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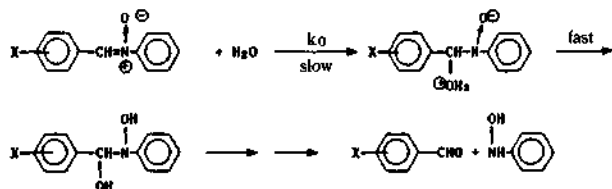
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the rate constant, k_{OH} should be more sensitive to change in σ than k_H ($\rho = 1.00$ at pH 3.0, $\rho = 1.36$ at pH 12.0).

On the other hand, at medium pH, the hydrolysis rate of nitrone is almost independent of pH change, therefore, it seems most reasonable to conclude that the addition of water to carbon atom is the rate controlling step.

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Electrochemical Behaviors of Sparteine-Copper (II) Dihalide

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Electrochemical behaviors of optically active sparteine-Cu(II) dihalide complexes were investigated by polarography and cyclic voltammetry (CV). These Cu(II) complexes are rather easier to be reduced to Cu(I) states when comparison is made with other nonplaner copper complexes. We have assigned the CV peaks and polarographic waves related to the redox processes for these complexes. We could also observe the exchange reaction of Cu(II) ion in the complex with mercury metal in the cell having mercury pool. The redox mechanism of these complelxes is as follows; The 1st wave appeared at $+0.47$ V/$+0.65$ V corresponds to the reaction of SpCuX$_2$+e $\rightleftarrows$ SpCuX$_2^-$ and the 2nd one at $+0.26$ V/$+0.21$ V does the reaction of SpCuX$_2^-$+e $\rightleftarrows$ SpCuX$_2^{2-}$. The 3rd one at -0.35 V/-0.27 V is due to the reduction of mercury complex formed via exchange reaction. Where, X is chloride ion.

Introduction

The copper (II) ion ($3d^9$) has one unpaired electron in the 3d shell, and a four-coordinated copper (II) complex usually maintains a planar structure to be attributed to the Jahn-Teller effect with the exception of a few compounds, which have pseudo-tetrahedral structure.[1-4] The tetrahalocuprate (II) ions have been found to posses a variety of geometries, *e.g.*, (a) pseudo-tetrahedral D$_{2d}$ symmetry in Cs$_2$CuCl$_4$[5,6]

(b) planar and pseudo-tetrahedral geometry in {(CH$_3$)$_2$CHNH$_3$}CuCl$_4$[7] (c) six coordinated tetragonal octahedral geometry (or 4+2 coordination) in (C$_6$H$_5$NH$_3$)$_2$CuCl$_4$[8] and (d) complexes associated to yield five-coordination in the dimeric anion, Cu$_2$Cl$_8^{4-}$ which can be isolated as the tris (ethylenediamine) cobalt (III) salt.[9] It has been considered that, based on the potential values reported for Cu(II)/Cu(I) redox couples, nonplanar bis-chelate complexes are easier to be reduced than their planar analogs, rigid planar four-coordinated com-

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plexes.[10]

Redox behaviors of Cu(II)/Cu(I) couple in copper metalloprotein were previously studied to find that the reduction potential is large and positive, and that the reduction process is very fast.[11] The kinetic lability of this redox couple is believed to be attributed to the coordination geometry of copper metalloprotein as well as the type of donor atoms around copper (II) ion. Sparteine copper (II) dihalide complex has been considered one of model compounds of these metalloprotein to maintain the pseudo-tetrahedral structure even in solution as well as solid.[12]

In this study, we investigated the redox properties of the Cu(II)/Cu(I) couple in the copper (II) dihalide complexes of sparteine (I, sp) *via* undertaking the peak assignment of the CVs and the assignment of waves in the polarograms of sparteine complexes, SpCuCl₂ and SpCuBr₂.

I
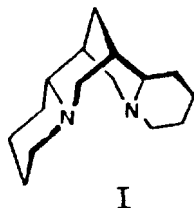
Experimental

Preparation of Sparteine-Cu (II) Dihalide Complex.

