

## THE POLAROGRAPHY OF THE NICKEL(II)-ETHYLENEDIAMINE SYSTEM\*

## II. EFFECTS OF VARIATION OF ETHYLENEDIAMINE CONCENTRATION

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## INTRODUCTION

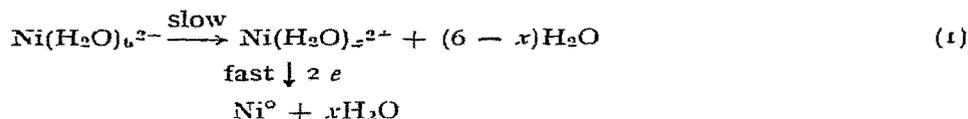
A previously reported study<sup>1</sup> showed that the polarographic reduction of  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ , in the presence of small amounts of ethylenediamine, exhibits a small pre-wave before the main metal ion wave. The general characteristics of this pre-wave were similar to those reported for the reduction of  $\text{Ni}^{2+}$  in the presence of certain aromatic organic compounds containing basic nitrogen such as pyridine<sup>1,2</sup> and *o*-phenylenediamine<sup>1,3,4</sup> in aqueous solution, and in the presence of chloride ion in acetonitrile<sup>5</sup>; the ethylenediamine pre-wave arises, however, at a somewhat more negative potential. It is believed that these pre-waves are probably the result of the reduction of mixed  $\text{Ni}^{2+}$  complexes formed with these added species and the differences in the pre-wave potentials are considered to be the result of differences in the stability constant of the complexes<sup>1</sup>.

It has also been reported that on increasing the concentration of a weak complexing agent such as pyridine<sup>6,7</sup>, chloride<sup>5,7</sup>, and *o*-phenylenediamine<sup>4</sup> so that it is in excess with respect to the  $\text{Ni}^{2+}$  ion concentration, the entire  $\text{Ni}^{2+}$  reduction wave shifts to the more positive reduction potential of the pre-wave. This would not be expected to occur, however, with excess of a strong complexing agent, such as ethylenediamine. Usually, the formation of a stable complex is expected to shift the reduction potentials of the central metal ion to more negative potentials<sup>8</sup>. For example, no wave is observed for the reduction of  $\text{Ni}^{2+}$  in the presence of an excess of tartrate ion<sup>7</sup> which forms complexes with  $\text{Ni}^{2+}$  of only slightly higher stability than ethylenediamine<sup>5</sup>. Thus, it was of interest to study the characteristics of the polarographic reduction of  $\text{Ni}^{2+}$  as a function of ethylenediamine concentration to determine if the reduction potential undergoes a second shift (in this case to more negative potentials) as the concentration of ethylenediamine is increased.

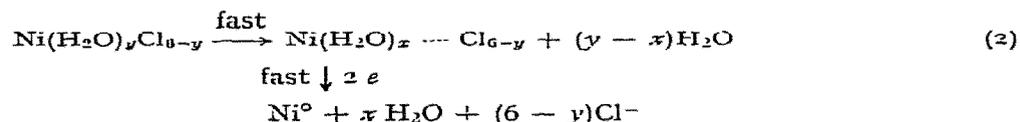
It was of interest also to attempt to characterize the nature of the electro-active species in the reduction reaction taking place at the more positive potentials corresponding to the pre-wave. DANDROY AND GIERST<sup>9</sup> showed that, in a non-complexing media,  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  itself was electro-inactive and the mechanism involved a slow

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dehydration reaction to produce the electro-active species,  $\text{Ni}(\text{H}_2\text{O})_x^{2+}$ :

