Comparison of chemical properties of Co(II) and Cu(II) Compounds with Bis-Phenol A(Endocrine Disruptor)

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The chemical behavior and properties of the redox state of environmental pollutants were investigated using electrochemical methods. Cyclic voltammograms were performed on the compounds to measure the variations in the redox reactions. Temperature and pH were established as influencing the redox potential and current. The electrode reactions were a mixture of quasi-reversible and irreversible processes, which changed according to the reaction current. Although the $Co(BPA)_2$ and $Cu(BPA)_2$ compounds were not found to dissociate in wastewater, they were very unstable(K=1.02).

Key words : cyclic voltammetry, charge transfer, reversible, potential, bis-phenol A, cathodic, anodic, diffusion control, endocrine disruptor

1. Introduction

The EPA(Environmental Protection Agency) project on multipathway, multichemical exposure is called the National Human Exposure Assessment Survey(NHEXAS). Conceptualized in 1991, NHEXAS consists of three pilot studies on the exposure of hundreds of U.S. residents to metals, pesticides, and volatile organic compounds. Two of the studies also include polycyclic aromatic hydrocarbons. The chemicals investigated in the studies were selected because they are either known to pose or are strongly suspected of posing health risks, are found in at least two environmental media(air, water, or soil), and are of concern to the EPA. NHEXAS also expanded on and replaced the EPA's National Human Adipose Tissue Survey, which ended in 1992 and involved monitoring human fat tissue for approximately 130 persistent organochlorine pesticides and polychlorinated biphenyls. During field work in 1995, researchers

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analyzed blood and urine samples taken from NHEXAS participants. The levels of the target chemicals were also measured in the air the volunteer breathed, the foods and beverages they consumed, and the soil and dust around their houses. A 1997 study connected to the NHEXAS project focused on the exposure of children to pesticides in six midwest states[1]. Part of this work involved determining the relationships between the activities reported by the participants and the measured environmental concentrations, exposure, and biomarkers. In 1995 a review[2] of the preliminary data from the pilot studies, EPA's Science Advisory Board(SAB) commented : "When completed, NHEXAS should provide a greatly improved understanding of human exposure to selected pollutants, which, in turn, will be helpful in determining the most effective strategies to reduce the public's risk to hazardous environmental chemicals." The same SAB review also declared NHEXAS as "an excellent project that has significant promise for improving public health in a cost-effective manner." Graham said NHEXAS will upgrade the scientific understanding of human exposure to pollutants[3]. The Kyunghyang Korean newspaper reported on statistical data(from 4. 1999 till 8. 2000) from research institutes in Korea and

expressed concern about the limited resources that have been allocated to analyze this data. An investigation was also conducted on the Sum-jin river(Hadong in Kyung won) and Eui Am lake (chun-Cheun in Kang Won), where researchers measured the level of target chemicals in the air, food, drinking water, soil, and dust around the local houses. The exposure of the local residents to metals, pesticides, and volatile organic compounds was also measured. 130 species were monitored for environmental contamination in the air, soil, river, and lake,[4] including persistent organochlorine pesticides, polychlorinated biphenyls, dioxine, bis-phenol A, di(2-ethylhexyl)phthalate, tributyltin, polybiphenylchloride, and hexachlorobenzene etc. As a result, an environmental hormone was reported from the synthesized materials.

