Polarographic Behavior of Cd (II) and Ni (II) Ions in the Presence of Imidazole Groups (II)*

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金俊容・申靜姬：Imidazole 및 그誘導體의
金屬錯鹽에 關한 Polarograph 研究 II

요 약

단백질과 전이금속 이온들과의 상호작용을 연구하는데 있어서 단백질중
의 이미다졸기 및 아미노산의 반응성은 중요하다. Cd(II)-2- 메틸이미다
졸 착물들의 경우 이미다졸 분자중의 결합축은 "피로올"형 보다 오히려
"피리딘"질소임을 알수 있다. 이 착물들의 환원파는 가역적이너 2전자반
응으로 나타난다.

그리고 이미다졸 존재하의 Ni(II) 이온은 촉매파를 나타내며 Ni(II) 이
온만의 환원파는 불가역성인 것에 비해 가역성을 보여주었다. 또한 그 반
파전위는 Ni(II) 이온만의 반파전위보다 수백 mV 양전위로 이동된다. 이
러한 성질은 전극 반응에 관여한 주물질이 전극 표면에서 흡착되어 환원
되기 때문이다. 이미다졸 농도의 대수값에 대해 반파전위를 도시했을 때
그 기울기가 30mV 로써 이론치와 일치한다.

한편 Cd(II)-2CH₃Im 의 단계적 생성항수 pK_1, pK_2, pK_3, pK_4,는 각
각 2.68, 4.01, 4.90, 5.36이었다.

The bonding of imidazole with transition metal ions is of interest because of this ligand's close relationship with biological system of a more complex nature involving histidine residues. Therefore, it is necessary to understand more fully the role of metal ions studying the coordinating properties of metalimidazole systems. [1]

Many workers have been investigated the complexes formed between imidazole and transition metal ions by means of infra-red spectra and proton magnetic resonance, [2] potentiometric pH method of Bjerrum[3] and polarographic method. [4] This paper presents the results on the cadmium (II) complexes of 2-methylimidazole using the method of

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polarography, as mentioned in previous report[5]. On the other hand, the polarographic behavior of nickel (II) ion in the presence of imidazole was investigated. It was found that the nickel ion had a catalytic wave which occurred at a more positive potential before the main free nickel (II) ion wave.

Such catalytic reduction of nickel ion in the presence of a number of amines and small quantity of pyridine has been reported by Mark[6] and Olson[7] respectively. The general physical and chemical requirements of a system that are necessary to give rise to a catalytic polarographic prewave and the mechanism for the reaction path will be discussed in detail. The effects of variation of metal ion and ligand concentration, and concentration of the supporting electrolyte, pH, maximum suppressor contents, etc. on the shape of the prewave and sensitivity of the measurement will be presented in this paper.

Experimental

Apparatus—Polarographic current-voltage curves were obtained with a Yanagimoto Model PA-102 Recording Polarograph. A Yokogawa D.C. Potentiometer Model P-IB was used to obtain voltage readings on the measurements of halfwave potential. The pH was measured with a Beckmann pH Meter Model 72 and Toyo pH test paper. The polarographic cell was a H-type cell with a sintered glass filter seperating the working compartment from the reference saturated caromel electrode. The capillary constants in an open circuit (h=38.5 cm) were t=3.75 second and m=1.422 mg per second.

Experimental procedure—Stock solutions were prepared to be 0.01M NiSO$_4$ and 0.01M CdCl$_2$. Imidazole solution was made by dissolving in 0.1 N potassium chloride. Polarographic test solutions were prepared by dilution of stock solutions. The concentration of metal ion solutions was taken a definite concentration 5×10^{-4}M, and 1×10^{-4}M to 1×10^{-1}M solutions of ligand were added to it. The ionic strength was adjusted with potassium chloride to maintain at 0.1. The change of pH in the presence of the excess imidazole was adjusted with 1N HCl and tested with pH test paper.

Results and Discussion

General Polarographic Wave Characteristics of Imidazole Groups and Metal Complex Formation—The Cd(II)-2-methylimidazole complexes were reduced directly to the amalgam. In this case, only single wave was observed.

The plots of log i/(i$_d$-i) versus the potential were straight lines and slopes indicate that the electrode reactions involve reversible two electron reductions in all cases.

Several studies have been made on the imidazole ring to determine, if possible, which nitrogen is involved in the binding to a transition metal ion.

However, in the presence of imidazole, Ni(II) ion gives a catalytic wave which occurred at a more positive potential before the main free nickel ion wave as shown in Figure 4. Polarograms of such systems exhibit "prewave" whose half wave potentials are, in some

instance, several hundred millivolts positive to that of the highly irreversible main hexaquo nickel complex wave. This may be due to the reduction overpotential of the complex species at the electrode.

