  $\text{H}_2\text{SO}_4$ .

Surface tension was measured by dropping mercury electrode by means of drop weight method. The apparatus was calibrated against standard values for the surface tension of mercury in contact with 0.1M KCl solution. Potentials were measured with a saturated calomel reference electrode (SCE), and all potentials are given relative to this scale. The dropping mercury electrode consisted of an extra long capillary and large mercury head to give as constant mercury flow rate as possible. The lower tip of capillary was immersed in test solution contained in the cell. The volume of the cell was 100 cm<sup>3</sup> which housed the working electrode connected by a side tube containing a sintered glass frit and an agar-salt bridge to a side tube which formed the saturated calomel reference electrode. The potential across the cell was controlled by general purpose polarograph E.I.I. Cambridge Model 0410 and digital multimeter, Thander TM 355. All potentials were measured with respect to a saturated calomel electrode, whose potential may be taken as 241.2 mV with respect to the saturated hydrogen scale of potential. The solutions were deoxygenated using nitrogen gas that had been scrubbed in vanadous chloride. A continuous nitrogen flow was maintained though the experiments.

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For each experiment, the dme was polarized to a fixed potential relative to the SCE and time taken for at least 10 drops to form which was measured with a stop watch. Measurements were made starting from the negative potentials (-1.6V) at 100 mV intervals. All potentials were repeated at least three times to check experimental accuracy and reproducibility. The experimental determination of drop time in 0.1M borate buffer gives reproducibility slightly better than  $\pm 1$  second over a time interval of about 120 seconds for the formation of 10 drops.

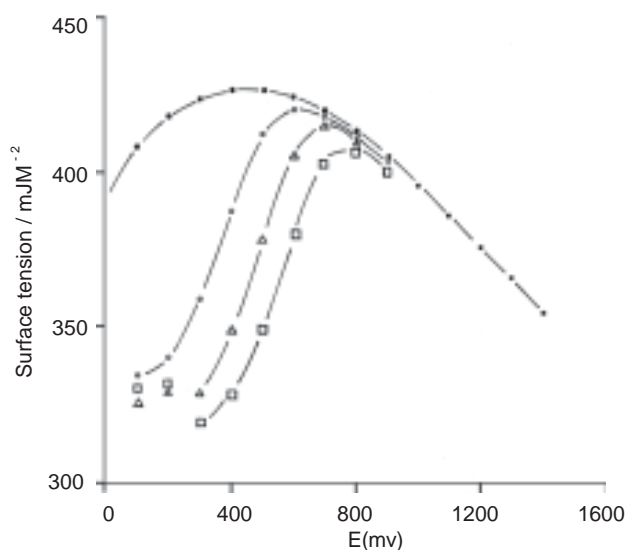
Flotation tests were performed in a Hallimond tube (height, 150 nm and internal diameter, 35 nm) with a magnetic stirrer, maintaining a constant speed for all the trials. Nitrogen gas was used at constant flow rate for flotation. A detachable mineral receiver was held in place by a general glass joint so that by changing receivers as required, the kinetic of flotation could be followed. The 5 grams samples of heazlewoodite used for the flotation studies were freshly ground (- 200, + 100  $\mu\text{m}$ ) and kept in vacuum out of air contact.

## Results and Discussion

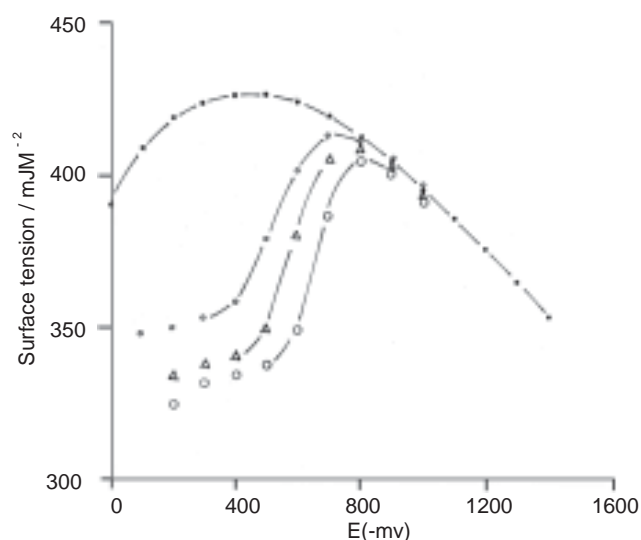
The electrocapillary curves for mercury determined in 0.1 M borate solution and in the presence of various additions of KETx and Dtp are shown in Fig 1 and 2. The mercury surface is initially observed as positively charged. On reducing this charge by means of applied potential, the surface tension increases, goes through maximum and then decreases. The maximum occurs at a potential at which the charge density changes from positive to negative values passing through zero. The potential at electrocapillary maximum (E.C.M.) is also known as the potential of zero charge (P.Z.C.) given by the symbol  $E_q = 0$ . On other side of P.Z.C, where the surface is either positively charged or the negatively charged, counter ions are adsorbed on the surface. The variation of surface tension with potential in the absence of electro active species, is presumably a result of orientation effects among water dipoles due to the surface charge on the mercury as contact adsorption of sodium or borate is unlikely. This is supported by the observation that the point of inflexion of curve coincides with P.Z.C. Electrocapillary curves may be differentiated with respect to the potential to give the surface charge ( $dr/dE = -qs$ ) where,  $qs$  is surface charge in electrolyte and redifferentiated to give the differential surface capacitance ( $dr^2/dE^2 = C$ ).

