

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

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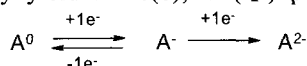
(Manuscript received 7 February, 2002 ; accepted 26 February, 2002)

The chemical behavior and properties on the redox state of environmental pollutant has been investigated by electrochemical methods. We carried out to measure the variations in the redox reaction of differential pulse polarogram and cyclic voltammogram. The results observed the influences on redox potential and current of various factors with temperature and pH. These were established factors as the effect of the redox reaction. It can be clearly recognized that the electrode reaction are from quasi-reversible to irreversible processes. Also, it was mixing with reaction current controlled. The bis-phenol A in the waste water was made to compound with cobalt ion and it take away from the separation into compound. The $\text{Co}(\text{BPA})_2$ compound was not found to be dissociation in waste water. However, this compound is a very unstable ($K=1.02$) and for a while, it was to be a dissociation. Therefore, we believed that it was likely to a toxic substance.

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

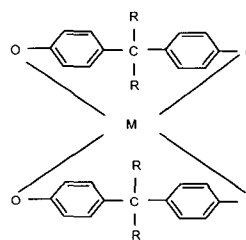
1. Introduction

To our knowledge, all synthetic copper complex that exhibit reversible reductions do so in (a) a one electron redox reaction presumably yielding a $\text{Co}(\text{I})$, $\text{Co}(\text{II})$ product¹⁾ or (b) two one electron steps with a significant potential separation presumably yield a $\text{Co}(0)$, $\text{Co}(\text{I})$ product.²⁾



The net result of this process is the transfer of two electrons at the same potential. The molecular exhibiting the peculiar electrochemical properties described here is the neutral, monocyclic cobalt(II) chelate(ligand) of bis-phenol A, $[\text{Co}(\text{BPA})_2]$. The cobalt(II) ions are strongly antiferromagnetic coupling with a singlet-triplet separation of 800 cm^{-1} . Thus, the compound is nearly diamagnetic

at room temperature. Structurally, the cobalt(II) compounds are best described as planar didentate ligand moieties with the cobalt(II) ions nearly in the planar and bridged by two hydroxide radical (oxygen) forming a four membered Co-O_4 ring. A schematic drawing is shown. In several earlier communications, as mentioned before, it reported some results of our studies of the bis-phenol A(environment pollutant).³⁾ This paper was studied that to the synthesis and chemical properties. Accordingly, it is focused the effects of contaminants on human health, environment, and ecological.



[Scheme]

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2. Materials and Methods

All reagents and solvents were purified according to the conventional procedures. Dimethylsulfoxide (DMSO) used in electrochemical measurements was distilled twice over P_2O_5 and then once over CaH_2 under nitrogen. $Co(BPA)_2$ complex was prepared by the literature method⁴⁾.

Elemental analysis were performed with Perkin-Elmer Model 240C Elemental Analyzer Conductance was measured with an ORION 142. Electron number was obtained with an EG & G PARC Model 279 Digital coulometer. Cyclic voltammetry(CV) and differential pulse voltammetry(DPV) were 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, a platinum wire counter electrode, and a $Ag/AgCl$ reference electrode was used. Tetraethylammoniumperchlorate(TEAP) was used as a supporting electrolyte.

2.1. Preparation of $[Co(Bis-Phenol A)_2]$

2.0 mM of ligand were dissolved in 100 ml of $MtOH$ at $50\text{ }^\circ C$ and then a solution of 0.1 M of $CoCl_2$ in the same solvent was added. The complex of $Co(II)$ precipitated immediately and we slowly evaporated solvent for a few hours at $50\text{ }^\circ C$. It was recrystallized from $MtOH$ to give 1.97 g of deep brown $[Co(BPA)_2]$ (yield 90 %). This complex was crystallized by slow evaporation. This salt was characterized by their IR spectrum and were a good agreement with theoretical and experimental values elemental analysis(C, H, O,

and Co).

The example, the $Cu(II)$ and $Co(II)$ ions are easily made a compounds with bis-phenol A, but the $Ni(II)$ and $Mg(II)$ ions are not to be complexes formation. Accordingly, only the bis-phenol A was known to be reactively with an elective affinity. Therefore, the bis-phenol A in the waste water was made to compound with cobalt ion and it take away from the separation into compounds.