Characteristic Polarograms of Ni(II) ion in the Presence of Low and High Concentration of Imidazole—Generally, in supporting electrolytes that do not form complexes with nickel, the halfwave potential of the hexaquo nickel ion is about-1.10 volts versus
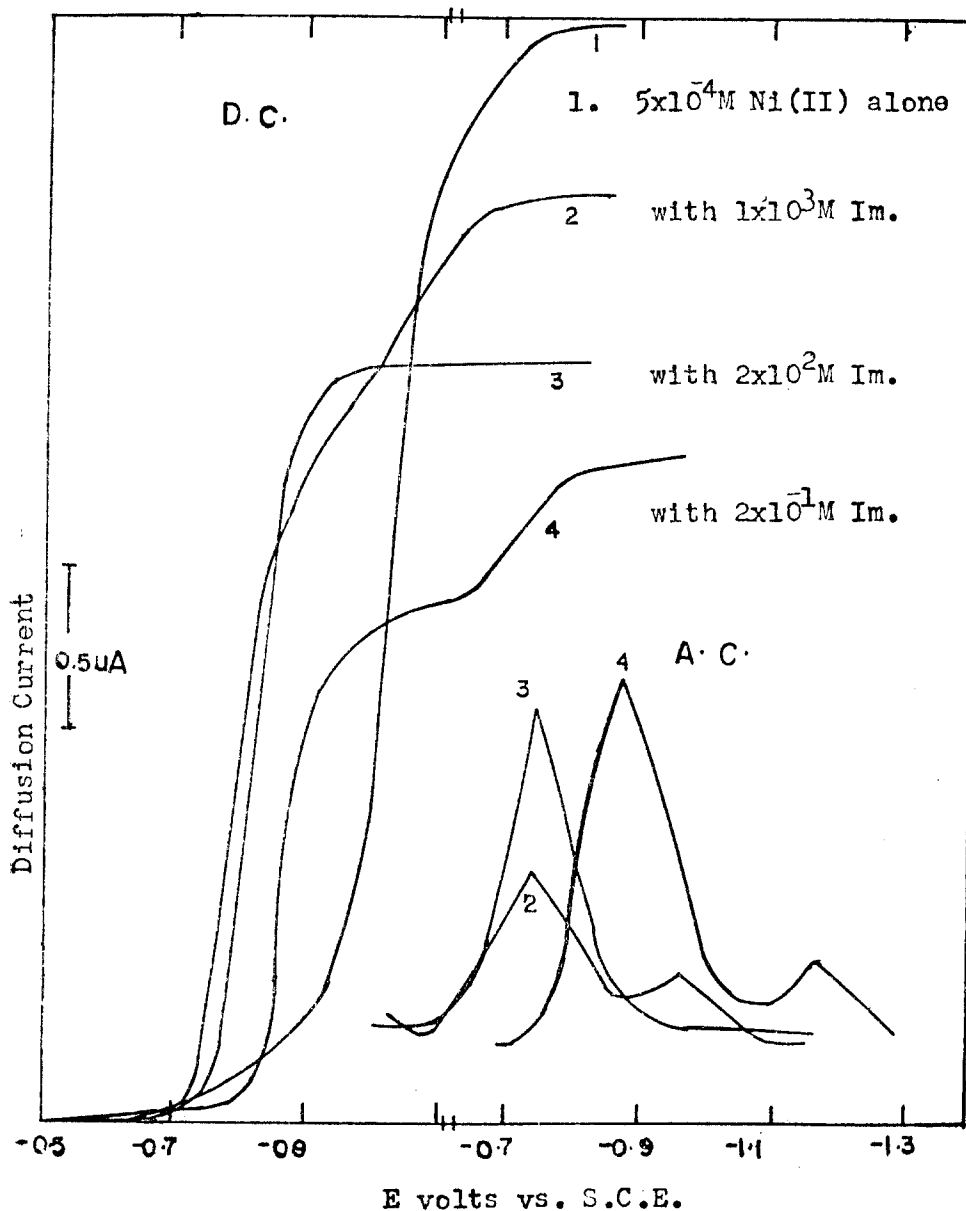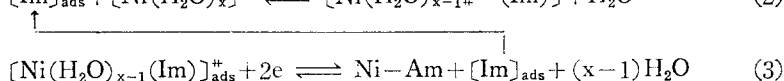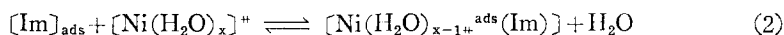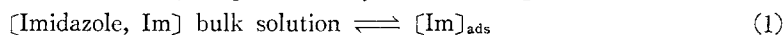

Fig. 1 Dependence of polarogram of Ni(II) on concentration of excess imidazole.

saturated calomel electrode.[10] The polarographic reduction of Ni(II) ion in dilute salt solutions generally shows an irreversible wave, and gives a catalytic wave which occurs at a more positive potential. This prewave is catalytic in nature as the limiting current in several orders of magnitude greatly than a diffusion limited process involving the metal complex.