A synthetic copper complex that exhibits reversible reductions does so based on (a) a single electron redox reaction, presumably yielding an M^+ and M^{2+} product[1] or (b) two one-electron steps with a significant potential separation, presumably yielding an M^0 and M^+ product.

$$M^0 \xrightarrow{+1e^-} M^- \xrightarrow{+1e^-} M^{2-}$$

The net result of this process is the transfer of two electrons at the same potential. The molecule exhibiting the peculiar electrochemical properties described here is the neutral, monocular M^{2+} chelate(ligand) of bis-phenol A, $[M(BPA)_2]$. The M^{2+} ions are strongly antiferromagnetic coupling with a singlet-triplet separation of 800 cm^{-1}. Thus, the compound is nearly diamagnetic at room temperature. Structurally, M^{2+} compounds are best described as planar didentate ligand moieties with the M^{2+} ions being nearly planar and bridged by two hydroxide radicals(oxygens) forming a four membered Co-O$_4$ ring. In several earlier communications, the current authors reported on results of studies on bis-phenol A(environment pollutant). The current study also investigates the detailed influence of various conditions on contaminate materials(compounds of bis-phenol A) and transition metals(Co$_{(II)}$ and Cu$_{(II)}$).

2. Materials and Methods

All reagents and solvents were purified according

to conventional procedures. The dimethylsulfoxide (DMSO) used in the electrochemical measurements was distilled twice over P_2O_5 and then once over CaH_2 under nitrogen. The Co(BPA)$_2$ and Cu(BPA)$_2$ complexes were prepared according to previous literature[6].

The elemental analyses were performed using a Perkin-Elmer Model 240C Elemental Analyzer. The conductance was measured with an ORION 142. The electron number was obtained using an EG & G PARC Model 279 Digital coulometer. The cyclic voltammetry(CV) was carried out with a PARC Model 303A static mercury dropping electrode(SMDE) and PARC 264A polarographic analyzer equipped with a PARC Model KE-0089 X-Y recorder. A three electrode cell consisting of a working electrode, platinum wire counter electrode, and Ag/AgCl reference electrode was used, with Tetraethylammoniumperchlorate(TEAP) as the supporting electrolyte.

2.0 mM of the ligand was dissolved in 100 ml of MtOH at 50 ℃, then a solution of 0.1 M of CoCl$_2$ and CuCl$_2$ in the same solvent was added. The complexes of Co(II) and Cu(II) precipitated immediately, then the solvent was left to slowly evaporate for a few hours at 50 ℃. The compounds[5] were recrystallized from the MtOH and yielded 1.97 g of deep blue [Co(BPA)$_2$] (yield 90 %) and 1.96 g of deep brown [Cu(BPA)$_2$](yield 88 %). These complexes were then crystallized by slow evaporation. The salts were characterized according to their IR spectrum, and the results were in good agreement with the theoretical and experimental values from the elemental analysis.

3. Results and Discussion

3.1 Electrochemical Methods

The electrochemical properties of the compounds were investigated using a cyclic voltammogram (CV) in a 0.1 M TEAP supporting electrolyte solution at a scan rate of 50~500 mV/s. All the electrochemical measurements were carried out under a nitrogen atmosphere. The cyclic voltammogram of the compounds is shown in Fig. 1 and Table 1. The curves of the peak separation in the CV of [Co(BPA)$_2$] and [Cu(BPA)$_2$] were presented in three and two steps, respectively. Evidence of a one-electron nature from the redox
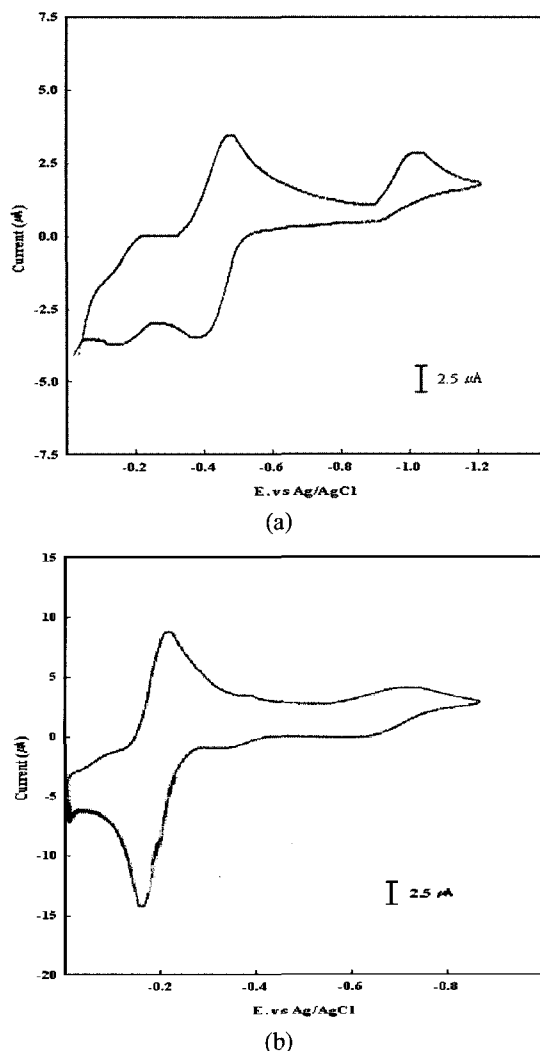
(a)