With the addition of KETx and Dtp, the curve shows variation of surface tension to a varying degrees depending on the nature and concentration of collectors. The E.C.M. are shifted to more positive potentials by about 60 mV for a ten fold degree in concentration. This is in agreement of surface capacitance reported by Hunter (1985) for different xanthate concentrations. Equating the decrease in surface tension to

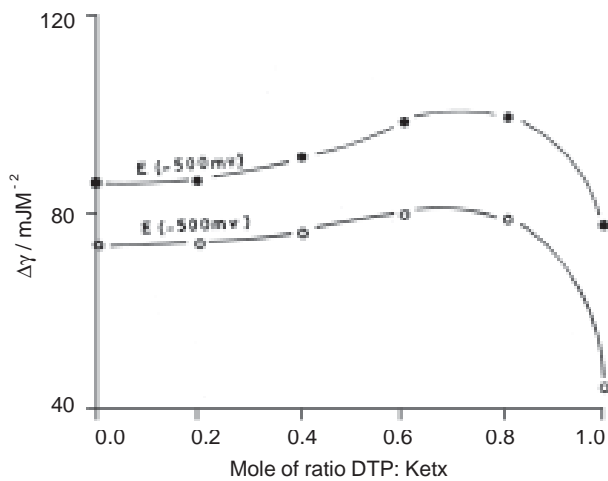
the extent of adsorption, it is noteworthy that measurable adsorption takes place at potentials several hundred millivolts negative to E.C.M. Where as, on negative charged surface, anion adsorption would not normally be expected to be significant. It may have been caused either by the weak affinity of sulphur in the polar group for mercury or by the chemisorption in which mercury atoms remain a part of metallic phase even after interaction with these collectors. The decrease in surface tension becomes greater with increasing concentration and applied potential. The magnitude of depression being proportional to the surface concentration of adsorbed xanthate or thiophosphate on the surface caused erratic be-



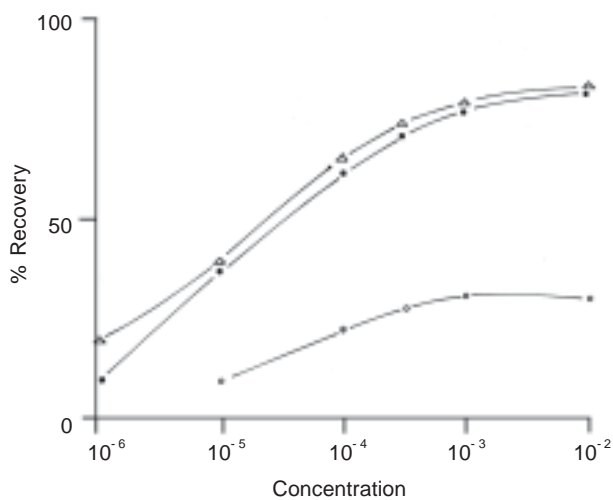
**Fig 1.** Surface tension of mercury in 0.1M borate solution in presence and absence of KETx  $10^{-4}\text{M}$  ( $\circ$ ), KETx  $10^{-3}\text{M}$  ( $\Delta$ ), KETx  $10^{-2}\text{M}$  ( $\square$ )



**Fig 2.** Surface tension of mercury in 0.1M borate solution in presence and absence of Dtp  $10^{-4}\text{M}$  ( $\circ$ ), Dtp  $10^{-3}\text{M}$  ( $\Delta$ ), Dtp  $10^{-2}\text{M}$  ( $\square$ )