From a detailed study of the mechanism of the electrode process with o-phenylendiamine as the amine, Mark[6] suggested that the electrode process was limited by the rate of prior cyclic chemical reaction involving the formation of complex between the ligand adsorbed on the electrode surface and nickel ion. Also, it was further suggested that the resulting complex was rapidly discharged with regeneration of the adsorbed ligand.

From the results of D.C. and A.C. polarograms as shown in Figure 1, it was found that the rate of dissociation of $[Ni(H_2O)_{x-1}(Im)]^+$ would be more rapid than that of diffusion because a diffusion-controlled wave, and the reversible well-defined wave was observed. The reduction must, therefore, be proceeded by the following mechanism.

$$[Imidazole, Im] \text{ bulk solution} \rightleftharpoons [Im]_{ads} \qquad (1)$$

$$[Im]_{ads} + [Ni(H_2O)_x]^+ \rightleftharpoons [Ni(H_2O)_{x-1}{}^{ads}(Im)] + H_2O \qquad (2)$$

$$[Ni(H_2O)_{x-1}(Im)]^+_{ads} + 2e \rightleftharpoons Ni-Am + [Im]_{ads} + (x-1)H_2O \qquad (3)$$

Vlcek[9] showed by oscillopolarography that the Ni(II)-ethylenediamine complex was reduced by this mechanism.

When $[Ni(H_2O)_{x-1}(Im)]^+$ ion is the principal diffusing species in the presence of low concentration of imidazole, the current-potential relationship is

$$E_{\frac{1}{2}} = E^{0\prime} - 0.0296 \ \log \frac{I_c K_{1:1}}{I_a} - 0.0296 \log C_{Im} \qquad (4)$$

where $E^{0\prime}$ is the formal potential of the $Ni^+_{ads} - Ni_{am}$ couple, I_c and I_a are the diffusion current constants of $[Ni(H_2O)_{x-1}(Im)]^+$ and Ni—am, respectively, and C_{Im} is the concentration of free imidazole. The equation 4 predicts the linear plots of $E_{\frac{1}{2}}$ vs. log C_{Im} with slope of 29.6mV in the region where is the predominant complex, $[Ni(H_2O)_{x-1}(Im)]^+$ ion, in solution. The experimental plot, shown in Figure 4, was in good agreement with theoretical consideration, having a linear region with slope of 30mV less than 0.01M imidazole concentration. In Table 1, there are shown polarographic data for the complexes formatoin of Ni(II) imidazole complexes at 25°C and 35°C. However, in the prseence of higher concentration of imidazole, from 1×10^{-2}M to 0.1M, the experimental slopes were determined to be 64 mV and 147 mV for the second and third step of curves, respectively (Figure 3). This experimental results show that the possibility of the formation of polymeric nickel imidazole complexes are the principal species in solution. This kind of polymeric structure was assumed by the X-ray diffraction method[13] and Raman spectra studies.

The characteristics of the metal-nitrogen bond in nickel imidazole complexes in higher concentration of imidazole, therefore, are expected to be intermediate between the metal-
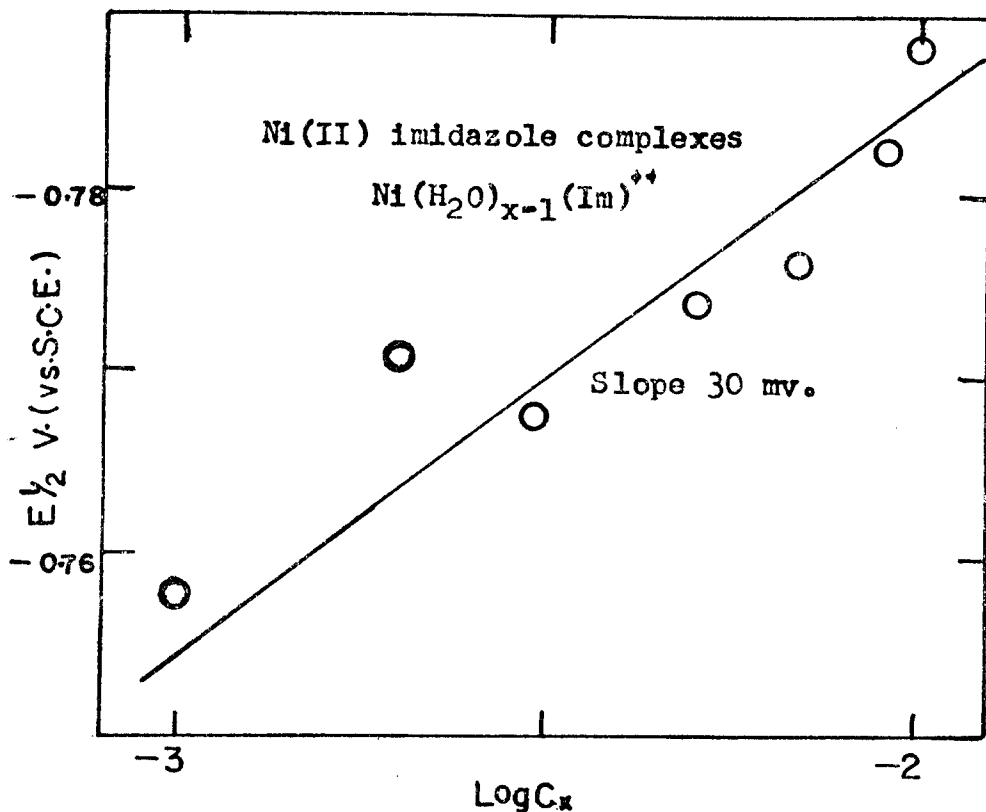
Fig. 2 Plot of $E_{1/2}$ vs. log imidazole concentration.