Sparteine sulfate, $C_{15}H_{26}N_2 \cdot O_4S \cdot 5H_2O$ (sp), $CuCl_2$ (99.999%) and $CuBr_2$ (99.95%) were obtained from Sigma and Aldrich Chemical Co. These were used without further purification. All other chemicals used in the preparation of halocuprate (II) complexes were of the best available reagents or spectroscopic grades. The preparation of the complex was undertaken as follows;

SpCuCl₂ and SpCuBr₂ were prepared by the method described previously.[13] To avoid possible decomposition, sparteine was isolated just before reaction with metal salts. An aqueous solution of the sparteine sulfate was treated with excess KOH and the resulting oil was extracted with ether, dried over MgSO₄, and then isolated in a Rotovac. The oil was then taken up in mixture solution of dehydrous methanol and trimethylorthoformate (5:1). Copper (II) halide complexes with sparteine, SpCuCl₂ and SpCuBr₂ were prepared by mixing methanol/trimethylorthoformate solutions of corresponding to copper (II) dihalide (previously dehydrated by heating at 110℃ for several hours) and the alkaloid oil in stoichiometric millimolar quantities. The precipitates settled down immediately and were crystallized from the mixture of trimethylorthoformate and dehydrous methanol solution. The crystal precipitated were filtered, and recrystallized in dehydrous methanol solution and dried in a vacuum oven. Analytical results for the complexes are summarized in Table 1.

Electrochemical Measurements.

Conventional *dc* polarograms were recorded in acetone with a Yanagimoto P-8 type polarography using 0.1 M tetraethylammonium perchlorate as supporting electrolyte. A three-electrode system was employed for all conventional dc measurements. The reference electrode was Ag/AgCl electrode (0.1 M LiCl in acetone and in DMF, respectively). Short controlled drop

Tabe 1. Analytical Results for Dihalides (II) Complexes

Compound	Color	% Calculate			% Found		
		C	H	N	C	H	N
SpCuCl₂	Green	48.84	7.12	7.60	49.00	7.30	7.40
SpCuBr₂	Orange	39.36	5.72	6.12	39.50	5.72	6.12

time polarograms (rapid polarogram) were recorded with a Yanaco P-8 type polarography (RT-8). The glass capillary dropping mercury electrode had the following characteristics in acetone/0.1 MEt₄NClO₄; at morcury column height of 67 cm; flow rate of mercury, $m = 1.645$ mg/s; drop time, $t = 4.60$ s and $m^{2/3} t^{1/6} = 1.797$.

The electrode has responsed quite accurately in the acetone/0.1 M Et₄NClO₄ medium, and exhibited the useful measurable range from + 0.8 V to − 2.5 V. This range is in good agreement with previous results. In case of DMF, it is also in good agreement with other report.[14]

All test solutions were thoroughly degassed with nitrogen saturated with acetone and a continuous stream of nitrogen was passed over the solutions while measurements were being taken. Test solutions were thermostated at 25.0± 0.1℃ and the H-type cell was used.

Cyclic voltammetric measurements were made with a three electrode system. The working electrodes were a glassy carbon (GCE, Tokai Co., area = 7.2 mm²), a mercury and a platinum electrode (area = 2.2 mm²). The auxiliary electrode was a platinum wire. The potentiostat used in cyclic voltammetric and coulommetric measurement was EG & G model 273 (PAR. Co., USA) and cyclic voltammograms were recorded with Kipp & Zonen model 13 BD 90 XY recorder. The working electrodes used for the controlled potential electrolysis was a mercury pool electrode and a platinum gauze. All test solutions were degassed with nitrogen to prevent from air oxidation.

Results and Discussion

Polarograms of Sparteine Copper (II) Dihalides.

