Pak. j. sci. ind. res., vol. 40, nos. 1-4, January-April 1997

THE CATALYTIC EFFECT OF SULPHUR ON SODIUM DIETHYL DITHIOCARBAMATE OXIDATION IN REACTION WITH PLATINUM AND HEAZLEWOODITE

M. Riaz, Mumtaz and Kamin Khan

PCSIR Laboratories, P.O. Peshawar University, Peshawar Pakistan

(Received October 16, 1995; revised March 31, 1997)

The cyclic voltammetric studies were carried out on platinum and heazlewoodite (Ni_3S_2) electrodes in 0.1 mol. dm^{-1} sodium tetra borate buffer with and without sodium diethyldithiocarbamat (DTC) and sodium sulphide (Na_2S_3) added separately or in combination under comparable conditions. The combination of DTC and Na_2S and the effect of sulphur so produced on DTC and its oxidation is described. Flotation experiments were also conducted to study the effect of Na_2S concentration on heazlewoodite recoveries. An increase of about 6% in flotation recovery was observed for addition of 10^{-4} mol.dm^{-3} Na_3S concentration.

Key words: Cyclic voltammetry, Sodium sulphide, Diethyldithiocarbamate, Flotation.

Introduction

The electrochemical techniques particularly cyclic voltammetry relating to flotation has been widely used [1-3] for studying surface reaction on noble metals and sulphide minerals. The behaviour of sulphide mineral is governed by the nature of its surface oxidation products. The reaction with oxygen may yield S° (elemental sulphur), $S_2O_3^{2-}$ (Thiosulphate), SO_6^{2-} (Thionate) and SO_4^{2-} (Sulphate). The adsorption and oxidation of sulphide on noble metals by anodic oxidation of hydrogen sulphide species, especially in relation to catalytic effect of sulphur containing surface layers towards the oxidation of organic and inorganic compounds has been the subject of a number of investigations [4-8].

The present paper describes the effects of sulphur on sodium diethyldithiocarbamate oxidation in reaction with platinum and heazlewoodite.

Experimental

All the measurements through out these studies were made in a base electrolyte solution of A.R. grade sodium tetra borate (0.1 mol.dm^{-3}) which gave constant pH and was also used as a supporting electrolyte to give constant ionic strength and conductivity. Reagent grade sodium sulphide was used to study the effect of sulphide ions. Commercially available sodium diethyldithiocarbamate was re-crystallized twice from acetone by addition of petroleum ether and dried under vacuum to avoid any atmospheric oxidation [9].

The potentiostat used was a 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, secondary or auxiliary electrode and reference electrode was used. The reference electrode with luggin capillary was inserted through the lid into the cylindrical round bottom glass cell (500 cm^3) containing base electrolyte to which appropriate reagents were added. The inert working electrode was of platinum foil with a surface area of 0.63 cm^2. This electrode was sealed to the end of a glass tubing with non-conducting "Araldite" epoxy. The electrode was cleaned prior to each run by rinsing with chromic acid dilute HCl and HNO_3 mixture and finally rinsed thoroughly with distilled water. A saturated calomel electrode with a luggin capillary was placed close to the working electrode surface (to reduce IR drop). This electrode was used as the reference electrode and all potentials were referred to the saturated calomel electrode. The inert auxiliary electrode used was a platinum foil attached to the end of a glass tube. This electrode was directly immersed in the test solution. For each experiment, the electrode was cleaned as described. The cell was filled with electrolyte having appropriate concentration of the reagents and deoxygenated by bubbling nitrogen gas.

The cyclic voltammograms of stationary platinum and heazlewoodite electrodes were recorded in pure borate solution within the pre-selected range of potential at selected scan rates. The current-potential curves of DTC and Na_2S were obtained separately and by addition of small aliquots of Na_2S to constant collector concentrations. The electrode potential was swept anodically starting from the open circuit potential. Flotation tests were performed in a Hallimond tube (height 150 mm and internal diameter 35 mm) with a magnetic stirrer maintained at a constant speed for all the trials. Nitrogen gas was used at a constant flow rate for flotation. A detachable mineral receiver was held by a ground glass joint so that by changing receivers as required, the kinetics of flotation could be followed. The 5 g samples of heazlewoodite (Ni_3S_2, synthesized and supplied by Johnson Matthey Research, Ltd.) used for flotation studies were ground to -200 + 100 µm.