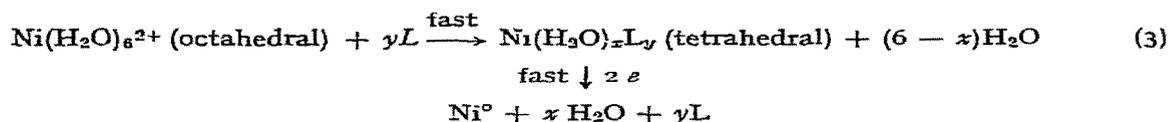


NELSON AND IWAMOTO<sup>5</sup>, in their study of the effect of chloride ion on the  $\text{Ni}^{2+}$  reduction in acetonitrile, concluded also that the rate-determining step in the electrode mechanism was a dehydration reaction to form the electro-active species; this reaction was accelerated by the presence of  $\text{Cl}^-$ . They noted that CONNICK<sup>10</sup> had demonstrated that the introduction of a foreign ligand in the primary solvation sphere of certain metal ions dramatically increased the lability of the remaining water molecules of the hydration sphere. They suggested, therefore, that the effect of  $\text{Cl}^-$  in shifting the reduction potential to more positive values was simply the result of the increase in the rate of the dehydration reaction by formation of a mixed complex to give the electro-active species:



(They did not consider whether the  $\text{Cl}^-$  ions remained in the first co-ordination sphere of the electro-active species).

A recent study of the  $\text{Ni}(\text{II})$ -*o*-phenylenediamine system<sup>4</sup> suggested another possible type of electro-active species in complexing media. The ultra-violet and visible spectra of the  $\text{Ni}(\text{II})$ -*o*-phenylenediamine system indicated that a small amount of a tetrahedral  $\text{Ni}^{2+}$  complex was forming in the bulk of the solution. This data, coupled with the fact that  $\text{NiCl}_4^{2-}$  (thought by some investigators to be the more easily reduced species in aqueous chloride media<sup>11,12</sup>) is also a tetrahedral complex<sup>13,14</sup>, indicates that the pre-waves may correspond to the reduction of a tetrahedral complex. It was suggested that the orbital configuration of the tetrahedral complex might be more closely analogous to that of the activated reduction intermediate than the orbital configuration of the octahedral  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  complex; this would result in the lowering of the activation energy of the reaction. The following mechanism could be considered:



where L is the added ligand. If a tetrahedral form of  $\text{Ni}(\text{II})$  is the electroactive species in complexing media, this might also be true of the reaction in non-complexing media (eqn. (1)). The species  $\text{Ni}(\text{H}_2\text{O})_x^{2+}$  proposed by DANDOY AND GIERST<sup>9</sup> might also be a tetrahedral complex.

It was impossible previously to distinguish between the two proposed mechanisms (represented by eqns. (2) and (3)) in the studies of  $\text{Ni}^{2+}$  in the presence of the weak complexing agents,  $\text{Cl}^-$ <sup>5</sup>, pyridine<sup>1</sup>, and *o*-phenylenediamine<sup>4</sup>. The stability constants of the species in aqueous media are sufficiently small to ensure that the mixed

complex is present in only small concentration. Furthermore, these mixed complexes appear to be very labile<sup>1,4</sup> so that it is impossible to say with any certainty that the tetrahedral complex is the electroactive species even if it does exist in large amounts in the bulk of the solution. For the Ni(II)-ethylenediamine system, however, there is the possibility of distinguishing between the two reaction mechanisms, as these complexes are quite stable<sup>15</sup> and relatively inert to the displacement of the ethylenediamine. As the species corresponding to the pre-wave in this system is probably the same as that existing in the bulk of the solution (probably a 1:1 Ni(II):ethylenediamine complex under conditions where  $[\text{Ni}^{2+}] \gg [\text{en}]$ ), ultra-violet and visible spectral studies would show if this complex exhibits tetrahedral character. The results of the electrochemical and spectrophotometric study of this system are reported in this paper.

#### EXPERIMENTAL

The dropping mercury electrode (D.M.E.) used in these experiments had a drop time of 3.10 sec at a height of 62.8 cm of mercury in 0.1 *M* KCl with no applied potential. Under these conditions, the outflow of mercury was 2.25 mg/sec. A saturated calomel electrode (S.C.E.) was used as the reference electrode, and its electrical contact with the sample solution in the polarograph cell was made through an agar-agar KCl bridge.