The SpCuCl₂ complex exhibits one polarographic oxidation wave at a potential of + 0.60 V (wave 1) *vs.* Ag/AgCl electrode, three reduction waves at + 0.46 V (wave 2), + 0.24 V (wave 3), − 0.38 V (wave 4) *vs.* Ag/AgCl, and one small post wave (+ 0.10 V) in close vicinity of reduction wave 3. The conventional polarogram of wave 4 reveal a slight inflection near the midpoint. Figure 1-a shows a typical polarogram of SpCuCl₂. The plot of the diffusion current, i_d *vs.* concentration, C is linear between 1×10^{-4} M and 1×10^{-3} M for all four redox waves(See Figure 2). The plot of i_d *vs.* the square root of the mercury column height, h is linear (See Figure 3). This indicates that the waves are diffusion controlled. The plots of E *vs.* $\log i/(i_d - i)$ are also linear for four waved. Figure 4 shows the plots of the logarithmic analysis for wave 2 and wave 4. The slopes of waves 1, 2, 3, and 4 are 40± 5 mV, 55± 5 mV, 67± 5 mV, and 130± 5 mV, respectively, which approximately show the electrode reaction of wave 2 and wave 3 are a reversible one-electron step, and that of wave 4 is a reversible consecutive two electron step, and electrode reactions of wave 1 is irreversible.
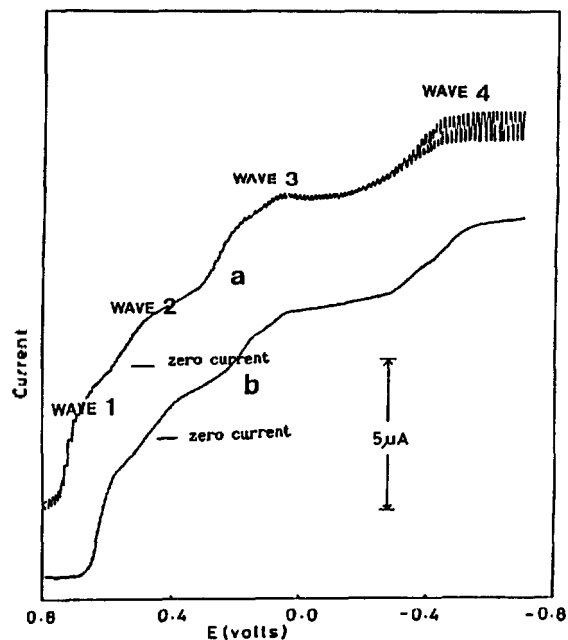
Figure 1. Conventional (a) and rapid (drop time: 1.06 sec) (b) polarograms of SpCuCl₂ (solvent; acetone/0.1 M TEAP, reference electrode; Ag/AgCl in 1 M LiCl).
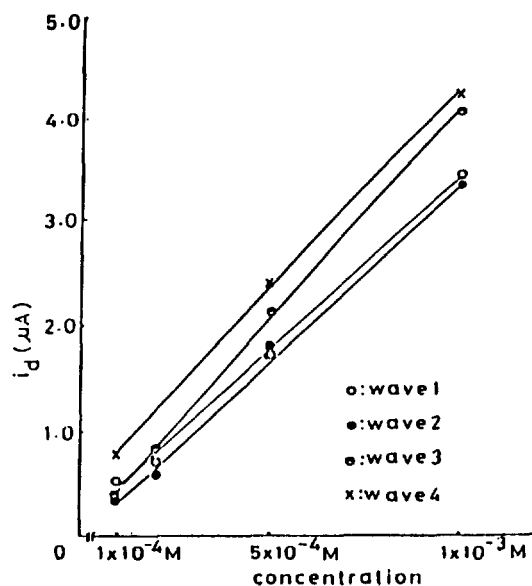

Figure 2. The plots of i_d vs. concentration for SpCuCl₂ complex.