Results and Discussion

The curve determined for a blank with background electrolyte solution only was expected on the basis of investigations carried out by various authors [10-13]. The electrochemical changes are described in Fig. 1. In the presence of DTC 10^{-3} mol. dm^{-3} (Fig. 2) the adsorption and desorption of hydrogen and oxygen were inhibited. There was an anodic current at the potential of +200mV, corresponding to the oxidation of DTC.

A typical voltammogram for a platinum electrode cycled in borate buffer containing 10^{-2} mol. dm^{-3} Na_2S is given in Fig.3. In the presence of Na_2S there was an anodic current beginning at -400 mV. This current developed into a plateau with poorly defined waves at +200 mV and +400 mV. During the cathodic scan the electrode was inactive until the appearance of a cathodic current below -700 mV. In the borate solution containing Na_2S, starting at potential of -950 mV with clean surface, a white film was deposited on the electrode at potential greater than -400 mV. Initial sulphide oxidation was accompanied by the deposition of a surface film that decreases the rate of sulphide oxidation on repeated scans. This process can be compared with that of passivation of active metals. The main reaction product within the potential ranges have considered was elemental sulphur [8], although the formation of poly sulphide was also possible, especially at higher Na_2S concentrations. The potential at which the anodic wave commenced was considerably below the reversible potential of sulphur formation for the reaction.

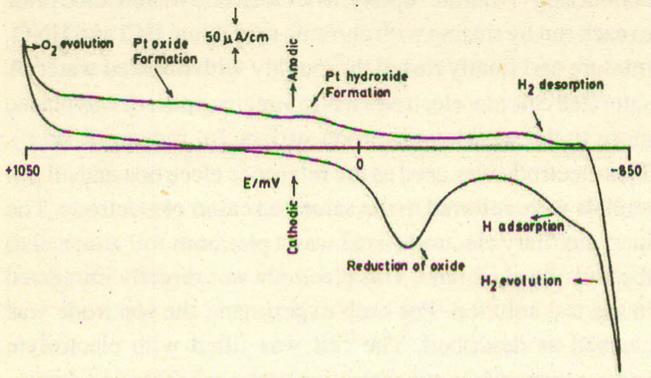

Fig. 1. Voltammogram for platinum electrode, potential sweep rate of 30 mV s^{-1}.

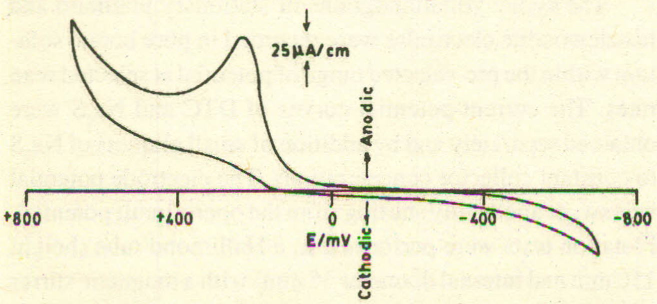

Fig. 2. Voltammogram for platinum electrode containing 10^{-3} mol. dm^{-3} DTC, potentials sweep rate of 30 mV s^{-1}.

$HS^- \longrightarrow S^\circ + H^+ + 2e^-$ ....(1)

E° (standard electrode potential) = 180 mV ....(2)

Er (reversible electrode potential) = 30 mV ....(3)

For example an anodic current began to flow at about -400 mV. This potential was 370 mV more negative than reversible potential of the HS^-/S couple at the experimental pH and concentration. It should be noted that the anodic charges passed on the positive going scan was greater than the cathodic charges. This charge imbalance could be due to the oxidation of some sulphide to thiosulphate, since thiosulphate is not reduced at the potentials of the return scan. However, as the formation of thiosulphate occurs at much higher potentials than the experimental potentials, it cannot account completely for the charge imbalance observed. This could also be due to the formation of a soluble intermediate during the reaction producing sulphur. Allen *et al.* [4] also suggested that the oxidation of sulphide ions in alkaline media proceeded via a series of polysulphides. Thus the formation of sulphur could be presented as a two step process.

$XS^{2-} \longrightarrow S_x^{2-} + (2x - 2)\,e^-$ ....(4)

$S_x^{2-} \longrightarrow S_x + 2e^-$ ....(5)

The voltammograms for solutions of polysulphides in sodium hydroxide were similar to those for sulphide ions [7]. This supported the interpretation of the voltammograms presented here in terms of reactions proceeding through polysulphide intermediates.

