

VOLTAMMATIC STUDIES OF THE REDOX REACTIONS OF SOME METAL CYANIDE COMPLEXES AT ROTATING DISK ELECTRODE IN DIMETHYLFORMAMIDE(DMF)

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Abstract

Electroactivity ,shown by the electroreduction of iron(III),manganese(III) and electrooxidation of molybdenum (IV)alkyl cyanide complexes has been studied at rotating disk electrodes of gold ,platinum and glassy carbon in dimethylformamide (DMF).All the compounds except molybdenum complexes display defined voltammetric wave at all electrode.the electrods kinetics parameter ,conditional potentials, diffusion coefficients have been determined and the influence of the solvent and the electrode material has been elucidated.comparison of the values obtained in the aqueous solution has been investigated.

Introduction

The cyanide complexes of iron(III) manganese (III) and molybdenum (IV) have been used ^{1,2} as coulometric reagents.The following standard potentials for these cyanide complexes can be found from Charlots tables ³ .

	<u>E_o vs S.H.E./V</u>
$[\text{MO}(\text{CN})_8]^{3-} + e \longrightarrow [\text{MO}(\text{CN})_8]^{4-}$	+0.84
$[\text{Fe}(\text{CN})_6]^{3-} + e \longrightarrow [\text{Fe}(\text{CN})_6]^{4-}$	+0.356
$[\text{Mn}(\text{CN})_6]^{3-} + e \longrightarrow [\text{Mn}(\text{CN})_6]^{4-}$	-0.244
$[\text{Mn}(\text{CN})_6]^{4-} + e \longrightarrow [\text{Mn}(\text{CN})_6]^{5-}$	-1.05

These reaction are therefore potentially useful coulometrically. The electrochemical behaviours of these complexes in aqueous solutions have been investigated by wright ⁴ ,who also determined the electrode kinetic parameters employing rotating disk voltammetry and faradaic impedance techniques. The effect of several non-aqueous solvents on the redox potentials of tetraethylammonium hexacyanoferrate(III) and hexacyanomanganate (III) have been recently studied ⁵⁻¹⁰ .the half wave potentials have also been measured ⁵⁻¹⁰ against bis(bi-phenyl)-chromium (I)/bis(bi-phenyl)chromium (0), and the variation in the

half wave potentials with the acceptor properties of the solvent has also been observed⁵⁻¹⁰.

However, no measurement of the electrode kinetic parameters for the above complexes in non-aqueous solvents appear to have been reported. Therefore, this investigation was undertaken to establish values of conditional potentials, electrode kinetic parameters and diffusion coefficients for the electroreduction of iron(III), manganese(III) and for the electron oxidation of molybdenum(IV) cyanide complexes in dimethylformamide (DMF), and also to compare them with values obtained in aqueous solutions at platinum, gold and glassy carbon rotating disk electrodes in the presence of tetraethylammonium perchlorate as supporting electrolyte.

Experimental

Chemicals and reagents

The purification of the solvent has been described⁴.

preparation of metal cyanide complexes

since alkali metal cyanomolybdate (IV), ferrate (III) and manganate (III) complexes are not soluble in dimethylformamide tetraalkyl complexes were used and prepared as described elsewhere in the literature⁶⁻¹⁰, followed by crystallization and dried at 50 °C under vacuum. Stock solution of the complexes was freshly prepared by dissolving the appropriate amount of each compound in the solvent. Dilute solutions were prepared from stock solution by the appropriate quantitative dilution. Tetraethylammonium bromide and tetra-n-butyl ammonium iodide, were obtained commercially from Fluka and used without further purification. Tetraethylammonium perchlorate was also obtained from Fluka and used as supporting electrolyte. All electrochemical measurements were carried out using a potentiostat of the type ST72, supplied by Gerhand Bank Electronic. The wave form generator used was of the type R.B.Z, supplied by Chemical electronic. The voltammograms were recorded using a 2900 A X-Y recorder. A three electrode cell was used, the working electrode was a rotating disk of the type B rucker ERS with gold, platinum and glassy carbon electrode. The reference electrode was a saturated calomel electrode (SCE) and the counter electrode was platinum wire. The normal voltammetric scan rate was 5 mV s⁻¹ and the geometric area of disk electrode was 0.28 cm².

