Electrochemical Investigation of Mo(VI)-MTB-ClO$_3^-$ System in Phosphate Buffer ☆

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Abstract : *The reduction mechanism of molybdenum-methyl thymol blue (MTB)-chlorate system has been investigated in water on a mercury electrode. As this system is very sensitive for ultra-trace determination of molybdenum, the actual mechanism involved was studied. Electrochemical techniques, including dc tast polarography and cyclic voltammetry were employed. It is shown that, the cathodic wave of molybdenum in the presence of methyl thymol blue and chlorate has an adsorptive catalytic character.*

KEY WORDS: *Electrochemical study, Mo-MTB-ClO$_3^-$ system, Mechanism, Cyclic voltammetry.*

INTRODUCTION

In recent years, adsorptive catalytic processes involving adsorption of metal complexes onto an electrode and catalytic effect of the adsorbed complex have attracted the attention of many electrochemists [1-8].

The catalytic effect of molybdenum in the presence of various ligands has been investigated or used for determination of molybdenum by several researchers [9-15]. However, the studies undertaken so far are mostly used for determination of molybdenum and little attention has been given on the mechanism of electrode processes.

Recently, we have reported a highly sensitive and selective method for the determination of ultra-trace concentrations of molybdenum by catalytic adsorptive stripping voltammetry [16]. The method was based on adsorptive accumulation of molybdenum (Mo)-methyl thymol blue (MTB) complex onto a hanging mercury drop electrode, followed by the reduction of adsorbed species by voltammetric scan using differential pulse modulation. The reduction current was seen to enhance by the presence of chlorate. The high selectivity and sensitivity of this method made us to investigate the actual mechanism, which is involved in such an electro-chemical system.

In the present work, the electrochemical behavior of Mo-MTB complex in the presence of chlorate is studied in phosphate buffer (pH 2.5) on a mercury electrode. The system has been investigated by dc tast polarography and cyclic voltammetry.

EXPERIMENTAL

Apparatus

Electrochemical measurements were performed using a Methrohm 693/694 VA processor electrochemical system. A multi-mode mercury electrode in DME mode (for polarographic measurements) or in HMDE mode (for cyclic voltammetry) was used as working electrode. The auxiliary and reference electrodes were platinum and Ag/AgCl (saturated KCl), respectively.

Electrochemical measurements were made in a solvent initially degassed with argon.

Unless otherwise stated, all measurements were made under 25°C and in 0.1 M phosphate buffer (pH=2.5) as supporting electrolyte.

Reagents

Reagents used in this study were analytical grade from Merck (Darmstadt, Germany) or Fluka (Buchs, Switzerland).

Stock solutions of MTB (1×10^{-3} M) were prepared fresh every three days by dissolving 0.0211g of MTB sodium salt in water and diluting to 25.0 mL.

Stock solutions of Mo(VI) (1×10^{-3} M) were prepared by dissolving 0.0242g sodium molybdate dihydrate in 100.0 mL. More dilute solutions were prepared by diluting this solution with water.

Phosphate buffer (pH 2.5) was prepared by dissolving 6.7 mL of phosphoric acid in water and diluting to 1.0 L. Appropriate volumes of this solution were adjusted to pH 2.5 with hydrochloric acid solution.

Triply distilled water was used throughout.

RESULTS AND DISCUSSION

Polarographic Study of Mo(VI)- MTB- ClO_3^- System

Fig. 1 shows direct current tast polarograms for different combinations of molybdenum(VI), methyl thymol blue and sodium chlorate in 0.1 M phosphate buffer solution (pH 2.5). As shown in Fig. 1 curve a, neither the reduction of MTB nor that of chlorate was observed in the potential window studied here. When Mo(VI) is mixed with MTB in the buffer solution, one wave with half wave potential at approximately – 0.4 V was obtained (curve b).