The small post wave near wave 3 appeared at about +0.10 V disappeared at the low concentration of complex (1×10^{-4} M below). The $(E_{1/4}\text{-}E_{3/4})$ values for wave 2, wave 3, and wave 4 of conventional polarogram are 76± 5 mV, 78± 5 mV, and 153± 5 mV, respectively. However, the $(E_{1/4}\text{-}E_{3/4})$ values for wave 1 varies slightly with change in concentration and time. This might also be attributed to the fact that the electrode reactions of wave 1 is irreversible. The $(E_{1/4}\text{-}E_{3/4})$ values for wave 2, wave 3, and ware 4 are relatively larger than theoretical values expected for complete reversibility. This indicates that these waves are not completely reversible. It may be caused by the mixed electrochemical process and or decomposition of ligand in acetone. Conventional po-
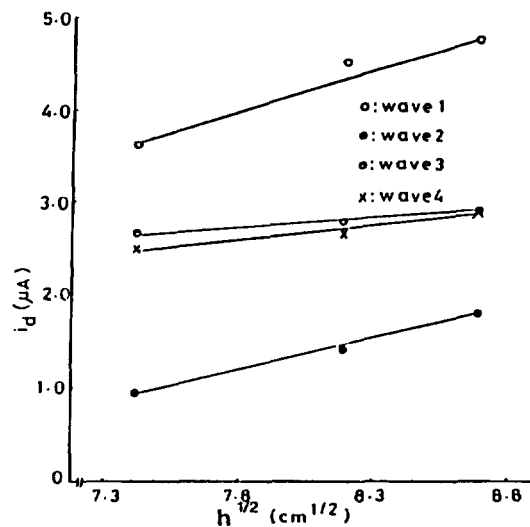

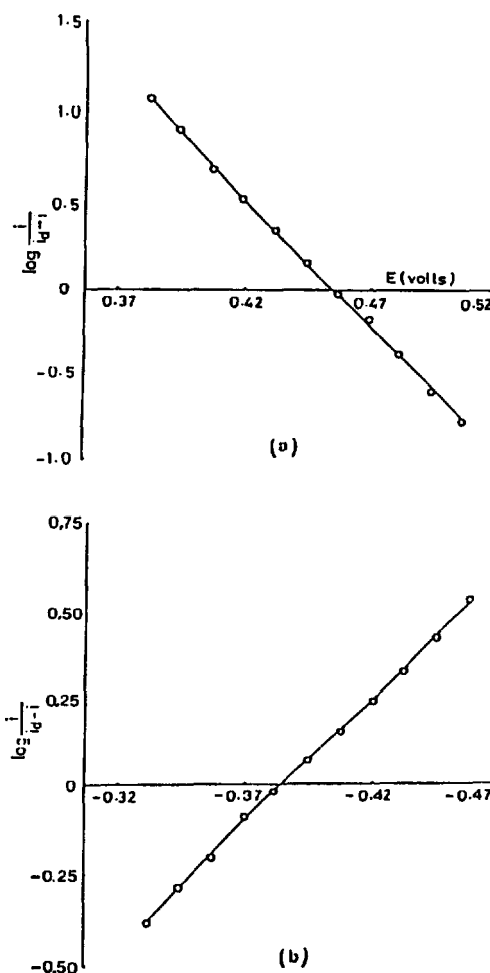**Figure 3.** Dependence of i_d on $h^{1/2}$ for SpCuCl₂ (5×10^{-4} M).

Figure 4. Logarithmic analysis for wave 2 (a) and wave 4 (b) of SpCuCl₂ complex (5×10^{-4} M).

larogram of wave 4 reveals reduction character with a slight inflection near the midpoint, suggesting some complexity involved in the electron transfer process. To obtain the detailed information on this phenomenon, rapid dc polarograms have been taken (see Figure 1-b). Inspection of Table 2

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Tabe 2. Variation of $E_{1/2}$ and $(E_{1/4}\text{-}E_{3/4})$ with Drop Time for $Cu(Sp)Cl_2$