3. Results and Discussion

3.1. Electrochemical Studies

The electrochemical properties of the compound was investigated by differential pulse polarography (DPP) and cyclic voltammogram(CV) in 0.1 M TEAP-DMSO solution at the scan rate of $50\sim 500$ mV/s. All electrochemical measurements were carried out under nitrogen. The differential pulse and cyclic voltammogram of the compound is shown in Fig. 1, 2 and table 1. The curves of the peak separation in DPP and CV methods of $[Co(BPA)_2]$ is presented to two step. To our knowledge, this $Co(II)$ compound exhibited two one-electron steps to redox processes.

Evidence of one electron nature from the redox processes was obtained by coulometric with $n = 1.02$ value. Here the techniques of differential pulse and cyclic voltammetry have been applied to the determination of response on experimental data. As shown in Table 1, $E_{1/2}$ and E_p values of DPP and CV(two method) are not coincidence to all the steps, but it is found that the difference of potential values(ΔE_p) by CV method are given in the region $-0.10V$, $-0.09V$, and $-0.90V$, re-

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

Complex	Redox Waves	Differential pulse polarography					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_{Pa}	$E_{Pc}^2-(E_{1/2})^1$	ΔE_p	$E_{Pc}^2-E_{P/2}^1$	n	K_c
$[Co(BPA)_2]$	1st wave	-0.16	-0.19				-0.16	-0.21	-0.11		-0.10			
	2nd wave	-0.37	-0.42	-0.26	-0.23	-0.33	-0.39	-0.43	-0.34	-0.27	-0.09	-0.34	1	1.02
	3rd wave	-0.87	-0.93				-0.88	-0.94	0.00		-0.90			

$\Delta E = E_p^2-(E_{1/2})^1$ (differential-pulse-half-wave potential; 1(first), 2(second)), $\Delta E_p(E_{Pc}-E_{Pa})$ (cyclic voltammetry; peak to peak separation), ΔE_p (differential 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 reaction), K_c (comproportionation), E_{Pc} : cathodic peak potential, E_{Pa} : anodic peak potential.

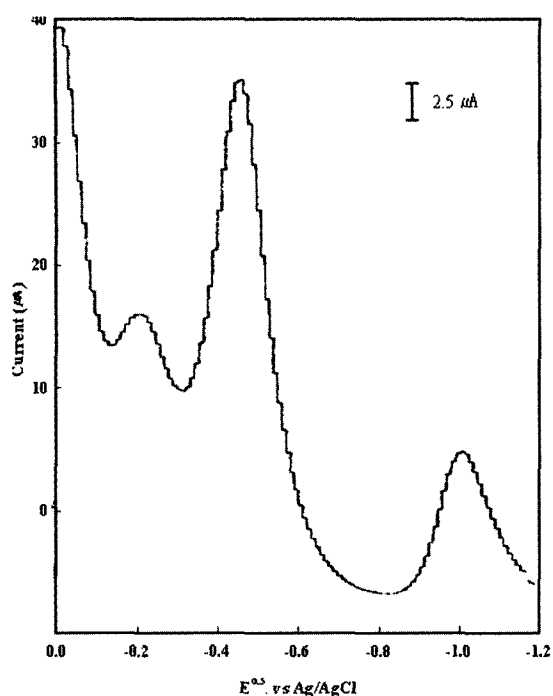


Fig. 1. Current-potential curve for differential-pulse polarography of 1 mM [Co(BPA)₂] (scan rate : 20 mV/s).