The polarograms were obtained with a Leeds and Northrup Type E Electrochemograph with no damping. The ultra-violet and visible spectral data were obtained with a Beckmann Model DB recording spectrophotometer using matched 1-cm silica cells.

The ethylenediamine was purified by recrystallization from concentrated hydrochloric acid. All other solutions were prepared with reagent-grade chemicals and de-ionized water.

All polarograms reported in this paper are drawn as the maximum current attained during drop life. All solutions were de-aerated with nitrogen gas purified according to standard practice<sup>16</sup>. The  $\text{Ca}^{2+}$  ion was added to the  $\text{Ni}^{2+}$  solutions as a maximum suppressor<sup>1,17,18</sup> for the  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  wave. Its presence did not affect the characteristics of the pre-wave but did increase its definition by decreasing the rate of rise of the foot of the background wave. The polarograph cell was thermostated and all experiments were run at  $25^\circ \pm 0.1$ .

#### RESULTS AND DISCUSSION

The effect of ethylenediamine concentration, over the range  $0-2.1 \times 10^{-2}$  *M*, on the polarograms of  $2.4 \times 10^{-3}$  *M*  $\text{Ni}(\text{Ac})_2$ ,  $4.8 \times 10^{-3}$  *M*  $\text{Ca}(\text{Ac})_2$ , and 0.10 *M* KAc solutions are shown in Figs. 1 and 2. The pH of the solutions was  $6.8 \pm 0.1$ . Figure 1 shows that as the concentration of ethylenediamine is increased to  $\sim 8.6 \times 10^{-4}$  *M*, a pre-wave, the current of which increases with ethylenediamine concentration in a non-linear manner, is observed to arise before the main  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  background wave. The characteristics of this pre-wave, such as wave shape and the fact that its "limiting" current is not proportional to concentration of ethylenediamine, are very similar to those observed for the pre-waves obtained for Ni(II) reduction in aqueous solution in the presence of pyridine<sup>1,2</sup> and *o*-phenylenediamine<sup>3,4</sup>, and in the presence of  $\text{Cl}^-$  in acetonitrile media<sup>5</sup>. The magnitude of the current,  $i_p$ , of the pre-wave at  $-0.90V$  vs. S.C.E. (the current was measured at this potential just prior to the onset

of the  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  reduction to eliminate the necessity for any correction resulting from the competing reductions of both the complex and  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  which occurs at more negative potentials<sup>1</sup>) appears to be catalytic in nature with respect to ethylenediamine concentration for  $[\text{en}]$  less than about  $4 \cdot 10^{-4} M$ . For example, the value of  $i_p$  obtained for a  $1.7 \times 10^{-4} M$  ethylenediamine concentration in a  $2.4 \times 10^{-3} M$   $\text{Ni}^{2+}$  solution was  $2.5 \mu\text{A}$ . The expected diffusion-controlled current would be about

