

## Study on Redox State of Environmental Pollutant

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The chemical behavior and properties related to the redox state of environmental pollutants were investigated using electrochemical methods. Measurements were taken of variations in the redox potential and cyclic polarization current. The results established the influence of various factors, including concentration, temperature, salt, and pH, on the redox potential and current. These factors were determined to effect the result of the redox reaction. Optimum conditions were also established for each case. It was clearly established that the electrode reaction was from a reversible to an irreversible process, plus it was also mixing reaction current controlled.

Key words : redox potential, cyclic polarization, mass transfer coefficient, irreversible

### 1. Introduction

Most toxicology and epidemiology studies on environmental contaminants focus on a single substance brought into the body by one means, for example, breathing, ingestion, or absorption through the skin. However, in the real world, people are exposed to a myriad of chemicals that can enter the body through more than one pathway. One unknown is whether the concentration of a pollutant in the environment is related to how much actually ends up in the human body. The US Environmental Protection Agency (US EPA) is attempting to gather information on human exposure through various pathways to several classes of chemicals, such as pesticides and metals. As such, the Agency is in the midst of a pilot effort designed to lay the groundwork on how such data can be gathered. Traditionally, the EPA has only monitored the concentration of a particular chemical contaminant in the environment. However, the new initiative will attempt to provide a link between environmental concentrations of pollutants and human exposure, as environmental contaminants do actually end up in human bodies. In addition, the EPA can use the data to determine exactly how people are exposed, for example, through diet, drinking water, air, or skin contact, and which

activities bring them into contact with a particular pollutant. The EPA 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 included polycyclic aromatic hydrocarbons. The chemicals investigated in the study 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 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 analyzed blood and urine samples taken from NHEXAS participants. The levels of the target chemicals were also measured in the air the volunteers breathed, in the foods and beverages they consumed, and the soil and dust around their houses. A 1997 study connected to the NHEXAS work in six midwest states focused on the exposure of children to pesticides<sup>1)</sup>. 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<sup>2)</sup> 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. This, 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<sup>3)</sup>. 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 these data. An investigation was also conducted on Sum Jin river(Hadong in Kyung Nam) and Eui Am lake(Chun-Cheum in Kang Won) where researchers measured the level of the 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<sup>4)</sup>, including persistent organochlorine pesticides, polychlorinated biphenyls, dioxine, bis-phenol A<sup>5)</sup>, di(2-ethylhexyl)phthalate, tributyltin, polybiphenylchloride, and hexachlorobenzene etc. As a result, an environmental hormone was reported from the synthesized materials. The current study also investigates the detailed influence of various conditions on contaminate materials(bis-phenol A).

## 2. Materials and Methods

### 2.1. Materials and Instrumentation

All reagents and solvents were purified according to conventional procedures. Reagent grade Bis-Phenol A (99.0 % purity : Aldrich Co) was used without any further purification and was kept in a glovebox under an argon atmosphere prior to use.

### 2.2. Electrochemical Experiments

All the chemical reagents were high purity grade. Tetraethylammoniumperchlorate(TEAP : Aldrich), used as a supporting electrolyte, was dried at 80 °C under a vacuum for 3 days. The experimental solutions were deoxygenated by purging for at least 15 min with prepurified nitrogen gas.

The cyclic voltammograms were recorded using a PARC Model-303A static mercury dropping electrode(SMDE) and PARC 264A polarographic analyzer equipped with a PARC Model KE-0089 XY recorder. A three-electrode cell consisting of a working electrode, platinum-wire counter electrode, and silver/silver chloride reference electrode was used. The reference electrode was kept in a compartment containing the appropriate supporting electrolyte(TEAP) freshly dropped with mercury, and a platinum wire as the counter electrode.

