Chemical Properties of Cu(II) Compound Containing Endocrine Disruptor, Bis-Phenol A

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The techniques of pulse and cyclic voltammetry were applied to the determination of $(E_{1/2})_2$-$(E_{1/2})_1$ for two-step electrochemical charge transfers. In addition, a simple amplitude was derived for the dependence of the differential pulse response on $(E_{1/2})_1$ and $(E_{1/2})_2$, and the use of peak to peak separation in cyclic voltammetry and differential pulse methods was evaluated. A comparison of the comproportionation constants(K_c) from differential pulse and cyclic voltammetry methods exhibited a good agreement within 5%.

Key words : differential pulse polarography, cyclic voltammetry, charge, transfer, reversible, potential, reaction control, cathodic, anodic, diffusion control.

1. Introduction

Currently, all synthetic copper complexes that exhibit reversible reductions would appear to so in (a) a one-electron redox reaction presumably yielding a Cu(I) or Cu(II) product[1] or (b) two one-electron steps with a significant potential separation presumably yielding a Cu(0) or Cu(I) product[2].

$$A^0 \underset{-1e^-}{\overset{+1e^-}{\rightleftharpoons}} A^- \xrightarrow{+1e^-} A^{2-}$$
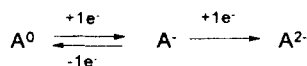
The net result of this process is the transfer of two electrons at the same potential. The molecule that exhibits these peculiar electrochemical properties is the neutral, monocular copper(II) chelate(ligand) of bis-phenol A, $[Cu(BPA)_2]$. The copper(II) ions are strongly antiferromagnetic coupling with a singlet-triplet separation of 800 cm^{-1}. As such, the compound is nearly diamagnetic at room temperature. Structurally, copper(II) compounds are best described as planar didentate ligand moieties in which the copper(II) ions are nearly planar and bridged by two hydroxide radical(oxygens), thereby forming a four-membered $Cu-O_4$ ring. A schematic drawing is shown below. In several previous reports, the current authors presented some results from earlier studies of bis-phenol A[3]. However, the current study focuses on the chemical characterizing and structurally stable transition of the metal complexes based on studying their synthesis and electrochemical properties.
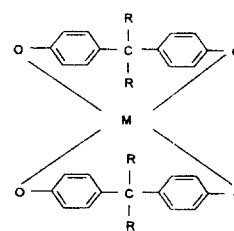
[Scheme]

2. Materials and Methods

All the 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 bis-phenol A copper(II) complex was prepared according to previous literature[4].

An elemental analysis was performed using a Perkin-Elmer Model 240C Elemental Analyzer, and the conductance was measured with an ORION Model 142. The electron number was obtained

using an EG & G PARC Model 279 Digital coulometer. The cyclic voltammetry(CV) and differential pulse voltammetry(DPV) were carried out with a PARC Model 303A static mercury dropping electrode(SMDE) and PARC 264A, respectively. In addition, a polarographic analyzer equipped with a PARC Model KE-0089 X-Y recorder was also used, plus a three-electrode cell composed of a working electrode, platinum wire counter electrode, and Ag/AgCl reference electrode with Tetraethylammoniumperchlorate(TEAP) as the supporting electrolyte.

2.1. Preparation of [Cu(Bis-Phenol A)₂]

2.0 mmol of bis-phenol A(BPA) was dissolved in 100 ml of MtOH at 50 ℃, then a solution of 0.1 M of $CuCl_2$ was added to the same solvent. The Cu(II) complex was immediately precipitated, after which the solvent was slowly evaporated for a few hours at 50 ℃. The complex was recrystallized from MtOH to produce 1.97 g of deep brown [Cu(BPA)₂](yield 88 %), which was then crystallized by slow evaporation. The compound were characterized by IR spectrometry and in all cases, the elemental analysis data were consistent with the proposed stoichiometries.