The voltammograms obtained on platinum and heazlewoodite electrodes in 10^{-3} mol.dm^{-3} DTC with varying concentrations of N_2S addition are given in Fig. 4a to 4e and Fig. 5 respectively. An increase in peak current related to DTC after subtracting the component due to N_2S is presented in Figs. 6 and 7 as a function of N_2S concentration. The hydrophobicity induced on platinum and heazlewoodite elecrodes was possibly due to the formation of sulphur film. The peak current remained constant. As sulphur is well known for its ability to form S—S bonds, it is, therefore, possible that the formation of adsorbed or oxidized sulphur layer on electrode surface resulted in the formation of S—S bonds with this sulphur containing compound. This can account for the

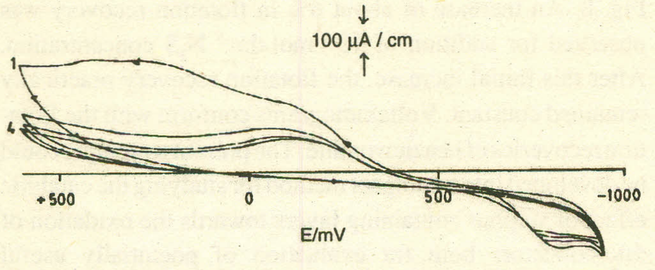

Fig. 3. Voltammogram for platinum electrode containing 10^{-2} mol. dm^{-3} Na_2S.Consecutive potentials cycling at 30 mV s^{-1}.

