THE CATALYTIC POLAROGRAPHIC CURRENT OF A METAL COMPLEX

II. THE NICKEL(II)–*o*-PHENYLENEDIAMINE SYSTEM

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INTRODUCTION

The polarographic reduction of Ni(II), in aqueous solutions containing small quantities of pyridine[1,2] as well as other organic amines[2,3] and in acetonitrile containing chloride ion[4], has previously been reported to exhibit a catalytic wave before the main free-metal ion wave. This pre-wave is thought to represent the reduction of Ni(II) which is complexed with the organic amine[1] or the chloride ion[4]. Because of the great sensitivity of a catalytic polarographic wave, the Ni(II)–complex catalytic pre-wave has been used successfully for the determination of small quantities of pyridine[2], ethylenediamine[5], and *o*-phenylenediamine[3]. Although it was postulated that the mechanism of this catalytic wave probably involved (i) the ability of the ligand to form a complex, (ii) adsorption of the ligand on the mercury surface, (iii) the ability of the ligand to act as a bridge which facilitates the electron transfer, and (iv) various competitive effects of protonation on certain of these processes[1,2], no conclusive experimental evidence has been previously found to substantiate such a mechanism.

An extensive investigation of the properties of the catalytic pre-wave observed when Ni(II) was reduced in the presence of *o*-phenylenediamine was undertaken in an effort to determine the details of the mechanism involved. This aromatic diamine was chosen because it gave the most well-defined pre-wave of any other substance studied[2,3]. The $E_{\frac{1}{2}}$ of this wave is approximately 0.30 V more positive than the $Ni(H_2O)_6^{2+}$ background wave and the catalytic enhancement of the wave is quite large[2]. This paper describes the experimental results of this study which indicate that the pre-wave current is limited by two factors: (i) the surface concentration of adsorbed *o*-phenylenediamine, and (ii) the rate of complexation of the free Ni(II) with the adsorbed diamine.

EXPERIMENTAL

Apparatus

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 Beckman Model-DB recording spectrophotometer using matched 1-cm silica cells. The current–time curves during the life-time of an individual drop were measured by recording, with a Tektronix Model-502 oscilloscope, the potential drop across a small resistor, 200 $\Omega \pm 0.1\%$, placed in series with the polarograph cell. A constant potential, corresponding to the potential of the peak pre-wave limiting current was applied to the series combination using the Electrochemograph as the potential source.

Reagents

The *o*-phenylenediamine was purified by recrystallization from concentrated hydrochloric acid[6]. Because of their susceptibility to air oxidation, stock solutions were prepared, just prior to taking measurements, with air-free deionized water. All other solutions were prepared with reagent-grade chemicals and deionized water.

Procedure

In order to minimize the magnitude of the air oxidation of the *o*-phenylenediamine, the sample solutions to be measured were actually prepared in the polarograph cell under a nitrogen atmosphere. The stock *o*-phenylenediamine solution was added in known volume, by means of a 5-ml microburette, to 40 ml of an air-free Ni(II)-supporting electrolyte solution, and the resulting solutions were measured. All polarograms 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[7]. Ca^{2+} ion was added as a maximum suppressor[2,8,9] for the $Ni(H_2O)_6^{2+}$ background wave. Its presence did not affect the limiting current of the pre-wave but did increase its definition by decreasing the rate of rise of the foot of the background wave.

A few polarographic experiments were performed with a stirred sample solution The stirring was accomplished by means of a variable speed magnetic stirrer. All experiments were performed at room temperature, $25° \pm 0.5$.

RESULTS AND DISCUSSION

The variation of the characteristics of the catalytic pre-wave as a function of concentration of both *o*-phenylenediamine and Ni(II) concentration, stirring of the sample solution, height of the mercury column, and pH were studied to establish the mechanism of the process. The characteristics of the current–time curves for individual drops were also determined. The spectra of the Ni(II)–*o*-phenylenediamine system was investigated as a function of pH and *o*-phenylenediamine concentration to determine if a complex is formed in the bulk solution. The electrocapillary curves were measured as a function of *o*-phenylenediamine concentration to determine if this species is absorbed on the electrode surface.

Effects of Ni(II) and o-phenylenediamine concentration

The effect of *o*-phenylenediamine concentration over a range $0–10^{-3}$ *M* on the

polarograms of 5×10^{-4} *M* $Ni(Ac)_2$, 1×10^{-3} *M* $Ca(Ac)_2$ and 1.00 *M* KAc solutions are shown in Fig. 1. The pH of the solutions was 6.8 $\pm$0.1. Note that the pre-wave actually reaches a peak current value rather than a limiting plateau. This current peak occurs at about —0.86 V *vs.* S.C.E. This peaking of the current could be the result