## 3. Results and Discussion

### 3.1. Electrochemical Studies

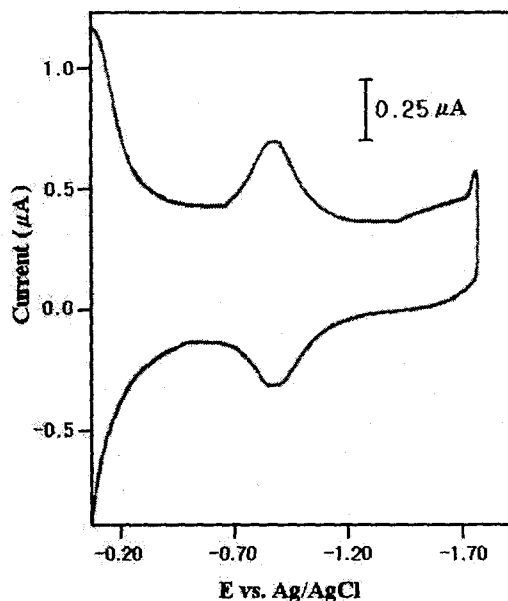


Fig. 1. Cyclic voltammogram for 1 mM bis-phenol A reduction in aqueous solution with 0.1 M TEAP supporting electrolyte at 25 °C.(scan rate : 500 mV/s)

The electrochemical measurements were performed under a nitrogen atmosphere. The concentration of the supporting electrolyte was typically 0.1 M TEAP. Fig. 1 shows a voltammogram of bis-phenol A, which clearly shows it to be distinct from a two wave. Plus, two well defined reduction processes were seen within the aqueous electrolyte limit with each redox process exhibiting evidence of chemical reversibility.

The first redox system only showed features of a couple of the organo materials, whereas the second system exhibited a single wave. Exhaustive electrolysis also showed the redox species to be stable under nitrogen, thereby enabling various physical measurements. Besides the bis-phenol A redox couple, a second cathodic wave appeared with a cathodic peak potential at -0.82 V (scan rate 500 mV/s). The first couple curve showed a distinct chemical reversibility with a redox peak, at -0.82 V. The second curve showed that the oxidation peak diminished from anodic and the reduction peak was only slight, plus there was a single cathodic peak at -1.60 V. Therefore, the second curve exhibited irreversibility. The above are two examples of reversibility from the redox potentials, further individual cases are discussed below in section 3.6.

### 3.2. Influence of Concentration on Redox Reaction

The cyclic voltammetry characteristics of bis-phenol A are summarized in Table 1. The 1st and 2nd waves relative to a variation in concentration are shown in Fig. 2, which were taken using the cathodic potentials at a scan rate of 500 mV/s. As shown in Fig. 2, the potential efficiency of the 1st wave exhibited negative potentials at all concentrations [1 mM( $E_p = -0.80$  V), 3 mM( $E_p = -0.16$  V), 5 mM( $E_p = -0.19$  V), 7 mM( $E_p = -0.22$  V), and 9 mM( $E_p = -0.25$  V)]. Except for 3 mM( $E_p = -0.16$  V), the cathodic potential progressively increased when increasing the concentration. Based on the data from this experiment, it would appear that the product of nonelectroactivity either impedes the oxidation of hydrogen ions in the solution or is exposed to a depleted reactant in the diffusion layer adjacent to the electrode.

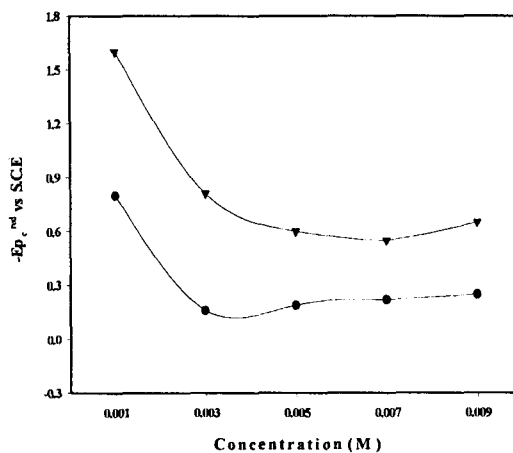


Fig. 2. Variation of concentration and reduction potential for bis-phenol A at 25 °C. (● : 1st wave, ▼ : 2nd wave)

As shown in Fig. 2, the potential efficiency of the 1st wave exhibited negative potentials at all concentrations [1 mM( $E_p = -0.80$  V), 3 mM( $E_p = -0.16$  V), 5 mM( $E_p = -0.19$  V), 7 mM( $E_p = -0.22$  V), and 9 mM( $E_p = -0.25$  V)]. Except for 3 mM( $E_p = -0.16$  V), the cathodic potential progressively increased when increasing the concentration. Based on the data from this experiment, it would appear that the product of nonelectroactivity either impedes the oxidation of hydrogen ions in the solution or is exposed to a depleted reactant in the diffusion layer adjacent to the electrode.