When chlorate was added to the solution one broad wave with a dip in the potential range of about – 0.5 to – 0.6V was observed (Fig. 1 c). The height of the wave in-creased and the dip became more pronounced with increasing chlorate concentration (Fig. 2) showing catalytic character of the wave [17].
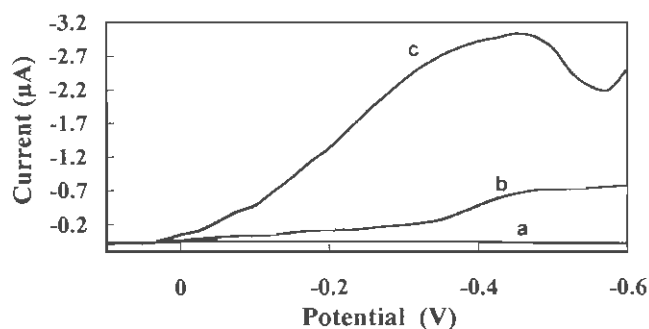

Fig. 1: Direct current tast polarograms of a mixture of MTB and chlorate (curve a); mixture of MTB and 1×10^{-4} M molybdenum (curve b) and mixture of MTB and 1×10^{-4} M molybdenum and 0.5 M chlorate (curve c) in 0.1 M phosphate buffer.
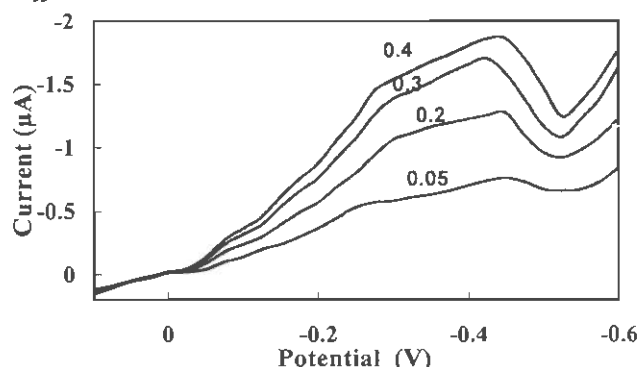

Fig. 2: Direct current tast polarograms of a Mo(VI)-MTB system in the presence of different chlorate concentrations. Conditions as in Fig. 1.

Fig. 3 shows the polarogram of Mo(VI)-MTB-chlorate system at different temperatures. As can be seen, at low temperatures, where the homogeneous chemical reaction is slow, the shape of polarogram is the same as that belonging to the pure diffusion controlled conditions. With increasing temperature, the effect of coupled chemical reaction increases and the shape of polarograms change from normal waves to a broad wave with a dip in the potential range of about – 0.5 to – 0.6 V. This behavior is characteristic of the kinetic behavior of the wave obtained [18].
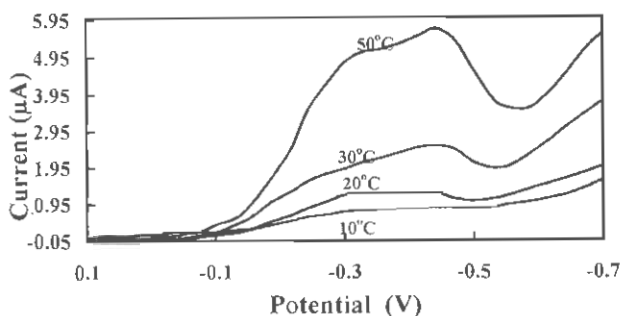
Fig. 3: Direct current tast polarograms of a Mo(VI)-MTB-ClO$_3^-$ system at different temperatures. Conditions as in Fig. 1