| Drop time	$E_{1/2}$ (V vs. Ag/AgCl)			i_d (μA)			$E_{1/4}\text{-}E_{3/4}$ (mV)		
	Wave 2	Wave 4	wave 2	wave 4			wave 2	wave 4	
Normal	0.47	−0.38		2.55	2.69		77	153	
3.20	0.46	−0.31	−0.45	1.88	0.88	2.30	65	36	90
1.60	0.45	−0.32	−0.47	2.08	1.02	1.10	66	44	54
1.06	0.46	−0.32	−0.44	1.56	0.90	0.90	55	44	44
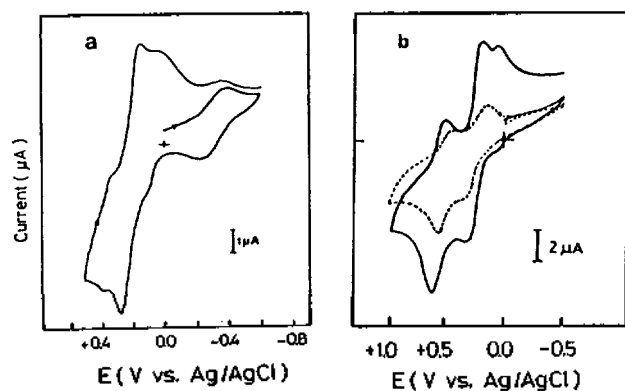
Figure 5. Cyclic voltammogram of $SpCuCl_2$ (solvent; DMF/0.1 M TEAP, scan rate; 100 mV/sec): (a); 1×10^{-3}M $SpCuCl_2$ with HMDE, (b) —; 1×10^{-3} M $SpCuCl_2$ with platinum electrode and —; 5×10^{-4} M $SpCuCl_2$ with platinum electrode.

shows that $E_{1/2}$ and $(E_{1/4}\text{-}E_{3/4})$ values of wave 2 and wave 4 are independent on drop time. It should be noted that the apparently large $(E_{1/4}\text{-}E_{3/4})$ value of wave 4 might indicate the presence of two separate but incompletely resolved, consecutive and reversible reduction steps.

The use of short controlled drop times of rapid polarography enabled us to observe the reduction wave 4 resolved into two waves (see Figure 1-b), of equal diffusion current, being approximately 100 mV apart. However, in the rapid polarography, the wave 3 and its post wave separated clearly in two waves, and the heights of two resolved waves are different. This says there is a irreversible chemical reaction or adsorption overlapped on the diffusion controlled wave. We confirmed that the post wave appeared after wave 3 is due to the adsorption process of reactants as post wave disappeared at the low concentration of the complex.

It is submitted that the oxidation of the ligand in metal complex takes place first and then other four reduction process occurs.

Cyclic Voltammetry of $SpCuCl_2$. Figures 5-a and 5-b show the cyclic voltammograms of $SpCuCl_2$ complex in dimethylformamide (DMF) obtained with HMDE and with platinum electrode. When the HMDE is used, this complex exhibits four quasi-reversible peaks, which appear at +0.34 V/ +0.40 V, +0.15 V/+0.28 V, −0.02 V/+0.05 V, and −0.37 V/ −0.23 V vs. Ag/AgCl electrode, respectively. However, when platinum electrode is employed in the same solution, only three quasi-reversible peaks appear at +0.53 V/+0.60 V, +0.21 V/+0.29 V, and −0.05 V/+0.09 V vs. Ag/AgCl electrode, respectively. One of these CV peaks at −0.02 V/+0.05 V and +0.05 V/+0.08 V vs. Ag/AgCl electrode with a HMDE and with a platinum electrode, respectively is due
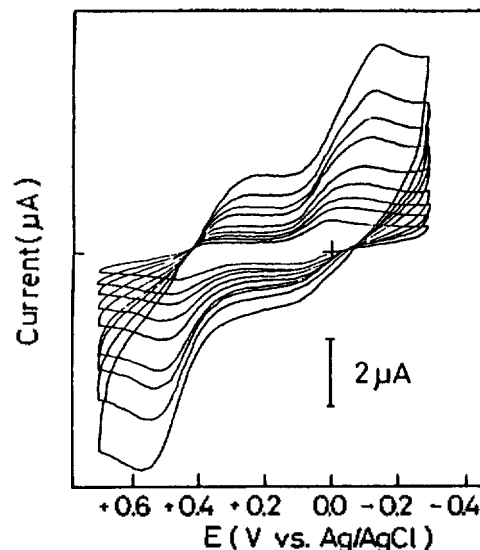
Figure 6. Cyclic voltammogram of 1×10^{-3} M $SpCuCl_2$ according to the change of scan rate (working electrode; glassy carbon, solvent; DMF/0.1 M TEAP).
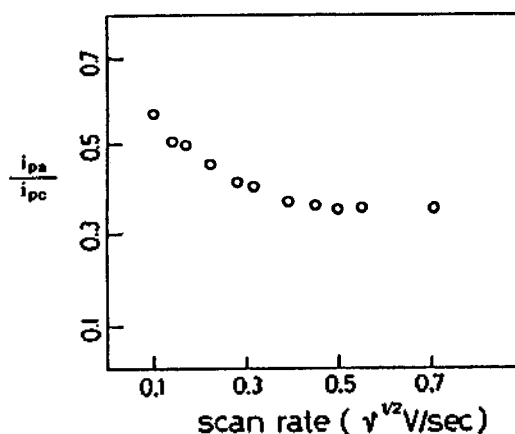
Figure 7. Variation of the 2nd peak current ratio with scan rate for cyclic voltammetry using a glassy carbon electrode.