Table I Polarographic Data of Ni(II)–Imidazole Complexes.

No	C_x (mole/1)	$E_{\frac{1}{2}}$ vs. S.C.E.		i_d (μA)		$E_{\frac{1}{2}}$ vs.
		at 25°C	at 35°C	at 25°C	at 35°C	log i/i_d-i
1	0	-1.04		3.06		
2	1×10^{-3}	0.758		2.66		0.0435
3	$2 \times$	0.771		2.29		0.044
4	$3 \times$	0.768		2.80		0.047
5	$5 \times$	0.774		2.88		0.040
6	$7 \times$	0.776		3.06	3.54	
7						0.034
8	$9 \times$	0.783	0.781	3.17	3.72	
9	1×10^{-2}	0.787	0.759	2.72	3.3	0.034
10	$2 \times$	0.802	0.772	2.68	3.36	
11	$3.5 \times$	0.791	0.791	2.81	3.26	
12	$5 \times$	0.826	0.806	2.58	3.36	

13	$6.5 \times$	0.812	0.809	3.18	3.56
14	$7.5 \times$	0.835	0.821	2.98	3.62
15	$8 \times$	0.860		1.95	
16	$9 \times$	0.856	0.869	2.52	3.15
17	1×10^{-1}	0.837	0.822	2.77	3.24
18	$2 \times$	0.895	0.865	2.41	3.12
19	$5 \times$	0.955		2.24	

pyridine type bond. The similar bonding in nickel triethylenetetramine has been reported by Olson[7].

Factors that govern Ni(II) imidazole

(a) **Effect of suppressor contents**—If the suppressor contents of gelatine were raised above 0.0006%, the half-wave potential was shifted to more negative potential as shown in Figure 4. Also, the diffusion current was rapidly decreased with increasing the concentration of the suppressor. The author found that gelatine was not able to suppress the maxima of Ni(II)-imidazole complex, in the case of very small concentration (less than 0.005%). In practical work the suppressive effect of gelatine on the diffusion current, when it was present at concentrations greater than about 0.005%, must be taken into account.

On the other hand, Electrocapillary curves of Ni (II)$^{++}$ ion in presence of imidazole are shown in Figure 5 along with a free Ni (II)$^{++}$ ion curve for comparison. The interfacial tension may be decreased as a result of their adsorption at the surface of the mercury. The curve 3 and 4 in Fig. 5, show the lower interfacial tension.

(b) **Effect of the height of Hg head**—The variation of the limiting current with the height of the mercury column above the capillary also was measured as represented in Table II. The current varied with the height of mercury; the value $i_d / \sqrt{h_{corr}}$' where h_{corr} is the height of the column after correction for the "back pressure", was fairly constant indicating that the electrode reaction was essentially diffusion-controlled.

Table II   Relation between the Diffusion Current and the Height of Mercury Reservior.