(b)

Fig. 1. Cyclic voltammograms for (a) 1 mM [Co(BPA)₂] and (b) 1 mM [Cu(BPA)₂] in 0.1 M TEAP-supporting electrolyte at 25 ℃.

processes was obtained by coulometry with an n = 1.02 value.

The two substances underwent multistep and electron charge transfer reactions. The relation of the concentrations at equilibrium was expressed by the comproportionation constant[7], K_c.

$$\left(K_c = \exp\left[\frac{(E^0_{1/2})_1 - (E^0_{1/2})_2\, n_1\, n_2 F}{RT} \right], \text{where } n_1 \right.$$

and n_2 designate 1(electron number), and $K_c = \exp$ ($\Delta E_{1/2}/$ 25.69) at 298 K), The K_c values of [Co(BPA)₂] and [Cu(BPA)₂] were obtained with 1.02 and 1.03. Myers and Shain previously suggested curves applicable to the region -80 mV < $\Delta E_{1/2}$ < 50 mV for the width of a multistep response, $\Delta E_{1/2}$, F or $n_1 = n_2 = 1$, which would appear to limit their method to $K_c \leq 7$.

Although the Co(BPA)₂ and Cu(BPA)₂ compounds did not become dissociated in waste water, they were very unstable($K_c = 1.02$ and $K_c = 1.03$) Therefore, these compounds would appear to be metal complexes and as such a focus of contamination for human health, the environment, and ecological research.

Table 1 summarizes the main cyclic voltammetry characteristics of the M(II)/M(I)/M(0) system in these complexes, at a scan rate of 100 mV/s. The measurements were focused on the variation in the $E_{1/2}$ values, which were taken as the average between the cathodic and anodic potential. As regards the half-wave potentials of [Co(BPA)₂], the half wave potential of three waves appeared at $E_{1/2} = -0.13$ V in the 1st wave, $E_{1/2} = -0.39$ V in the 2nd wave, and $E_{1/2} = -0.88$ V in the 3rd wave. As regards the half wave potential of [Cu(BPA)₂], the half-wave potentials of the two waves appeared at $E_{1/2} = -0.18$ V in the 1st wave

Table 1. Electrochemical characteristics of 1 mM [Co(BPA)₂] and 1 mM [Cu(BPA)₂] in DMSO solvent at 25 ℃(scan rate : 100 mV)