Results and Discussion

A-Cathodic behaviour of tetraethylammonium hexacyanoferrate (III) and tetraethylammonium hexacyanomanganate(III) in 0.1 M tetraethylammonium perchlorate.

Voltammetry

Current-potential curves were recorded for the reduction of 0.004 M tetraethylammonium perchlorate hexacyanoferrate (III) and 0.004 M tetraethylammonium hexacyanomanganate(III) separately at platinum, gold and glassy carbon electrode rotating at 50 Hz using a scan speed of 5 mV s⁻¹. The resulting voltammograms (Figure 1) for the alkyl ferrocyanide complex show one cathodic wave (0.52V) at gold electrode, two cathodic waves at platinum (-0.57 V, -

0.75 v) and three cathodic waves at glassy carbon (-0.46, -0.75, -0.86 v)/ the first wave is due to reduction of hydrogen of the solvent. It does not appear at the gold because it emerge with second cathodic wave produce slight kink. The second wave is observable at all electrode with very well defined limiting currents which correspond to the reduction of $[\text{Fe}(\text{CN})_6]^{3-}$ to $[\text{Fe}(\text{CN})_6]^{4-}$. Moreover at glassy carbone another wave (-0.74v) appeared which probably may be due to reduction of some organic species on this material. This waves did not appear if the electrode was previously cathodically activated. (Figure 2) exemplifies the cathodic voltammograms at various rotation speeds. The limiting currents are mass transfer dependent. The Levich Plots for platinum, gold and glassy carbone (Figure 3a) give straight lines passing through the origine. This indicate a mass transfer controlled reaction. The diffusion coefficients were evaluated from the slopes. The values obtained are given in table 1

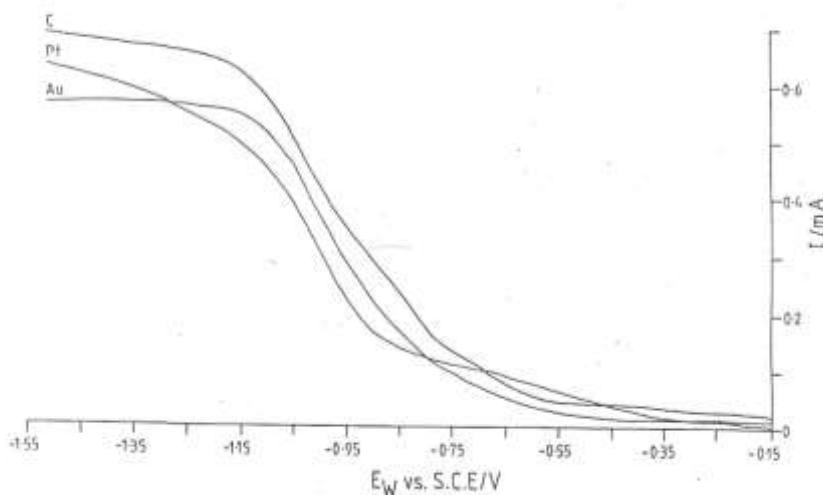
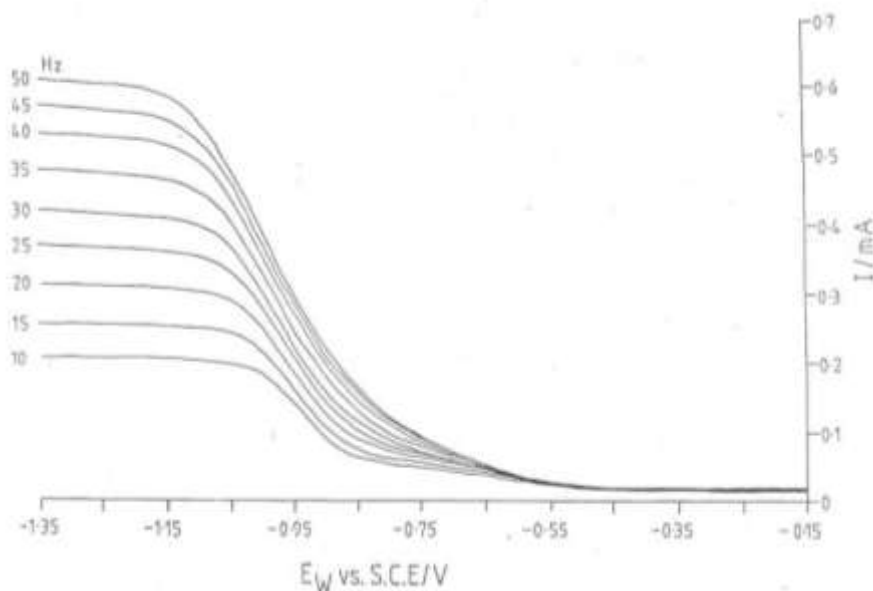