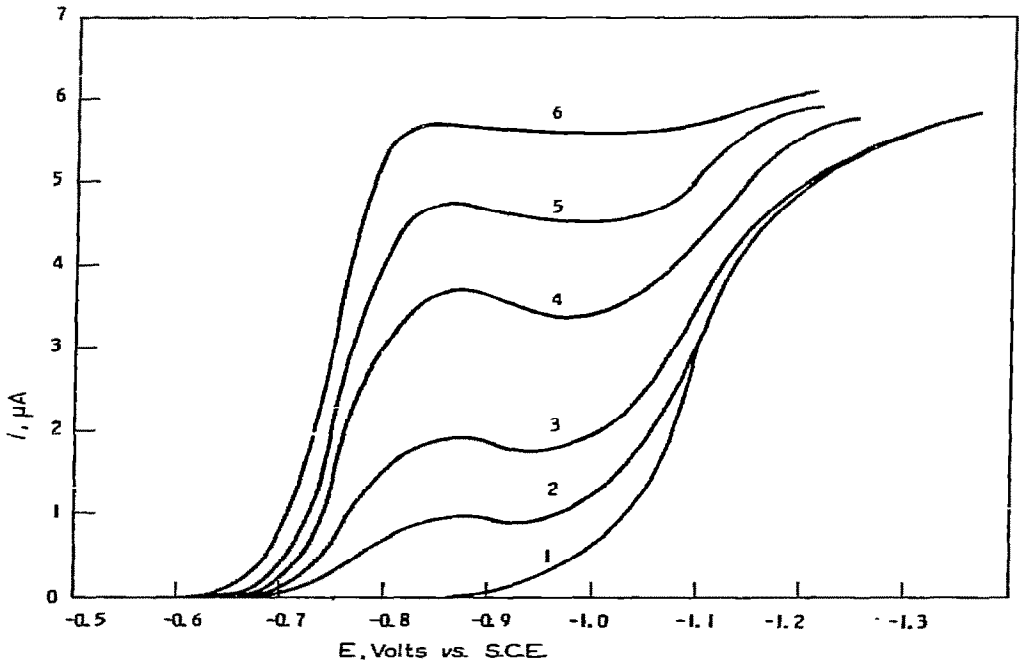

Fig. 1. Effect of concn. of *o*-phenylenediamine on the polarograms of Ni(II). $[Ni^{2+}] = 5 \times 10^{-4}$ *M*, $[Ca^{2+}] = 1 \times 10^{-3}$ *M*, [KAc] = 1.0 *M*, pH = 6.8 $\pm$0.1. [*o*-pda]: curve 1, 0 *M*; curve 2, 0.35×10^{-4} *M*; curve 3, 0.81×10^{-4} *M*; curve 4, 2.20×10^{-4} *M*; curve 5, 4.4×10^{-4} *M*; curve 6, 11.6×10^{-4} *M*.

of a slight polarographic maximum, or it could indicate that the electrode mechanism involves some adsorbed species which is partially desorbed at potentials more negative than —0.8 V *vs.* S.C.E. The catalytic hydrogen waves of some organic sulfhydral compounds[10,11] and amines[12] exhibit peaks which have been attributed to a mechanism involving an adsorbed species[12–14].

The theoretical treatment of MAĬRANOVSKIĬ[14a] predicts that catalytic reactions involving adborbed species will exhibit a peak current.

The height of the pre-wave, measured at the current peak, i_p, is shown in Fig. 2 as a function of the concentration of *o*-phenylenediamine for Ni(II) solutions of 5 different concentrations. The peak current does not vary linearly with concentration of the diamine, which is typical of catalytic waves[14]. Although the *o*-phenylenediamine concentration has a very large effect on i_p up to a concentration of about 4×10^{-4} *M*, further increase does not greatly affect i_p.

Figure 3 shows plots of i_p *vs.* Ni(II) concentration for four different constant concentrations of *o*-phenylenediamine. As expected for a catalytic wave, i_p increases with increasing Ni(II) ion concentration[14]. It is interesting to note that i_p is almost linear with $[Ni^{2+}]$ over the range of 0 to 8×10^{-3} *M* $[Ni^{2+}]$. A similar plot for the Ni (II)–pyridine pre-wave was considerably less linear[2].