Complex	Redox waves	$E_{1/2}$	E_{Pc}	E_{Pa}	ΔE_p	iP_c	iP_a	iP_a/iP_c	n	K_c
		(V)				(μA)				
[Co(BPA)₂]	1st wave	-0.13	-0.21	0.12	0.09	5.0	1.00	0.50		
	2nd wave	-0.39	-0.45	0.36	0.09	3.8	5.00	1.40	1.00	1.02
	3rd wave	-0.88	-0.94	0.00	0.94	2.5	0.00	2.50		
[Cu(BPA)₂]	1st wave	-0.18	-0.22	-0.18	0.44	10.00	11.25	1.00	1.00	1.03
	2nd wave	-0.68	-0.75	0.00	0.75	1.50	0.00	0.00		

and $E_{1/2}$ = -0.68 V in the 2nd wave. The compound was E_{Pc} = -0.22 V, E_{Pa} = -0.18 V(1st wave) and E_{Pc} = -0.75 V, E_{Pa} = +0.00 V(2nd wave). The 1st wave was 440 mV and the 2nd wave was 750 mV. Consequently, the 1st and 2nd waves were both estimated to be irreversible, although the compounds were not dissociated. Accordingly, Bis-phenol A could be removed from contaminates polluted with Co and Cu complexes.

3.2 Redox Dependence Relative to Temperature

Fig. 2 shows a plot of the half-wave potential $(E_{1/2})$ value relative to temperature based on the data in Table 2 obtained from the redox potentials derived using voltammogram curves relative to temperature. The reactions exhibited negative potentials at all temperatures. As such, the waves were maintained by a negative potential at all temperatures. The redox half-wave potential of Co(BPA)$_2$ shifted with the 1st and 2nd curves as follows : 20 °C((E$_{1/2}$)$_1$ = 0.00 V, (E$_{1/2}$)$_2$ = -0.04 V), 30 °C((E$_{1/2}$)$_1$ = -0.08 V, (E$_{1/2}$)$_2$ = -0.29 V), 40 °C((E$_{1/2}$)$_1$ = 0.00 V, (E$_{1/2}$)$_2$ = -0.20 V), and 50 °C((E$_{1/2}$)$_1$ = -0.17 V, (E$_{1/2}$)$_2$ = -0.24 V), respectively. (where, 1, 2 : waves). The 1st wave of the redox tests distinctly exhibited only zero potential values at 20 °C and 40 °C, seemingly the product of non-electroactivity. The highest redox potential value for Co(BPA)$_2$ was obtained at 20 °C, and the lowest at 30 °C, with reduced values from 40 °C to 50 °C. Accordingly, the most rapid oxidation or reduction and decomposition occurred at 20°C, while the slowest occurred
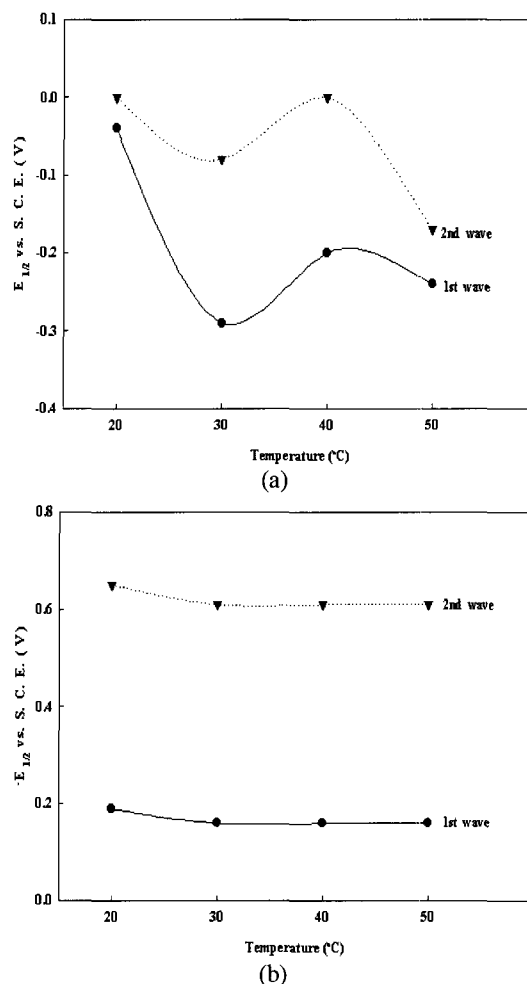

(a)

(b)

Fig. 2. Plot of E½ vs. temperature for redox couple reaction of (a) 1 mM [Co(BPA)$_2$] and (b) 1 mM [Cu(BPA)$_2$] at 25 °C.

