Polarographic Study of Nickel (II) Perchlorate and Copper (II) Nitrate in the presence of 2,2'-Bipyridyl in Acetonitrile Solvent.

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Summary: The polarographic study of nickel (II) perchlorate hexahydrate in the presence of 2,2'-bipyridyl gave an evidence for oxidation of nickel (II) to nickel (III) while in the case of copper (II) nitrate study with 2,2'-bipyridyl as a ligand, gave an oxidation wave around 2V which corresponds to the oxidation of nitrate and the ligand rather than copper (II).

Introduction

The evidence for the existence of nickel in the 3.6 oxidation state is reported by Vogel[1] using an eletrochemical method in a molten KOH-H_2O medium. Olson and Vasilevakis[2,3] have claimed the preparation of nickel (III) and copper (III) complexes with cyclic amine ligands, trans-tetramine and trans-diene in acetonitrile by an electrochemical technique. Copper (III) complexes with tellurate and periodate are also reported by Lister[4], where the oxidation is achieved through an oxidizing agent rather than by an electroxidation method. Of these preparations of copper (III) and nickel (III), our interest was directed towards the approach of Olson and Vasilevskis[2,3], because we had already done a successfull eletrochemical study of silver (I) salts with polypyridyls in acetonitrile solvent and suggested an interesting mechanism and prepared and isolated a variety of silver (II) complexes[5,6].

Results and Discussion

Polarographic data for $Ni(ClO_4)_2.6H_2O$ and $Cu(NO_3)_2.3H_2O$ were obtained with 0.1M tetra-n-butylammonium perchlorate as supporting electrolyte in acetonitrile. The solvent system used in this work gave an anodic limit of 2.9 V vs S.C.E.[5] compared to 2.0 V vs silver reference electrode used by Olson and Vasilevskis[2,3] Nickel (II) perchlorate hexahydrate did not give any oxdation wave whereas copper (II) nitrate trihydrate did show a single oxidation wave around 2.1 V, thought to be due to nitrate ion oxidation. i.e. copper ion seems to remain unoxdised. Table I gives details of a polarographic study for different concentrations of copper (II) nitrate. The plot of i_L vs NO_3 is given in Fig. I from which the slope was determined as 1.2 μA mM^{-1}. Although this value is appreciably lower than the value determined for iodide ion oxidation[5], the value is considered to correspond to the one-electron oxidation of the nitrate. This discrepency might be due to the incomplete dissociation of copper (II) nitrate in acetonitrile. The absence of a copper (II)/copper (III) wave within the anodic limit of the solvent system is somewhat surprising. This implies that the copper (III) ion in acetonitrile is much less strongly solvated than copper (II) ion, a situation which would not be expected on purely electrostatic grounds. The following argument might be used to explain this anomaly. If the specific solvation of copper (II) by acetonitrile is attributed to the back-bonding from the copper ion to the NC-group, this effect might be considerably reduced when the copper is in the tripositive state, the extra positive charge reducing the π-donor properties of the copper ion and thereby reducing the strength of the copper (III)/acetonitrile bond.

Fig. I. i_L vs $[NO_3^-]$

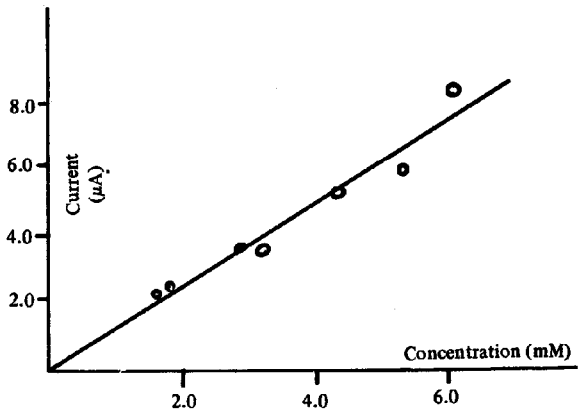

Table I *Anodic polarography of copper (II) nitrate solutions.*

C_M(mM)	0.93	1.00	1.55	1.42	2.00	2.63	2.93	5.43
i_L(uA)	2.5	2.7	3.5	3.5	4.8	6.0	7.6	15.2
$E_{½}$ (V)	2.09	2.14	2.05	2.12	2.15	2.09	2.15	2.20

Table II *Anodic polarography of copper (II) nitrate/bipy solutions.*

C_M(mM)	0.96	0.96	0.96	1.00	1.00	1.42	1.42	1.42	1.42	2.00	2.93	2.93
C_L(mM)	1.85	5.13	6.62	1.59	3.89	3.85	7.85	13.18	17.59	6.00	6.41	9.74
i_L(uA)	3.8	9.1	9.7	3.8	8.1	6.3	10.0	12.0	12.6	11.0	11.2	16.9
$E_{½}$ (V)	2.05	2.06	2.08	2.05	2.04	2.03	2.07	2.06	2.06	2.05	2.10	2.12

Solutions of copper (II) nitrate in the presence of 2,2'-bipyridyl gave a single wave having a half-wave potential identical to that obtained in the absence of the ligand. Values of the limiting current, however, are much larger than those given in the absence of the ligand. Table II giving details of the complete set of polarographic experiments. At this stage it seems reasonable to assume, since this oxidation wave occurs at the same half-wave potential as that of the nitrate ion, that the wave is associated with the oxidation of the nitrate ion to the nitrate radical. This radical might then oxidise the ligand with the regenerationof the nitrate ion giving a catalytic wave. The assumption of catalytic oxidation is supported to a certain extent by the fact that the amount of electricity passed during electrolysis was extremely large and on the basis of total copper (II) percentage gave an electron change/molecule of about 7 to 8.