In Fig. 4 the effect of drop time on the shape of polarograms is shown. As can be seen from this figure increasing the drop time leads to an increase in the wave height and also in the dip in the polarograms. In addition, increasing the drop time leads to the appearance of a prewave at approximately – 0.1 V. The appearance of pre-wave at high drop times is an evidence for adsorptive characteristic of the wave [19].
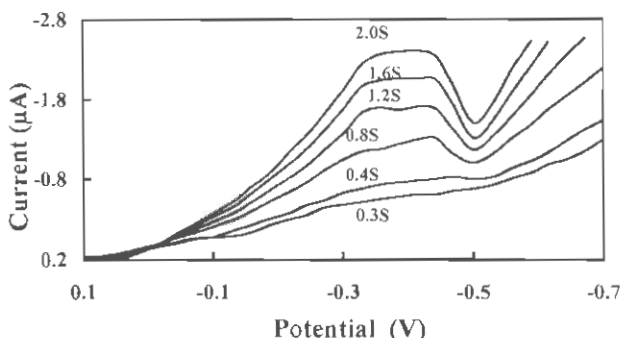

Fig. 4: Direct current tast polarograms of a Mo(VI)-MTB-ClO$_3^-$ system at different drop times. Conditions as in Fig. 1.

In order to reach a deeper understanding of the adsorption behavior, the electrocapilary curves were obtained [20] by measuring the drop times at various potentials. The decrease in the surface tension upon addition of MTB and Mo(VI)-MTB complex indicates adsorption of MTB and Mo-complex (Fig. 5).

Cyclic Voltammetric Study of Mo(VI)-MTB-ClO$_3^-$ System

Fig. 6 shows cyclic voltammograms for 2×10^{-4} M molybdenum in phosphate buffer containing 2×10^{-4} M MTB, at different scan rates. In the potential region of
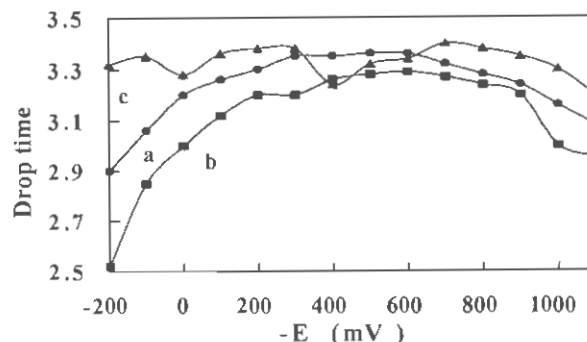

Fig. 5: Electrocapilary curve of solutions containing 0.5 M chlorate in pH 2.5 (a), a + 1 ×10^{-4} M MTB (b) and b + 1×10^{-4} M molybdenum (c).
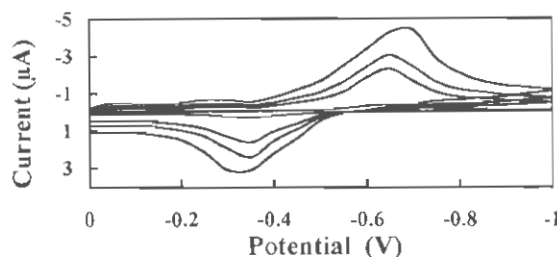

Fig. 6: Cyclic voltammograms of mixture of 2×10^{-4} M molybdenum and 2×10^{-4} M MTB in 0.05 M phosphate buffer (pH 2.5) at different scan rates (from 20 to 1000 mV/s).

about – 0.55 to – 0.8 V, a cathodic peak is observed. An anodic peak was observed upon scanning in the positive direction. A plot of the resulting cathodic current and peak potential vs. sweep rate is shown in Fig. 7. The peak current increases linearly with the increase in the scan rate. The peak potential shifts towards more negative potentials with the increase in the scan rate. This is an indication of the quasi reversibility of the electrochemical reaction.
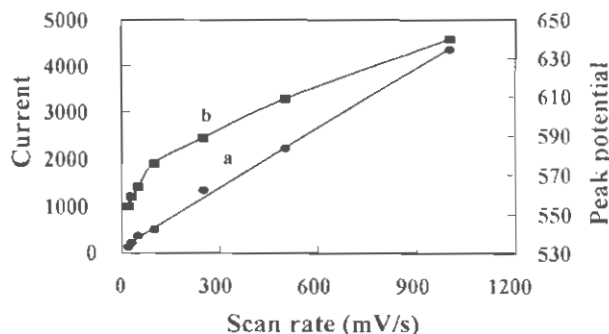

Fig. 7: Variation of i$_p$ (a) and E$_p$ (b) vs. potential sweep rate. Conditions as in Fig. 6.

