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Depolarising Action of Mo^{VI} at DME in Organic Acids

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Results are reported on the polarographic behaviour of Mo^{VI} in various organic acids. Experimental factors such as pH, ligand concentration, mercury pressure, temperature, and viscosity etc. have been varied and the data thus obtained have been interpreted in the present manuscript.

Introduction

The electro-chemical behaviour of Mo^{VI} in various organic acids[1-7] have been investigated by several authors who assumed that the polarographic reduction of hexavalent molybdenum is irreversible. A cursory examination of literature reveals that so far Mo-Malic acid, adipic acid, succinic acid and oxalic acid systems have not been investigated polarographically. Hence it has been thought worthwhile to study the cathodic action of Mo^{VI} in these supporting electrolytes. Full electro-chemical investigations are discussed in the present paper.

Experimental Section

All the reagents used were of reagent grade and all solutions were prepared in double distilled water. Mo^{VI} in the form of alkali molybdate (Na_2MoO_4) was used for the experimental work throughout the course of investigations. A manual polarograph with a scalamp galvanometer as current recorder was employed in all these determinations. The Dropping Mercury Electrode had the following characteristics $m = 2.306$ mg. per sec., $t = 3.22$ sec. in 0.1 *M* Potassium chloride solution at -1.00 volts.

Purified hydrogen was used to expel the dissolved oxygen from the polarographic solutions. An H-type cell fitted with a saturated calomel electrode and an agaragar saturated potassium chloride salt bridge were used. All polarograms were taken at 25±1°C. Use of maxima suppressor was found to be of no use except in case of oxalic acid. Maxima observed in this case is suppressed by the addition of 0.004% gelatin.

Discussion

Mo^{VI} is reduced in oxalic, succinic, adipic and malic acids giving two, one, one and two waves respectively. The values of various half wave potentials of Mo^{VI} at particular concentration of organic acids have been presented in Table I.

Table I.

Name of Organic Acid	No of Waves	$E_{1/2}$ *vs.* SCE (V) I	II
Oxalic Acid	2	−0.06	−0.33
Succinic Acid	1	−0.45	
Adipic Acid	1	−0.52	
Malic Acid	2	−0.23	−0.51

Effect of Height. Several polarograms at various heights were taken to find whether the waves are diffusion controlled. The constant values of $\frac{i_d}{h_{eff.}^{1/2}}$ in each case proves that each wave is diffusion controlled. The values of $\frac{i_d}{h_{eff.}^{1/2}}$ have been tabulated in Table II.

Table II. Effect of Height

Name of Organic Acid	$\frac{id}{h^{1/2}_{eff.}}$	
Oxalic Acid	9.114±0.057	[A constant value in each case]
Succinic Acid	5.529±0.03	
Adipic Acid	6.365±0.04	
Malic Acid	5.26 ±0.01	

Effect of Temperature. Several polarograms were taken at different temperatures varying from 30°–45°C to investigate the effect of temperature on the wave. The values of temperature coefficients have been tabulated in Table III. This value of the temperature coefficient shows that the wave is probably irreversible. Its probability is further increased by the fact that slope of the plot of $E_{d.e.}$ *vs.* log $\frac{i}{i_d - i}$ is 120 mV.

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Effect of Mo^{VI} Concentration. Solutions containing 0.05 *M* of oxalate, succinate, adipate, and malate ions and various amounts of Mo^{VI} were polarographed. All the results have been presented in Table IV. Below 0.5 m*M* of Mo^{VI}, $\frac{i_d}{c}$ constancy does not hold good in each case. The values of $D^{1/2}$ have also been determined assuming an electron transfer of 3.

In case of succinic acid, the diffusion current is not proportional to concentration.

The different values of diffusion coefficient show that molybdate ion exists in different aggregated species in different organic acids.

Table III. Effect of temperature

Oxalic Acid = 0.05 *M*
Concentration of Mo^{VI} = 7×10^{-4} *M*.

Temperature (°C)	$E_{1/2}$ *vs.* SCE (V)		Total i_d in div.	Temp. coeff.
45	–0.07	–0.335	86.0	—
40	–0.07	–0.34	81.0	1.2%
35	–0.07	–0.35	78.0	2.8%
30	–0.07	–0.36	59.0	3.3%

Succinic Acid = 0.05 *M*
Concentration of Mo^{VI} = 9×10^{-4} *M*.