In contrast, with the 2nd wave higher reduction potentials occurred at all concentrations, [(1 mM( $E_p = -1.60$  V), 3 mM( $E_p = -0.81$  V), 5 mM( $E_p = -0.60$  V), 7 mM( $E_p = -0.55$  V), and 9mM ( $E_p = -0.65$  V)]. Accordingly, the results were not concentration dependent, thereby implying the presence of both surface and bulk solution processes<sup>6</sup>.

### 3.3. Influence of Temperature on Redox Reaction

As shown in Fig. 3 and Table. 1, Fig. 3 was

Table 1. Electrochemical data for Bis-phenol A in aqueous solution

Condition Redox steps	Concentration				Temperature				Temperature (0.35% Salt)				pH					
	(1 mM)				(°C)				(°C)				(1 mM, 25°C)					
	1	3	5	7	9	25	35	45	55	25	35	45	55	3.0	5.0	7.0	9.0	11.0
1st wave	-0.80	-0.16	-0.19	-0.22	-0.25	-0.16	-0.15	-0.14	-0.13	-1.01	-1.01	-0.98	-1.01	-0.13	-0.14	0.00	0.00	0.00
2nd wave	-0.16	-0.81	-0.60	-0.55	-0.65	-0.85	-0.82	-0.81	-0.80	-1.53	-1.53	-1.46	-1.53	-0.83	-1.13	-0.78	-1.05	-1.25

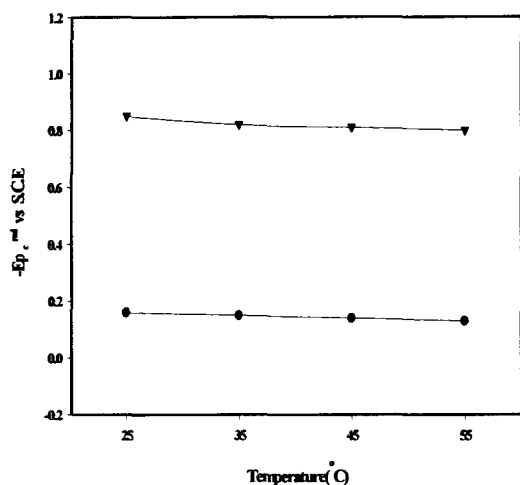


Fig. 3. Variation of reduction potential relative to temperature for 1 mM bis-phenol A. (● : 1st wave, ▼ : 2nd wave)

based on redox potential data derived from voltammogram curves relative to temperature. Therefore, as previously mentioned, the reactions all exhibited a negative potential in the bis-phenol A solution. The redox processes consisted of two-step waves that were chemical reduction processes. Fig. 3 shows that for each peak potential value, the series of redox tests produced their own distinct negative potential values. The results are summarized in Table 1. Fig. 3 and Table 1 will be discussed in more detail below. Reduction did occur with the 1st and 2nd curves as follows at 25°C ( $E_{pc1} = -0.16$  V ;  $E_{pc2} = -0.85$  V), 35°C ( $E_{pc1} = -0.15$  V ;  $E_{pc2} = -0.82$  V, 45°C ( $E_{pc1} = -0.11$  V ;  $E_{pc2} = -0.81$  V), and 55°C ( $E_{pc1} = -0.13$  V ;  $E_{pc2} = -0.80$  V). These results were based on the fact that the cathodic reaction at all temperatures consisted of a reduction of hydrogen ions to hydrogen in an aqueous solution. Reduction tests were carried out to determine the effect of temperature variation on the reduction potential and compare the potential differences at different temperatures. A shift in the potential was observed with an increase in temperature. However, this was less than the negative potential. The reduction potential gradually indicated lower values when the temperature increased regularly. Accordingly, the reduction efficiency of temperature was that it gradually decreased with an increase in temperature.