The cyclic voltammograms of the above solution in the presence of 0.2 M chlorate is illustrated in Fig. 8. As can be seen, one broad cathodic peak is observed at -0.6 V during negative going scan. Scanning in the reverse direction also exhibits a cathodic peak. This is a good indication of the presence of a catalytic process in this system [21].
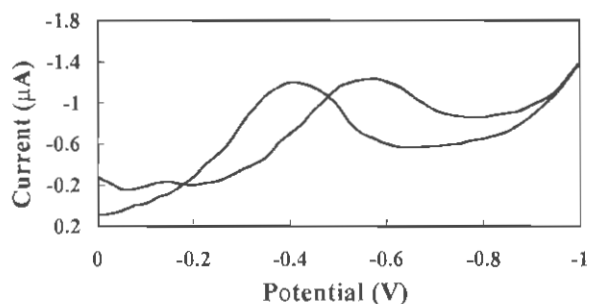

Fig. 8: Cyclic voltammogram of Mo(VI)-MTB-ClO$_3^-$ system. Conditions: 2 × 10^{-4} M MTB and Mo(VI), 0.2 M ClO$_3^-$ in 0.05 M phosphate buffer (pH 2.5) at scan rate of 100 mV/s.

Variation of chlorate concentration at constant experimental conditions caused the cathodic peak height (at -0.6 V) for molybdenum to increase with the chlorate concentration. For catalytic currents, the reduction current should be proportional with the square root of the oxidant concentration. The following relationship was used to verify the catalytic nature of the process [22]:

$$i_{pc}/i_p = f([ClO_3^-]^{1/2})$$

where i_{pc} is the catalyzed current and i_p is the current in the absence of chlorate. Experimental relationship was found to be linear over the chlorate concentration, demonstrating the catalytic nature of the process (Fig. 9).

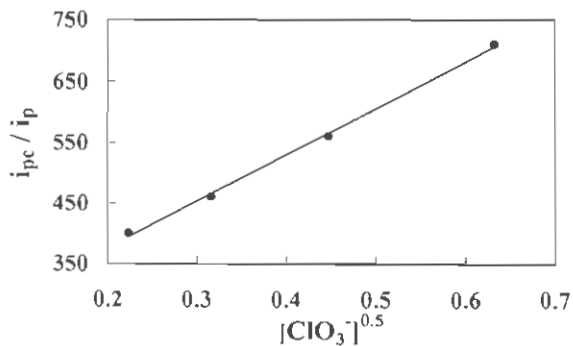The effect of scan rate on the shape, peak current and

Fig. 9: Variation of i$_{pc}$/i$_p$ vs. square root of chlorate concentration.