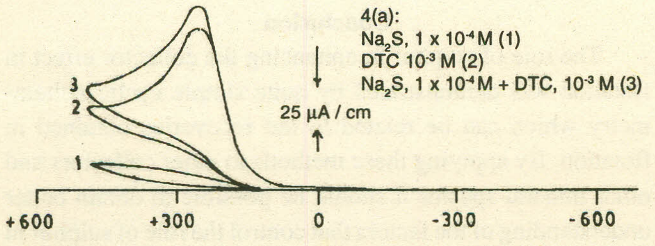

Fig. 4a

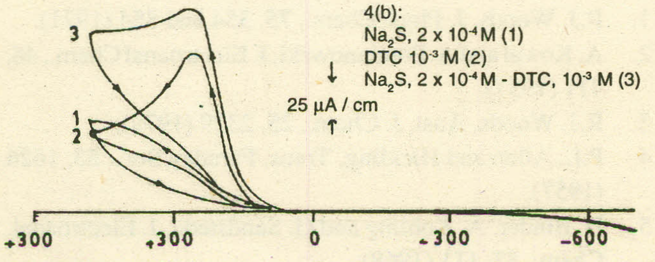

Fig. 4b

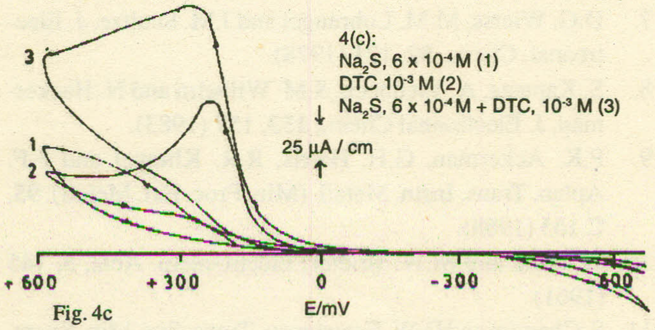

Fig. 4c

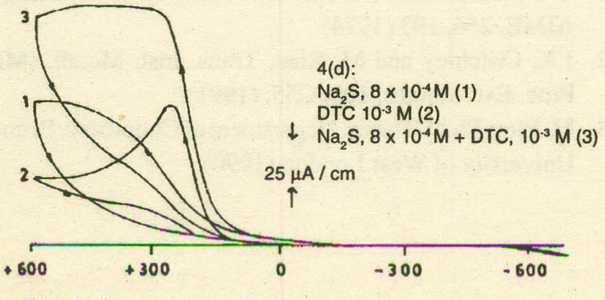

Fig. 4d

E/mV

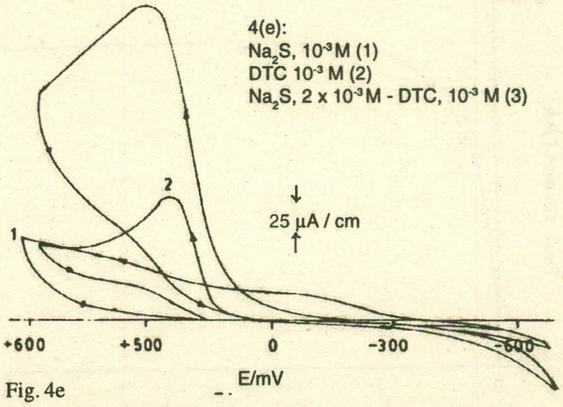

Fig. 4e

Fig. 4(a,b,c,d,e). Superimposed voltammograms for platinum electrode representing the effect of various Na_2S concentrations with and without DTC containing (10^{-3} mol. dm^{-3} potentials sweep rate 30 mV s^{-1}.

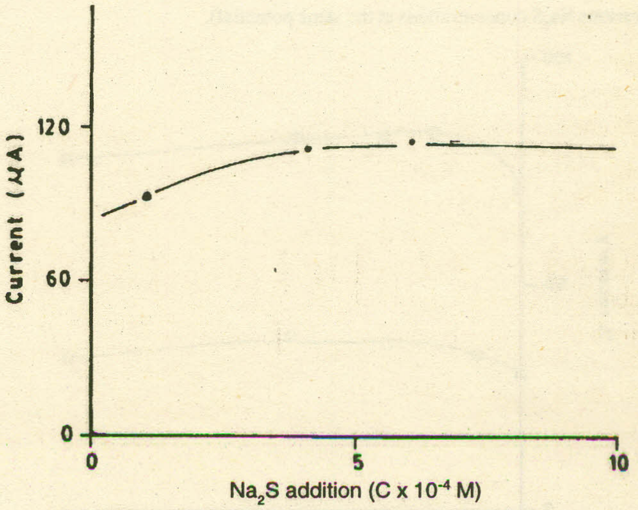

Fig. 5. Effect of Na_2S addition on anodic peak current at 265 mV corresponding to oxidation of 10^{-3} mol.dm^{-3} DTC for platinum electrode.

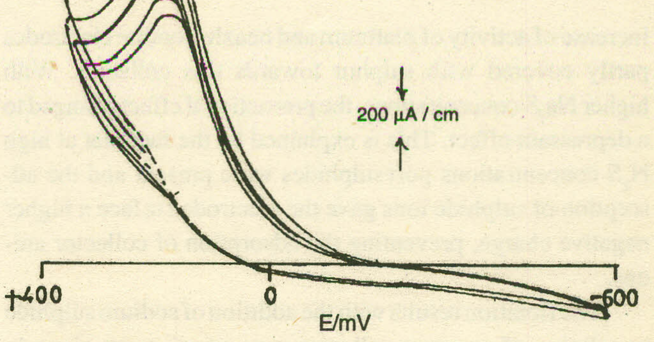

Fig. 6. Voltammograms for Ni_3S_2 electrode (A=1.87 cm^2) representing the effect of various concentrations of Na_2S addition 1 x 10^{-4} mol.dm^{-3} (2); 2 x 10^{-4} mol.dm^{-3} (3); 3 x 10^{-4} mol.dm^{-3} (4), 5 x 10^{-4} mol.dm^{-3} (5), 10^{-3} mol. dm^{-3} (6), with and without 5 x 10^{-3} mol.dm^{-3} DTC (1), potential sweep rate of 30 mVs^{-1}.

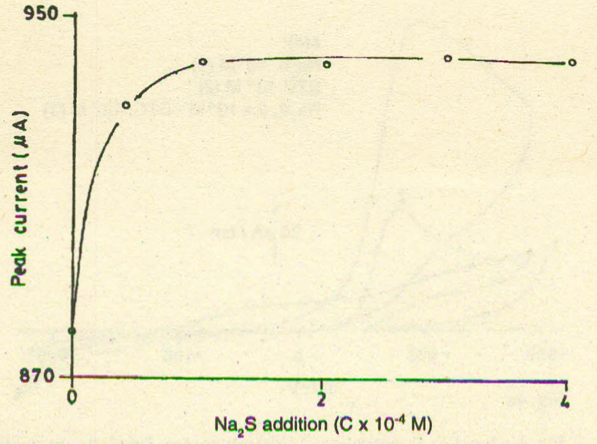

Fig. 7. Effect of Na$_2$S addition on peak current, associated with DTC (5 x 10^{-3} mol.dm^{-3}) oxidation at Ni$_3$S$_2$ electrode (A=1.87 cm^2). (The peak current for DTC oxidation was obtained after subtracting the current associated with various Na$_2$S concentrations at the same potential).