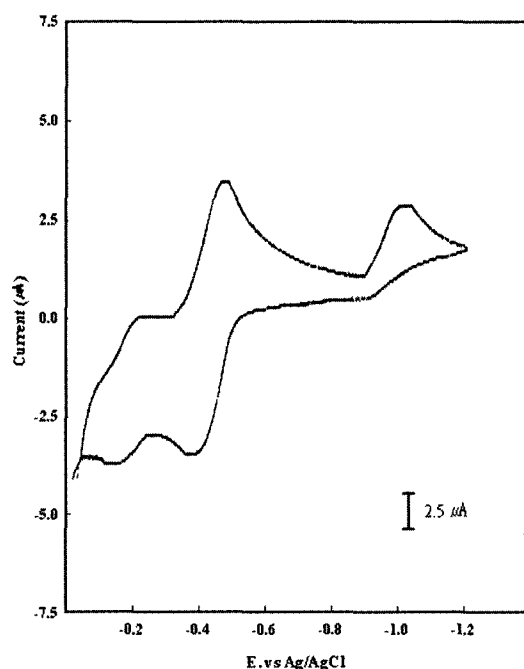


Fig. 2. Cyclic Voltammogram for 1 mM [Co(BPA)₂] in DMSO solvent with 0.1 M TEAP at 25°C (scan rate : 100 mV/s).

spectively and the potential value of D.P.P method is -0.23V. From the two methods, these values are found a good agreement with reversible processes. However, $(E_{pc})_2 - (E_{1/2})_1 = -0.57$ V and $\Delta E_p = -0.53$ V values were found by two methods. Here, we are obtained with $(E_{pc})_2 - (E_{1/2})_1 = -0.26$ V from DPP and $(E_{pc})_2 - (E_{1/2})_1 = -0.27$ V from CV. But, when here are compared with $(E_{pc})_2$ vs $(E_{1/2})_1$, it can be seen that the potential value of CV method indicated a more negative potential (-0.01 V) than DPP method. It can be seen that the difference value of potential is just 0.01V. Accordingly, we are recognized that the potential efficiency exhibited due to the more wave width than pulse amplitudes. Since instruments for cyclic voltammetry are relatively simple and more widely available than pulse instruments, we have examined the use of the cyclic voltammetry.

In general, good agreement (1 mV) was found between the $\Delta E_{1/2}$ values determined by the width methods of cyclic and pulse voltammetric. The peak difference of cyclic voltammetric method often resulted in $\Delta E_{1/2}$ values as much as 10 mV different from the width methods.⁵⁾ From the two examples, the latter was found with good agreement. Many substances can undergo multistep charge transfer reactions. The relation of the concentrations at equilibrium is expressed by the comproportionation constant, K_c .

$$K_c = \exp \left[\frac{(E_{1/2}^0)_1 - (E_{1/2}^0)_2}{RT} \right], \text{ where } n_1 = n_2 = 1 \text{ (electron number), } K_c = \exp(\Delta E_{1/2} / 25.69)$$

at 298 K, with that method, value of $K_c = 1.02$ [Co(BPA)₂] was obtained. Myers and Shain⁶⁾ have given a curve applicable to the region $-80 \text{ mV} < \Delta E_{1/2} < 50 \text{ mV}$ for the width of a multistep response, $(E_{pc} - E_{p/2})$ vs. $\Delta E_{1/2}$. For $n_1 = n_2 = 1$, this would appear to limit their method to $K_c \leq 7$. We will show, however, that their method can be extended to any value of $\Delta E_{1/2}$. They can be applied over the whole experimentally accessible range of $\Delta E_{1/2}$ values⁷⁾.

The Co(BPA)₂ compound was not found to be dissociation in waste water. However, this compound is a very unstable ($K=1.02$) and for a while, it was to be a dissociation. Therefore, we believed that it was likely to a toxic substances. Accordingly, it is focused the effects of contaminants on human health, environment, and

Table 2. Cyclic voltammetry characterization of Co(II) complex redox couples in DMSO solvent(scan rate : 100 mV/s).

Complex	Redox Waves	$E_{1/2}$	E_{Pc}	E_{Pa}	ΔE_p	iP_c	iP_a	iP_a/iP_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
	3rd wave	-0.88	-0.94	0.00	0.94	2.5	0.00	2.50

ecological research.