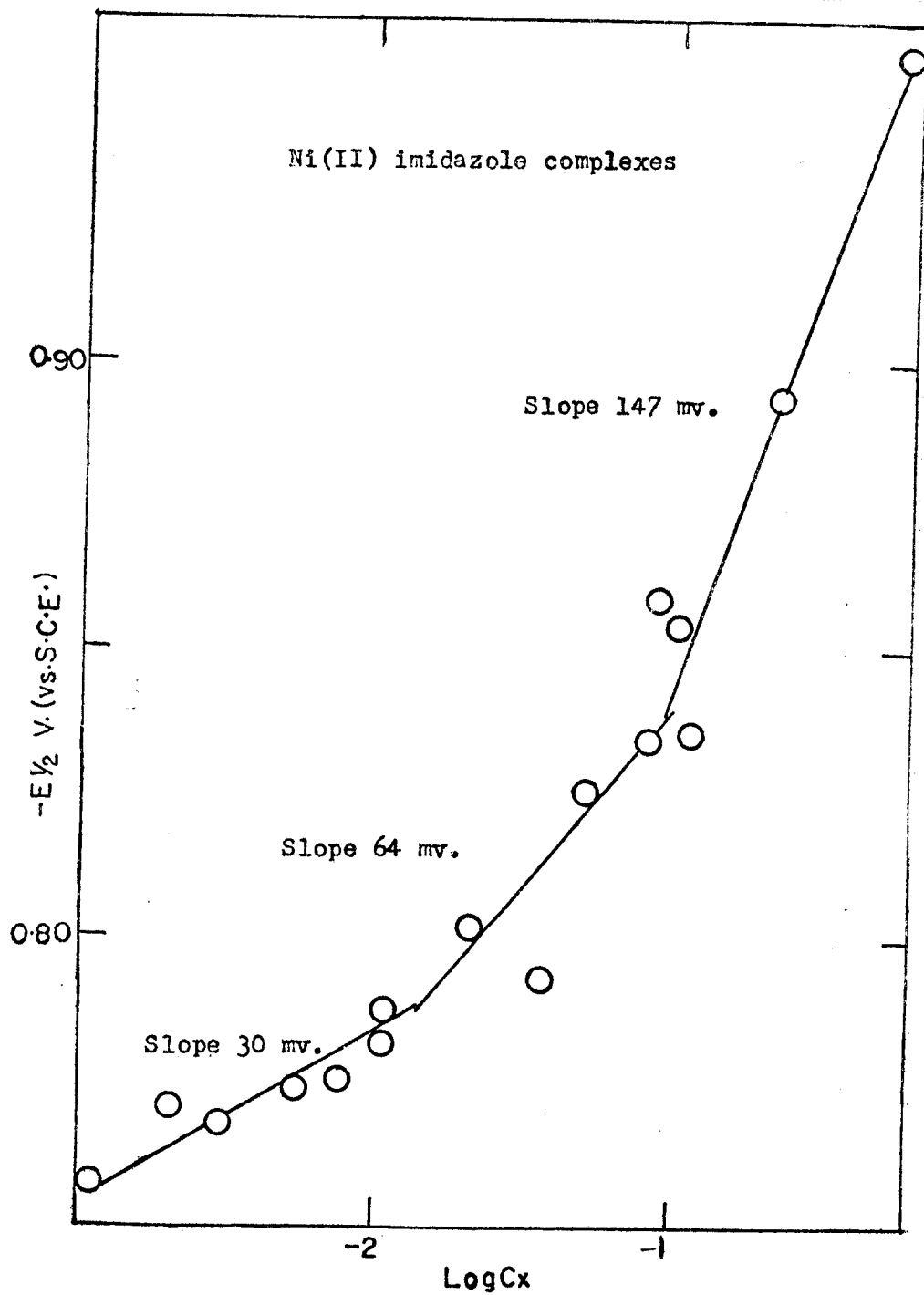| Height of mercury head (h)	$h_{corr.}$	Diffusion currents (uA)	$i_d / \sqrt{h_{corr}}$
35 (cm)	5.76	2.36	0.41
40	6.18	2.66	0.43
45	6.57	2.84	0.439
50	6.94	2.98	0.43
60	7.13	3.44	0.48