In the presence of 2,2'-bipyridyl, the nickel (II) perchlorate system gave a single oxidation wave having a half-wave potential of 1.85 V. Fig. II shows a representative polarogram for a 2.68 mM nickel (II) solution containing 4.1 mM bipyridyl; details of other polarograms are given in Table III. The polarograms obtained were much less reproducible than those for the corresponding silver (I) system[5], although the maximum current effect of the silver (I) perchlorate system was absent. The values of limiting current are much smaller than expected for one-electron oxidation of nickel (II) based on the total concentration of nickel (II) present; and it seems likely that a similar explanation in terms of an electroactive intermediate complex species[5] might be found.

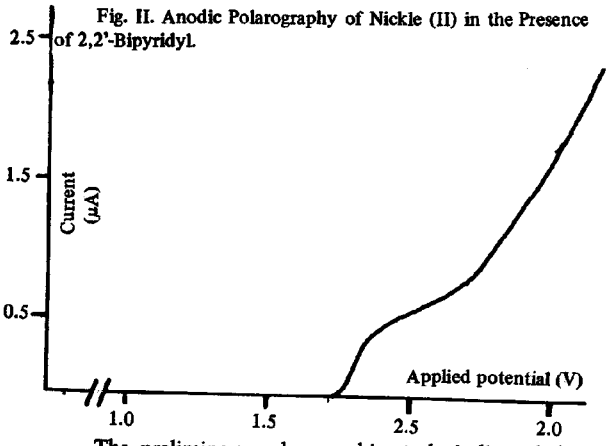

Fig. II. Anodic Polarography of Nickle (II) in the Presence of 2,2'-Bipyridyl.

The preliminary polarographic study indicated that controlled potential electrolysis of nickel (II)/bipy solutions at 1.85 V might yield a nickel (III) complex. Table IV gives details of controlled potential electrolysis for this system and includes calculation of the number of electrons involved per molecule in the electrode reaction. During electrolysis, the anode compartment solution changed from the light pink colour to a very dark green. Removal of the acetonitrile solvent from the oxidised solution gave a dark-green viscous liquid which on exposure to the atmosphere quickly reverted to the light pink colour of the original unoxidised solution. Unfortunately, attempts to isolate the oxidation product from the dark green viscous liquid were unsuccessful; even with careful handling, the dark-green colour gradually disappeared.

Table III *Anodic polarography of nickel (II)/Bipy solutins.*

C_M(mM)	2.22	2.68	4.84	4.84	4.84	4.84	5.02	5.10	5.10	5.33	5.33
C_L(mM)	7.49	4.10	0.67	2.62	5.85	11.85	12.06	11.13	14.00	11.90	14.46
i_L(uA)	0.3	0.7	0.2	0.6	1.2	2.4	2.2	1.1	2.6	2.1	3.0
$E_L/2$(V)	1.90	1.85	1.86	1.85	1.83	1.80	1.82	1.84	1.9	1.85	1.90

Table IV *Coulometry of Nickel (II)/Bipy solution.*

(A)	Weight of nickel (II) perchlorate hexahydrate electrolysed	= 0.0364 g
	Initial current	= 3.1 mA
	Electrolysis time	= 143 min.
	Total quantity of electricity consumed	= 12.23 coulombs
	Molecular ratio of Bipy: $Ni(ClO4)_2.6H_2O$	= 9.2:1
	n = 1.27 electron / mole	
(B)	Weight of nickel (II) perchlorate hexahydrate electrolysed	= 0.0370 g
	Initial current	= 3.1 mA
	Elcctrolysis time	=110 min.
	Total quantity of electricity consumed	= 11.19 coulombs
	Molecular ratio of Bipy: $Ni(ClO4)_2.6H_2O$	= 9.9:1
	n = 1.15 electron / mole	

*The applied anodic potential for the sets mentioned above was 1.9V and the concentration of n-tetrabutyl ammonium perchlorate was taken as 0.1M.

This study, while indicating that oxidation of nickel (II)/bipy solutions occurred, was not successful in isolating a nickel (III) complex. However, the study was of use in giving direction to the future investigations, since it appears that the product of the oxidiation of nickel (II)/bipy solution is sensitive to small amounts of water oxygen. Olson and Vasilevskis[2] were able to overcome the difficulty of isolating the nickel (III) complexes of trans-tetramine and trans-diene from acetonitrile solvent by using a very large quantity of nickel (II) complex, and for this reason as the oxidation proceeded the nickel (III) complex started precipitating out.

This work suggests that if stronger ligands, like 2,2',2"-terpyridyl are used, the half wave for the oxidation of Ni(II)/Ni(III) couple might come very much within the anodic limit of the system used.

References

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