

POLAROGRAPHIC BEHAVIOUR OF SOME METAL IONS IN PRESENCE OF PYRUVATE

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The polarographic reduction of Bi^{III} , Fe^{III} , Hg^{II} , Cu^{II} and UO_2^{II} at the dropping mercury electrode has been investigated in pyruvate solution. A single reduction wave has been observed with each metal ion. It has been proved that pyruvate forms complexes of the type 1:1 and 2:1 ligand to metal ratio with Fe^{III} and UO_2^{II} and 1:1 ligand to metal complexes with Bi^{III} , Hg^{II} and Cu^{II} . The stability constants have been determined. The effect of pH, the nature of the electrode process and the reduction mechanism have been discussed. The stoichiometry of the complexes has been confirmed by conductometric titration.

Key words: Polarographic reduction, Pyruvate-metal ion complexes, Polarographic behaviour.

INTRODUCTION

The polarographic behaviour of metal ions in pyruvate solutions are scarcely studied. This may be due to the early appearance of the pH dependent reduction wave of pyruvic acid or pyruvate [1] which vitiate most polarographic waves of metal ions. It is thought that by controlling the pH of the solution, the polarographic reduction of many metal ions in pyruvate solution can be studied. Only In (III) [2] and pb (II), Cd (II), and Cu (II) [3] ions have previously been investigated by polarography. The interaction of some metal ions with pyruvic acid has been studied by a variety of other techniques [4]. It is of interest to get informations of the polarographic characteristics of Bi(III), Cu (II), Fe (III), Hg (II) and U (VI) as UO_2^{II} (II) in the presence of pyruvate due to the essential biological role of pyruvic acid.

EXPERIMENTAL

Pyruvic acid (Prolabo), perchloric acid (BDH), copper (II) chloride (Prolabo), uranyl chloride (BDH), mercury (II) chloride (camberian chemicals) and iron (III) chloride (BDH) were of reagent grade and the solutions were prepared by using redistilled water.

Average current-potential curves were recorded by a Sargent-Welch polarograph model XVI. The solutions were deoxygenated by bubbling pure nitrogen before electrolysis. The reference electrode was saturated calomel electrode (S.C.E.). The dropping mercury electrode (D.M.E.) had the following characteristics: rate of flow of mercury (m) = 1.76 mg Sec^{-1} , drop time (t) = 4.3 sec. in 0.1 M KCl as

supporting electrolyte at a mercury height of 60 cm (open circuit) and the value of $m^{2/3}t^{1/6} = 1.84 \text{ mg}^{2/3} \text{ sec}^{-1/2}$.

The temperature of the cell was maintained at 30°C . Triton X-100 was used as maximum suppressor. The polarograms were taken at constant ionic strength viz 0.2 and constant pH values ($5.5 <$) adjusted with sodium hydroxide and perchloric acid solutions. 0.5 mM of the metal ion was polarographed. Orion research digital ionalyzer model 601 A was used to measure the pH of the solutions. CM 25 Safron Walden (WPA) England conductivity bridge was used in the conductometric titrations.

RESULTS AND DISCUSSION

A single reduction wave was observed with the title metal cations viz, Bi^{II} , Cu^{II} , Fe^{III} , Hg^{II} and UO_2^{II} in the presence of pyruvate. The pyruvic acid itself or pyruvate anion is reduced at the D.M.E. and the half-wave potential is pH-dependent [1]. Thus appearance of any other reduction step, if any, for the above mentioned metal cations is vitiated by the pyruvate reduction step.

From the slopes of the plots of $\log i$ (limiting current) vs $\log h$ (effective mercury head), it is indicated that the reduction processes are controlled mainly by diffusion since the values of the slopes are in the range of 0.45-0.51 for all the systems under investigation. Furthermore, the effect of concentration of each metal ion ($1.25 \times 10^{-4} - 2.5 \times 10^{-3} \text{ M}$) on the height of its polarographic reduction wave gave linear plot that passes through the origin indicating the applicability of the Ilkovic equation.