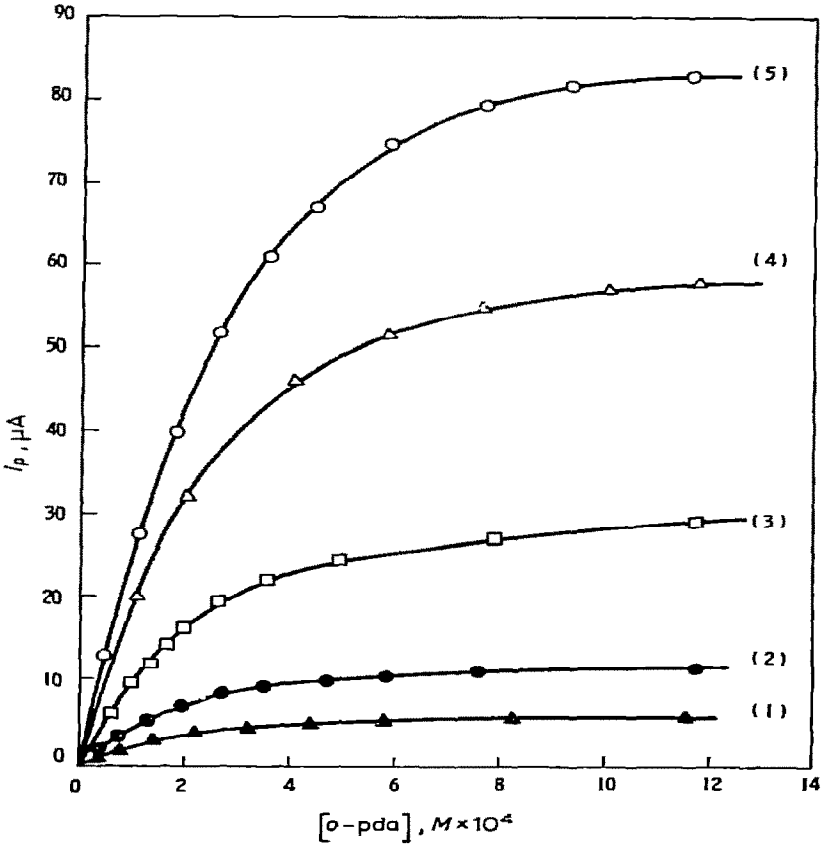

Fig. 2. Variation of peak pre-wave height, i_p, with concn. of *o*-phenylenediamine, pH = 6.8 ±0.1. [Ni^{2+}]: curve 1, 0.5×10^{-3} *M*; curve 2, 1.0×10^{-3} *M*; curve 3, 2.5×10^{-3} *M*; curve 4, 5.0×10^{-3} *M*; curve 5, 7.5×10^{-3} *M*.

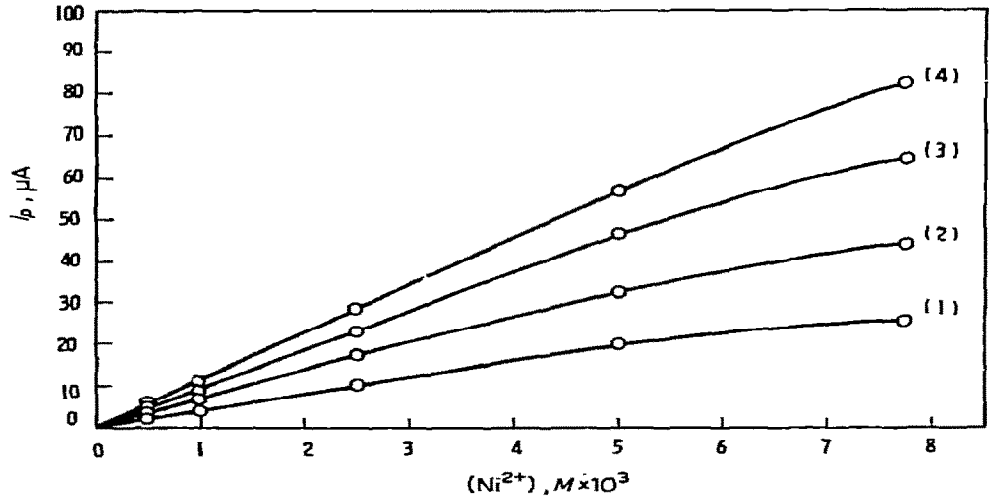

Fig. 3. Variation of peak pre-wave height, i_p, with concn. of Ni(II), pH = 6.8 ±0.1. [*o*-pda]: curve 1, 1.0×10^{-4} *M*; curve 2, 2.0×10^{-4} *M*; curve 3, 4.0×10^{-4} *M*; curve 4, 10.0×10^{-4} *M*.

Effect of o-phenylenediamine on the electrocapillary curve

The electrocapillary curves of the D.M.E. in 1.0 *M* KAc solution, and 1.0 *M* KAc solution which is 0.2 *M* in *o*-phenylenediamine, are given by curves A and B respectively of Fig. 4. The presence of *o*-phenylenediamine in the solution decreases the drop time of the D.M.E. to an appreciable extent as potentials approach the region