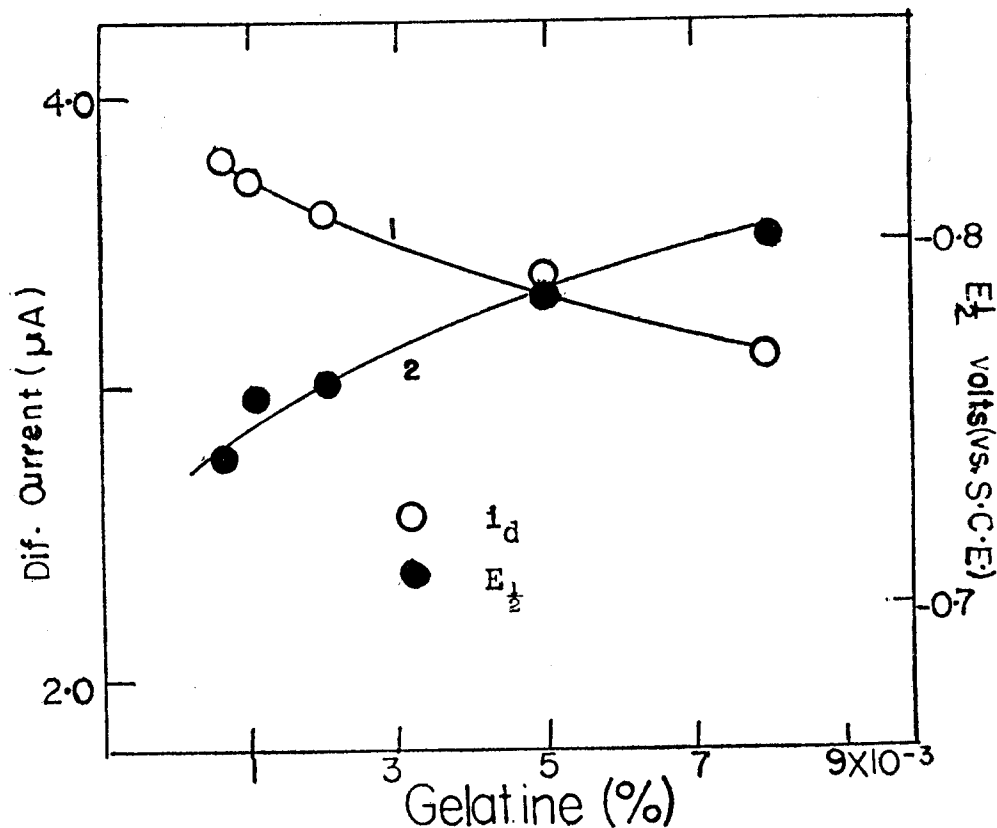Fig. 3 Dependence of $E_{1/2}$ of Ni (II) on concentration of excess imidazole.

Fig. 4 Effects of suppressor concentration on diffusion current and half wave potential
of Ni (II) imidazole in 0.1M KCl solution.
5×10^{-4}M Ni (II) with 3×10^{-3}M imidazole.

(c) **Effect of pH**—The pH of solutions containing 5×10^{-4}M Ni (II) ion and 1.5×10^{-1}M imidazole was varied from 3.2 to 8.5 in the supporting electrolyte as shown in Figure 6. This results indicate that the imidazolium ion, in solution or adsorbed on the electrode doesn't take part in the catalytic mechanism because the catalytic wave disappears as the pH becomes less than the pK_a of imidazole, $7.0^{[12]}$. It was found that only weak complex formation was occurred at the pH 7-8.

(d) **Effects of the concentration of imidazole and supporting electrolyte**—The author has studied the effect of imidazole concentration on the polarography of nickel ion. As shown in Figure 1, it was observed that the free nickel ion wave decreased with increasing imidazole concentration and increasing the reversibility of electrode reaction. In presence of high concentration of imidazole, however, two waves were observed which both waves were shifted to more negative potentials. At a constant metal ion concenration, the prewave height also rose linearly with small addition of the imidazole.
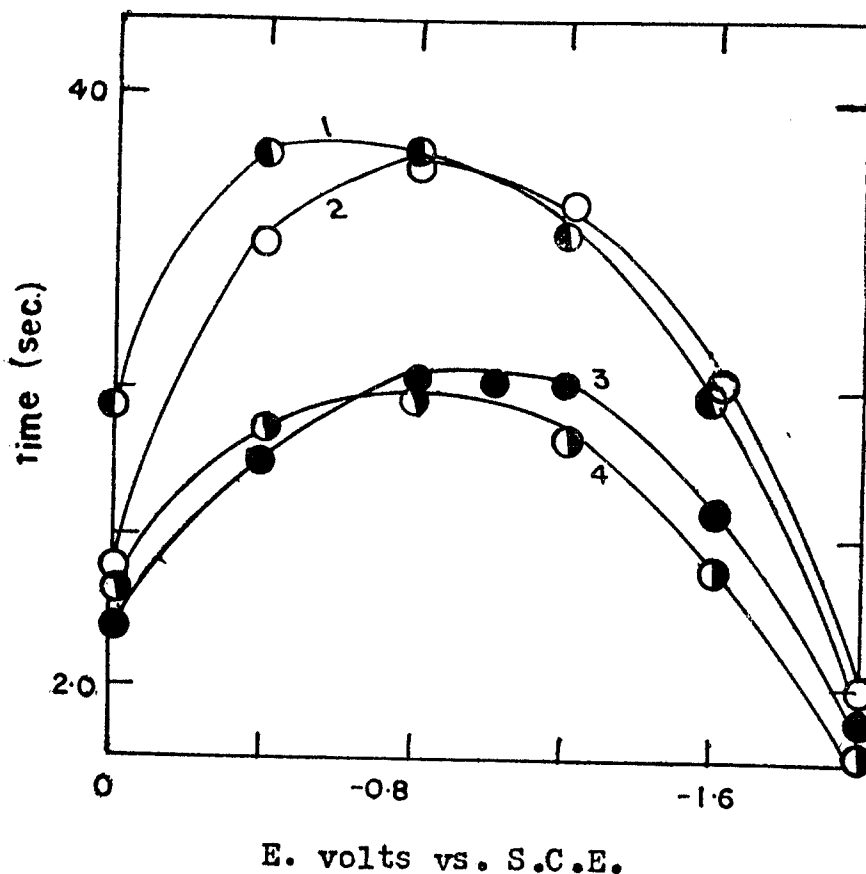
Fig. 5　Electrocapillary curves in absence and presence of imidazole.
Curve 1. Ni (II) ion without gelatine
〃　2. Ni (II) ion with 0.005%
〃　3. Ni (II) ion 1×10^{-3}m imdazole without gelatine
〃　4. Ni (II) ion $1 \times 10^{-}$m imidazole with 0.005%.