#### 3.4. Influence of Temperature plus Added Sodium Chloride on Redox Reaction

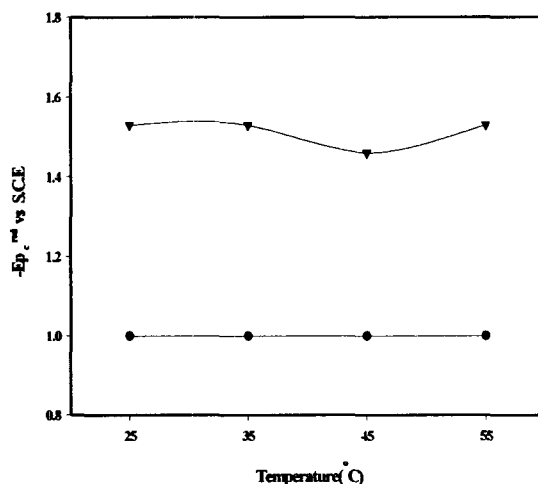


Fig. 4. Variation of temperature and reduction potential in the presence of 0.35 % NaCl with 1 mM bis-phenol A. (● : 1st wave, ▼ : 2nd wave)

As shown in Fig. 4, the two reduction processes observed clearly corresponded to the first two reduction steps observed in the aqueous solution. Finally, it should be noted that there was a complex formation between the magnesium ion existing in the salt and the bis-phenol A in the aqueous solvent. However, there was a significant potential variation. As shown in Fig. 4 and Table 1, the 1st and 2nd curves exhibited consistent values at 25°C ( $E_{pc1} = -1.01$  V ;  $E_{pc2} = -1.53$  V), 35°C ( $E_{pc1} = -1.01$  V ;  $E_{pc2} = -1.53$  V), and 55°C ( $E_{pc1} = -1.01$  V ;  $E_{pc2} = -1.53$  V), respectively. Yet this occurred at a value lower than negative potential at 45°C ( $E_{pc1} = -0.98$  V ;  $E_{pc2} = -1.46$  V). Overall, this means that the lines representing the anodic dissolution only shifted slightly in the inert potential direction based on the pH and temperature<sup>7,8</sup>. Accordingly, the reduction efficiency of salt exhibited a slow reduction due to a complex formation with magnesium ion within the salt. Therefore, it was concluded that the immobilization of the electroactivity<sup>9</sup> of the added salt was successful.

#### 3.5. Effect of pH on Redox Reaction

From Fig. 5 and Table 1, the potential efficiency

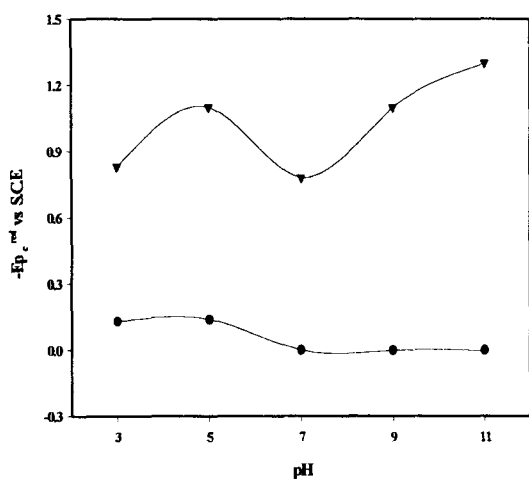


Fig. 5. Variation of reduction potential relative to pH at 25 °C. (● : 1st wave, ▼ : 2nd wave)

of the 1st and 2nd curves relative to the pH was maintained as an cathodic potential with various pHs. The reduction potential shifted to a negative potential with the 1st and 2nd curves as follows : pH 3.0( $E_{pc1} = -0.13$  V ;  $E_{pc2} = -0.83$  V), pH 5.0( $E_{pc1} = -0.14$  V ;  $E_{pc2} = -1.13$  V), pH 7.0( $E_{pc1} = 0.00$  V ;  $E_{pc2} = -0.78$  V), pH 9.0( $E_{pc1} = 0.00$  V ;  $E_{pc2} = -1.05$  V), and pH 11.0( $E_{pc1} = 0.00$  V ;  $E_{pc2} = -1.25$  V), respectively. At first, two reduction steps were observed in the acid solution(from pH 3.0 to 5.0). From the results in

Fig. 5, at pH 5.0 the reduction potential values started to indicate a more negative value than at pH 3.0( $E_{pc1} = -0.14$  V ;  $E_{pc2} = -1.13$  V) they shifted to a negative potential. In contrast, two reduction steps were observed in the alkaline solution(from pH 9.0 to 11.0). There was a significant variation in the potentials at pH 9.0( $E_{pc1} = 0.00$  V ;  $E_{pc2} = -1.05$  V) and at pH 11.0( $E_{pc1} = 0.00$  V ;  $E_{pc2} = -1.25$  V). The 1st step curve maintained a consistent linear dependence on the potential, yet the 2nd step curve exhibited a higher value than the negative potentials. These results were based on the fact that  $H^+$  and  $OH^-$  ions are active in the aqueous solution relative to the pH. As such, reduction reactions were confirmed at pH 3.0 and pH 11.0.

