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Polarography of Hexavalent Molybdenum in Hypophosphorous Acid Solutions

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The polarographic behaviour and determination of Mo(VI) in hypophosphorous acid solutions of concentrations varying from 0.1 to 5.0 mol l^{-1} and $T = 25 \pm 0.1$ °C have been investigated. It was shown that reduction of MoO_4^{2-} takes place along a single or two waves depending upon the acid concentration. Microcoulometric experiments have been performed at the limiting region of the different waves obtained at different acid concentrations. A scheme for the mechanism of reduction occuring at the *DME* has been deduced. A method for analytical determination of Mo(VI) on both the micro- and macro-scales in hypophosphorous acid solutions has been reported. Analysis of a binary mixture Mo(VI)/Cd(II) and a tertiary mixture Mo(VI)/Cd(II)/Zn(II) in mol l^{-1} hypophosphorous acid has been investigated.

(Keywords: Hexavalent molybdenum; Polarography; Hypophosphorous acid)

Zur Polarographie von sechswertigem Molybdän in Hypophosphorsäure

Es wurde das polarographische Verhalten und die Bestimmung von Mo(VI) in hypophosphoriger Säure bei einer Konzentration zwischen 0.1 und 5.0 mol l^{-1} und einer Temperatur von 25 ± 0.1 °C untersucht. Es zeigte sich, daß die Reduktion von Mo_4^{2-} je nach Säurekonzentration über eine oder zwei Wellen verläuft. In den Grenzgebieten der Wellen wurden bei verschiedenen Säurekonzentrationen mikrocoulometrische Messungen durchgeführt. Es wurde ein Schema für den Mechanismus der Reduktion an der tropfenden Quecksilberelektrode abgeleitet. Es wird über eine Methode für die analytische Bestimmung von Mo(VI) sowohl im Mikro- als auch im Makrobereich berichtet. Die Analyse einer binären Mischung Mo(VI)/Cd(II) und einer ternären Mischung Mo(VI)/Cd(II)/Zn(II) wurde ebenfalls untersucht.

Introduction

Molybdenum finds extensive use in the ferrous and nonferrous metallurgical industries. Its determination at trace level in plants, animals, waters and geological samples has been the subject of wide spread study.

Therefore, numerous studies have been performed for the polarographic behaviour and determination of molybdenum in different acid media [1–11]. This prompted us to study the reduction of Mo(VI) at *DME* in hypophosphorous acid solutions in continuation of the authors work on the polarographic reduction and determination of oxygenated anions [12–14]. The reduction states have been established conclusively by the coulometric analysis technique based on controlled potential electrolysis with a large mercury cathode.

Experimental

All chemicals used were of BDH grade.

A stock $0.05\,\text{mol}\,l^{-1}$ sodium molybdate solution was prepared by dissolving the proper amount of AnalR Na_2MoO_4, BDH grade, in doubly distilled water. The resulting solution was then standardized as recommended [15].

A stock $5\,\text{mol}\,l^{-1}$ acid solution was prepared by diluting A.R. hypophosphorous acid solution (50% H_3PO_2) with bidistilled water. The resulting acid solution was then standardized by titration against a standard sodium hydroxide solution. Acid solutions of lower concentrations were then prepared by accurate dilution.

Polarographic measurements were carried out with a Tacussel PRG3 apparatus equipped with three Tacussel RMO6 electrodes and a thermostat cell. A saturated calomel electrode served as the reference electrode. The dropping mercury working electrode had the following characteristics: $m = 1.894\,\text{mg}\,\text{s}^{-1}$ and $t = 3.9\,\text{s drop}^{-1}$ in hypophosphorous acid solutions.

Results

Current Potential Curves

The polarographic behaviour of $0.5\,\text{m mol}\,l^{-1}$ Mo(VI) in hypophosphorous acid solutions of concentrations varying from 0.1 to $5.0\,\text{mol}\,l^{-1}$ is illustrated by the polarograms shown in Fig. 1. The results show that reduction of Mo(VI) at the *DME* occurs along a double-wave polarogram within the investigated range of concentration. However, the polarogram obtained from $0.1\,\text{mol}\,l^{-1}$ acid solution is shown to consist of a main wave together with signs of appearance of a small first wave. At all acid concentrations the height of the second wave is twice that of the first wave. The first wave becomes well developed in the polarogram obtained from $1\,\text{mol}\,l^{-1}$ acid solution, whereas its plateau becomes ill-defined when the acid concentration is raised to $5\,\text{mol}\,l^{-1}$ or decreased to $0.1\,\text{mol}\,l^{-1}$. In the $0.1\,\text{mol}\,l^{-1}$ acid solution the rising portion of the second wave is very sloping so that the plateau is ill-defined narrow and thus vitiated by hydrogen evolution.