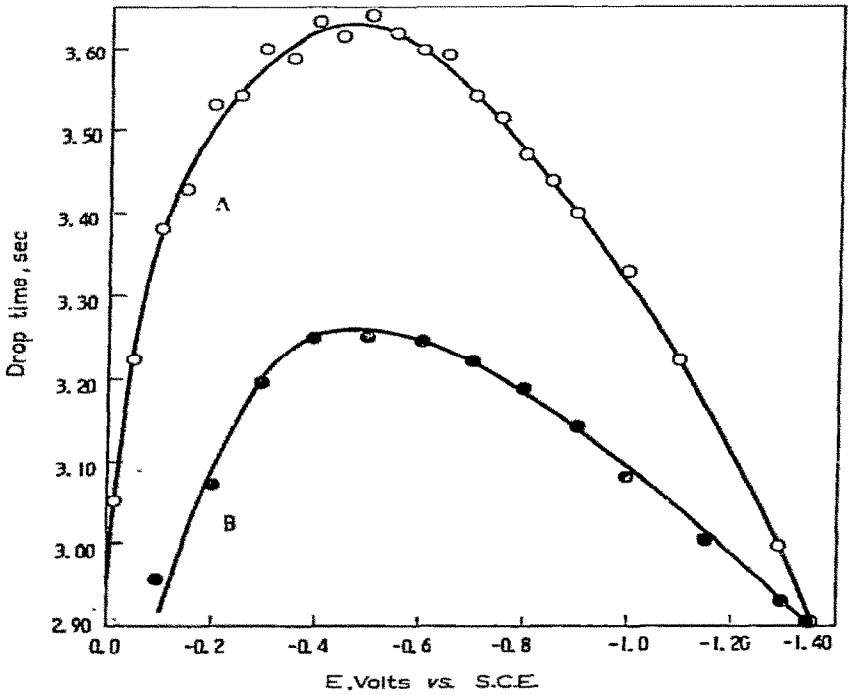

Fig. 4. Electrocapillary curve of *o*-phenylenediamine in 1.0 *M* KAc, pH = 6.8 ± 0.1: curve A, without *o*-phenylenediamine; curve B, with 0.2 *M* *o*-phenylenediamine.

of the electrocapillary maximum and this effect decreases at potentials remote from it. This phenomenon is a typical effect resulting from the adsorption of a neutral species on the electrode surface. Such specific adsorption lowers the interfacial tension (proportional to drop time)[18,19]. Complete desorption of *o*-phenylenediamine at potentials more negative than that of the electrocapillary maximum occurs at −1.35 V *vs.* S.C.E. where curves A and B coincide.

The i–t curves and effect of drop time

The current–time curves of individual drops obtained at the potential of the peak current and the effect of drop time (height of the mercury column) were investigated to determine if the electrode process was diffusion- or kinetic-controlled.

Curve A of Fig. 5 shows a typical *i–t* wave obtained for a solution which was 2.3×10^{-4} *M* in *o*-phenylenediamine, 7.5×10^{-3} *M* in $Ni(Ac)_2$, 1.5×10^{-3} *M* in $Ca(Ac)_2$, and 1.0 *M* in KAc. The slope of the log *i*–log *t* plot of the data of curve A had a value of 0.61 as shown by curve B. This value is very close to the value of 0.67 expected for a pure kinetic-controlled electrode mechanism[19] ($i \approx t^{2/3}$) and well beyond the

value of 0.167 expected for a diffusion-controlled mechanism ($i \approx t^{1/6}$), as predicted by the Ilkovič equation[21,22].

It was found that the height of the pre-wave was totally independent of the height of the mercury column (varied from 24–85 cm) up to concentration of $1 \times 10^{-4} M$ *o*-phenylenediamine (for all $[Ni^{2+}]$ concentrations studied). In this concentration range, the height of the pre-wave wave was only a small fraction, ~25% or less, of the total Ni(II) ion limiting current. The limiting current of a pure kinetic-controlled process is generally independent of height of the mercury column[20]. As the concentration of *o*-phenylenediamine is increased and the pre-wave becomes a more appreciable portion of the total limiting current of Ni(II) species, the wave height begins to