Temperature (°C)	$E_{1/2}$ (V)	i_d in div.	Temp. coeff.
45	–0.445	64.5	1.8%
40	–0.44	59.0	1.8%
35	–0.435	51.5	2.9%
30	–0.435	47	1.6%

Adipate ion = 0.05 *M*
Concentration of Mo^{VI} = 11×10^{-4} *M*.

Temperature (°C)	$E_{1/2}$ (V)	i_d in div.	Temp. coeff.
45	–0.60	100.5	—
40	–0.60	87.5	2.7%
35	–0.60	73.5	3.5%
30	–0.585	60	4.0%

Malic Acid = 0.05 *M*
Concentration of Mo^{VI} = 9×10^{-4} *M*.

Temperature (°C)	$E_{1/2}$ *vs.* SCE (V) I	II	i_d I	II	Total i_d	Temp. coeff.
45	–0.22	–0.515	19	24	52	—
40	–0.23	–0.52	18	27.5	57	0.4%
35	–0.24	–0.52	16	22.5	47.5	1.4%
30	–0.24	–0.52	15	19.5	44.5	1.3%

Effect of pH. One of the important factors which affect the half wave potential and diffusion current is pH. In order to study the effect of pH, solutions containing 9×10^{-4} *M* Mo^{VI} and 0.05 M of the respective organic acids were polarographed at various hydrogen ion concentrations. In case of oxalate ions, two waves have been obtained from which it can be inferred that the first step is due to the reduction of Mo^{VI} and second step is for $Mo^{V} \rightarrow Mo^{III}$. The plateau of the first step is not well defined. Since the first step tends to merge into the second wave, an error may be possible in the evaluation of separate diffusion currents. Because of this uncertainty, the diffusion currents of first and second waves separately are of semi-quantitative significance only while the total height of both the waves varies within an error of 2%. Half wave potentials of both the waves go on shifting to more negative values as the pH is increased. The slight decrease in the limiting region is due to the fact that all the ions reaching the electrode are not reduced. Table V lists the data thus obtained. In succinate media only one wave is obtained with an $E_{1/2}$ of –0.45 volts. Value of $E_{1/2}$ goes on shifting to more negative values with increase of pH thus showing the involvement of hydrogen ions in the process of reduction. Diffusion current increases from 2.6 to 4.1, thereby it remains constant at 4.3, finally it falls down. Results have been reported in Table V.

The reduction has been found to be a single step one with the use of three electrons $Mo^{VI} \rightarrow Mo^{III}$ in adipate media. In the lower pH range from 3.6-3.8, $E_{1/2}$ is constant at –0.52 V. Further it goes on increasing towards more negative values up to pH 4.6.

Table IV. Effect of conc. of Mo^{VI}

Oxalic Acid = 0.05 *M*
Temperature = 21°C Height = 60 cm

Conc. of Mo^{VI} (m*M*)	i_d in µA I	II	Total i_d in µA	$E_{1/2}$ vs. SCE (V) A	B	$D^{1/2} \times 10^{-3}$
0.9	2.585	3.525	8.46	–0.06	–0.33	2.435
0.7	2.115	2.115	6.580	–0.05	–0.33	2.434
0.5	1.598	1.222	4.888	–0.055	–0.325	2.533
0.3	1.034	0.846	3.008	–0.07	–0.305	2.594

Adipic Acid = 0.05 *M*
Temperature = 21°C Height = 60 cm

Conc. of Mo^{VI} (m*M*)	$E_{1/2}$ *vs.* SCE (V)	i_d in µA	$D^{1/2} \times 10^{-3}$
1.5	–0.585	6.533	1.13
1.1	–0.585	4.794	
0.9	–0.585	3.238	0.933
0.7	–0.575	2.632	0.9738
0.5	–0.565	2.303	1.196

Malic Acid = 0.05 *M*

Conc. of Mo^{VI} (m*M*)	i_d in µA I	II	Total i_d in µA	$D^{1/2} \times 10^{-3}$
0.83	2.604	5.115	7.614	2.379
0.7	2.046	2.79	6.46	2.392
0.5	1.488	1.720	4.6070	2.386
0.3	0.930	1.581	2.85	2.460
0.1	—	0.548	0.95	2.460