Table 2. Electrochemical characteristics relative to temperature and pH

Complex	Redox steps	Temperature (°C) $E_{1/2}$				pH $E_{1/2}$				
		20	30	40	50	2.0	4.0	6.0	8.0	10.0
[Co(BPA)$_2$]	1st wave	-0.04 (0.00)	-0.29 (-0.08)	-0.20 (0.00)	-0.24 (-0.17)	-0.19 (0.09)	-0.32 (0.09)	-0.39 (0.09)	-0.38 (0.09)	break down
	2nd wave					0.00 (0.00)	-0.32 (0.24)	-0.39 (0.30)	-0.39 (0.32)	break down
[Cu(BPA)$_2$]	1st wave	-0.19 (0.15)	-0.16 (0.12)	-0.16 (0.12)	-0.16 (0.12)	-0.10 (0.06)	-0.18 (0.14)	-0.21 (0.17)	-0.23 (0.18)	0.00 0.00
	2nd wave	-0.65	-0.61	-0.61	-0.61	-0.44	-0.59	-0.67	-0.78	-0.66

(   ) : oxidation potential

at 30 ℃, thereby indicating the natural phenomenon of oxidation or reduction and decomposition with potential($E_{1/2}$) responses relative to temperature. The redox half-wave potential of Cu(BPA)$_2$ shifted with the 1st and 2nd curves as follows: 20 ℃ (($E_{1/2}$)$_1$ = -0.19 V, ($E_{1/2}$)$_2$ = -0.65 V), 30 ℃ (($E_{1/2}$)$_1$ = -0.16 V, ($E_{1/2}$)$_2$ = -0.61 V), 40 ℃ (($E_{1/2}$)$_1$ = -0.16 V, ($E_{1/2}$)$_2$ = -0.61 V), and 50 ℃ (($E_{1/2}$)$_1$ = -0.16 V, ($E_{1/2}$)$_2$ = -0.61 V), respectively. (where 1, 2 : waves). The 1st and 2nd half-wave potentials of Cu(BPA)$_2$ were most negative at 20 ℃ and lowest at temperatures in between. Cu(BPA)$_2$ exhibited the same potentials at 20 ℃ Therefore, the natural oxidation or decomposition was found to occur more rapidly at temperatures between 30 ℃ and 50℃ than at 20 ℃.

3.3 pH Dependence of Co(II) and Cu(II) Compounds

The pH dependence of the Co(II) and Cu(II) compounds is shown in Fig. 3. The experimental data were obtained from pH-dependent cyclic voltammetric measurements. The diagram indicates the dominant form of the compounds with regard to their oxidation state and proton composition in the various pH potential regions. In the labeling, scheme abbreviations are used, such as [Co(II)(BPA)$_2$](H$^+$), [Co(II)(BPA)$_2$](OH$^-$) and [Cu(II)(BPA)$_2$](H$^+$), [Cu(II)(BPA)$_2$](OH$^-$). The proton compositions of the compounds were inferred by comparing the slopes of $E_{1/2}$ vs. S. C. E(V).