Microcoulometric experiments performed at the limiting region of the different waves obtained at different acid concentrations showed that

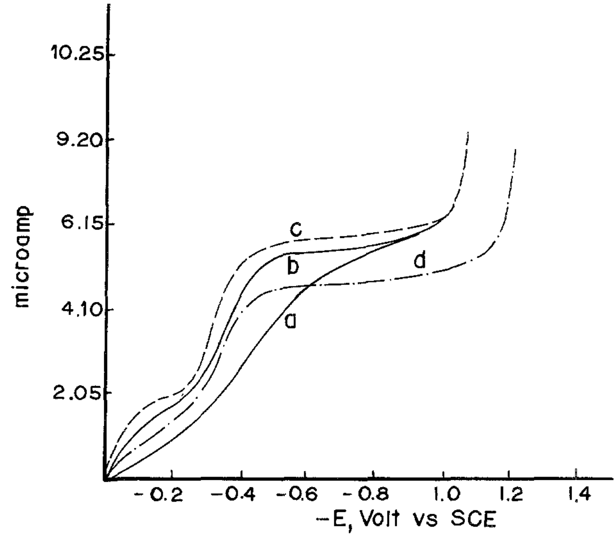

Fig. 1. Polarograms of $5 \cdot 10^{-4}$ mol l^{-1} Mo(VI) in H_3PO_2 solutions; *a* 0.1 mol l^{-1} acid, *b* 0.5, *c* 1.0, *d* 5.0

three electrons participate in the overall reduction and one electron in the first wave at 0.1 mol l^{-1} acid concentration.

It has been inferred by several authors [2, 5] that reduction of Mo(VI) at the dropping mercury electrode in dilute acid solutions occurs along two consecutive steps leading to the formation of Mo(V) and Mo(III) along the first and second waves respectively. The polarogram obtained from the 1.0 mol l^{-1} acid solution consists of two waves at the height ratio 1.95 : 3.89. Accordingly, the first wave represents the uptake of a single electron to yield Mo(V), two electrons were consumed along the second wave leading to Mo(III). The marked variations in the values of the limiting currents observed in 5 mol l^{-1} acid solutions may be ascribed to viscosity effects in the manner described before by the *Einstein-Stokes* relation [16].

Coulometric reduction of a 1.5 m mol l^{-1} solution of Mo(VI) in hypophosphorous acid solutions of concentrations 0.1, 0.5, 1.0 and 5.0 mol l^{-1} was established with a large mercury cathode whose potential was maintained at − 0.80 V and − 0.70 V vs. *SCE* respectively by an automatic potentiostat. The reduction product was the green form of Mo(III). Solutions of Mo(III) in hypophosphorous acid solutions of concentrations varying from 0.1 to 5.0 mol l^{-1} show no cathodic wave, but an incompletely developed anodic wave appears.

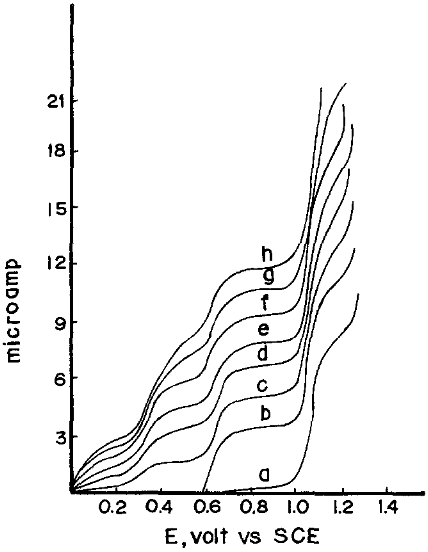

Fig. 2. Polarograms of X mM Mo(VI) in 1.0 mol l^{-1} H_3PO_2 solution containing *a* 1 mM $ZnSO_4$, *b* 0.5 mM $CdSO_4$; curve *c* X = 0.19, *d* 0.37, *e* 0.55, *f* 0.72, *g* 0.90, *h* 1.07

Controlled potential reduction of Mo(VI) solution at a mercury cathode in 1 mol l^{-1} hypophosphorous acid at a potential − 0.20 V between the first and second waves produced a solution of Mo(V) which showed only the second wave observed in this acid medium. It was shown that the second reduction wave of Mo(VI) in 1 mol l^{-1} hypophosphorous acid solution is too wide and thus it can accommodate other depolarizer waves. Based upon this fact, a procedure has been developed for the simultaneous polarographic determination of the two elements in this medium.