The logarithmic analyses plots i.e., $\log (i/i_{d,i})$ vs $E_{d,e.}$ for each wave were drawn. The slopes of the logarithmic analysis were used to assess the reversibility or other-

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wise of the electrode processes. Besides the logarithmic analysis plots, the number of electrons can be deduced by comparison of the wave heights of the systems under investigation, with those obtained in non-complexing medium i.e.: perchlorate where the behaviour of these metal ions is well-known.

The information concerning the complexation of the metal ion with pyruvate were gathered from the effect of ligand concentration, (pyr), at constant pH and ionic strength (0.2) on the half-wave potential. The effect of pH at constant ligand concentration, led to the estimates of the number of H^+ ions participating in the reduction mechanism.

Bi^{III}-Pyruvate system. The polarographic characteristics of Bi^{III} reduction at the D.M.E. are shown in Table 1. The slopes of the logarithmic analysis plots of the wave viz, 0.022-0.023, indicate that Bi^{III} is reduced reversibly with the consumption of 3 electrons. However, the reduction of Bi (III) proceeds in a quasireversible manner at pH = 3.05 in the absence of the ligand since the logarithmic analysis plot is curved around the abscissa [5]. The $E_{0.5}$ value in this case was found from the extrapolation of the asymptote of the wave. It is clear from the data that on increasing either the concentration of the ligand at constant pH or raising the pH at constant ligand concentration, a shift in the $E_{0.5}$ towards more electronegative potential is observed. This indicates complex formation and hydrogen ion participation in the reduction mechanism respectively.

From the slopes of the linear plot [6] of $\Delta E_{0.5}$ i.e., $E_{0.5}(\text{complex}) - E_{0.5}(\text{simple})$, vs $\log [\text{pyr}]$, the values of p (number of ligands bound to the metal ion), were found to be 1.85 and 1.91 at pH values 1.2 and 3.05 respectively. This means that the complex $\text{Bi}(\text{pyr})_2^{1+}$ is predominant and $\log B_2$ are 4.00 and 4.70 respectively.

The plot of $E_{0.5}$ vs pH at 0.05 M pyruvic acid is linear (c.f. Fig. 1) and had a slope of 0.036. This indicates that

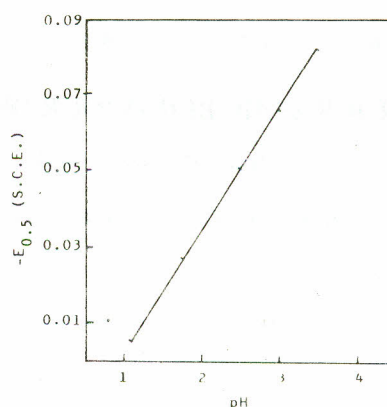
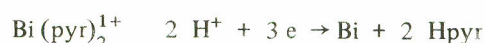


Fig. 1. Effect of pH on the half-wave potential of Bi^{III}-reduction wave in presence of 0.05 M pyruvate.

the number of H^+ ions participating in the reduction mechanism is ~ 2 . The electrode reaction may be written as follows:



However, the existence of hydrolysed species of Bi^{III} is highly probable in the pH range investigated. It can be assumed that these species may not have any effect on the final results concerning the stoichiometry and the stability of the complexes formed.

Cu^{II}-Pyruvate system. From the polarographic characteristics shown in Table 2, it is observed that Cu²⁺ ion is reduced reversibly in pyruvate medium upto pH ~ 3.5 where the slopes of the logarithmic analyses are very close to the theoretical value of the reversible 2-electron reduction step viz, 0.03. At higher pH values, the reduction proceeds irreversibly with a value of $0.06/a n_a = 0.046 \pm 0.002$ v. The limiting current remains constant and it is not affected by both pH variation or pyruvate concentration indicating that the reduction product is Cu(Hg).