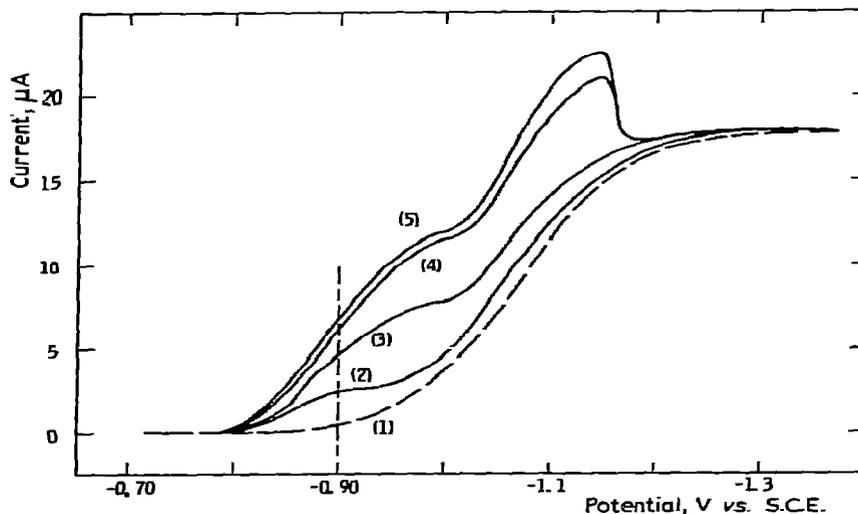


Fig. 1. Effect of ethylenediamine concn. on the polarograms of  $\text{Ni}(\text{II})$ , ( $[\text{en}]:[\text{Ni}^{2+}] < 0.5$ ).  $[\text{Ni}^{2+}]$ ,  $2.4 \times 10^{-3} M$ ;  $[\text{Ca}^{3+}]$ ,  $4.8 \times 10^{-3} M$ ;  $[\text{KAc}]$ ,  $0.10 M$ ; pH, 6.8.  $[\text{en}]$ : curve 1,  $0 M$ ; curve 2,  $1.7 \times 10^{-4} M$ ; curve 3,  $3.4 \times 10^{-4} M$ ; curve 4,  $5.1 \times 10^{-4} M$ ; curve 5,  $8.5 \times 10^{-4} M$

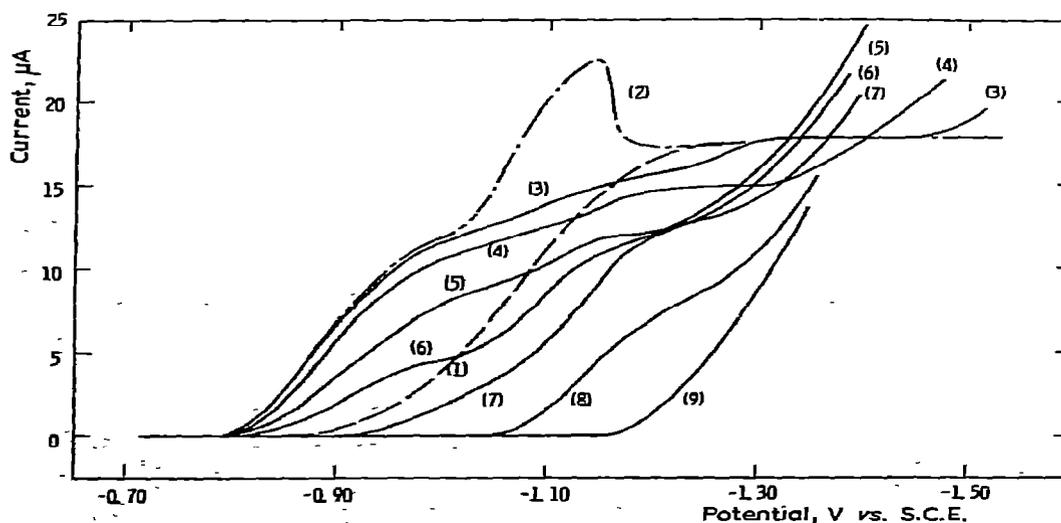
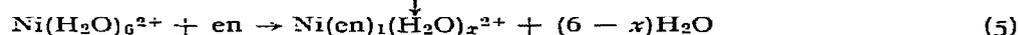


Fig. 2. Effect of ethylenediamine concn. on the polarograms of  $\text{Ni}(\text{II})$ , ( $[\text{en}]:[\text{Ni}^{2+}] > 0.5$ ).  $[\text{Ni}^{2+}]$ ,  $2.4 \times 10^{-3} M$ ;  $[\text{Ca}^{3+}]$ ,  $4.8 \times 10^{-3} M$ ;  $[\text{KAc}]$ ,  $0.10 M$ ; pH, 6.8.  $[\text{en}]$ : curve 1,  $0 M$ ; curve 2,  $8.5 \times 10^{-4} M$ ; curve 3,  $1.7 \times 10^{-3} M$ ; curve 4,  $2.1 \times 10^{-3} M$ ; curve 5,  $3.4 \times 10^{-3} M$ ; curve 6,  $4.3 \times 10^{-3} M$ ; curve 7,  $5.6 \times 10^{-3} M$ ; curve 8,  $8.6 \times 10^{-3} M$ ; curve 9,  $2.1 \times 10^{-2} M$ ; curves 1 and 2 are the same as in Fig. 1.