3. Results and Discussion

3.1 Electrochemical Studies

The electrochemical properties of the compound were investigated by differential pulse polaro a 0.1 M TEAP-DMSO solution at a scan rate
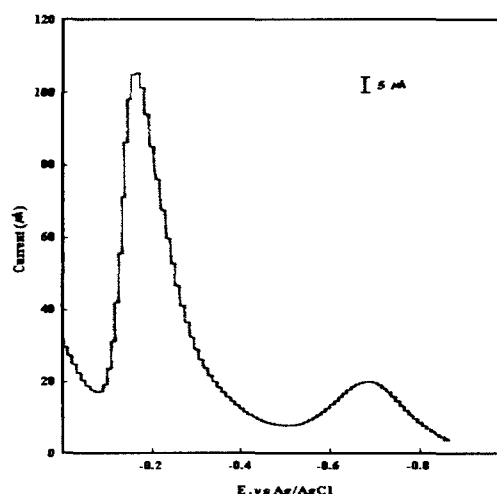

Fig. 1. Current-potential curve for differential pulse voltammetry of 1 mM [Cu(BPA)₂] (scan rate 20 mV/s).

Table 1. Comparison of parameters with differential pulse polarography and cyclic voltammetry methods.

Complex	Redox steps	Differential pulse polograpy					Cyclic voltammetry						
		$E_{1/2}$	E_{Pc}	$E_{Pc}^2-(E_{1/2})^1$	ΔE_p	$E_{Pc}^2-E_{P/2}^1$	$E_{1/2}$	E_{Pc}	$E_{Pc}^2-(E_{1/2})^1$	ΔE_P	$E_{Pc}^2-E_{P/2}^1$	n	K_c
[Cu(BPA)₂]	1st wave	-0.15	-0.19	-0.57	-0.53	-0.63	-0.18	-0.22	-0.57	-0.53	-0.64	1.00	1.03
	2nd wave	-0.65	-0.72				-0.68	-0.75					

ΔE = E_P^2 - $(E_{1/2})^1$(differential-pulse-half-wave potential; 1(first), 2(second)), $\Delta E_P(E_{Pc}-E_{Pa})$ (cyclic voltammetry; peak to peak separation), ΔE_P(diffential pulse method; $E_P^2-E_P^1$), $E_{P/2}$ (half peak potential) ; (| $E_{Pc}-E_{P/2}$| width of wave), n(electron number of redox reacion), K_c (comproportionation), E_{Pc} : cathodic peak potential,E_{Pa} : anodic peak potential.

Table 2. Cyclic voltammetry characterization of bis-phenol A and Cu(II) complex redox couples in DMSO with 0.1 M TEAP(scan rate : 100 mV).

Complex	Redox Steps	$E_{1/2}$	E_{Pc}	E_{Pa}	ΔE_p	iP_c	iP_a	iP_a/iP_c
		(V)				(μ A)		
[Cu(BPA)₂]	1st wave	-0.18	-0.22	-0.18	0.44	10.00	11.25	1.00
	2nd wave	-0.68	-0.75	0.00	0.75	1.50	0.00	0.00

of 50~500 mV/s. All electrochemical measurements were carried out under a nitrogen atmosphere, and the results are shown in Figs. 1 ~ 5 and Tables 1 and 2. The differential pulse and cyclic voltammograms of the compound are shown in Figs. 1 and 2. The curves of the peak to peak separation in the DPP and CV methods are presented as a two-step electrochemical charge transfer. As such, it would appear that this Cu(II) compound used two one-electron steps in the redox processes.
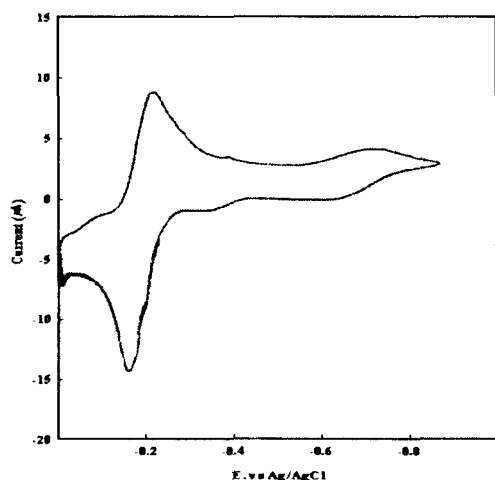