The shift in the reversible half-wave potentials (pH = 2.29) on increasing the ligand concentration is small,

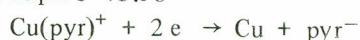
Table 1. Polarographic characteristics of Bi^{III}-pyruvate system.
 $\mu = 0.2$ (NaClO₄) Temp. = 30°C, [Bi^{III}] = 0.5 mM.

pH	[Hpyr] = 0.05 M			pH = 1.20				pH = 3.05		
	$-E_{0.5}$ V	Slope	i_d μA	Hpyr M	$-E_{0.5}$ V	Slope	i_d μA	$-E_{0.5}$ V	Slope	i_d μA
1.08	0.004	0.002	5.04	0.00	-0.018	0.022	5.40	0.022	0.022	4.26
1.75	0.026	0.022	5.04	0.02	0.002	0.023	5.01	—	—	—
2.40	0.050	0.023	5.04	0.04	0.015	0.023	4.86	0.056	0.023	4.71
2.95	0.065	0.023	4.98	0.06	0.021	0.023	4.86	0.062	0.023	4.71
3.45	0.081	0.023	4.50	0.80	0.026	0.023	4.86	0.068	0.023	4.71
—	—	—	—	0.10	0.032	0.023	4.86	0.073	0.023	4.71

indicating that Cu-pyruvate complex is weak. The number of pyruvate anion bound to the Cu^{2+} ion is one and the value of $\log K_1 = 1.20$ as they are determined from the present polarographic data. This is in close agreement with the previous results obtained by potentiometry [4,7] viz, $\log k_1 = 1.64$ at $\mu = 0.11$ and $\log K_1 = 1.35$ at $\mu = 2$ M (NaClO_4). The formation of 1:2 metal to ligand complex is not detected by the present polarographic technique due to the low overall stability value viz $\log \beta_2 = 2.03$ as obtained from potentiometric method [7]. However, there is a difference between our results and those obtained by Palrecha and Gaur [3] where three complexes were detected by polarography at $\mu = 1.0$ (NaClO_4) with $\log K_1 = 2.77$, $\log \beta_2 = 4.82$ and $\log \beta_3 = 5.19$.

The $E_{0.5}$ -pH plot had two segments with a break at $\text{pH} = 3.5$. The slopes of these segments are 0.007 and 0.025 giving number of H^+ ions less than unity which can be approximated to 0 and 1 H^+ ion. Consequently the reduction mechanism may be formulated as follows:

at $\text{pH}'s < 3.50$



and at $\text{pH}'s > 3.5$ the reduction became irreversible and the method, developed by Matsuda and Ayabe [5,8] was followed to identify the complex that directly reduced at the electrode surface and that is predominating in the bulk of the solution. Our results indicate that $\text{Cu}(\text{pyr})^+$ is the prevailing species whereas $\text{Cu}(\text{pyr})_2^{2+}$ is subjected to the reduction. However, the overall reduction may be written as:



Uranium^{VI} dioxide-pyruvate system. Two waves were observed for the polarographic reduction of UO_2^{2+} at the D.M.E. in presence of 0.1 M HClO_4 and 0.1 M NaClO_4 . The height of the second wave is twice as that of the first wave. The $E_{0.5}$ values are -0.176 and -0.843 V. The reduction products are U(V) and U(III) respectively [9]. On the addition of pyruvic acid, the $E_{0.5}$ value of the first wave shifted to more electronegative potentials on increasing either ligand concentration or pH values as seen from the data listed in Table 3. The slope of the logarithmic analysis plots of the wave indicates its reversibility and a

Table 2. Polarographic characteristics of Cu^{II} -pyruvate system.
 $\mu = 0.2$ (NaClO_4) Temp. = 30°C, $[\text{Cu}^{\text{II}}] = 0.5$ mM.