(a)

(b)

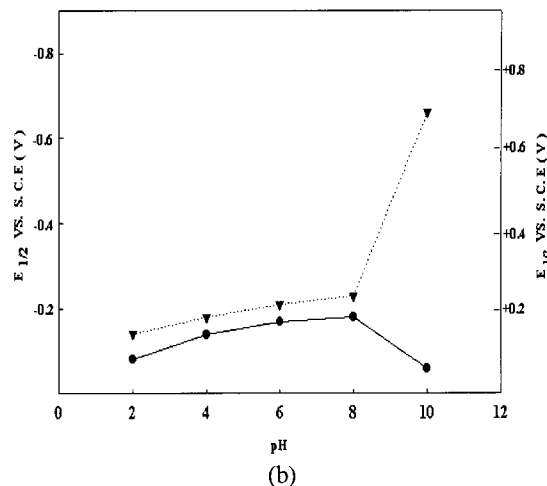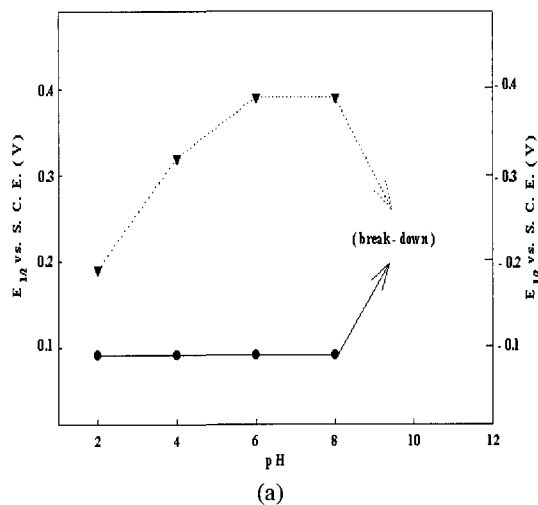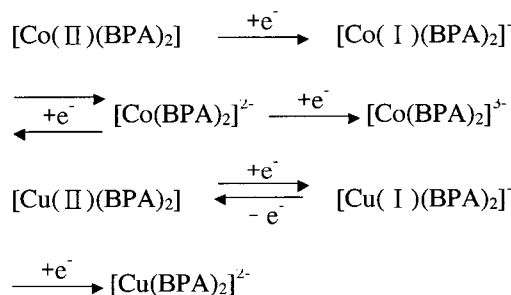Fig. 3. Plot of E½ vs. pH for redox couple reaction of (a) 1 mM [Co(BPA)$_2$] and (b) 1 mM [Cu(BPA)$_2$] at 25 ℃.

The pH line values were calculated using the Nernst equation; $E_{1/2} = E^0_{1/2} - (0.059 \, m/n)pH$, where $E^0_{1/2}$ is the half-wave potential at pH $\simeq 0$ and m is the number of protons gained when n electrons are gained. As regards the proton content, the compounds varied based on the equation below from pH 2.0 to pH 10.0.

$$[Co(II)(BPA)_2] \xrightarrow{+e^-} [Co(I)(BPA)_2]^-$$

$$\xrightleftharpoons{+e^-} [Co(BPA)_2]^{2-} \xrightarrow{+e^-} [Co(BPA)_2]^{3-}$$

$$[Cu(II)(BPA)_2] \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [Cu(I)(BPA)_2]^-$$

$$\xrightarrow{+e^-} [Cu(BPA)_2]^{2-}$$

From Fig. 3 and Table 2, the potential efficiency of the 1st curve relative to pH was maintained as an cathodic and anodic potential. From the results in Fig. 3, at pH 2.0, the 1st reductive half-wave potential at $E_{1/2}$ = -0.19 V, while the oxidative half-wave potential at $E_{1/2}$ = 0.09 V. At pH 4.0, the 1st reductive half-wave potential at $E_{1/2}$ = -0.32 V, the oxidative half wave potential at $E_{1/2}$ = -0.32 V, and the oxidative half wave potential $E_{1/2}$ = 0.09 V. Meanwhile, the 2nd reductive half-wave