The prewave current was a function of the metal ion concentration and was also strongly affected by the concentration of the supporting electrolyte. It was observed that the prewave decreased with increasing supporting electrolyte. However, in addition of a large quar tity of supporting electrolyte to the metal-imidazole complex solution, the half-wave potential was shifted to more positive potential than that of the $[Ni\ (H_2O)_{x-1}\ (Im)]^{++}$ ion species.

Determination of the Formation Constant (9, 10) of Cd(II)-2-methylimidazole Complexes—The coordination number and over-all formation constants of the complexes were determined by application of the following equations, [10]

$$-\frac{\varDelta E_{1/2}}{\varDelta \log C_x} = -(p)\frac{0.059}{n}\ (\text{at }25°C) \tag{5}$$

$$(E_{1/2})_c - (E_{1/2})_s = \frac{-0.059}{n}\log\ K_f - p\frac{0.059}{n}\log\ C_x - \frac{0.059}{n}\log\frac{f_c k_s}{f_s k_c} \tag{6}$$
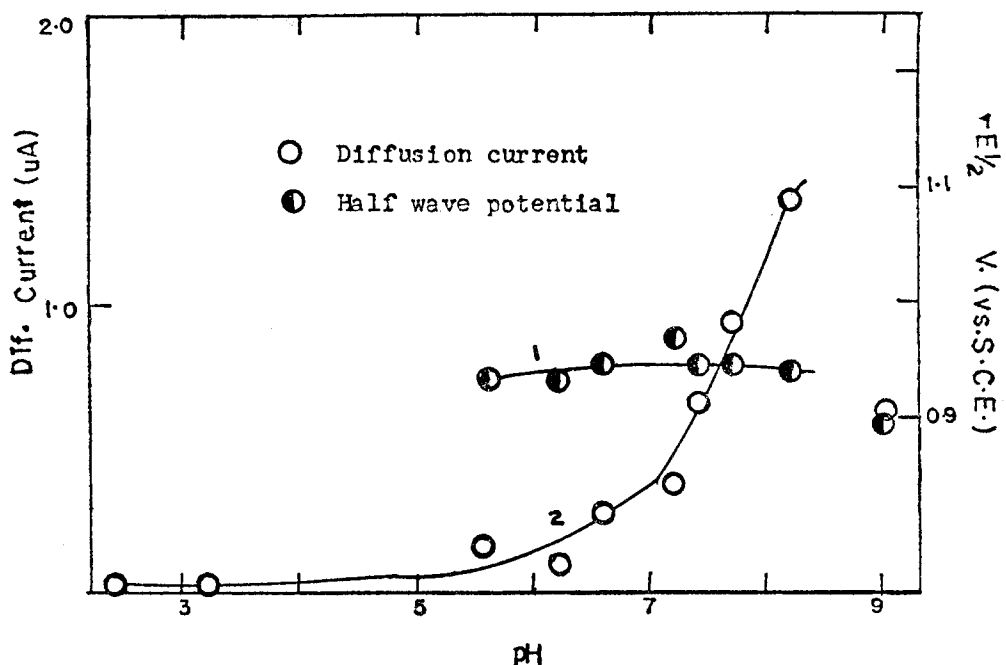
Fig. 6 Dependence of pH on diffusion current of Ni (II) imidazole complexes.

where, f is the activity coefficient, k is constant proportional to the square root of the diffuson coefficient of the metal ions, and n is the number of electrons transfered in the reduction. The subscripts and refer to simple metal ions and the complex, respectively. The ratio, $f_c k_s / f_s k_c$ was assumed to be unity.

The equation 6 is the usually used to calculate K_f. In most cases, however, a plots of $\Delta(E_{1/2})$ versus $\log C_x$ does not yield a straight line, but rather yields a curved plot. This indicates that there exists a mixture of complexes. In other words, complexes exist in which p has different values depending upon the coordination of the ligand. The entire polarographic waves are reversible and have the theoretical slope $E_{d.e.}$ vs. $\log i/(i_d - i)$ of 30 mV for a two electron reaction.