pH	[Hpyr] = 0.05 M			Hpyr M	pH = 12.49			$-E_{0.5}$ V	pH = 4.33		
	$-E_{0.5}$ V	Slope	i_d μA		$-E_{0.5}$ V	Slope	i_d μA		Slope	i_d μA	
1.24	-0.002	0.036	2.34	0.00	-0.01	0.033	2.44	-0.01	0.033	2.44	
2.34	0.002	0.036	2.34	0.02	-0.004	0.034	2.34	0.007	0.044	2.34	
2.86	0.006	0.036	2.34	0.04	0.001	0.035	2.34	0.025	0.048	2.34	
3.54	0.012	0.036	2.34	0.06	—	—	—	0.035	0.048	2.34	
4.36	0.028	0.046	2.19	0.08	0.006	0.035	2.34	0.041	0.048	2.34	
5.05	0.037	0.046	2.13	0.10	0.010	0.036	2.34	—	—	—	

Table 3. Polarographic characteristics of UO_2^{II} -pyruvate system.
 $\mu = 0.2$ (NaClO_4) Temp. = 30°C, $[\text{UO}_2^{\text{II}}] = 0.5$ mM.

pH	[Hpyr] = 0.05 M			Hpyr M	pH = 2.47			$-E_{0.5}$ V	pH = 4.36		
	$-E_{0.5}$ V	Slope	i_d μA		$-E_{0.5}$ V	Slope	i_d μA		Slope	i_d μA	
2.01	0.185	0.062	1.41	0.00	0.176	0.062	1.53	1.178	0.061	1.53	
2.47	0.196	0.064	1.41	0.02	0.181	0.063	1.41	0.256	0.068	1.41	
2.74	0.206	0.064	1.41	0.04	0.192	0.063	1.41	0.284	0.065	1.41	
3.20	0.216	0.066	1.41	0.06	0.198	0.061	1.41	0.294	0.066	1.41	
3.70	0.236	0.062	1.41	0.08	—	—	—	0.308	0.065	1.41	
4.30	0.283	0.066	1.41	0.10	0.204	0.061	1.41	0.320	0.065	1.41	

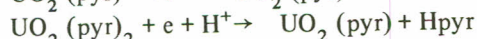
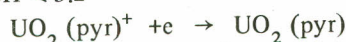
single electron process is involved. The reduction product being U(V) species.

Since the reduction product is a lower oxidation state i.e., U(V), with a number of q pyruvate anions bound to it, the polarographic data permit the determination of $(p - q)$ and $\log(\beta_{\text{ox}}/\beta_{\text{red}})$ where p is the number of pyruvate anions bound to U(VI) before its reduction and β_{ox} and β_{red} are the stability constants of the oxidised and reduced forms respectively. From the $\Delta E_{0.5}$ vs $\log[\text{pyr}]$ plot, the values of $(p - q)$ were determined viz, 0.5 and 1.5 at pH values 2.47 and 4.63 respectively. The values of $\log(\beta_{\text{ox}}/\beta_{\text{red}})$ are 0.95 and 3.33 at the corresponding pH values respectively.

The $E_{0.5}$ -pH plot had two segments with a break at pH = 3.2. The corresponding slopes were 0.03 and 0.06. These slopes indicate the uptake of one proton per two complexed uranyl species at pH < 3.2 and one proton per one complex species at pH > 3.2.

The non-integer numbers of $p-q$ at both pH values and of the number of H^+ ions consumption at pH values < 3.2 indicate the formation of more than one complex between UO_2^{2+} and pyruvate. The spectrophotometric and potentiometric [4, 10] data reveal the formation of 1:1 and 1:2 metal to ligand complexes with $\log K_1 = 1.88$ and $\log \beta_2 = 3.69$ ($\log K_2 = 1.81$) [4]. The nearly identical stability constants give an information that both complexes are reduced simultaneously in a single polarographic step. consequently, the reduction mechanism may be written as follows:

(i) at pH < 3.2



with $\log K_{\text{red}} \cong 0.90$

(ii) at pH > 3.2



Fe^{III}-Pyruvate system: A single reversible reduction wave was observed for the reduction of Fe^{III} in the presence of 0.2 M HClO_4 with $E_{0.5} = +0.204$ with a slope equals 0.062 indicating to Fe^{II} . On addition of pyruvic acid (at pH = 3.5), the logarithmic analysis pilot of the waves became curved around the abscissa indicating that the reduction of Fe^{III} to Fe^{II} in presence of pyruvate proceeds in a quasireversible manner [5]. The reversible half-wave potential $E_{0.5}^r$ was determined using the Matsuda-Ayabe method [5, 8]. The slopes of the lower and upper parts of the logarithmic analysis plot are recorded in Table 4. The slopes of the lower part indicate that a single electron is involved in the reduction process.