Figure (1) ..Carhodic reduction of 0.004 M $[\text{Fe}(\text{CN})_6]^{-3}$ in DMF



Figure(2).. Cathodic reduction of 0.004 M of $[\text{Fe}(\text{CN})_6]^{-3}$ at gold at different rotation speeds in DMF

Table 1. diffusion coefficient for iron(111) and manganese cyanide complexes

<u>Metal complex</u>	<u>electrode</u>	<u>$D/\text{cm}^2 \text{ s}^{-1}$</u>	<u>$D/\text{cm}^2 \text{ s}^{-1}$ reported values⁴</u>
$[(\text{C}_2\text{H}_5)_4\text{Fe}(\text{CN})_6]$	pt	2.3×10^{-7}	2.7×10^{-6}
	Au	2.2×10^{-7}	—
	C	2.5×10^{-7}	—
$[(\text{C}_2\text{H}_5)_4\text{Mn}(\text{CN})_6]$	pt	3.5×10^{-7}	3.3×10^{-6}
	Au	2.9×10^{-3}	-
	C	3.2×10^{-7}	—

The diffusion coefficient tabulated in table 1 are found to be lower in dimethylformamide than aqueous solutions. This can be attributed to higher viscosity of dimethylformamide compared to water .

Figure 4 shows current-potential curves obtained for the reduction of manganese complex at three above electrode with same experimental condition used for iron complex. Two cathodic wave were observed at each electrode .The second wave is of a well defined current at gold and glassy carbon ,but in the case of platinum , it is accompanied by a maximum . This cathodic wave corresponds to the reduction of $[\text{Mn}(\text{CN})_6]^{-3}$ to $[\text{Mn}(\text{CN})_6]^{-4}$.No indication of the reduction to lower oxidation state has been observed . Furthermore enhanced mass transfer was observed at each electrode material which could be due to a potential .dependent adsorption of the product or adsorption of cyanide and/or disporporation of manganese (III) complex to manganese (II) and managanese (IV) . The limiting

current – rotation speed give straight line of Levich Plots (Figure 3b). The diffusion coefficient are shown in table 1. The values are slightly effected by the nature of electrode material.