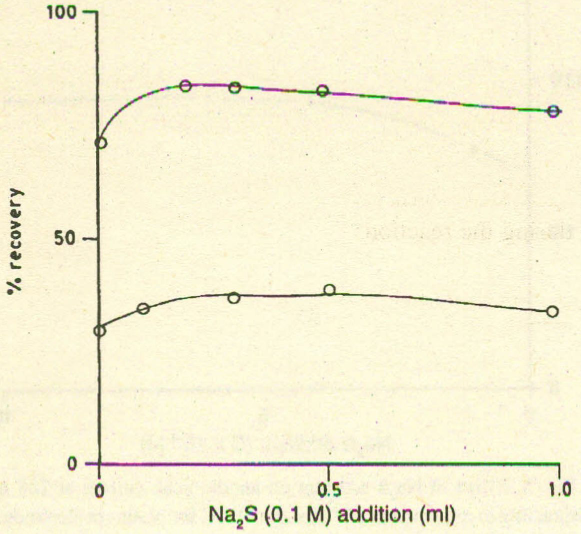

Fig. 8. Effect of various concentrations of Na$_2$S addition on flotation recovery; (DTC, 5 x 10^{-4} mol.dm^{-3}, flotation time 10 and 20 minutes).

increase of activity of platinum and heazlewoodite electrodes partly covered with sulphur towards this collector. With higher Na$_2$S concentrations, the promotional effect changed to a depressant effect. This is explained by the fact that at high N$_2$S concentrations polysulphides were present and the adsorption of sulphide ions gave the electrode surface a higher negative charge, preventing the adsorption of collector anions.

The flotation results with the addition of sodium sulphide in solution of constant collector concentration are given in Fig. 8. An increase of about 6% in flotation recovery was observed for addition of 10^{-4} mol.dm^{-3} N$_2$S concentration. After this initial increase, the flotation recovery practically remained constant. Voltammograms conform with the flotation recoveries of heazlewoodite. The present technique could be developed into a compact method for studying the catalytic effect of sulphur containing layers towards the oxidation of thio-collectors both for evaluation of poetntially useful systems and for a better understanding of the underlying theoretical principles.

Conclusion

The role of sulphur in enhancing the collector effect in flotation was demonstrated by quite simple cyclic voltammetry which can be related to the recoveries obtained in flotation. By applying these methods to other collectors and other mineral species it should be possible to obtain better understanding of the factors that control the role of sulphur in flotation for a particular system.

References

1. R.J. Woods, J. Phys. Chem., **75**, 354 and 854 (1971).
2. A. Kowal and A. Pomianowski, J. Electroanal Chem., **46**, 411 (1937).
3. R.J. Woods, Aust. J. Chem., **25**, 2329 (1972).
4. P.L. Allen and Hickling, Trans. Faraday Soc., **53**, 1626 (1957).
5. H. Binder, A. Kohling and G. Sandstede, J. Electroanal. Chem., **17**, 111 (1968).
6. M. Farooque and I.Z. Fahidy, J. Electrochem. Soc., **124**, 1191 (1977).
7. D.G. Wierss, M.M. Lohrengel and J.M. Scultze, J. Electroanal. Chem., **92**, 121 (1978).
8. S. Kapusta, A. Viehbeck, S.M. Wilhelm and N. Hackerman, J. Electroanal Chem., **153**, 157 (1983).
9. P.K. Ackerman, G.H. Harris, R.R. Klimpel and F.F. Aplan, Trans. Instn. Metall. (Min. Proc. Ext. Metall), **95**, C 165 (1968).
10. W. Bold and M.W. Brieter, Electrochem. Acta, **5**, 145 (1961).
11. S. Chander and D.W. Fuerstenau, Trans. Soc. Min. Engrs. AIME, **256**, 193 (1974).
12. J.K. Critchley and M. Riaz, Trans. Inst. Metall. (Min. Proc. Ext. Metall), **100**, C55, (1991).
13. M. Riaz, Ph.D. Thesis, Department of Chemistry, Brunel, University of West London (1990).