Table V. Effect of pH

Oxalic Acid = 0.05 M
Conc. of Mo^{VI} = 9×10^{-4} M
Temperature = 25°C
height = 65 cm

pH	$E_{1/2}$ vs. SCE (V)		i_d in μA		Total i_d in μA
	I	II	I	II	
1.9	−0.06	−0.33	2.914	3.204	8.554
1.95	−0.065	−0.34	2.914	3.243	8.648
2.0	−0.08	−0.355	2.914	3.204	8.460
2.1	−0.08	−0.365	2.820	3.572	8.336
2.2	−0.08	−0.365	2.632	3.290	7.990
2.4	−0.125	−0.395	2.679	3.243	7.708
2.7	−0.155	−0.440	2.538	2.632	7.238
3.1	−0.21	−0.460	2.914	2.914	7.990
3.4	−0.24	−0.505	1.332	3.102	4.653
3.6	−0.27	−0.52	1.974	2.397	5.264
3.9	−0.305	−0.57	1.410	3.102	5.546
4.1	−0.31	−0.615	1.269	3.290	Uupper plateau not well defined

Succinic Acid = 0.05 M
Conc. of Mo^{VI} = 9×10^{-4} M

pH	$E_{1/2}$ vs. SCE (V)	i_d in μA
2.6	−0.45	4.136
3.4	−0.505	5.311
3.7	−0.52	5.452
3.9	−0.54	5.546
4.1	−0.55	5.922
4.3	−0.56	6.016
4.5	−0.58	5.358
4.7	ill defined	—

Adipic acid = 0.05 M
Conc. of Mo^{VI} = 9×10^{-4} M
Temperature = 25°C
height = 65 cm

pH	$E_{1/2}$ vs. SCE (V)	i_d in μA
3.6	−0.52	5.546
3.7	−0.52	5.969
3.8	−0.52	5.969
3.9	−0.53	6.345
4.0	−0.535	6.439
4.1	−0.54	6.392
4.2	−0.54	6.016
4.3	−0.545	6.063
4.5	−0.565	5.828
4.6	−0.560	5.733

Malic acid = 0.05 M
Conc. of Mo^{VI} = 9×10^{-4} M

pH	$E_{1/2}$ vs. SCE (V)		i_d in μA		Total i_d in μA
	I	II	I	II	
2.3	−0.24	−0.525	2.773	3.572	7.614
2.65	−0.275	−0.56	2.961	3.619	7.567
2.85	−0.30	−0.59	3.995	3.995	7.379
3.00	−0.31	−0.61	2.867	4.230	7.426
3.35	−0.33	−0.64	2.773	3.572	6.439
3.50	−0.35	−0.655	2.585	3.384	5.922
3.70	−0.36	−0.66	2.538	2.303	4.700
4.20	−0.39	−0.76	2.162	1.269	3.431

Mo^{VI} is reduced in two steps in presence of 0.05 M malate ion. The first step corresponds to $Mo^{VI}\rightarrow Mo^{V}$ whereas the second step corresponds to $Mo^{V}\rightarrow Mo^{III}$. All the results have been summarised in Table V which reveals that half wave potential is shifted to more negative values with increase of pH. At lower pH, the plateau of first wave is not well defined but on increasing pH, this plateau becomes well defined. The height of the second wave also decreases.

Effect of Increase of Concentration of Organic Acid. The half wave potentials of both the steps of the reduction of Mo^{VI} in oxalic acid shift to more positive values on increasing the amount of oxalic acid. Data thus collected has been shown in Table VI.

A peculiar behaviour of the reduction of Mo^{VI} in succinic acid has been observed. Up to 0.1 M succinic acid single step reduction occurs while appearance of two waves is noted in 0.2 M and 0.3 M succinic acid (Table VI). Since polymerised molybdate gives stepwise polarographic waves with diffusion coefficient of about 5×10^{-6} cm^2 sec^{-1}, it will be asumed here that single wave here in 0.1 M and 0.05 M of succinic acid is probably due to monomeric species while at higher concentration of succinic

Table VI. Effect of organic acid concentrations.