The results obtained in studying the analysis of the binary depolarizer mixture Mo(VI)/Cd(II) indicate possibilities to account for tertiary mixtures. Figure 2 illustrates the effect of increasing concentration of Mo(VI) on the electroreduction of a solution containing Cd(II) and Zn(II) in 1 mol l^{-1} hypophosphorous acid solution.

Nature of the Reduction

The reduction of Mo(VI) in hypophosphorous acid solutions of varying concentrations was irreversible, judging from the log-plot of the wave analysis, which was obtained by means of the plots of the values of

Table 1. *Kinetic parameters and microcoulometric data for the reduction waves of* Mo(VI) *in hypophosphorous acid solutions*

[Acid] mol l^{-1}	Wave	i_d (μA)	$E_{1/2}$, V *SCE*	Slope Volt^{-1}	αn_a	K^0 cm s^{-1}	ΔG^* kJ	$K^0 D^{-1/2}$	Microcoulometric data	
									E vs. (*SCE*)	*n*
0.1	main	5.23	− 0.38	3.88	0.23	1.3×10^{-4}	217.0	0.63	− 0.80	2.825
0.5	1st	1.85	− 0.08	7.43	0.45	1.57×10^{-4}	215.0	0.51	− 0.80	2.837
	2nd	3.58	− 0.30	12.00	0.72	5.26×10^{-5}	226.5	0.17		
1.0	1st	1.95	− 0.05	13.70	0.82	1.0×10^{-4}	219.7	0.30	− 0.18	0.830
	2nd	3.89	− 0.28	17.10	1.03	1.7×10^{-4}	213.9	0.52	− 0.80	2.841
5.0	1st	1.64	− 0.07	8.00	0.48	1.2×10^{-4}	217.8	0.45	− 0.80	2.827
	2nd	3.28	− 0.33	13.30	0.80	3.7×10^{-6}	230.3	0.14		

$\log i/i_d - i$ vs. E. These plots were utilized in the evaluation of the corresponding values of the kinetic parameters [17, 18] and wave characteristics including slope, αn_a (α = transfer coefficient and n_a = number of electrons involved in the rate determining step K^0 (standard rate constant), ΔG^* (energy of activation) and $KD^{-1/2}$. Table 1 summarises the kinetic parameters and microcoulometric data for the reduction of Mo(VI) in hypophosphorous acid solutions. These results, coupled with the direct proportionality of the diffusion current to the square root of the effective height of the mercury column, indicated that the reduction of Mo(VI) in hypophosphorous acid solutions is irreversible and entirely diffusion-controlled.

Effect of Concentration

Plots of i_l vs. concentration for the different reduction waves of molybdate ions at different acid concentrations are shown in Fig. 3. The limiting currents are directly proportional to the concentration of the depolarizer indicating an accurate application for the *Ilkovic* equation. Figures 4 and 5 show plots of i_l vs. concentration for the binary mixtures of Mo(VI)/Cd(II). These plots are straight lines coming through the origin

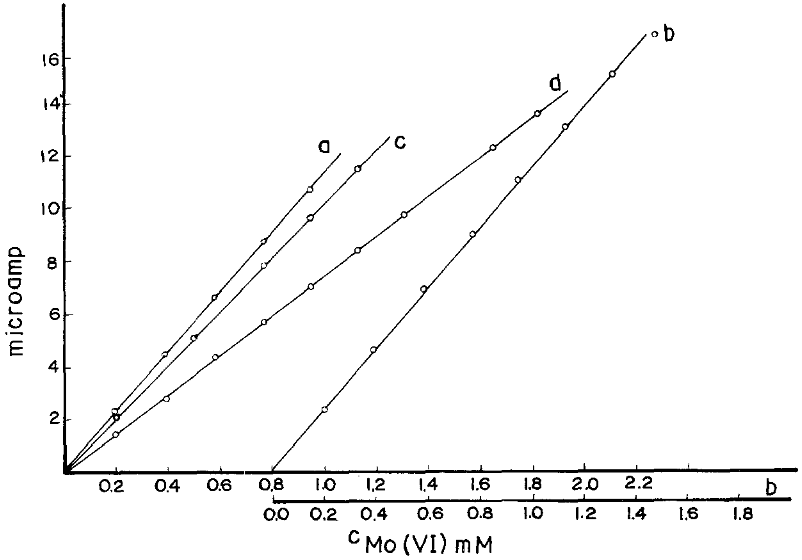

Fig. 3. Effect of [Mo(VI)] in hypophosphorous acid solutions; *a* 0.1 $\mathrm{mol\,l^{-1}}$ acid, *b* 0.5, *c* 1.0, *d* 5.0

indicating the validity of *Ilkovic* equation in analysing of such mixtures. Plots of i_l vs. concentration of Mo(VI) in presence of Cd(II) and Zn(II) in 1 mol l^{-1} hypophosphorous acid solution are shown in Fig. 6. It is quite clear that the quantitative determination of Mo(VI) in this tertiary mixture is successful.