peak potential of cyclic voltammograms of the system was studied at different chlorate concentrations. The shape of voltammogram depends on the [chlorate]/scan rate ratio. At low [chlorate]/scan rate ratios, where the effect of chemical reaction is small, the shape of voltammograms are similar to the case when chlorate is absent (Fig. 10 a). With increasing the [chlorate]/scan rate ratio, anodic peak current decreased to zero (Fig 10 b). Further increase in [chlorate]/scan rate ratio leads to observation of a cathodic peak in positive going scan (Fig. 10 c). At high [chlorate]/scan rate ratios the height of this peak is
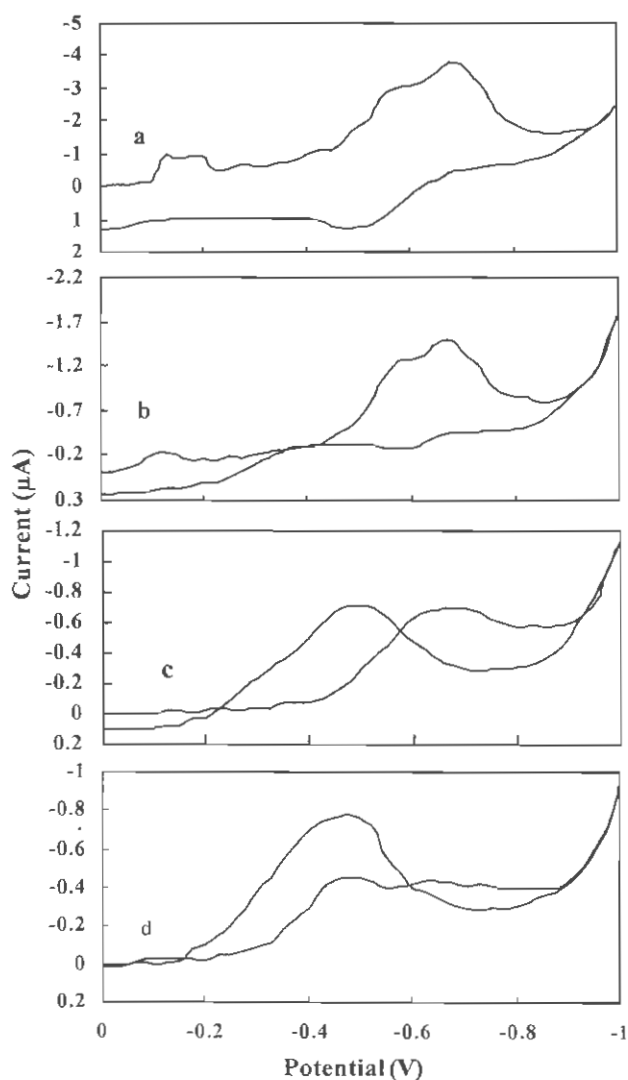

Fig. 10: Effect of scan rate on the shape of cyclic voltammogram of Mo(VI)-MTB-ClO$_3^-$ system in the presence of 0.1 M ClO$_3^-$ at scan rates a) 1000 mV/s; b) 250 mV/s; c) 50 mV/s and d) 30 mV/s. Other conditions as in Fig. 8.

greater than the cathodic peak in negative going scan.

The effect of scan rate on the half peak potential and peak current were studied at different chlorate concentrations. Fig. 11 shows variations of the half peak potential versus scan rate. As can be seen from this figure, variation of the half peak potential is different at different scan rates. At low scan rates where the system is in kinetic region, the slope of variation of peak potential vs. scan rate is higher than at high scan rates where the system is in the diffusion region.

Variation of $i_p/v^{1/2}$ with scan rate is shown in Fig. 12 for a 0.2 M chlorate solution. In all chlorate concentrations, the ratio of $i_p/v^{1/2}$ decreases to a plateau value with the increase in scan rate due to loss of the catalytic effect at high scan rates, causing the charge transfer to become faster than chlorate diffusion [23].

CONCLUSION

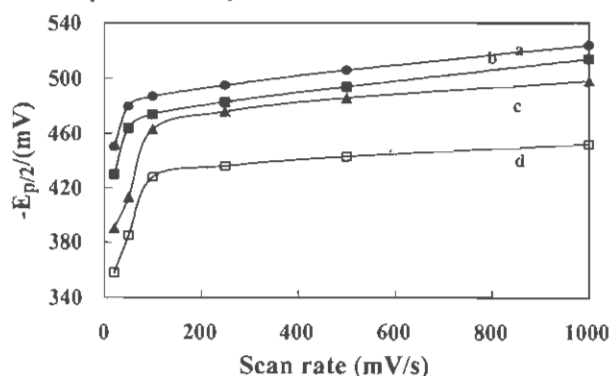The present study demonstrates that reduction of

