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Electrochemical Properties of Tetraethylammonium Tetrathiomolybdate(VI), $[(C_2H_5)_4N]_2MoS_4$

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The thiomolybdate(VI) ions, $[MoO_xS_{4-x}]^{2-}$, (x = 0–3), are believed to be active intermediates in the copper–molybdenum antagonism that afflicts ruminants [1–4]. Administration of MoS_4^{2-} is known to cause symptoms of copper deficiency in monogastric animals [5]. The MoS_4^{2-} ion is also believed to be involved in the active site of nitrogenase as well as other molybdenum containing enzymes [6]. In these cases redox reactions occur at the thiomolybdate centre. The chemical and physical properties of the thiomolybdates are well documented [7–9], but little information is available on the electrochemical properties of the thiomolybdate ions themselves.

In our earlier papers the nature of the reaction between Cu(II) compounds and MoS_4^{2-} was investigated. The reaction of thiomolybdate ions with Cu(II) generates an insoluble Cu containing product which is thought to offer a plausible explanation as to how Mo can cause Cu deficiency in ruminants [3, 4]. The reaction of Cu(II) with MoS_4^{2-} produces a Cu(I)–Mo(V)–S containing species involving a two electron internal redox reaction [4]. Similar two electron redox reactions have been reported by Stiefel *et al.* [10] involving organic oxidants.

Results have recently been reported of an investigation of the electrochemistry of the thiomolybdates in aqueous media [11]. We wish to report the results of a study of the electrochemistry, using cyclic voltametry, of MoS_4^{2-} in non-aqueous media.

Experimental

Tetraethylammonium tetrathiomolybdate was prepared by the method of McDonald *et al.* [12], purity was checked by elemental analysis, ultraviolet/visible and infrared spectrometry, and was found to be satisfactory. Tetrabutylammonium tetrafluoroborate was purchased from Sigma (Laboratory Reagent), dimethylformamide and acetonitrile were from BDH (General Purpose). Solvents were distilled, and dried over molecular sieves, prior to use.

Cycle voltammograms of tetraethylammonium tetrathiomolybdate (5×10^{-3} mol dm^{-3}) were measured in dimethylformamide or acetonitrile with tetrabutylammonium tetrafluoroborate (0.1 mol dm^{-3}) as the background electrolyte.

Cyclic voltammograms were recorded at room temperature, under anaerobic conditions, using a three electrode system with a platinum or vitreous carbon button working electrode, a platinum wire auxiliary electrode and a saturated calomel electrode (SCE) as the reference. Potentials were also referenced to the ferrocene/ferricinium system. The apparatus used consisted of a Ministat Potentiostat, a Hi-Tec Waveform Generator and a Bryans X–Y recorder.

Results and Discussion

The cyclic voltammogram of MoS_4^{2-}, using a platinum working electrode, shows an irreversible reduction at −2.46 V in dimethylformamide or −2.55 V in acetonitrile, *versus* SCE, Fig. 1. When a vitreous carbon working electrode is used a reversible one electron reduction is observed at −2.50 V in dimethylformamide, Fig. 2. The apparent difference in behaviour may be due to fast follow up reactions occurring at the platinum electrode surface, which does not happen when using the relatively inert vitreous carbon electrode. Cyclic voltammograms of the tetraethylammonium salts of trithiomolybdate and tetrathiotungstate did not show any reductions over the same range. It is known that upon increasing oxy-substitution of Mo–S containing systems the cathodic reduction potential becomes

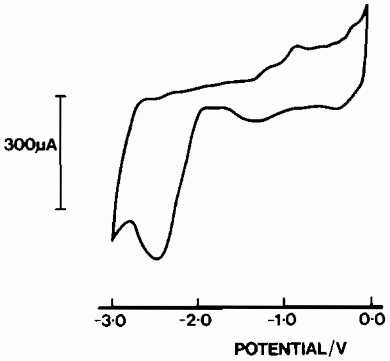

Fig. 1. Cyclic voltammogram of *ca.* 5×10^{-3} mol dm^{-3} $[N(C_2H_5)_4]_2MoS_4$ in a solution of 0.1 mol dm^{-3} $[N(C_4H_9)_4]BF_4$ in dimethylformamide at room temperature, at a platinum disc electrode; scan rate 100 mV s^{-1}.

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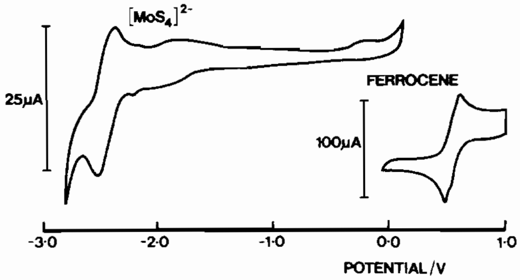

Fig. 2. Cyclic voltammogram of *ca.* 5×10^{-3} mol dm^{-3} $[N(C_2H_5)_4]_2MoS_4$ and ferrocene in a solution of 0.1 mol dm^{-3} $[N(C_4H_9)_4]BF_4$ in dimethylformamide at room temperature, at a vitreous carbon electrode; scan rate 100 mV s^{-1}, $[N(C_2H_5)_4]_2MoS_4$; 300 mV s^{-1}, ferrocene.

increasingly negative [13, 14]. In aqueous solution thiomolybdates were reported [11] to exhibit irreversible waves; a value of -1.08 V was quoted for ammonium tetrathiomolybdate.

We have observed that reaction of Cu(II) with MoS_4^{2-} results in the formation of a Cu(I)–Mo(V)–S containing species [4], however, reaction of Cu(II) with WS_4^{2-} produces what appears to be a Cu(I)–W(VI)–S containing species [15]; no evidence for W(V) is observed. The large reduction potential of MoS_4^{2-} can be explained in terms of extensive electron delocalization stabilizing the metal centre towards reduction. The lack of reduction of WS_4^{2-} was expected from the general redox behaviour of Mo and W analogues.

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