Table 2 summarizes the main cyclic voltammetry characteristics of the Co(II)/Co(I)/Co(0) system in this complex, at a scan rate of 100 mV/s. We focused first on the variation of $E_{1/2}$ values, which were taken as the average between the cathodic and anodic potential. Half wave potentials of [Co(BPA)₂], half wave potential of the three waves appear at $E_{1/2} = -0.13$ V of 1st wave, $E_{1/2} = -0.39$ V of 2nd wave and $E_{1/2} = -0.88$ V of 3rd wave. As showed by the data in Table 2, compound was $E_{Pc} = -0.21$ V(1st wave), -0.45 V(2nd wave), and -0.94 V(3rd wave), and $E_{Pa} = +0.12$ V(1st wave), 0.36 V(2nd wave), and 0.00 V(3rd wave), respectively. Therefore, 1st wave and 2nd waves are 90 mV(quasi-reversible) and 3rd wave is 940 mV(irreversible). The ratio of the cathodic peak current to the anodic peak current(iP_a/iP_c) value of about 1 at 100 mV/s. Accordingly, 1st wave was quasi-reversible but the 2nd and 3rd wave were irreversible.

A reversibility of Co(BPA)₂ was estimated by current values. From above experimental data, the Co(BPA)₂ can be found the quasi-reversible and irreversible reaction. A previous results are shown unstable compound that the values between current and potential gives a relative of the degree.

Fig. 3 shows these variation effects of the scan rate on the chemical reversibility of the Co(II)/Co(I)/Co(0) system of compound. All facts of these observation indicate that molecular oxygen reacts with the Co(I) state of compound and removes it from the electrode surface.

As shown in Fig. 4, the shape and scan rate dependence of the responses is markedly different for dissolved compound. In Fig. 3, 1st and 2nd waves couple reaction gives for the Co(II)/Co(I)/Co(0) couple. Additionally, there is not an approximately linear relationship between peak

current(iP_c) and scan rate(ν) (rather than with $\nu^{1/2}$) over the range 50~500 mV/s for both processes. The main features of the voltammetric response of Fig. 4 were not consistent with diffusion control. Rather, they have the characteristics of thin layer electrochemistry.⁸⁾ This may originate from complete electrolysis of particles which are sufficiently small that diffusion is not relevant and or from the presence of thin layers of electroactive materials on the outer surface of relatively large particles. From the known electrode area, and observed current, we can draw some tentative

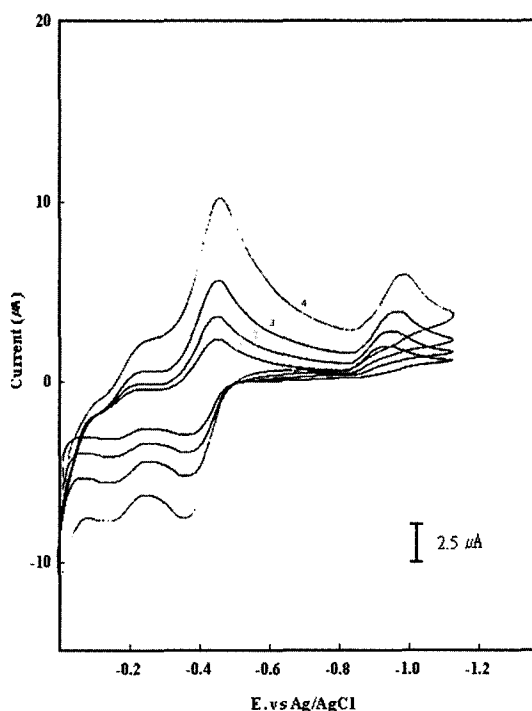


Fig. 3. Cyclic Voltammogram for 1 mM [Co(BPA)₂] redox non-aqueous solution with 0.1 M TEAP supporting electrolyte at 25 °C (scan rate : ① 50, ② 100, ③ 200, ④ 500 mV/s).