1.2  $\mu\text{A}$  (this is assumed to be the same as the diffusion-controlled limiting current of a  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  solution of the same concentration). The magnitude of catalytic enhancement of the pre-wave current is approximately the same as that reported in a previous study<sup>1</sup>. The catalytic reaction mechanism is presumably the same as that suggested for the  $\text{Ni}(\text{II})$ –pyridine<sup>1</sup> and *o*-phenylenediamine pre-waves<sup>4</sup> where the electroactive species is a mixed complex of unknown composition.



As the concentration of ethylenediamine is increased from  $4 \cdot 10^{-4}$  to about  $9 \cdot 10^{-4} M$ , the rate of change of  $i_p$  with  $[\text{en}]$  decreases sharply, and at  $[\text{en}] = 9 \cdot 10^{-4} M$ ,  $i_p$  is approximately equal to the value of the diffusion-controlled current for the reduction of a 1:1  $\text{Ni}(\text{II})$ :ethylenediamine complex. Also, a polarographic maxima is observed in this concentration range.

As the concentration of ethylenediamine is increased beyond  $9 \cdot 10^{-4} M$ , a sharp change occurs in the characteristics of the polarograms, as shown by the curves of Fig. 2. The polarographic maximum disappears and the magnitude of the pre-wave begins to decrease. Also, a new wave starts to appear which has a half-wave potential of about  $-1.15 \text{ V vs. S.C.E.}$  and does not appear to correspond to the reduction of  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  (which has a half-wave potential of about  $-1.06 \text{ V vs. S.C.E.}$  under these conditions). The magnitude of this second wave increases as the ethylenediamine concentration increases to about  $6 \cdot 10^{-3} M$ . In this same concentration range the magnitude of the pre-wave decreases essentially to zero. With further increase of ethylenediamine concentration above  $6 \cdot 10^{-3} M$ , the magnitude of the second wave begins to decrease and is essentially zero at  $[\text{en}] = 2.1 \times 10^{-2} M$ . At this point, curve (9) of Fig. 2, only a background wave is observed.  $\text{Ni}(\text{II})$  has been converted to a complex, presumably  $\text{Ni}(\text{en})_3^{2+}$ , which because of its large stability constant is reduced at potentials more negative than that of the reduction of the medium itself.

Thus, polarography indicates that there are at least four species of  $\text{Ni}(\text{II})$  formed in this system below an ethylenediamine concentration of  $2 \cdot 10^{-2} M$ : species (I) corresponding to the  $\text{Ni}(\text{II})$  wave in the absence of ethylenediamine; species (II) corresponding to the pre-wave (see Fig. 1); species (III) corresponding to the wave at  $-1.15 \text{ V vs. S.C.E.}$  (see Fig. 2); species (IV) corresponding to the "non-reducible" form of  $\text{Ni}(\text{II})$ .