Since the reduction product is Fe^{II} -species, the shift in the half-wave potential with the increase in the ligand concentration gives the differences in the coordination number between the depolarizer (oxidized form) and the product (reduced form) i.e., $(p-q)$. The stability constants will be obtained in this case as $\log(\beta_{\text{ox}}/\beta_{\text{red}})$. The values of $(p-q)$ and $\log(\beta_{\text{ox}}/\beta_{\text{red}})$ for the $\text{Fe}^{\text{III}}-\text{Fe}^{\text{II}}$ system are 2 and 4.34 respectively. The reduction product; $\text{Fe}(\text{II})$ forms a very weak complex as $\text{Fe}(\text{pyr})^+$ with $\log K_1 = 0.69$ at $\mu = 3.0$ M NaClO_4 as obtained by e.m.f. measurements [11]. It can be assumed that this complex may not be formed during the drop life and the simple Fe^{II} is produced. If this assumption is true, the value of q is 0 and the value of K_{red} is 1. Consequently the values of P and $\log \beta_{\text{ox}}$ are 2 and 4.34 respectively.

It is worthy to mention that in quasi-reversible process, polarographic measurements permit determination of the

Table 4. Polarographic characteristics of Fe^{III} -pyruvate complex.
 $\mu = 0.2$ (NaClO_4) Temp. = 30°, $[\text{Fe}^{\text{III}}] = 0.5$ mM.

pH	[Hpyr] = 0.05 M			pH = 3.5						
	$E_{0.5}^r$	Slope		$-\log K_e^o$	Hpyr	$E_{0.5}^r$	Slope		$-\log K_e^o$	i_d
		A	Lower				Upper	M		
2.40	0.204	0.061	0.135	0.37	0.00	0.20	0.062	—	—	1.26
3.00	0.160	0.061	0.135	0.41	0.02	0.144	0.062	0.137	0.42	1.25
3.45	0.131	0.061	0.135	0.36	0.04	0.126	0.060	0.133	0.40	1.25
4.20	0.073	0.061	0.135	0.44	0.06	0.104	0.059	0.131	0.38	1.26
5.20	0.007	0.062	0.135	0.68	0.08	0.91	0.059	0.131	0.36	1.26

number of ligands in the complex prevailing in the bulk of the solution as well as in the complex that is reduced, permit determination of the stability constants for the complex, and give information about the kinetics of the electrode process [5]. Therefore, the values of p and q are the number of ligands prevailing in the bulk of the solution for the depolarizer and the reduction product in the present case.

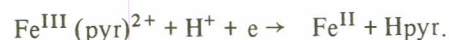
According to Matsuda and Ayabe's treatment [5, 8] the plot of $\log K_e^0$ (standard rate constant) against the concentration of the complexing agent permits determination of the composition of the complex subject to the electrode process. However, in the present case, this treatment gives the differences in the number of ligands between the oxidised and reduced form. The relation adapted by Matsuda and Ayabe [5, 8] may be modified and rewritten as

$$(i-i') = (1-\alpha)(p-q) + \frac{\Delta \log K_e^0}{\Delta \log [X]}$$

where i and i' are the number of pyruvate anions bound to Fe(III) subjected directly to the reduction and that bound to Fe(II) as the product respectively. α viz; 0.42 in the present case, and K_e^0 are the transfer coefficient and rate constant of the process respectively. The present data give $i-i' = 1$. It is assumed the $i' = 0$, then the value of $i = 1$ i.e., $\text{Fe}^{\text{III}}(\text{pyr})_2^+$ is predominating in the solution whereas $\text{Fe}^{\text{III}}(\text{pyr})_1^{2+}$ is the species that reduced at the electrode surface.