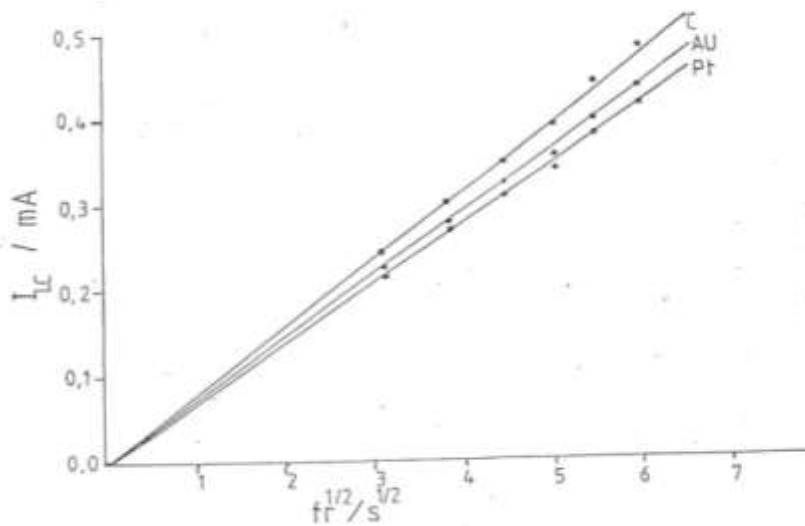


Figure 3 a: Levich plots for the reduction of $[\text{Fe}(\text{CN})_6]^{-3}$ in DMF

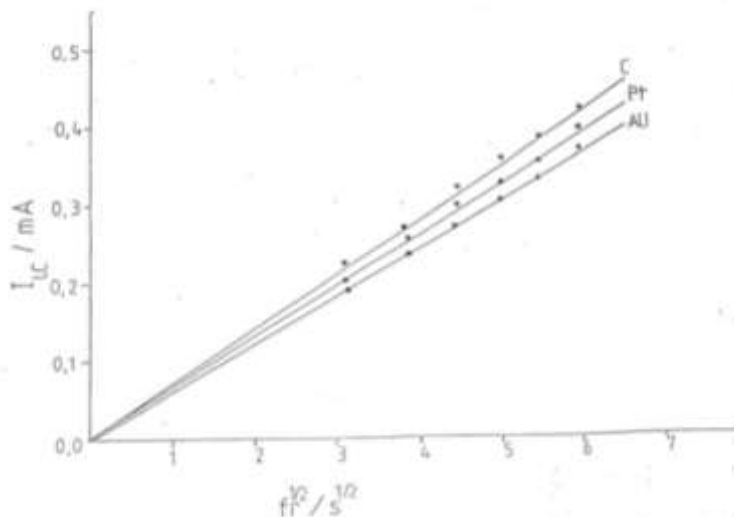


Figure 3b : Levich plots for the reduction of $[\text{Mn}(\text{CN})_6]^{-3}$ in DMF

Determination of n and E^o

The number of electrons (n) and the conditional potentials (E^o) were determined using the half-electrolysis method⁵ for the complexes and n was found to be one which confirms our postulation of the reduction of [Fe(CN)₆]⁻³ to [Fe(CN)₆]⁻⁴ and the reduction of [Mn(CN)₆]⁻³ to [Mn(CN)₆]⁻⁴. The conditional potentials were measured for the half reduction solution at each electrode. The values obtained are listed in table 2.

Table 2: The condition potential for the couples [Fe(CN)₆]⁻³ / [Fe(CN)₆]⁻⁴ and Mn(CN)₆]⁻³ / [Mn(CN)₆]⁻⁴

<u>Complex</u>	<u>electrode</u>	<u>E^o vs S.C.E./V</u>	<u>reported values⁴</u>
[Fe(CN) ₆] ⁻³ / [Fe(CN) ₆] ⁻⁴	Pt	-0.6725	0.23/v
	Au	-0.6721	
	C	-0.6722	0.23/v
[Mn(CN) ₆] ⁻³ / [Mn(CN) ₆] ⁻⁴	Pt	-0.78	0.49/v
	Au	-0.89	
	C	-0.75	-0.47/v

The conditional potentials given in table2 are found to be not affected by the nature of electrode material. Moreover the markedly lower potentials in (DMF) compared to those in water could be explained on the basis of doner-accepter interaction between the metal hexacyano ions and the solvent molecules, and between the above ions with cation of the supporting electrolyte.

Electrode kinetic parameters

The kinetic parameters were evaluated by the mass transfer extrapolated method¹³. The values obtained in DMF and in water are summarized in table3a and 3b.