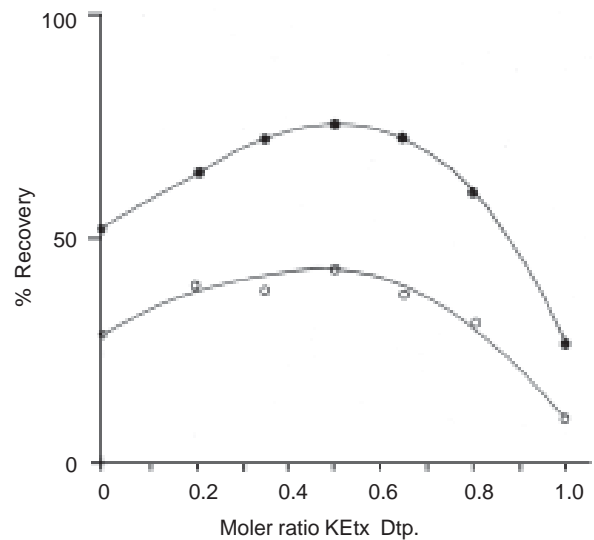
**Fig 3.** Change in surface tension of mercury on addition of collector as function of the ratio of KEtx Dtc ( $10^{-2}\text{M}$ ).



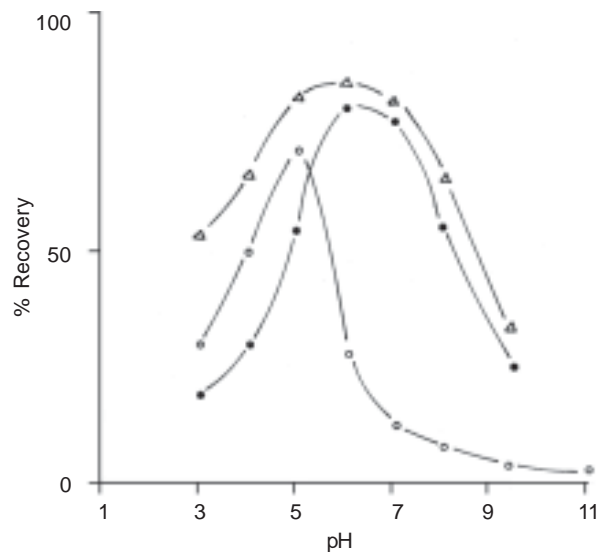
**Fig 4.** Cumulative % age recoveries as a function of concentration for flotation of  $\text{Ni}_3\text{S}_2$  with use Dtc (o), KEtx (•) and KEtx + Dtp equimolar mixture ( $\Delta$ ).

havior in the curves. However, at potentials more negative than  $-900\text{ mV}$  (S.C.E.), all the curves tend to coincide with that of electrolyte.

A collectors mixtures show synergism when they contain a greater lowering of surface tension at a given total concentration than that of separate components of mixture at the same concentration. In Fig 3, the change in surface tension (measured at fixed potential) brought about by the addition of a mixture of PEtx and Dtp to a total concentration of  $10^{-2}\text{M}$  is plotted as a function of the ratio of the two collectors. It can be seen that, the decrease in surface tension is significantly greater than that would be expected from a linear interpretation from the results for the separate reagents. The maximum synergistic effect occurring at an approximately 7:3 concen-



**Fig 5.** Recovery as a function of molar ratio of KEtx to Dtp at constant total concentration of collector and for flotation time lower curve (10 min), upper curve (20 min).



**Fig 6.** Recovery as a function of pH for flotation of  $\text{Ni}_3\text{S}_2$  with KEtx (•), Dtp  $10^{-4}\text{M}$  (o) and 1: 1 molar ratio mixture at constant total concentration  $10^{-4}$  ( $\Delta$ ).

tration of Dtp and KEtx collectors, respectively. The observed synergistic effect could be, as a result of molecular interaction between the components of mixture or the mercury surface charge modification. From the present work, it can be suggested that the component KEtx adsorbable at lower potential, modifies the mercury surface charge for other component. Dtp normally adsorbable at higher potentials, resulting in a greater reduction of surface tension.

Flotation recoveries obtained with KEtx and Dtp separately at a concentration of  $5 \times 10^{-2}\text{M}$  and for mixture (1 : 1) at the same

total concentration for the flotation time of 20 minutes as a function of concentration are given in Fig 4, in which the synergistic effect is evident. Recoveries after 10 and 20 minutes for the mixed collectors are shown as a function of the molar ratio KETx:Dtp in Fig 5, in which the synergistic effect is clearly evident, this is at a maximum at ration of 1: 1. In Fig 6 flotation recoveries are plotted as a function of pH for KETx and Dtp separately and for a mixture at a molar ratio 1 : 1 and the same total collector concentration. It is apparent that the synergistic effect extends over the whole pH range with in which significant flotation is observed.

It is evident from these limited experiments that synergism between collectors is important factor in the selection of reagents in flotation. It has been demonstrated that its occurrence can be readily explored by quite simple electrocapillary 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 should be possible to obtain a fuller understanding of factors that control synergism, both in general terms and in particular systems. The methods should also be capable of developing into a useful industrial tool for the improvement of plant performance thus it is hoped to develop this asept of the work further.

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