Different polarograms were recorded for the Fe^{III} -pyruvate system at different pH values viz, 2.40, 3.00, 3.45, 4.20 and 5.20 in the presence of 0.05 M pyruvic acid and $\mu = 0.2$. The $E_{0.5}^r$ values were determined from the logarithmic analyses plots of the quasireversible reduction waves. The $E_{0.5}^r$ -pH plot was linear with a slope equals

0.061. Consequently, a single proton is consumed in the reduction mechanism which can be written as follows:



Hg^{II}-Pyruvate system. Polarograms obtained during the oxidation of mercury or the reduction of mercury ions are unique in that the electrode itself constitutes the reduced form. A composite anodic-cathodic wave was observed at different pH values viz 1.18-4.94 in the presence of 0.04 M pyruvic acid at $\mu = 0.02$. The excellent continuity of the wave across the zero current axis indicated a reversible electrode reaction. In the case of Hg(II) reduction the analysis of the wave was carried out by plotting $\log(i_d - i)$ vs $E_{d,e}^{12}$. The value of the slope of the logarithmic analysis plots of the wave was 0.03, proving the electrode reaction to be essentially a reversible two-electron transfer. The polarographic characteristics are shown in Table 5.

The observed half-wave potential for the reversible reduction of Hg(II) complex in the presence of an excess of the ligand is not the true half-wave potential because a very large anodic portions of the composite wave is neglected. This apparent half-wave potential is, as pointed out by Kolthoff and Miller [13], a function of the concentration of the mercury complex as well as that of the ligand. The apparent $E_{0.5}$ values are pH-independent ($E_{0.5} = -0.12$ V) and therefore no protons are involved in the reduction of Hg(II)-pyruvate complex.

From the shift in the $E_{0.5}$ values by increasing of the ligand concentration (0.01-0.1 M) it was observed that one pyruvate anion bound to Hg(II) ion in the complex with $\log K_1 = 1.28$. However, at low concentrations of pyruvate viz, 0.04 M, the shift was too small to indicate complex formation. The potentiometric data [4] indicated the formation of 1:1 complex with $\log K_1 = 1.69$ at $\mu = 0.11$.

Table 5. Polarographic characteristics of Hg^{II}-pyruvate system.
 $\mu = 0.2$ (NaClO₄) Temp. = 30°C, [Hg^{II}] = 0.5 mM.

pH	[Hpyr] = 0.05M			pH = 3.89			
	$E_{0.5}$ V	Slope	i_d^* μA	[Hpyr] M	$E_{0.5}$ V	Slope	i_d^* μA
1.88	0.210	0.03	4.6	0.00	0.214	0.028	4.6
2.00	0.210	0.03	4.6	0.02	0.212	0.028	4.6
2.60	0.210	0.03	4.6	0.06	0.210	0.029	4.6
3.89	0.210	0.03	4.6	0.08	0.208	0.029	4.6
4.94	0.210	0.03	4.6	0.10	0.204	0.028	4.6

The reduction of Hg(II)-pyruvate complex may follow the following equation.



Conductometric titrations. Conductometric titrations were performed to trace the formation of the complexes which are liable to be formed from the reaction of UO_2^{II} , Cu^{II} , Hg^{II} and Fe^{III} with pyruvic acid in aqueous media in order to determine the stoichiometry of the complexes and to confirm the results obtained by the previous pH-metric [4] and the present polarographic methods 50 ml of 0.002 M metal ion was titrated with 0.02 M pyruvic acid. The conductance was measured after stirring the solution for about two minutes. The conductance was corrected for dilution and plotted as a function of ml added of the ligand. The results indicated the formation of 1:1 metal to ligand complexes with Hg(II) and Cu(II) whereas both Fe(III) and UO_2^{II} form 1:1 and 1:2 metal to ligand complexes.

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