In order to determine the nature of the species present in the bulk of the solution at different concentrations of ethylenediamine, the visible and ultra-violet spectra of  $0.044 M \text{ Ni}(\text{Ac})_2$ ,  $0.088 M \text{ Ca}(\text{Ac})_2$ , and  $0.10 M \text{ KAc}$  ( $\text{pH} = 6.8$ ) solutions containing  $0-0.16 M$  ethylenediamine were determined. The resulting spectra are shown in Fig. 3. When the ratio of  $[\text{en}]:[\text{Ni}^{2+}]$  is less than 1:1, the spectra (curves 1–3) show a peak growing at about  $640 \text{ m}\mu$  and a slight shift of the peak in the  $400 \text{ m}\mu$  range to shorter wave lengths without any appreciable change in its molar absorptivity. This change in the spectra probably corresponds to the formation of a 1:1  $\text{Ni}(\text{II})$ :ethylenediamine complex. When the ratio of  $[\text{en}]:[\text{Ni}^{2+}]$  is greater than 1:1 but less than 2:2 (curves 4 and 5) both peaks of the spectrum have shifted to shorter wave lengths and both show increases in the molar absorptivity, which indicates that a 1:2  $\text{Ni}(\text{II})$ :ethylenediamine complex is probably forming, as would be expected from the magnitude of the

stability constant of the 1:2 complex<sup>15</sup>. The increase of ethylenediamine concentration to 0.16 *M* (in excess of a 3:1 [en]:[Ni<sup>2+</sup>] ratio) results in a spectrum (curve 6) which is identical to those reported by ROBERTS AND FIELD<sup>18</sup> and JØRGENSEN<sup>19</sup> for the Ni(en)<sub>3</sub><sup>2+</sup> complex, which again would be expected from the magnitude of the Ni(en)<sub>3</sub><sup>2+</sup> stability constant<sup>15</sup>.

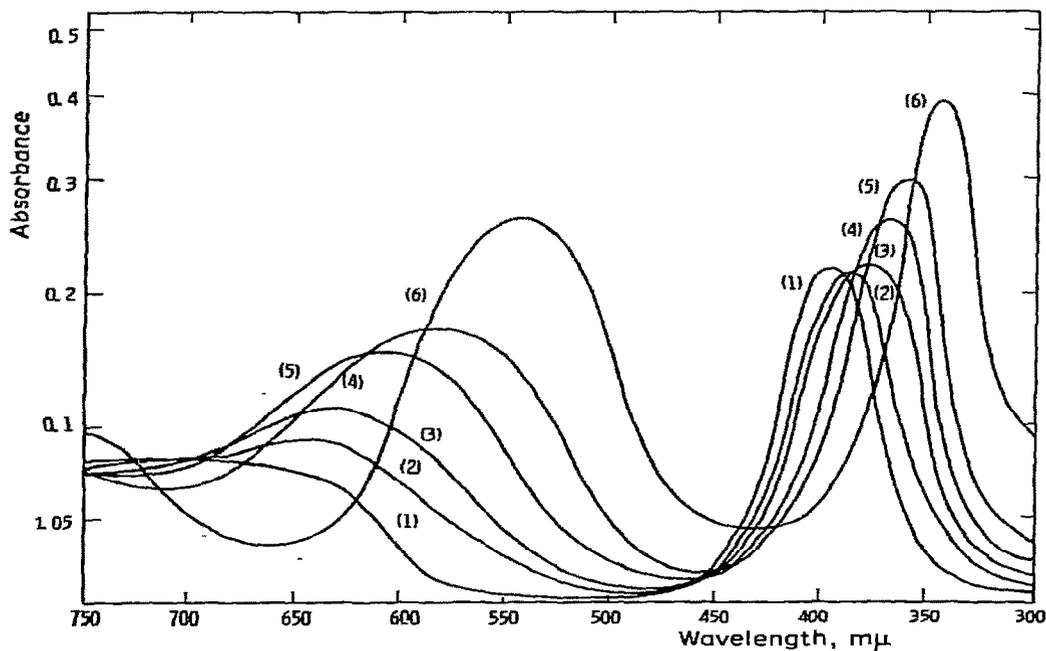


Fig. 3. Ultra-violet and visible absorption spectra of 0.044 *M* Ni(Ac)<sub>2</sub> and 0.088 *M* Ca(Ac)<sub>2</sub> in 0.10 *M* KAc in the presence of ethylenediamine. pH, 6.8 ± 0.1. [en]: curve 1, 0 *M*; curve 2, 0.01 *M*; curve 3, 0.02 *M*; curve 4, 0.04 *M*; curve 5, 0.06 *M*; curve 6, 0.16 *M*