Table3 a. Kietic parameters for thr reduction of [Fe(CN)₆]⁻³

<u>Electrode</u>	<u>0.1M TEAP/DMF</u>		<u>0.1 M TEAP/water</u>	
	<u>k/cm s-1</u>	<u>α</u>	<u>k/cm s-1</u>	<u>α</u>
Pt	7.9x10 ⁻³	0.49	1.5x10 ⁻²	0.58
Au	8.7x10 ⁻³	0.58	-	-
C	6.8x10 ⁻³	0.43	-	-

Table3 b. Kietic parameters for thr reduction of [Mn(CN)₆]⁻³

<u>Electrode</u>	<u>0.1M TEAP/DMF</u>		<u>reported values⁴</u>	
	<u>k/cm s-1</u>	<u>α</u>	<u>k/cm s-1</u>	<u>α</u>
Pt	12.2x10 ⁻³	0.56	6x10 ⁻²	0.76
Au	13.3x10 ⁻³	0.54	-	-
C	15.2x10 ⁻³	0.59	7x10 ⁻³	0.4

It can be seen that both K and α follow the sequence Au > Pt > C. Moreover, the charge transfer proceeds at slower rate in DMF than water. This indicates a higher free energy of activation of the transition state in DMF than water. For [Mn(CN)₆]⁻³ reduction K follows the sequence C > Au > Pt while α are in the order C > Pt > Au. The charge transfer reaction proceeds faster at platinum in aqueous media while its

proceed slower at glassy carbon. This may be due to some adsorption at glassy carbon in aqueous media.

B-Anodic behaviour of tetra-n-butylammonium octacyanomolybdate(IV).

Voltammetry

The current potential curves were recorded for the oxidation of 0.001 M tetra-n-butylammonium octacyanomolybdate(IV) at platinum, gold and glassy carbon disk electrode rotating at 50 Hz. A scan speed of 5Mv s^{-1} was used. The anodic voltammograms are shown in figure 5. One anodic wave together with the background wave were observed at platinum (0.74v) and at glassy carbon (0.78v) whereas two waves (0.58, 0.9 v) appeared at gold electrode. The first wave at each electrode is probably due to the oxidation of molybdenum (IV) complex to molybdenum (V) and the second wave before the background wave at gold might be due to oxidation of molybdenum(V) to molybdenum(VI). However, the current potential curves at all three electrode are of very poor reproducibility and repeated scans seem to affect the anodic oxidation potential at all three electrode.

Conclusion

From the electrochemical investigation of the systems studied in this work the following conclusion have been drawn:

- 1- The conditional potential for both iron (III) / iron (II) and manganese(III)/ manganese (II) cyano complex were found to be of markedly lower values in dimethylformamide than in water.
- 2- The above two electrode reactions are fast in DMF at all three electrode and with exception of glassy carbon in the case of manganese (III) complex it was found that both iron (III) and manganese (III) complexes reduced at slower rate in dimethylformamide than in water.
- 3- The charge transfer rate constant K at all three electrode falls in the order $[\text{Mn}(\text{CN})_6]^{-3} > [\text{Fe}(\text{CN})_6]^{-3}$.
- 4- The current -potential curves were not reproducible for oxidation of molybdenum (iv) complex and the calculation of the kinetic parameters were not reported for this system because of the lack of complete certainty of the nature of the electrode reaction mechanism for the oxidation process.