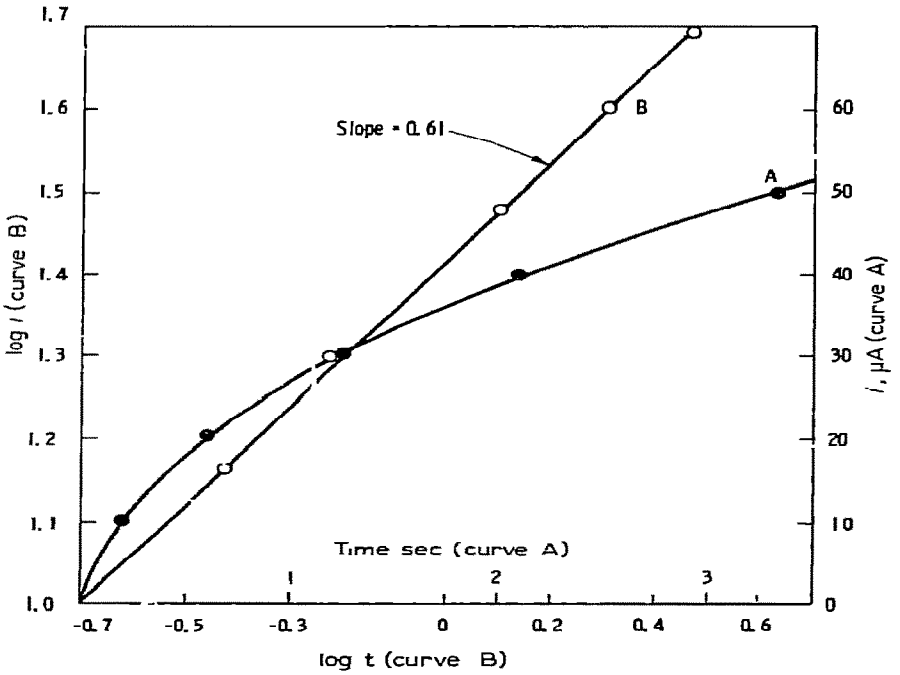

Fig. 5. Current–time curve of an individual drop. Applied potential = −0.87 V *vs.* S.C.E., $[Ni^{2+}] = 7.5 \times 10^{-3} M$, $[Ca^{2+}] = 15.0 \times 10^{-3} M$, [KAc] = 1.0 *M*, [*o*-pda] = $2.3 \times 10^{-4} M$, pH = 6.8: curve A, *i*–*t* plot; curve B, log *i*–log *t* plot (slope = 0.61).

vary with the height of the column, indicating that the process now has an appreciable contribution from a diffusion-controlled reaction. At large *o*-phenylenediamine concentrations, i_p was found to be proportional to the square root of column height as expected for a diffusion-controlled mechanism[20].

Effect of stirring

Some Ni(II) solutions containing various amounts of *o*-phenylenediamine were stirred at a rate that was found to increase a Cd^{2+} diffusion plateau threefold (stirring was not vigorous enough to appreciably affect the drop time). It was found that the pre-wave current in the region, 0–0.5×10^{-4} *M* *o*-phenylenediamine, was essentially *independent* of stirring (only a 2–5% increase in i_p was observed in this region). As the concentration of *o*-phenylenediamine increased, the percentage increase in i_p

was proportional to [*o*-phenylenediamine]. It should be noted that this stirring rate increased the $Ni(H_2O)_6^{2+}$ background wave about threefold in all cases. Thus, it appears that the magnitude of the current of the electrode mechanism of the pre-wave is controlled by some process, in the *o*-phenylenediamine concentration range between 0 and $\sim 1 \times 10^{-4}$ *M*, which does *not* involve the formation of a concentration gradient of some reactive species in the vicinity of the electrode.

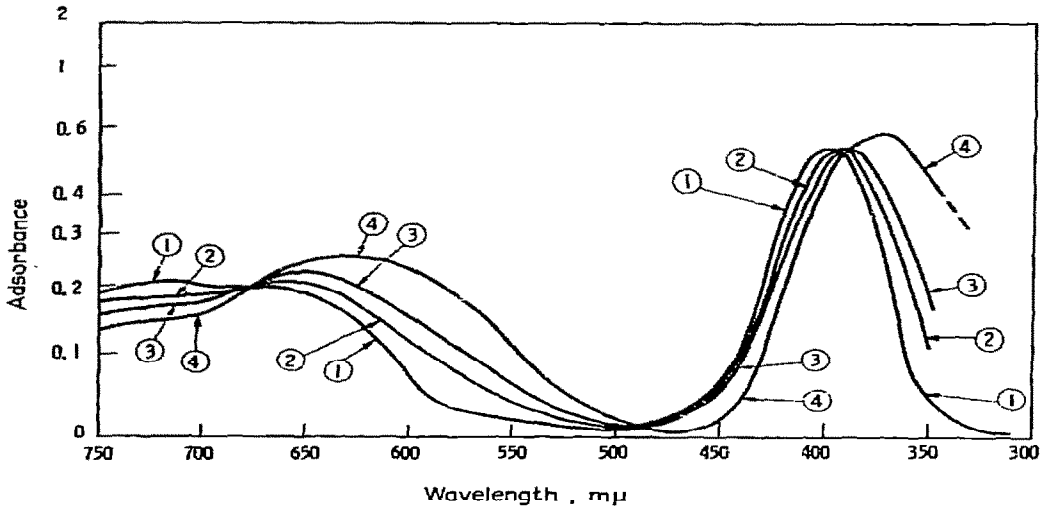

Fig. 6. Ultra-violet and visible adsorption spectra of 0.1 *M* $Ni(Ac)_2$ and 0.2 *M* $Ca(Ac)_2$ in 1.0 *M* KAc in the presence of *o*-phenylenediamine, pH = 6.8 ±0.1 [*o*-pda]: curve 1, 0; curve 2, 0.025 *M*; curve 3, 0.050 *M*; curve 4, 0.10 *M*.