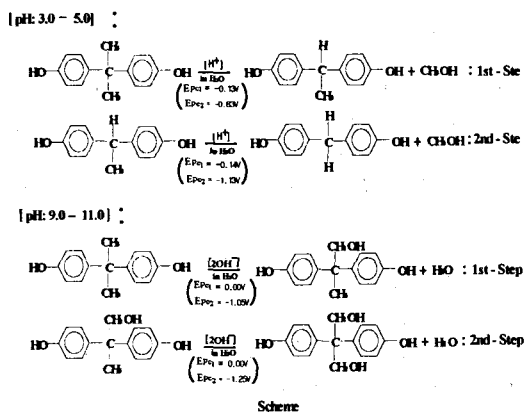
### 3.6. Reversibility of Potentials Relative to Scan Rate in Redox Reaction

From Table 2 showing two redox(single or couple) processes, the  $E_{1/2}$  values are obtained using  $E_{1/2} = E_{pc} + E_{pa}/2$  equation from the cyclic voltammogram<sup>10</sup>.

A comparison of the half wave potential for each condition revealed that with aspects of the electrochemical method there was a significant variation in the currents and potential( $\Delta E_p$ ) values. Except for the temperature(25 °C : 0.16 V) and

Table 2. Electrochemical data to the optimum for Bis-phenol A in aqueous solution

Condition	Redox steps	$E_{1/2}$	$E_{pc}$	$E_{pa}$	$\Delta E_p$	$iP_c$	$iP_a$	$iP_a/iP_c$ (sweep rate)					
								$iP_d/v^{1/2}$	$iP_a/v^{1/2}$	$iP_c/v^{1/2}$	$iP_a/v^{1/2}$	$iP_c/v^{1/2}$	$\mu A/(mV/S)^{1/2}$
Concentration (1 mM)		-0.72	-0.80	-0.78	0.02	0.20	0.18	0.90	0.01	0.02	0.01	0.01	0.03
Temperature (25 °C)	1st wave	-0.09	-0.16	0.00	0.16	1.00	0.00	0.90	0.01	0.02	0.03	0.05	0.04
pH(5.0)		-0.28	-0.13	0.05	0.08	0.13	0.15	0.15	0.01	0.01	0.02	0.01	0.03
Salt (0.35% NaCl)		-0.83	-1.01	-0.96	0.05	0.15	0.14	0.93	0.01	0.02	0.03	0.01	0.02
Concentration (1 mM)		-0.85	-1.60	-1.38	0.22	0.18	0.05	0.30	0.01	0.01	0.03	0.01	0.02
Temperature (25 °C)	2nd wave	-0.85	-0.85	-0.81	0.04	0.25	0.15	0.60	0.01	0.02	0.02	0.01	0.03
pH(5.0)		-0.99	-0.13	-1.10	0.03	0.13	0.15	0.15	0.01	0.03	0.03	0.01	0.02
Salt (0.35% NaCl)		-1.38	-1.53	-1.46	0.07	0.18	0.03	0.17	0.01	0.02	0.02	0.01	0.03



added NaCl(0.35 % : 0.22 V), see Table 2, the varying conditions were generally smaller than the expected values for diffusion controlled processes. Larger  $\Delta E_p$  values were associated with larger currents than the reaction currents. There was always an approximate value dependence between the cathodic and anodic potentials. A qualitative inspection of the 1 mM concentration experiment clearly indicated a reversible with the 1st wave(20 mV) process and an irreversible with the 2nd wave(220 mV) process. The  $\Delta E_p$  values for the 1st and 2nd potentials with a temperature of 25 °C were distinct with an irreversible(1st wave : 160 mV) and reversible(2nd wave : 40 mV) process. Plus, the  $\Delta E_p$  values for the 1st and 2nd potentials at pH 5.0 were obtained through a quasi-reversible(1st wave : 80 mV) and reversible(2nd wave : 30 mV) process. Also, the  $\Delta E_p$  values for the 1st and 2nd potentials with added salt(0.35 % sodium chloride) were distinct with an reversible(1st wave : 50 mV) and quasi-reversible(2nd wave : 70 mV) process.