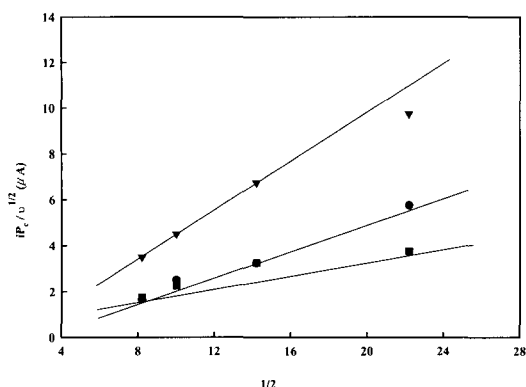


Fig. 4. Plot of the cathodic peak current vs. the square root of the scan rate from cyclic voltammogram for the reduction processes of 1 mM[Co(BPA)2] at 25 °C.

conclusions concerning the physical nature of the electrode state.

3.2. pH Dependence of the Co(II)/Co(I)/Co(0) Couple-Single

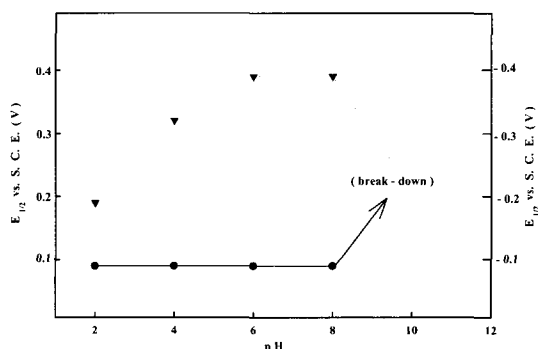


Fig. 5. Plot of $E_{1/2}$ vs. pH for redox couple reaction of [Co(BPA)₂] complex (▲ : reduction ; ● : oxidation ; 1st wave).

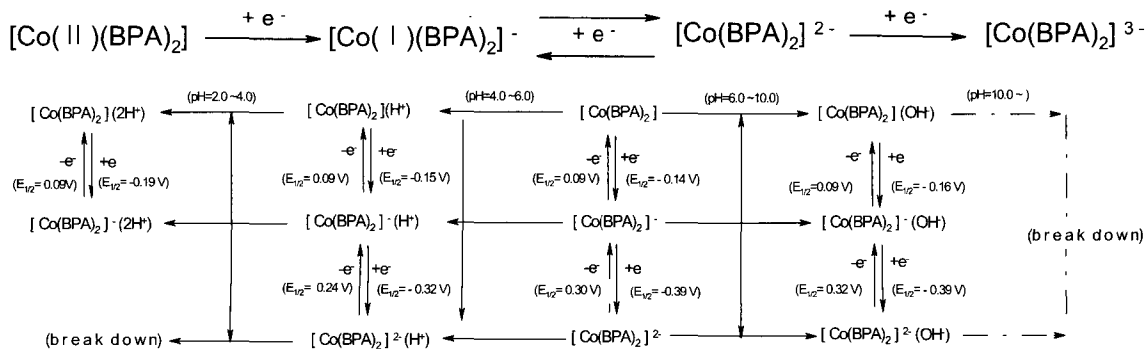
The pH dependence of the Co(II)/Co(I)/Co(0) couple-single for the compound is shown in Fig. 5. The experimental data were obtained from pH dependent cyclic voltammetric measurements. In the diagram the dominant form of the couple with regard to oxidation state and proton composition in the various pH potential regions is indicated. In the labeling scheme abbreviations such as [Co(II)(BPA)₂](H⁺) and [Co(II)(BPA)₂](OH⁻) are used. The proton compositions of the compound was interred by comparing the slopes of the $E_{1/2}$ vs. S. C. E(V). pH lines to values calculated from 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 0 and m is the number of protons gained when n electrons are gained. In term of proton content, the couple varies from below equation at pH 2.0 to at pH 10.0.

3.3. Redox State of Couples

A 1st wave of [Co(BPA)₂] appears at $E_{1/2} = 0.09$ V and $E_{1/2} = 0.19 \sim 0.15$ V(at pH 2.0~4.0) in organo acid(HCOOH). As shown by chemical redox couple by Co(II) the redox process that occurs at this wave is a one electron process corresponding to redox.