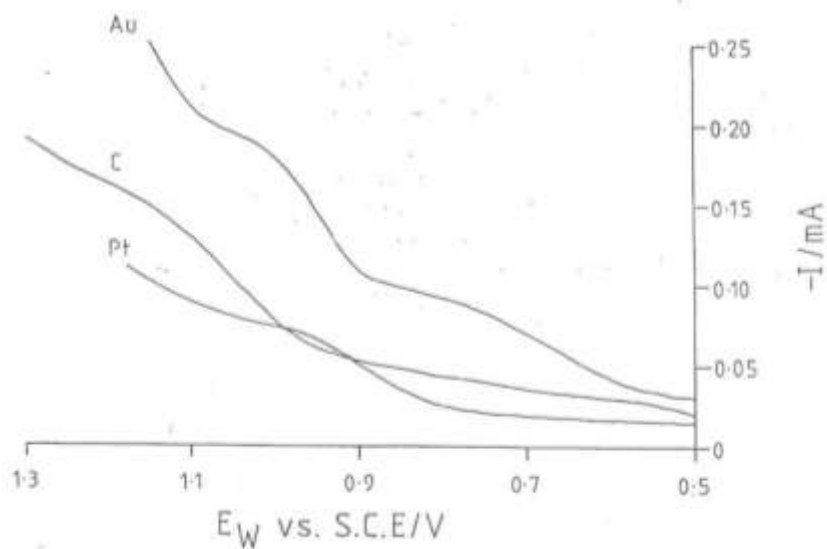


Figure 4: Cathodic reduction of $0.002\text{M } [\text{Mn}(\text{CN})_6]^{3-}$ in DMF

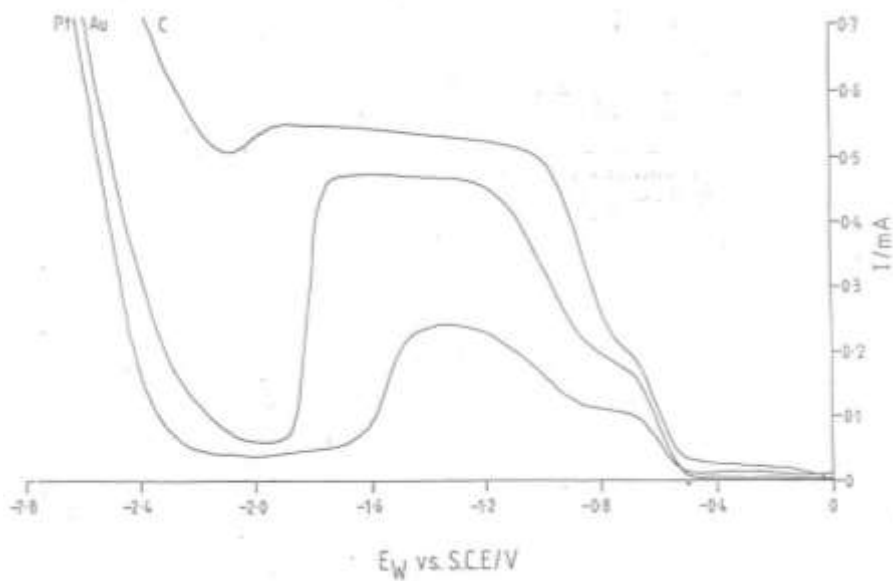


Figure 5: Anodic oxidation of $0.001\text{M } [\text{Mo}(\text{CN})_8]^{4-}$ in DMF

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دراسة فولتا مترية لتفاعلات الأكسدة والاختزال لبعض معقدات الكيل السيانيد الفلزية على أقطاب قرصية في مذيب ثنائي تثيل فورما مايد.

ا.د فتحي احمد عبيد

قسم الكيمياء-كلية العلوم □ جامعة اب

الملخص:

تمت دراسة الفعالية الكهربية لاختزال كل من الحديد الثلاثي والمنغنيز الثلاثي واكسدة الموليبدنم الرباعي لمعقدات الكيل السيانيد لهذه الفلزات على اقطاب قرصية دوارة من الذهب والبلاتين والكربون الزجاجي في مذيب ثنائي فورمامايد .
لقد اعطت جميع المركبات باستثناء معقدات الموليبدنم موجات فولتامترية واضحة المعالم لجميع الاقطاب. تم ايجاد معاملات القطب الحركية. الجهد الظرفي ومعامل الانتشار واستنتاج تأثير المذيب والقطب على تلك القيم. تم مقارنة النتائج التي تم الحصول عليها في هذه الدراسة مع النتائج في المحلول المائي.