Oxalic acid
Conc. of Mo^{VI} = 7×10^{-4} *M*

Conc. of Oxalic acid	$E_{1/2}$ *vs.* SCE (V)	
	I	II
0.4 *M*	–0.02	–0.285
0.2 *M*	–0.02	–0.305
0.1 *M*	–0.035	–0.32
0.05 *M*	–0.06	–0.33

Succinic acid
Conc. of Mo^{VI} = 9×10^{-4} *M*

Conc. of Succinic acid	$E_{1/2}$ *vs.* SCE (V)	
	I	II
0.2 *M*	–0.40	–0.705
0.3 *M*	–0.39	–0.66
0.1 *M*	–0.425	only one wave
0.05 *M*	–0.45	only one wave

Malic Acid
Conc. of Mo^{VI} = 9×10^{-4} *M*.

Conc. of Malic acid.	$E_{1/2}$ *vs.* SCE (V)	
	I	II
0.4 *M*	–0.195	–0.48
0.3 *M*	–0.20	–0.49
0.2 *M*	–0.215	–0.49
0.1 *M*	–0.23	–0.50
0.05 *M*	–0.24	–0.525

acid (0.2 *M*) presence of two waves signifies the presence of polymerised species. Shift of half wave potential to more positive values is also noticed on increasing the concentration of malic acid (0.1 *M*–0.4 *M*) (Table VI).

Polarographic Characteristics of Mo^{VI} in Aqueous-Alcoholic and Aqueous-DMF Mixtures. Non aqueous solvents usually influence the diffusion current and sometimes the shape of the wave and the half wave potential. These effects are chiefly due to changes in solvation and in the diffusion coefficients.

Well defined waves can be obtained in non-aqueous solvents for the metal ions that yield ill defined waves in aqueous media. Hence in order to investigate the possibility of improving the waves of Mo^{VI} in various organic acids, different mixtures of various solvents with water were employed. Solvents like methanol, ethanol, propanol, T. Butanol and DMF were used.

Addition of various alcohols and DMF is found to have little effect on the nature of the molybdenum waves. They are more or less similar. In general on increasing the percentage of solvent, i_d decreases

Table VII. Diffusion current in μA

% Methanol	Mo^{VI} = 0.7 m*M* 0.05 *M* Oxalate	Mo^{VI} = 0.9 m*M* 0.05 *M* Succinate	Mo^{VI} = 1.1 m*M* 0.05 *M* Adipate	Mo^{VI} = 0.83 m*M* 0.05 *M* Malate
0	6.580	4.136	4.794	7.614
10	6.016	3.713	4.042	7.050
20	5.546	3.102	3.337	6.016
30	4.794	2.679	2.538	5.123
40	4.042	2.444	see fig. 2A	3.854
50	4.275	—	—	—
60	4.136	3.290	—	—
80	4.512	—	—	see fig. 3A

Table VIII. Diffusion current in μA

% Ethanol	Mo^{VI} = 0.7 m*M* 0.05 *M* Oxalate	Mo^{VI} = 0.9 m*M* 0.05 *M* Succinate	Mo^{VI} = 1.1 m*M* 0.05 *M* Adipate	Mo^{VI} = 0.83 m*M* 0.05 *M* Malate
0	6.580	4.136	4.794	7.614
10	5.076	3.431	see fig. 2B	5.405
20	3.243	2.726	—	see fig. 3B
30	2.955	2.021	—	—
40	2.726	1.739	—	—
50	3.008	—	—	—
60	2.955	see fig. 1A	—	—
80	—	—	—	—

Table IX. Diffusion current in μA

% Propanol	Mo^{VI} = 0.7 m*M* 0.05 *M* Oxalate	Mo^{VI} = 0.9 m*M* 0.05 *M* Succinate	Mo^{VI} = 1.1 m*M* 0.05 *M* Adipate	Mo^{VI} = 0.83 m*M* 0.05 *M* Malate
0	6.580	4.136	4.794	7.614
2.5	—	—	—	6.110
5.0	—	—	3.102	see fig. 3C
10.0	4.136	3.102	see fig. 2C	—
20	3.196	2.209	—	—
30	2.254	1.598	—	—
40	2.538	1.222	—	—
50	1.665	—	—	—
60	—	No wave	—	—
80	1.620	—	—	—