Fig. 2. Cyclic voltammogram for 1 mM [Cu(BPA)₂] in DMSO solvent with 0.1 M TEAP at 25 ℃(scan rate : 100 mV/s).
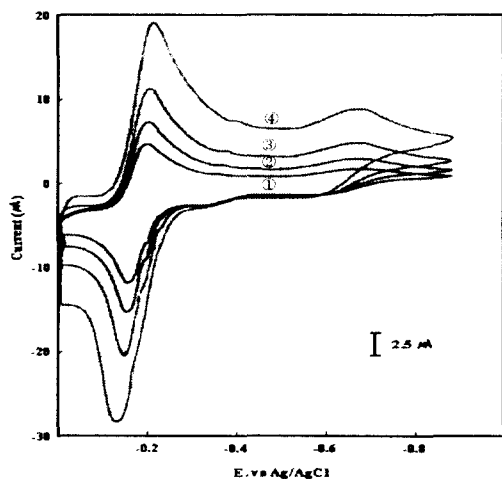

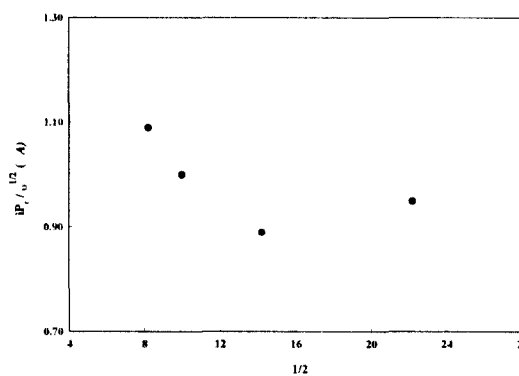Fig. 3. Cyclic voltammogram for 1 mM [Cu(BPA)₂] in DMSO solvent with 0.1 M TEAP at 25 ℃(① 50, ② 100, ③ 200, ④ 500 mV/s).

Fig. 4. Plot of the cathodic peak current vs. the square root of the scan rate from cyclic voltammogram for the reduction processes of 1 mM [Cu(BPA)₂] in DMSO solvent with 0.1 M TEAP at 25 ℃.

Evidence of a one-electron transfer in the redox processes was obtained using a coulometric when $n = 1.02$. Here, the techniques of differential pulse and cyclic voltammetry were applied to the experimental data to determine the response. As shown in table 1 , the E_P values of DPP and $E_{1/2}$ of CV(two methods) did not coincide with all the steps, but rather a difference in the potential values was found in the region 0.03 V. However, the values obtained by the two methods were clearly in good agreement with $(E_{Pc})_2$ - $(E_{1/2})_1$ = -0.57 V. With a constant, $\triangle E_p$ can not be compared with the E_P values because it would not be expected to exhibit an anodic peak potential(E_{Pa}) with a dpp measurement method. In the current study, $(E_{Pc})_2$ - $(E_{1/2})_1$ = -0.63 V (DPP) and $(E_{Pc})_2$ - $(E_{1/2})_1$ = -0.64 V(CV) were obtained. However, when these results are compared with $(E_{Pc})_2$ vs $(E_{1/2})_1$, it is clear that the potential value of the CV method exhibited a more negative potential (-0.01 V) than the DPP method. Accordingly, it would appear that the potential efficiency exhibited was due more to the wave width than the pulse amplitudes. Since instruments for cyclic voltammetry are relatively simple and more widely available than pulse instruments, the use of cyclic voltammetry was examined.

In general, a good agreement(± 2 mV) was found between the $\varDelta E_{1/2}$ values determined by the cyclic and pulse voltammetric width methods. The peak difference from the cyclic voltammetric method

often resulted in $\Delta E_{1/2}$ values that differed by as much as 10 mV from the width method values.[5] From the two examples, the latter was found to be in good agreement. Many substances can undergo multistep charge transfer reactions. The relation of the concentrations at equilibrium can be expressed by the comproportionation constant, K_c.