to the adsorption process. These peaks disappeared at the low concentration condition (See Figure 5-b) as shown in the polarogram. This adsorption process is also validated by experimental results shown in Figure 6 and Figure 7. Figure 6 is the cyclic voltammogram of the $SpCuCl_2$ complex, in which the scan rate is varied and glassy carbon electrode is used. As the scan rate increase, the height of the post peak at about −0.1 V increases linearly. These results clearly indicate that the post peak is due to the adsorption of

Tabe 3. Polarographic Data for SpCuX₂ Complex

	Half-wave potential $E_{1/2}$		Reaction mechanism	Remark
	SpCuCl₂	SpCuBr₂		
Wave 1	+0.63	+0.61	SpCuX₂ ⇌ (SpCuX₂)⁻ + e	Solvent; acetone
Wave 2	+0.46	+0.41	SpCuX₂ + e ⇌ (SpCuX₂)⁻	
Wave 3	+0.14	−0.06	adsorption wave of (SpCuX₂)⁻	reference; Ag/AgCl
Wave 4	−0.38	−0.28	SpCuX₂ + Hg ⟶ SpHgX₂ + Cu²⁺	(1 M LiCl in acetone)
			(chemical reaction)	
			SpHgX₂ + 2e ⇌ SpHgX₂²⁻	

the reactant on the electrode. Figure 7 is the plot of the variation of scan rate vs. the ratio of current for anodic and cathodic peaks which appeared around −0.1 V with the glassy carbon electrode. This type of the plot should clarify the existence of an adsorption process in electrode reaction.[15]

The peaks in CV obtained with HMDE appeared at −0.37 V/−0.23 V vs. Ag/AgCl electrode should be related in part with the mercury metal. Since this peak has not revealed in CV obtained with the platinum or the glassy carbon electrodes, but have been observed only in case of presence of mercury metal in the measuring solution. The peak in respect to the presence of mercury metal has also been appeared in the polarogram of the copper (II)-sparteine complexes. The potentials of this wave of polarography and CV peaks are similar to the potential values obtained for mercury (II)-sparteine dihalide complexes (SpHgX₂). This clearly indicates that the copper (II) ion in the SpCuX₂ complexes can exchange with mercury metal in solution. For example, Bond and coworkers[16] recently reported the exchange reaction of Te (II) dithiocarbamate complexes with mercury metal. So far, no exchange reaction has been reported for the complex having nitrogen donor atoms. We have confirmed this exchange reaction as follows; to testify the effect of mercury in this copper (II) complex solution, we obtained the cyclic voltammograms of the SpCuCl₂ and SpCuBr₂ complexes in DMF solution containing mercury metal pool with platinum electrode as working electrode. A normal cyclic voltammograms for the complexes have been obtained with initial voltage cycling. However, after the several minute, the peaks related to the copper complex become gradually smaller, but the fourth peak related to mercury appears and the peak height gradually increases. Besides, as the measuring time increases, the yellowish-green color of SpCuCl₂ solution was dimmed in the presence of mercury.