Table X. Diffusion current in μA

% T. Butyl alcohol	Mo^{VI} = 0.7 m*M* 0.05 *M* Oxalate	Mo^{VI} = 0.9 m*M* 0.05 *M* Succinate	Mo^{VI} = 1.1 m*M* 0.05 *M* Adipate	Mo^{VI} = 0.83 m*M* 0.05 *M* Malate
0	6.580	4.136	4.794	7.614
2.5	—	5.136	—	7.614
5.0	—	—	see fig. 2D	5.076
10.0	3.854	—	—	see fig. 3D
20.0	3.008	2.726, fig. 1C	—	—
30.0	2.162	wave ill defined	—	—
40.0	2.256	—	—	—
60.0	—	—	—	—
80.0	1.80	—	—	—

Table XI. Diffusion current in μA

% DMF	Mo^{VI} = 0.7 m*M* 0.05 *M* Oxalate	Mo^{VI} = 0.9 m*M* 0.05 *M* Succinate	Mo^{VI} = 1.1 m*M* 0.05 *M* Adipate	Mo^{VI} = 0.83 m*M* 0.05 *M* Malate
0	6.580	4.136	4.794	7.44
10	4.935	3.102	1.645	5.922
20	4.183	2.444	see fig. 2E	4.794
30	3.431	2.820	—	2.632
40	2.632	1.598	—	2.162
60	—	see fig. 1B	—	Wave not well defined, fig. 3E

and in some cases the wave is ill defined or completely obscured as is clear from the Figure 1, 2, 3. The reason for this distortion probably lies in the fact that a portion of the voltage is the effective voltage (E_c) which brings about electrolysis. The remainder is used to overcome the resistance in the cell circuit as is evident from the following equation

$$E_a = E_c + iR.$$

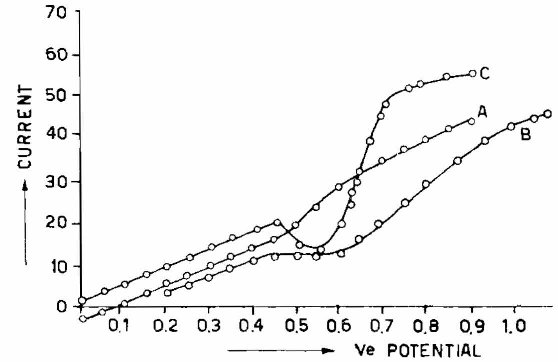

Figure 1.

Analytical Applications. Among all these acids the reduction waves of Mo^{VI} in malic acid have been found to be of analytical importance. Mo^{VI} can be estimated in presence of W^{VI} provided its concentration is 200 times less than that of Mo^{VI}. Beyond that it would interfere. Copper does not interfere as it is reduced at more positive potentials. Nickel is reduced at more negative otentials hence its presence does not interfre Cr^{VI} oxidizes the malic acid on keeping the solution for 6-8 hours and with the result that Mo^{VI} can be determined in its presence.

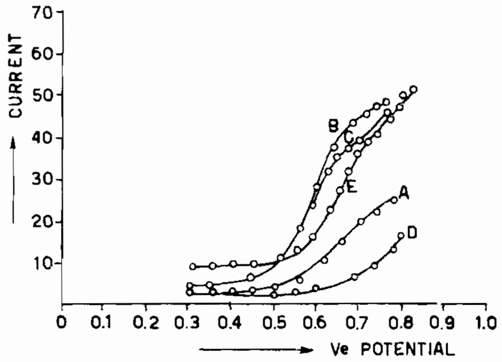

Figure 2.

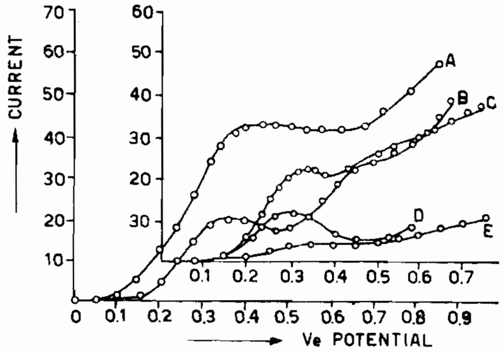

Figure 3.

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