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

= n_2 = 1(electron number) and K_c = $\exp(\Delta E_{1/2}/25.69)$ at 298 K. Using this method, the value of K_c = 1.03 can be obtained within a range 0.16 V < $\Delta E_{1/2}$ < 0.65 V. Myers and Shain[6] produced a curve applicable to the region -80 mV < $\Delta E_{1/2}$ < 50 mV for the width of the multistep response, $(E_{Pc} - E_{P/2})$ vs. $\Delta E_{1/2}$. As such, when F or n_1 = n_2 = 1, this would appear to limit this method to $K_c \leq 7$. However, the current study shows that this method can be extended to any value of $\Delta E_{1/2}$ across the entire experimentally accessible range of $\Delta E_{1/2}$ values.[7]

Table 2 summarizes the main cyclic voltammetry characteristics of the $Cu(II)/Cu(I)/Cu(0)$ system in the complex, at a scan rate of 100 mV/s. The initial focus was on the variation in the $E_{1/2}$ values, which were taken as the average between the cathodic and anodic peak potentials. Half wave potentials of the two waves appeared at $E_{1/2}$ = -0.18 V in the 1st wave and $E_{1/2}$ = -0.65 V in the 2nd wave. In Fig. 2, the voltammogram shows a reduction in the 1st wave at E_{Pc} = -0.04 V with an oxidation wave at E_{Pa} = +0.01 V and a reduction in the 2nd wave at E_{Pc} = -0.54 V with an oxidation wave at E_{Pa} = +0.00 V. As indicated by the data in Table 2, the 1st wave was reversible as the peak potential difference($\triangle E_P$=30mV) was smaller than 60.0mV, while the 2nd wave was irreversible because of the larger peak potential difference at $\triangle E_P$=540mV. When the sweep rate was increased, i.e. the ratio of the cathodic peak current to the anodic peak current, the iP_a/iP_c of the 1st wave was 1(reached a value of about 1 at 100 mV/s). Accordingly, the 1st wave was determined to be reversible. In contrast, for the 2nd wave, since no anodic current was observed on the reverse negative scan at a scan rate of 100 mV/s, it was determined to be irreversible.

Fig. 3 shows the effects of variations in the scan

rate on the chemical reversibility of the $Cu(II)/Cu(I)$ system of the compound. The results indicated that molecular oxygen reacted with the $Cu(I)$ state of the compound, thereby removing it from the electrode surface. As shown in Figs. 3 and 4, the shape and scan rate dependence of the responses were markedly different for the dissolved compound. Fig. 3 shows the results for all the scan rates examined(50~500 mV/s). The voltammetry of the 1st wave couple reaction produced much sharper peaks for the $Cu(II)/Cu(I)$ couple. The ΔE_P value was also very small 40 mV. 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 a range of 50~500 mV/s for both processes. The main features of the voltammetric response in Fig. 4 were not consistent with diffusion control. Rather, they exhibited characteristics of thin layer electrochemistry.[8] This may have resulted from the complete electrolysis of the particles which became 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. Accordingly, based on the known electrode area and observed current, certain tentative conclusions could be drawn concerning the physical nature of the electrode state.
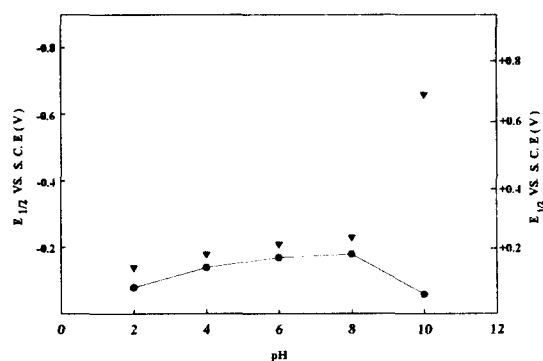
3.2. pH Dependence of Cu(II)/Cu(I)/Cu(0) Couple Single

Fig. 5. Plot of $E_{1/2}$ vs pH for redox couple reaction [Cu(BPA)₂] complex.