Spectral studies and pH effects

The visible and ultraviolet spectra of 0.1 *M* $Ni(Ac)_2$, 0.2 *M* $Ca(Ac)_2$ and 1.0 *M* KAc solutions (pH = 6.8) containing various amounts of *o*-phenylenediamine (from 0–0.1 *M*) were measured to determine if a complex of Ni(II) and *o*-phenylenediamine was formed. Figure 6 shows that there is a definite change in the adsorption spectra

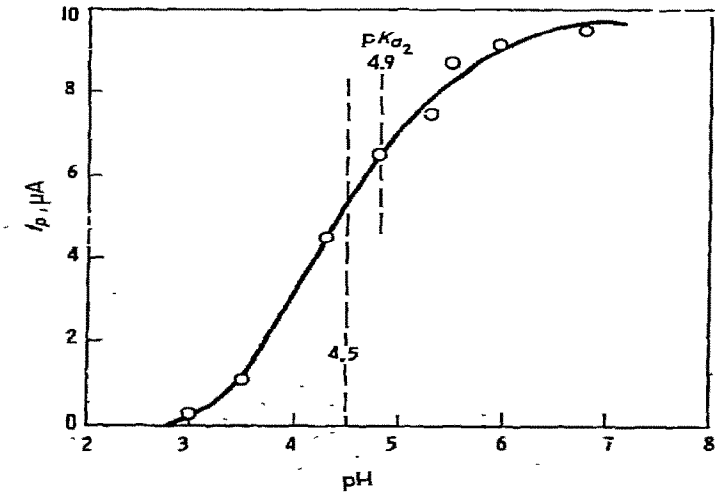

Fig. 7. Variation of peak pre-wave height, i_p, with pH. $[Ni^{2+}] = 2.5 \times 10^{-4}$ *M*, $[Ca^{2+}] = 5.0 \times 10^{-3}$ *M*, [*o*-pda] = 7.6×10^{-5} *M*.

of the Ni(II) ion as the concentration of *o*-phenylenediamine increases, which indicates that a complex does form under these conditions. A similar change in the spectrum would be expected if a small amount ($\sim 1\%$) of a tetrahedral Ni(II) complex was formed in the solution[23,24]. The molar extinction coefficient of a tetrahedral complex would be expected to be of the order of 100 times that of the octahedral $Ni(H_2O)_6^{2+}$ complex[24]. A detailed study of this complex formation was not possible under the conditions of this investigation, because a precipitate was observed to form at ratios of [*o*-phenylenediamine]: [Ni(II)] greater than 2:1.

If the assumption that only a small fraction of the Ni(II) forms a tetrahedral complex even when the ratio of [Ni]:[*o*-phenylenediamine] is 1:1 is true, the stability constant of this complex must be quite small. Evidence to support this conclusion was obtained by studying the effect of pH on both i_p and the adsorption spectrum of the Ni(II)–*o*-phenylenediamine system.

The pH of solutions containing 2.5×10^{-3} *M* $Ni(Ac)_2$, 5.0×10^{-3} *M* $Ca(Ac)_2$ and 7.6×10^{-5} *M* *o*-phenylenediamine was varied from 6.80 to 3.00 by varying the ratio of potassium acetate to acetic acid in the supporting electrolyte. The total acetate concentration was kept constant at 1.0 *M* in all solutions. The results are shown in Fig. 7. It appears likely that the mono-protonate form of *o*-phenylenediamine, H_3N^+—C$_6$H$_4$—NH_2, does not take part in the catalytic mechanism, because the pre-wave disappears as the pH becomes less than the pK_{a_2} of the mono-protonated species ($pK_{a_2} = 4.9$[6,25,26]). This suggests that a complex must be involved in some step in the catalytic process. The fact that the mid-point of the i_p–pH curve of Fig. 7 occurs at pH 4.5 rather than pH 4.9 also suggests that a weak complex is involved in the mechanism.

Qualitatively, it was also observed that the spectra of 0.1 *M* $Ni(Ac)_2$ and 0.1 *M* *o*-phenylenediamine solutions shifted from that corresponding to curve 4 of Fig. 6 to spectra more closely resembling curve 1 (Ni(II) only at pH = 6.8) as the pH was varied from 6.8 to 3.0 (ratio, acetic acid: potassium acetate concentration, varied; total acetate ion = 1.0 *M*). This supports the electrochemical inference that the tetrahedral complex is not very stable and is easily dissociated by lowering the pH.