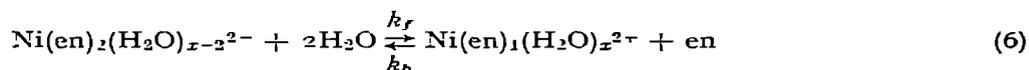
#### CONCLUSIONS

Calculations based on the successive stability constants of the Ni(II)-ethylenediamine complexes,  $pK_1 = 7.6$ ,  $pK_2 = 6.5$ ,  $pK_3 \approx 4.6$ <sup>15</sup> show that a 1:1 nickel:ethylenediamine complex is, as expected, the predominant species in the solution for concentration ratios of [en]:[Ni<sup>2+</sup>] less than 1. Similarly the 1:2 complex predominates in the concentration region where [en]:[Ni<sup>2+</sup>] is greater than 1 but less than 2, and the 1:3 complex is the predominant species when the concentration ratio exceeds about 2.5:1. The spectral data given, support these calculations. Thus, the concentration ratio region where the catalytic pre-wave is observed ([en]:[Ni<sup>2+</sup>] < 1) also corresponds qualitatively with the same concentration region where the Ni(en)<sub>1</sub><sup>2+</sup> form of Ni<sup>2+</sup> predominates. As the  $pK_1$  of this complex is large, it can be calculated that essentially all the ethylenediamine is complexed to Ni<sup>2+</sup>, and it is reasonable to assume, as stated before, that the electroactive species corresponding to the pre-wave is a Ni(en)<sub>1</sub>(H<sub>2</sub>O)<sub>2</sub> mixed complex. As this species is reduced at the D.M.E., the ethylenediamine released by the reaction (eqn. (4)) is available to react with Ni(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> in the vicinity of the electrode to reform the electroactive species according to eqn.

(5) (as shown by previous study of the ethylenediamine catalytic hydrogen wave<sup>20</sup>, some of the ethylenediamine freed by the reduction of the complex is probably actually adsorbed on the mercury surface). As this concentration of  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  in the bulk of the solution is decreased with respect to  $\text{Ni}(\text{en})_1(\text{H}_2\text{O})_{x-2}^{2+}$  (as the ratio of  $[\text{en}]:[\text{Ni}^{2+}]$  increased above 0.5, see curves 3-6 of Fig. 2), the accumulated ethylenediamine at or near the electrode surface will begin to react with the  $\text{Ni}(\text{en})_1(\text{H}_2\text{O})_{x-2}^{2+}$  to form a 1:2 Ni(II)-ethylenediamine complex which would be expected to be reduced at more negative potentials than the 1:1 complex. Therefore, the wave which begins to appear at  $-1.15$  V *vs.* S.C.E. when the  $[\text{en}]:[\text{Ni}^{2+}]$  ratio becomes larger than  $\sim 0.5$ , probably corresponds to the reduction of a  $\text{Ni}(\text{en})_2(\text{H}_2\text{O})_{x-2}^{2+}$  species.

A similar process is repeated as the concentration of  $\text{Ni}(\text{en})_2(\text{H}_2\text{O})_{x-2}^{2+}$  begins to exceed the concentration of  $\text{Ni}(\text{en})_1(\text{H}_2\text{O})_{x-2}^{2+}$ . The freed ethylenediamine at the electrode surface begins to react with  $(\text{Ni}(\text{en})_2(\text{H}_2\text{O})_{x-2})$  to form the  $\text{Ni}(\text{en})_3^{2+}$  complex which is reducible only at potentials more negative than the background reduction. Hence, the magnitude of the wave at  $-1.15$  V *vs.* S.C.E. begins to decrease as the ratio of  $[\text{en}]:[\text{Ni}^{2+}]$  increases above 2.5 (see curve 8 of Fig. 2). When the ethylenediamine concentration is increased to a ten-fold excess (see curve 9), the  $\text{Ni}^{2+}$  in the bulk of the solution is essentially completely in the  $\text{Ni}(\text{en})_3^{2+}$  form which does not exhibit a wave.