The pH dependence of the $Cu(II)/Cu(I)$ couple in the compound is shown in Fig. 5. The ex-
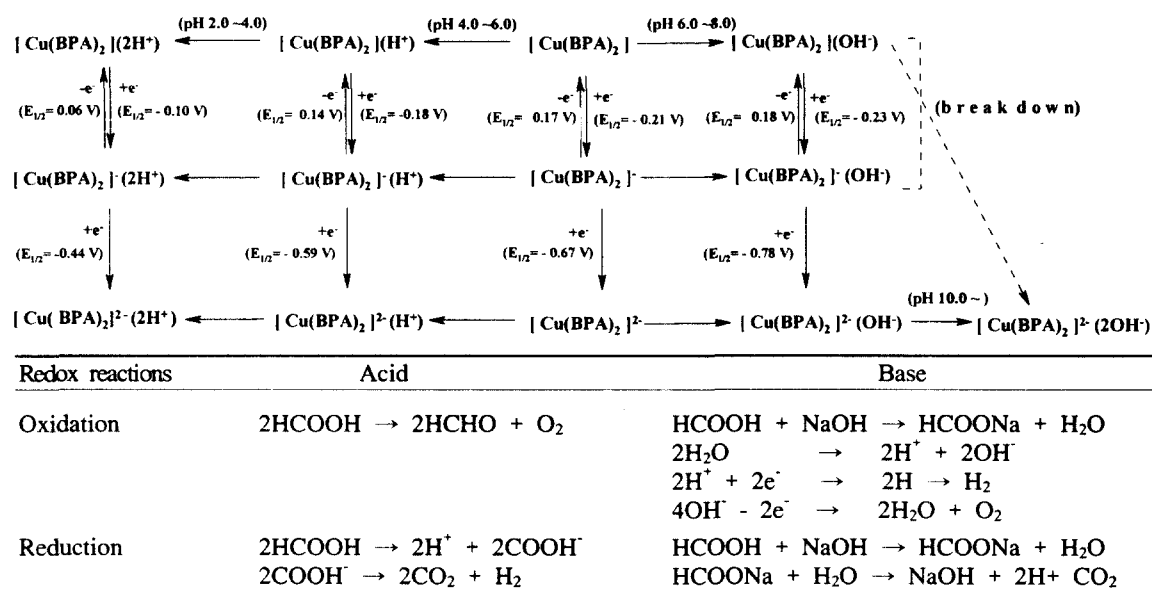
perimental data were obtained from pH dependent cyclic voltammetric measurements. In the diagram the dominant form of the couple is indicated with regard to the oxidation state and proton composition in the various pH potential regions. Abbreviations such as [Cu(Ⅱ)(BPA)₂](H⁺) and [Cu(Ⅱ)(BPA)₂] (OH⁻) are used in the labeling scheme. The proton compositions of the compound were inferred by comparing the slopes of the $E_{1/2}$ vs. pH lines with the values 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 the pH and m is the number of protons gained when n electrons are gained. In terms of the proton content, the couple varied from the equation below from pH 2.0 to pH 10.0.

$$[Cu(Ⅱ)(BPA)_2] \xrightleftharpoons[\text{-e}]{\underset{(H^+)}{\text{+e}}} [Cu(Ⅰ)(BPA)_2]^- \xrightarrow{\text{+e}} [Cu(BPA)_2]^{2-}$$
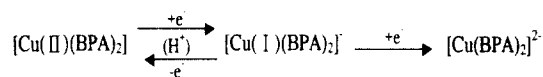
3.3. Redox State Couples