potential at $E_{1/2}$ = -0.32 V and the oxidative half-wave potential at $E_{1/2}$ = 0.24 V. At pH 6.0, the 1st reductive half-wave potential at $E_{1/2}$ = -0.39 V and the oxidative half-wave potential at $E_{1/2}$ = 0.09 V. At pH 8.0, the 1st reductive half-wave potential at $E_{1/2}$ = -0.38 V and the oxidative half wave potential at $E_{1/2}$ = -0.09 V. Meanwhile, the 2nd reductive half-wave potential at $E_{1/2}$ = -0.39 V and the oxidative half-wave potential at $E_{1/2}$ = 0.32 V. Accordingly, the compounds exhibited break-down potentials of more than ±0.5 V. From these results, the $Co(BPA)_2$ compound exhibited a slower redox reaction at pH 6.0~8.0 than at pH 2.0~6.0 and thus more potential for oxidative and reductive decomposition. Consequently, this compound does not easily degrade or decompose in waste water, plus it does not easily exist in a gaseous phase in nature with non-volatile properties. As such, it can be readily adsorbed by particulate matter and removed from water in an increased sediment concentration.[9]

From the results of $Cu(BPA)_2$, at pH 2.0, the 1st reductive wave was observed at $E_{1/2}$ = -0.10 V and the oxidative wave at $E_{1/2}$ = +0.06 V. Meanwhile, the 2nd reductive half- wave potential at $E_{1/2}$ = -0.44 V. At pH 4.0, the 1st reductive half-wave potential at $E_{1/2}$ = -0.18 V and the oxidative half-wave potential at $E_{1/2}$ = +0.14 V. At pH 6.0, the 1st reductive half-wave potential at $E_{1/2}$ = -0.21 V and the oxidative half-wave potential at $E_{1/2}$ = +0.17 V. Meanwhile, the 2nd reductive half-wave potential at $E_{1/2}$ = -0.67 V. At pH 8.0, the 1st reductive half-wave potential at $E_{1/2}$ = -0.38 V and the oxidative half-wave potential at $E_{1/2}$ = +0.18 V. Meanwhile, the 2nd reductive half-wave potential at $E_{1/2}$ = -0.78 V. Above pH 10.0, break-down potentials were observed, and the oxidative half-wave potentials of the 2nd wave from pH 2.0 to pH 8.0 were diminished.
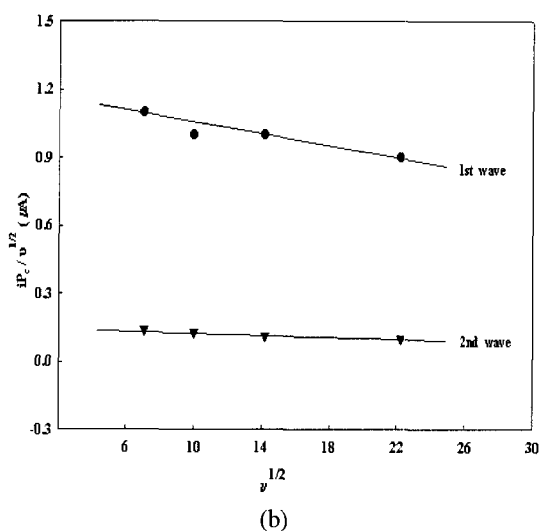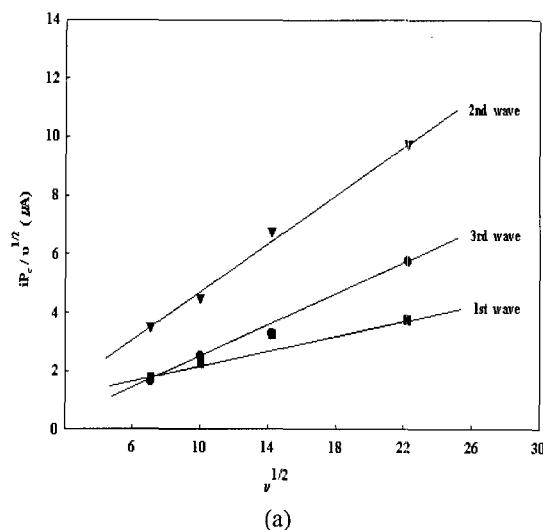
3.4 Reversibility of Co(II) and Cu(II) Compounds

(a)

(b)

Fig. 4. Plot of cathodic peak current vs. square root of scan rate from cyclic voltammograms for reduction processes of (a) 1 mM $[Co(BPA)_2]$ and (b) 1 mM $[Cu(BPA)_2]$ at 25 °C.