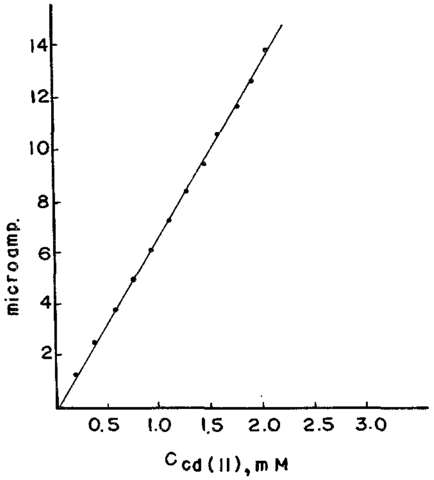

Fig. 4. Effect of [Cd(II)] in 1 mol l^{-1} H_3PO_2 containing 0.5 mM Mo(VI)

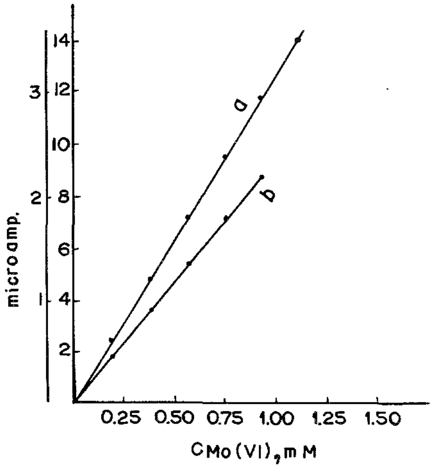

Fig. 5. Effect of [Mo(VI)] in 1 mol l^{-1} H_3PO_2 containing 0.5 mM $CdSO_4$; *a* E, Volt (*SCE*) = −0.25, *b* −0.55

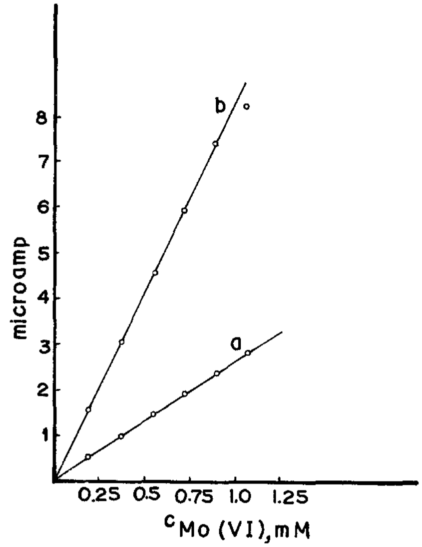

Fig. 6. Effect of [Mo(VI)] in 1.0 mol l^{-1} H_3PO_2 containing 1 mM $ZnSO_4$ and 0.5 mM $CdSO_4$; *a* at -0.2 V vs. *SCE*, *b* at -0.55 V vs. *SCE*

Discussion

The foregoing results concerning the polarographic behaviour of Mo(VI) in hypophosphorous acid solutions of different concentrations varying from 0.1 mol l^{-1} reveal that reduction occurs along a double-wave polarogram in accordance with the following mechanism:

$$H_2MoO_4 + e^- + 2\,H^+ = MoO_2^+ + 2\,H_2O \qquad (1^{st}\ \text{wave})$$

$$MoO_2^+ + 2\,e^- + 4\,H^+ = Mo^{3+} + 2\,H_2O \qquad (2^{nd}\ \text{wave})$$

Thus, the first step represents the uptake of one electron whereas two electrons are involved in the second step to produce the final reduction state, Mo(III).

The polarographic determination of Mo(VI) is quite feasible and successful on both the micro- and macro scales in hypophosphorous acid solutions. This fact has been confirmed by the very good straight lines passing through the origin, obtained for the plots of the limiting current vs. concentration of the depolarizer which verifies the validity of *Ilkovic* equation. This is also manifested by the constancy of the current-concentration coefficient throught the hypophosphorous acid concentration range 0.1–5.0 mol l^{-1}.

Polarographic analysis of the binary mixture Mo(VI)/Cd(II) and of the tertiary mixture Mo(VI)/Cd(II)/Zn(II) in 1 mol l^{-1} hypophosphorous acid solution is successful. This fact has been confirmed by the very good straight lines obtained for the plots of the limiting current vs. concentration of the depolarizer, which verifies the validity of the *Ilkovic* equation.

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