CONCLUSIONS

The results of the investigation of the *i*–*t* curves of an individual drop and the effect of height of the mercury column on i_p under conditions where the pre-wave is small compared to the $Ni(H_2O)_6^{2+}$ background wave, clearly indicate that the mechanism of the catalytic wave involves a chemical reaction which preceeds the electron transfer step. The rate of this reaction controls the magnitude of the catalytic wave. The lack of any effect of stirring of the solution indicates also that the limiting process does *not* involve any reaction which results in depletion of the concentration of a species (resulting in concentration gradient) in the vicinity of the electrode. The electrocapillary measurements show definite adsorption of *o*-phenylenediamine and suggest that the limiting current is also a function of the surface coverage of *o*-phenylenediamine. These properties of the pre-wave (observed when pre-wave $\ll Ni(H_2O)_6^{2+}$ wave) suggest that the mechanism involves a very rapid adsorption equilibrium of *o*-phenylenediamine which controls the effective (or reactive) surface area of the electrode. If the equilibrium between the bulk concentration of *o*-phenylenediamine and the surface concentration excess were sufficiently rapid, stirring

of the solution would have no appreciable effect on the surface excess Γ. This evidence also implies that the adsorbed *o*-phenylenediamine reacts with $Ni(H_2O)_6^{2+}$ to form a complex at the surface prior to electron transfer. This complexation reaction is probably relatively slow as the limiting current is kinetic-controlled. Stirring has no appreciable effect on the rate of complexation as, under these conditions, there is a large excess of $Ni(H_2O)_6^{2+}$ ions available at the electrode surface. Stirring effects on the pre-wave would only become appreciable under conditions where the pre-wave is an appreciable portion of the total Ni(II) limiting wave. The concentration of $Ni(H_2O)_6^{2+}$ at the surface, under these conditions, has undergone considerable depletion. It should be noted that the lack of stirring effects also suggest that the stability constant of the Ni(II)-*o*-phenylenediamine complex in the bulk of the solution must be very small, as was postulated from the spectral data. The reaction mechanism of the catalytic wave can probably be represented by the following sequence (*o*-pda refers to *o*-phenylenediamine):

$$\{Ni(o\text{-pda})_y(H_2O)_{4-2y}^{2+}\}_{x>0} \underset{\text{rapid}}{\overset{K_{st}\text{ small}}{\rightleftharpoons}} \{Ni(H_2O)_6\}_{x>0} + (o\text{-pda})_{x>0} \underset{\text{rapid}}{\overset{K_{ads}}{\rightleftharpoons}} (o\text{-pda})_{x=0} \qquad (1)$$

$$y'(o\text{-pda})_{x=0} + \{Ni(H_2O)_6^{2+}\}_{x=0} \xrightarrow[\text{slow}]{k_{chem}} \{Ni(o\text{-pda})_{y'}(H_2O)_{4-2y'}^{+}\}_{x=0} + 2 + 2y'H_2O \qquad (2)$$

$$\left\{Ni(o\text{-pda})_{y'}(H_2O)_{4-2y'}\right\}_{x=0} + 2e \xrightarrow[\text{fast}]{k_{el}} Ni^0 + y'(o\text{-pda})_{x=0} + 4 - 2y'H_2O \qquad (3)$$

where the subscripted x represents the linear distance from the electrode surface, K_{st} the effective stability constant of the Ni(II)–*o*-pda complex in the bulk of solution, K_{ads} the *o*-pda adsorption equilibrium constant, and k_{chem} and k_{el} the rate constants of reactions (2) and (3) respectively. Reaction (1) represents the rapid competitive equilibrium that is stabilized between the Ni(II) complex and the *o*-phenylenediamine in the bulk of the solution (shifted far toward free ligand) and that between the bulk and adsorbed *o*-phenylenediamine. As experimental evidence indicates that the adsorption equilibrium is rapidly established, *o*-phenylenediamine is probably a weakly adsorbed species[16,18,27]. The cyclic regeneration of the *absorbed* ligand in the sequence of reactions (2) and (3) accounts for the catalytic enhancement; the rate must be finite in order that a limiting current is attained.

If it is assumed that the layer of adsorbed *o*-phenylenediamine is a mono-layer, the adsorption of the system can be described by a *Langmuir isotherm*[15].

$$\Gamma = \frac{C\Gamma_m}{a + C} \qquad (4)$$

where Γ_m is the maximum surface excess concentration of *o*-phenylenediamine that can be attained, C the bulk concentration of *o*-phenylenediamine, and a a constant for the particular adsorbate. Also, if the assumption that the active surface area of the electrode is actually that covered with adsorbed *o*-phenylenediamine, is correct, the limiting current, i_p, of the pre-wave should be proportional to the surface

coverage, and a plot of C/i_p *vs.* C should be linear[28]. Such a plot was found to be linear, as shown in Fig. 8.