Thus, we have conclusively interpreted the electrochemical reaction for these complexes as follows;

1) The oxidation wave of polarogram appeared at +0.60 V vs. Ag/AgCl is related to the oxidation of ligand donor atoms of SpCuCl₂ complex. The 1st reduction wave of +0.36 V corresponds to SpCuCl₂ + e ⇌ SpCuCl₂⁻. The 2nd reduction wave (wave 3) which is completely split into two wavelets when short controlled drop times of rapid polarography is applied is the mixed wave arisen from the reactions of SpCuCl₂⁻ + e ⇌SpCuCl₂²⁻ and of adsorption of SpCuCl₂⁻. When rapid polarographic technique is applied, the 3rd wave is also splitted into two wavelets, indicating a consecutive steps. This consecutive one electron reduction waves is due to the two step reduction of mercury complex formed
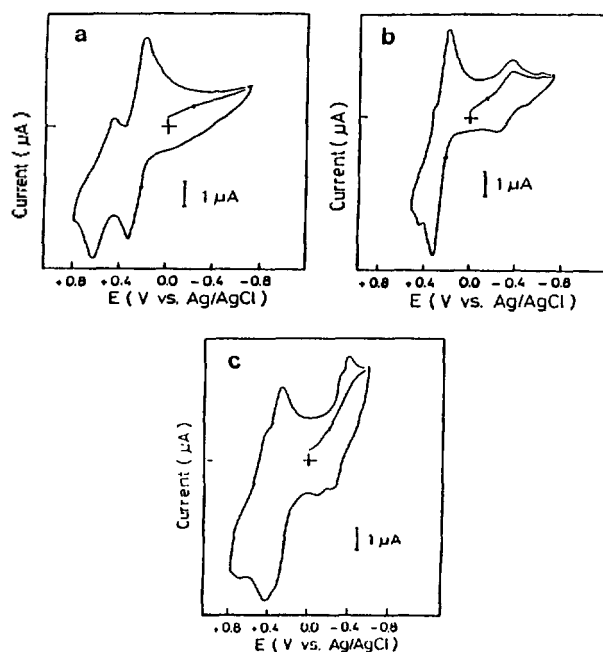

Figure 8. Cyclic voltammogram of 1×10⁻³M SpCuBr₂ with platinum electrode (a), HMDE (b), and Pt electrode in the cell containing Hg pool (c) (solvent; DMF/0.1 M TEAP, scan rate; 100 mV/sec).

in SpCuCl₂ solution via the replacement of Cu (II) ion in the complex by Hg. Thus, 3rd reduction wave is due to the reaction of SpHgCl₂ + 2e ⇌SpHgCl₂²⁻ (See Table 3).

2) The cyclic voltammogram of SpCuCl₂ obtained using HMDE is quite similar to the one obtained using platinum electrode with exception of the reduction peak of mercury complex (See Figure 5-a).

3) In case of CV of SpCuCl₂ with platinum electrode, the first CV peaks at +0.53 V/+0.62 V vs. Ag/AgCl is due to the one-electron diffusion process which was verified by employing the coulommetry. This process is arisen from the reaction of SpCuCl₂ + e ⇌SpCuCl₂⁻. The 2nd quasi-reversible peaks at +0.21 V/+0.29 V vs. Ag/AgCl is due to the reaction of SpCuCl₂⁻ + e ⇌SpCuCl₂²⁻. Such a process is evidenced by the succeeding experiment; the exhausting electrolysis of this complex with platinum gauze electrode at +0.4 V vs. Ag/AgCl is undertaken, which is correspond to the reduction potential of SpCuCl₂ into SpCuCl₂⁻.