Redox reactions	Acid	Base
Oxidation	$2HCOOH \rightarrow 2HCHO + O_2$	$HCOOH + NaOH \rightarrow HCOONa + H_2O$
		$2H_2O \rightarrow 2H^+ + 2OH^-$
		$2H^+ + 2e^- \rightarrow 2H \rightarrow H_2$
		$4OH^- - 2e^- \rightarrow 2H_2O + O_2$
Reduction	$2HCOOH \rightarrow 2H^+ + 2COOH^-$	$HCOOH + NaOH \rightarrow HCOONa + H_2O$
	$2COOH^- \rightarrow 2CO_2 + H_2$	$HCOONa + H_2O \rightarrow NaOH + 2H^+ + CO_2$

As regards the ratio of the cathodic peak current to the anodic peak current, the iP_a/iP_c of [Co(BPA)₂] was 0.50 for the 1st wave, 1.40 for the 2nd wave, and 2.50 for the 3rd wave. Not all the waves reached values of about 1.0 at 100 mV/s. Accordingly, all three waves were irreversible, plus the above results for the two examples represent the relative degrees. The iP_a/iP_c of [Cu(BPA)₂] was 1.00 for the 1st wave and 0.00 for the 2nd wave. In contrast, from above experimental data, the 1st wave was determined to be reversible and the 2nd wave an irreversible reaction.

As shown in Fig. 4, the shape and scan rate dependence of the responses was markedly different for the dissolved compound. Fig. 4 shows the 1st, 2nd, and 3rd waves for Co(Ⅱ)/Co (Ⅰ)/Co(0) and Cu(Ⅱ)/Cu(Ⅰ)/Cu(0). In addition, there was no approximate linear relationship between the peak current(iP_c) and the scan rate(ν) (rather than with $\nu^{1/2}$) over the range 50~500 mV/s for either process. The main features of the voltammetric response of Fig. 4 were inconsistent with diffusion control. Rather, they exhibited characteristics of thin layer electrochemistry[7]. This may have resulted from complete electrolysis of particles that were sufficiently small so that diffusion was irrelevant and/ or from the presence of thin layers of electroactive materials on the outer surface of the relatively large particles. Therefore, from the known electrode area and observed current, certain tentative conclusions were drawn concerning the physical nature of the electrode state.

4. Conclusions

One electron charge transfer from the redox processes was obtained by coulometry with an n = 1.02 value. Comproportionation constants(K_c) were obtained for Co(BPA)₂(K_c = 1.02) and Cu(BPA)₂(K_c = 1.03). The redox reactions of the compounds were a couple reaction for the 1st step wave and a single reaction for the 2nd step wave. As such, the 1st wave was quasi-reversible, while the 2nd wave was irreversible. Plus, the two waves were observed to be kinetically slower based on the diminished peak heights of the anodic and cathodic peak current compared to those of the

Co(Ⅱ)/Co(Ⅰ) couple reaction. Above pH 10.0, the two waves were also diminished. Accordingly, the compound exhibited break-down potentials of more than ±0.5 V. In wasterwater, Bis-phenol creates a compound with cobalt and copper ions. These compounds were not found to dissociate in waste water, and are not naturally found in an aqueous phase due to their non-volatile properties. However, since they were readily absorbed by particulate matter, they can be removed from water in an increased sediment concentration. In addition, rapid oxidation or reduction and decomposition was observed at 20 ℃, while Cu(BPA)₂ exhibited the highest oxidation or decomposition above at 30 ℃.

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