Although this study has indicated the sequence of reactions that are probably involved in the mechanism of the catalytic pre-wave, it has not provided any conclusive evidence as to the exact nature of the Ni(II)–*o*-phenylenediamine complex involved. Nor does it explain why this complex is reduced at potentials considerably more positive than the hexaquo complex. Such behavior is difficult to understand as the effective stability constant of the Ni(II)–*o*-phenylenediamine complex must be slightly larger than that of the $Ni(H_2O)_6^{2+}$ complex under the conditions used. The fact that the spectrum of the Ni(II)–*o*-phenylenediamine system (Fig. 6) hints that a tetrahedral Ni(II) complex might be forming, leads to the speculation that

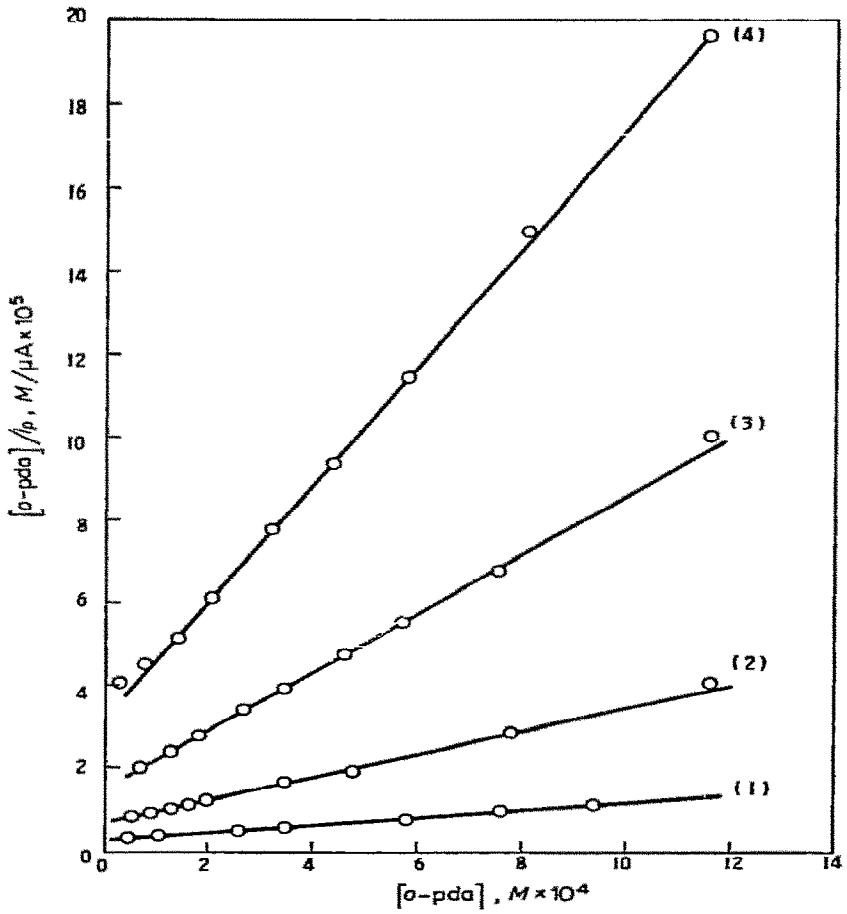

Fig. 8. Langmuir adsorption isotherm plots. $[Ni^{2+}]$: curve 1, 7.5×10^{-3} *M*; curve 2, 2.5×10^{-3} *M*; curve 3, 1.0×10^{-3} *M*; curve 4, 0.5×10^{-3} *M*.

Ni(II) in a tetrahedral configuration might be more easily reduced than in the octahedral configuration. Simply, the orbital configuration of the tetrahydral complex might be more closely analogous to that of the activated reduction intermediate (or reduction product) than that of the octahedral complex, which would lower the

activation energy of the reaction. ANSON[29] has proposed a similar explanation of the effect of Br^- ions which facilitate the electro-oxidation of Co(II) complexes. He suggested that the presence of Br^- perturbed the ligand field of CoY complexes near the electrode. The fact that Cl^- ions also shift the Ni(II) reduction potential to more positive values in aqueous solution[30-33] also supports this idea. There is some evidence[33,34] that the $NiCl_4^{2-}$ ion is the electroactive species (in their study of the Ni(II)–Cl^- system in acetonitrile; NELSON AND IWAMOTO[4] suggested that actually four complexes are reduced at more positive potentials: $NiCl^+$, $NiCl_2$, $NiCl_3^-$, and $NiCl_3^{2-}$). In this reaction, it is, therefore, interesting that GRUEN AND MCBETH[35] have prepared $NiCl_4^{2-}$ in in a fused $NiCl_2$–LiCl system and have shown that this complex is tetrahedral[24,35]. Further study of the tetrahedral Ni(II) complexes is in progress.

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SUMMARY

The catalytic current observed as a pre-wave when Ni(II) is reduced polarographically in the presence of small quantities of *o*-phenylenediamine is studied as a function of Ni(II) ion and *o*-phenylenediamine concentration. The effect of pH, stirring, and mercury height on the pre-wave are described. The *i–t* curves of an individual drop and the effect of *o*-phenylenediamine concentration on the electrocapillary curve are discussed. On the basis of the experimental evidence, a mechanism which involves a rapid adsorption equilibrium between bulk and adsorbed *o*-phenylenediamine and a complexation reaction of Ni(II) with the adsorbed diamine is proposed. The complexation reaction is thought to be the rate-determining step. A possible explanation as to why the adsorbed complex is more easily reduced than $Ni(H_2O)_6^{2+}$ is proposed.

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