The 1st wave appeared at $E_{1/2} = 0.06 \sim 0.14$ V and $E_{1/2} = 0.10 \sim 0.18$ V(at pH 2.0 ∼ 4.0) in an organo acid(HCOOH) solution for the compound at an activated electrode. As shown by the chemical redox couple in Cu(Ⅱ), the redox process that occurred at this wave was a one-electron process corresponding to the redox of the Cu(Ⅱ) compound. Although the wave appeared to be

reversible, it was kinetically slow, as shown by the diminished peak heights of the anodic and cathodic peak currents compared to those of the Cu(Ⅱ)/Cu(Ⅰ) couple. From Fig. 5, the potential efficiency of the 1st curve relative to the pH was maintained as an cathodic and anodic potential with various pHs. From the results in Fig. 5, 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. This wave was a reversible process with a peak splitting of $\Delta E_P = E_{Pc} - E_{Pa} = 40$ mV, whereas the 2nd reductive wave appeared to be irreversible at $E_{Pc2} = -0.65$ V and $E_{1/2} = -0.50$ V. At pH 4.0, the 1st reductive wave at $E_{1/2} = -0.18$ V and oxidative wave at $E_{1/2} = +0.14$ V were observed to be reversible at 60 mV, whereas the 2nd reductive wave appeared to be irreversible at $E_{Pc2} = -0.65$ V and $E_{1/2} = -0.59$ V. At pH 6.0, the 1st reductive wave at $E_{1/2} = -0.21$ V and oxidative wave at $E_{1/2} = +0.17$ V were observed to be reversible at 50 mV, whereas the 2nd reductive wave appeared to be irreversible at $E_{Pc2} = -0.73$ V and $E_{1/2} = -0.67$ V. At pH 8.0, the 1st reductive wave at $E_{1/2} = -0.23$ V and oxidative wave at $E_{1/2} = +0.18$ V were observed to be reversible at 50 mV, whereas the 2nd reductive wave appeared to be irreversible at $E_{Pc2} = -0.80$ V and $E_{1/2} = -0.78$ V. At pH 10.0, the 1st reductive wave at $E_{1/2} = -0.66$ V and oxidative wave at $E_{1/2} = +0.03$ V were observed

Redox reactions	Acid	Base
Oxidation	2HCOOH → 2HCHO + O₂	HCOOH + NaOH → HCOONa + H₂O 2H₂O → 2H⁺ + 2OH⁻ 2H⁺ + 2e⁻ → 2H → H₂ 4OH⁻ - 2e⁻ → 2H₂O + O₂
Reduction	2HCOOH → 2H⁺ + 2COOH⁻ 2COOH⁻ → 2CO₂ + H₂	HCOOH + NaOH → HCOONa + H₂O HCOONa + H₂O → NaOH + 2H+ CO₂

to be irreversible at 630 mV, whereas the 2nd reductive wave was not.

3.4. Redox Dependence relative to pH

These assignments are based on the fact that H^+ and OH^- ions are active relative to the pH in a nonaqueous solution. The redox reactions are thus proposed as follows :

4. Conclusions

A one-electron charge transfer in redox processes was obtained by coulometry when n = 1.02. The $E_{1/2}$ and E_P values of the DPP and CV methods did not coincide for all the steps, however, a difference in the potential values was exhibited in the region 0.03 V. In contrast, the value$(E_{Pc})_2$ - $(E_{1/2})_1$ = -0.57 V was obtained by both methods. The comproportionation constant(K_c) obtained by the differential pulse polarography method was 1.03. The redox reaction of the compound was found to be a couple consisting of a 1st step wave and single consisting of a 2nd step wave. The 1st wave was reversible while the 2nd was irreversible. However, the redox process was found to be kinetically slow based on the diminished peak heights of the anodic and cathodic peak current compared to those of the $Cu(II)/Cu(I)$ couple

reaction. In terms of the proton content, the couple varied from the equation below between pH 2.0 and pH 10.0.

$$[Cu(II)(BPA)_2] \xrightarrow[\substack{+e \\ \longleftarrow \\ -e}]{(H^+)} [Cu(I)(BPA)_2]^- \xrightarrow{+e} [Cu(BPA)_2]^{2-}$$
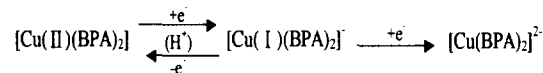
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