3.4. Redox Dependence Relative to pH

From Fig. 5 and Table 3, the potential efficiency of the 1st curve relative to pH was maintained as an cathodic and anodic potential on various at pH. From results in Fig. 5 at pH 2.0, 1st reductive half wave potential at $E_{1/2} = -0.19$ V and oxidative half wave potential at $E_{1/2} = 0.09$ V are observed. In Fig. 2, the voltammogram shows a reduction in the 1st wave at $E_{Pc} = -0.29$ V with an oxidation wave at $E_{Pa} = -0.11$ V and a reduction. And ox-



idation in the 2nd wave at E_{Pc} and $E_{Pa} = 0.0$ V. As above mentioned by the values, the 1st wave was irreversible because of the larger than potential difference at $\Delta E_P = 0.18$ V and the 2nd wave were diminished. A comparison of 0.059 V with $\Delta E_P = 0.18$ V, it was irreversible process because of the larger peak potential difference. At pH = 4.0, 1st reductive half wave potential at $E_{1/2} = -0.32$ V and oxidative half wave potential at $E_{1/2} = -0.32$ V and oxidative half wave potential $E_{1/2} = 0.09$ V And 2nd reductive half wave potential at $E_{1/2} = -0.32$ V and oxidative half wave potential at $E_{1/2} = 0.24$ V are observed. The 1st wave at $E_{Pc} = -0.38$ V and $E_{Pa} = -0.12$ V were observed, whereas the 2nd wave at $E_{Pc} = -0.37$ V and $E_{Pa} = 0.27$ V appeared. These waves were a irreversible process with a peak potential difference of $\Delta E_P = E_{Pc} - E_{Pa} = 0.26$ V (1st wave) and $\Delta E_P = E_{Pc} - E_{Pa} = 0.10$ V(2nd wave). At pH=6.0, 1st reductive half wave potential at $E_{1/2} = -0.39$ V and oxidative half wave potential at $E_{1/2} = 0.09$ V are observed. The 1st wave at $E_{Pc} = -0.44$ V and $E_{Pa} = -0.11$ V, and the 2nd wave at $E_{Pc} = -0.44$ V and $E_{Pa} = -0.35$ V appeared to be irreversible at $\Delta E_{P1}=0.33$ V(1st wave) and $\Delta E_{P2} = 0.09$ V (2nd wave). At pH = 8.0, the 1st reductive half wave potential at $E_{1/2} = -0.38$ V and oxidative half wave potential at $E_{1/2} = -0.09$ V. And 2nd reductive half wave potential at $E_{1/2} = -0.39$ V and oxidative half wave potential at $E_{1/2} = 0.32$ V are observed. These waves were a irreversible process with a peak potential difference of $E_P = E_{Pc} - E_{Pa} = 0.32$ V (1st wave) and $E_P = E_{Pc} - E_{Pa} = 0.09$ V (2nd wave). Above at pH = 10.0 were diminished the two waves. Accordingly, the compound exhibit break down potentials by more than ± 0.5 V. From these results,

we was known that Co(BPA)_2 compound exhibited slowly redox reaction to at pH = 6.0~8.0 more than pH = 2.0~6.0. At this point, the compound showed clearly from potentials of oxidative and reductive decomposition. This compound in waste water is not easy to be degradation and decomposition. On the other hand, from proportionation constant($K_c = 1.02$). This compound is the unstable. And so, it is not easy to be gaseous phase in natural because of it non-volatile properties. But it are readily adsorbed to particulate matters and it may be removed from water in increased sediment concentration.

3.5. Redox Dependence Relative to Temperature

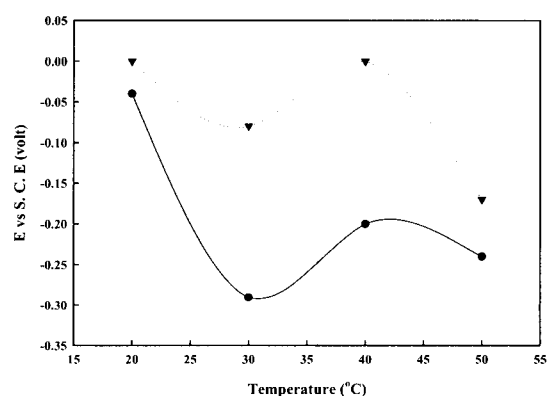


Fig. 6. Plot of $E_{1/2}$ vs. temperatures redox reaction of Co(II) complex(where ; \blacktriangle : 1st wave ; \bullet : 2nd wave).