Fig. 11: Variation of half peak potential with scan rate at 0.05(a), 0.1(b), 0.2(c), and 0.4(d) M chlorate concentrations. Other conditions as in Fig. 10.
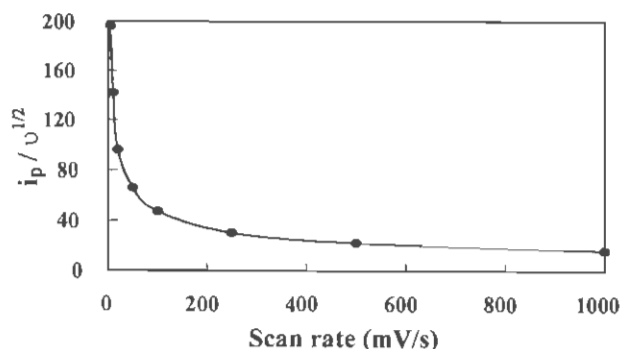

Fig. 12: Variation of $i_p/v^{1/2}$ with scan rate 0.2 M chlorate concentration. Other conditions as in Fig. 10.

molybdenum in the presence of methyl thymol blue and sodium chlorate in phosphate buffer has an adsorptive catalytic character. The adsorptive characteristic of molybdenum peak obtained in the present study is apparent from the fact that there exists a linear relationship between i_p and scan rate. Moreover, the electrocapilary curve revealed some adsorption in the potential range where molybdenum peak is obtained.

The study on the effect of temperature on the molybdenum peak makes clear that the system is kinetically controlled most probably by a coupled catalytic reaction. The catalytic nature of the coupled reaction was further proved by the observation of a cathodic peak in the reverse scan of the cyclic voltammogram (Fig. 10) from a solution of molybdenum-MTB containing chlorate. In the absence of chlorate, molybdenum-MTB system shows a quasi reversible redox couple. Thus, it is concluded that chlorate is taking part in the catalytic reaction proposed here. In order to further make clear the role of chlorate, the variation of i_{pc}/i_p vs. $[chlorate]^{0.5}$ was plotted. The graph shows a linear dependency between i_{pc}/i_p and square root of chlorate concentration. This can be considered as a good evidence that molybdenum has a catalytic effect on the chlorate reduction. The presence of the coupled catalytic reaction was further illustrated by the fact that plot of $i_p/v^{1/2}$ decreased to a plateau value with increasing scan rates. This is due to the fact that at high scan rates the effect of the coupled catalyzed reaction on the charge transfer process will be less significant.

It should be noted that the catalytic Mo-MTB-ClO_3^- system was worked at pH 2.5 in phosphate buffer. When phosphate buffer was changed to an acetate buffer with the same pH value, no catalytic behavior was observed in the system. However, addition of a phosphate salt to the above solution caused the appearance of the catalytic peak, which was previously observed with phosphate buffer. Analyzing the effect of concentration of phosphate on molybdenum peak revealed the fact that not only addition of phosphate results in appearance and enhancement of the catalytic peak, but the molybdenum reduction peak has also moved to less negative potentials by increasing the phosphate concentration. This is supportive of the fact that, as it is expected, in the presence of phosphate and at the acidic pH value of 2.5, phosphate is

also incorporating into Mo-MTB complex, and the complex which is adsorbed on the mercury is a molybdenum complex containing both phosphate and MTB. In fact the presence of MTB in the complex is also essential for the complex to be adsorbed at the electrode surface.

What can be concluded is that, at first Mo-MTB-phosphate complex is adsorbed on the electrode surface where it undergoes a reduction process. The reduced molybdenum species can then catalyze the reduction of chlorate and becomes reoxidized by this catalytic cycle, where it is rereduced electrochemicaly in the reverse scan.

However, it was not possible at this juncture to predict the exact stoichiometry of the complex adsorbed on the electrode, because phosphate tends to form different types of complexes with Mo(VI), and similar molybdenum system in the presence of phosphate is usually reported to be very complex.

Acknowledgment

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