The fact that a slight wave corresponding to the  $\text{Ni}(\text{en})_1(\text{H}_2\text{O})_{x-2}^{2+}$  reduction is observed even when the ratio  $[\text{en}]:[\text{Ni}^{2+}]$  is 2-2.5 (see curves 6 and 7) can be explained by considering that the equilibrium



(although shifted to the left) is established in the solution. As the potential reaches the reduction potential of the 1:1 complex and the equilibrium concentration of the 1:1 complex is reduced, depleting its concentration at the electrode surface, the rate of the dissociation reaction of the 1:2 complex,  $k_f$ , is probably sufficiently large to shift the equilibrium to the right, thus providing additional 1:1 complex in the diffusion layer at the electrode. The wave is therefore much larger than would be anticipated from a calculation of the equilibrium concentration of the electroactive species in the system under the above concentration conditions. Such behavior, is typical of a reaction where a rapid equilibrium is established in the bulk of the solution between an electroactive and non-electroactive species<sup>21</sup>.

It is interesting to note that the spectra of the  $\text{Ni}^{2+}$  solutions obtained when the ratio  $[\text{en}]:[\text{Ni}^{2+}]$  is 1 or less (curves 1-4 of Fig. 3) are almost identical with those reported previously for the same concentration ratios for the Ni(II)-*o*-phenylenediamine system. Thus, the orbital configuration of the central Ni(II) ion of the complexes in the bulk of the solution is essentially the same for both systems. This substantiates the theory that the resulting change in the orbital configuration of the central atom on complexation is responsible for the decrease in the activation overpotential<sup>4,22</sup>. However, this does not exclude the possibility that the overpotential change results from the increased lability of the remaining water molecules in the complex<sup>5</sup>. It does tend to rule out, however, the speculation that the spectral change in the *o*-phenylenediamine case was the result of the formation of a small

fraction of a tetrahedral Ni(II) complex which had a large molar absorptivity coefficient<sup>4</sup>. Because the ethylenediamine added to excess Ni<sup>2+</sup> solutions can be considered to be about 100% associated (no data on the stability constants of Ni-*o*-phenylenediamine complex could be found in the literature so no calculation was possible in that case) as a 1:1 complex under these conditions<sup>1,20</sup>, the spectral changes in the Ni(II)-ethylenediamine system cannot be the result of formation of a tetrahedral complex. The molar absorptivity for the observed complex in the 640 m $\mu$  region is only slightly greater than that of Ni(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> and much smaller than that expected for a tetrahedral complex ( $\sim 100$  times that of the Ni(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> complex<sup>14</sup>). Further investigation of the spectra of mixed ligand-Ni(II) complexes is now in progress to determine if there is any correlation in all cases between the spectra and the decrease in the activation overpotential.

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#### SUMMARY

The effect of variation of ethylenediamine concentration from  $0-2.1 \times 10^{-2} M$  on the polarography of  $2.4 \times 10^{-3} M$  Ni<sup>2+</sup> solutions is studied. Two new waves are observed over this concentration range; a pre-wave arising before the Ni(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> wave for low concentrations of ethylenediamine, and a wave occurring at a slightly more negative potential than the Ni(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> wave for intermediate ethylenediamine concentrations. At high concentration of ethylenediamine, the Ni<sup>2+</sup> wave is not observed. The nature of the species and reactions corresponding to these waves is described. The visible and ultra-violet spectra of the system are also reported for the same ratios of Ni<sup>2+</sup>: ethylenediamine concentrations and are compared with the spectra obtained for the Ni(II)-*o*-phenylenediamine system which also exhibits a pre-wave.

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