Table 3 and Fig. 6 is plotted of half-wave potential($E_{1/2}$) value against at the temperatures. It was based on data Table 3 obtained from redox

Table 3. Redox Characterization of Co(II) complex in DMSO Solvent(scan rate : 100 mV/s)

Redox waves	pH					°C				
	2.0	4.0	6.0	8.0	10.0	20	30	40	50	
1st	-0.19 (0.09)	-0.32 (0.09)	-0.39 (0.09)	-0.38 (0.09)	break down	-0.04 0.0	-0.29 -0.08	-0.20 0.0	-0.24 -0.17	
2nd	0.0 (0.0)	-0.32 (0.24)	-0.39 (0.30)	-0.39 (0.32)	break down					

() : oxidation potential value

Redox reactions	Acid	Base
Oxidation	$2\text{HCOOH} \rightarrow 2\text{HCHO} + \text{O}_2$	$\text{HCOOH} + \text{NaOH} \rightarrow \text{HCOONa} + \text{H}_2\text{O}$ $2\text{H}_2\text{O} \rightarrow 2\text{H}^+ + 2\text{OH}^-$ $2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H} \rightarrow \text{H}_2$ $4\text{OH}^- - 2\text{e}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2$
Reduction	$2\text{HCOOH} \rightarrow 2\text{H}^+ + 2\text{COOH}^-$ $2\text{COOH}^- \rightarrow 2\text{CO}_2 + \text{H}_2$	$\text{HCOOH} + \text{NaOH} \rightarrow \text{HCOONa} + \text{H}_2\text{O}$ $\text{HCOONa} + \text{H}_2\text{O} \rightarrow \text{NaOH} + 2\text{H}^+ + \text{CO}_2$

potentials derived with the voltammogram curves relatives to temperature. These reactions would appear to negative potentials of the all temperatures. These waves were maintained by the negative potential at all temperatures. Redox potential 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). From the 1st wave of redox tests exhibited distinctly an only zero potential values at 20 °C and 40 °C. It conclude that the product of non-electroactive. The redox potential values of compound were obtained highest at 20 °C, lowest at 30 °C, and less than from at 40 °C to 50 °C. Here, we was known that it exhibited rapidly of oxidative or reductive and decomposition at 20°C. However, it showed slowest at 30 °C. Therefore, at this point, such a phenomenon which occurs in natural is given by temperature and it showed clearly of oxidative or reductive and decomposition with potential($E_{1/2}$) responses.

These assignments were based on the fact that at pH are actively H^+ and OH^- ion in nonaqueous solution. Redox reactions, we can be proposed as the follows.

4. Conclusions

One electron charge transfer from the redox processes was obtained by coulometric with $n = 1.02$ value. $E_{1/2}$ and E_p values of DPP and CV method are not coincidence to all the steps, but it is found that the difference of potential values are given in the region 0.03 V. However, (E_p)₂ - ($E_{1/2}$)₁ = -0.57 V value obtained by two method was found with a good agreement clearly. The comproportionation constant(K_c) obtained by differential pulse polarography method was 1.03. The redox reaction of compound was obtained to

couple of 1st step and single of 2nd step wave. The 1st wave was a quasi-reversible and with a irreversible of 2nd wave. We was known kinetically slow by the diminished peak heights of the anodic and cathodic peak current compared to those of the Co(II)/Co(I) couple reaction. Above at pH = 10.0 were diminished the two waves. Accordingly, the compound exhibited break down potentials by more than ± 0.5 V. The bis-phenol A in the waste water was made to compound with cobalt ion and it take away from the separation into compound. This compound was not found to be dissociation in waste water. It was focused the effects of contaminants on human health, environment, and ecological research. It is not easy to be aqueous phase in natural because of its non-volatile properties. But it was readily absorbed to particulate matters and it may be removed from water in increased sediment concentration. We was known that it exhibited rapidly of oxidative or reductive and decomposition at 20 °C.

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