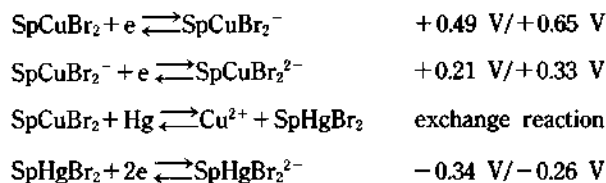In this case, when the time of electrolysis is long enough, the 2nd peaks become gradually enhanced. This says that

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Tabe 4. Cyclic Voltammetric Data for SpCuX₂ Complex in DMF (Reference Electrode; Ag/AgCl 1 M LiCl in DMF)

Working electrode	Potential				Electrode reaction mechanism
	SpCuCl₂		SpCuBr₂		
	E_{pc}	E_{pa}	E_{pc}	E_{pa}	
HMDE	+0.33	+0.40	+0.38	+0.44	$SpCuX_2 + e \rightleftarrows (SpCuX_2)^-$
	+0.15	+0.28	+0.22	+0.32	$(SpCuX_2)^- + e \rightleftarrows (SpCuX_2)^{2-}$
	−0.02	+0.05	−	−	adsorption wave of $(SpCuX_2)^-$
	−0.37	−0.23	−0.34	−0.26	$SpCuX_2 + Hg \longrightarrow SpHgX_2 + Cu^{2+}$ (chemical reaction)
					$SpHgX_2 + 2e \rightleftarrows (SpHgX_2)^{2-}$
Platinum	+0.53	+0.62	+0.49	+0.65	$SpCuX_2 + e \rightleftarrows (SpCuX_2)^-$
	+0.21	+0.29	+0.24	+0.31	$(SpCuX_2)^- + e \rightleftarrows (SpCuX_2)^{2-}$
	−0.05	−0.08	−	−	adsorption wave of $(SpCuX_2)^-$
Glassy carbon	+0.38	+0.45	+0.38	+0.47	$SpCuX_2 + e \rightleftarrows (SpCuX_2)^-$
	+0.01	+0.07	+0.09	+0.14	$(SpCuX_2)^- + e \rightleftarrows (SpCuX_2)^{2-}$ and post adsorption wave of $(SpCuX_2)^-$

the 2nd peak related to the reduction of the SpCuCl₂⁻ complex into SpCuCl₂²⁻.

The 3rd peaks of +0.05 V/+0.08 V might be caused by the adsorption of SpCuCl₂⁻ species. We could validate this adsorption reaction at previous section.

We have also studied electrochemical behavior of the SpCuBr₂ complex. It is similar to the electrochemical behavior of SpCuCl₂ except that the peak potential is slightly more negative than that of SpCuCl₂. The typical cyclic voltammogram of SpCuBr₂ in DMF is shown in Figure 8. In case of SpCuBr₂ complex, the adsorption peak of SpCuBr₂ species is so small that it is difficult to observe. Figure 8-b is a cyclic voltammogram of the SpCuBr₂ obtained in the presence of mercury in DMF. It reveals the peak of mercury complex, which indicate the presence of exchange reaction of copper (II) ion with mercury in the copper complex solution. Cyclic voltammogram of SpCuBr₂ is very similar to that of SpCuCl₂ except that for a couple of 2nd peaks observed on CV corresponding to the adsorption reaction of SpCuCl₂⁻ is not shown. Couple of 3rd peak was also observed and these peaks are attributed to the mercury exchange reaction when platinum electrode having mercury metal pool (See Figure 7). Thus, we have assigned the CV peaks of SpCuBr₂ of Figure 8 as follows;

$SpCuBr_2 + e \rightleftarrows SpCuBr_2^-$ +0.49 V/+0.65 V

$SpCuBr_2^- + e \rightleftarrows SpCuBr_2^{2-}$ +0.21 V/+0.33 V

$SpCuBr_2 + Hg \rightleftarrows Cu^{2+} + SpHgBr_2$ exchange reaction

$SpHgBr_2 + 2e \rightleftarrows SpHgBr_2^{2-}$ −0.34 V/−0.26 V

We summarized the reaction mechanism of the redox reaction of sparteine-Cu (II) dihalide complexes and polarographic data in Table 3, and cyclic voltammetric data in Table 4, respectively.

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