A plot of $E_{\frac{1}{2}}$ vs. $\log C_x$ in the concentration range from 1.5×10^{-3} M to 0.35 M 2-methylimidazole shows that the curve can be interpreted as the composite of four straight lines as shown in Figure 7. When the concentration of 2-methylimidazole is higher than 0.1 M, the line is steepest, and the coordination number is four. This is represented as the following reaction;

$$Cd^{++} + 4(2-meIm) \rightleftharpoons Cd(2-meIm)_4^{++} \qquad (7)$$
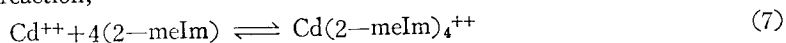
The value for p, given in Fig. 7 and Table 3, are obtained from the least squares treatment of the polarographic data. In Table IV, the formation constants and coordination number are presented.
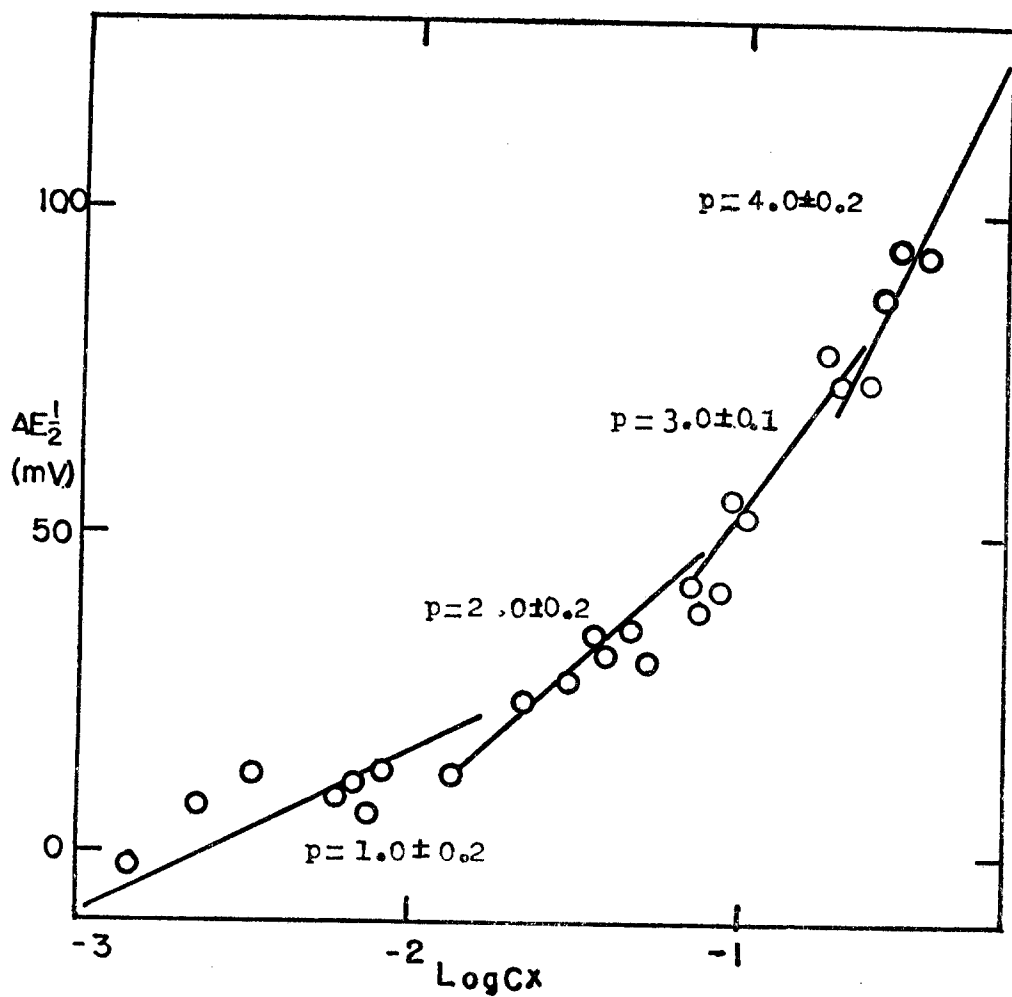
Fig. 7 Cd (II) 2-methylimidazole complexes.

Table IV Formation Constants of Cd (II) 2-Methylimidazole Complexes at 25°C.

Metal Complexs	pK_f pK_j values	Coordination No. P	$E\frac{1}{2}$/log i/i_d-i
Cd (II)-2-methyl	pK_1 2.68	1.0±0.2	0.028
	pK_2 4.01	2.0±0.2	0.027
	pK_3 4.90	3.0±0.1	0.029
	pK_4 5.36	4.0±0.2	0.028

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