Table 3. Electrochemical data for Bis-Phenol A<sup>a</sup> in aqueous solution

Redox steps	Sweep rate(mV/s)	$E_{Pc}$	$E_{Pa}$	$\Delta E_p$	$i_{Pc}$	$i_{Pa}$	$i_{Pa}/i_{Pc}$	$i_{Pd} \nu^{1/2}$
		(V)	(V)	(mV)	( $\mu A$ )	(V)		( $\mu A/(mV/S)^{1/2}$ )
1st wave	50	-0.78	-0.74	40	0.04	0.03	0.75	0.01
	100	-0.79	-0.75	40	0.06	0.05	0.83	0.01
	200	-0.81	-0.77	40	0.10	0.08	0.80	0.01
	500	-0.82	-0.79	30	0.28	0.25	0.89	0.01
	1000	-0.83	-0.81	20	0.67	0.50	0.75	0.02
2nd wave	50	-1.50	0.00	0.00	0.08	0.00	0.00	0.01
	100	-1.54	0.00	0.00	0.08	0.00	0.00	0.01
	200	-1.56	0.00	0.00	0.08	0.00	0.00	0.01
	500	-1.58	0.00	0.00	0.15	0.00	0.00	0.01
	1000	-1.60	0.00	0.00	0.25	0.00	0.00	0.01

### 3.7. Kinds of Current in Redox Reaction

Parts ① to ⑤ in Fig. 6 show the cyclic voltammograms recorded at a respective scan rate of 1 mM bis-phenol A. As such the peaks can be assigned to forward and reverse reactions. A linear dependence of the cathodic peak current( $i_{Pc}$ ) on the square root of the scan rate( $\nu^{1/2}$ ) was found. Based on the current characteristics from a plot of  $i_{Pc}$  with  $\nu^{1/2}$ , as shown in Fig. 7 and Table

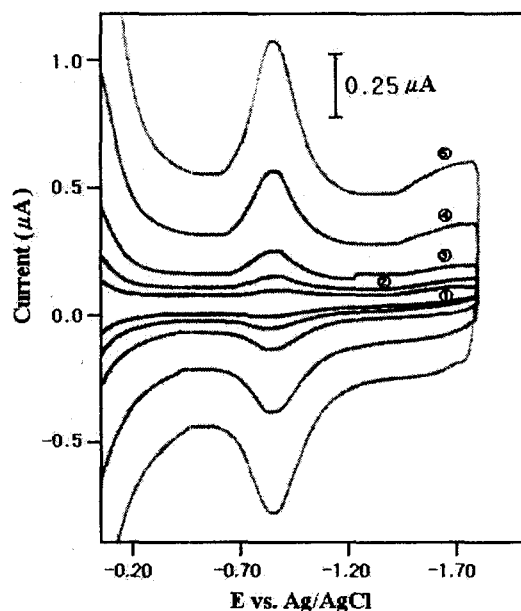


Fig. 6. Cyclic voltammogram for 1 mM bis-phenol A reduction in aqueous solution with 0.1 M TEAP supporting electrolyte at 25 °C.(scan rate: ① 50 mV/s ② 100 mV/s, ③ 200 mV/s, ④ 500 mV/s, ⑤ 1000 mV/s)

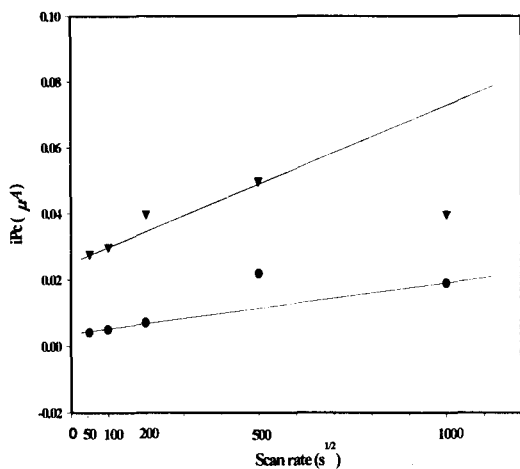


Fig. 7. Plot of cathodic peak current ( $iP_c$ ) vs. a square root of scan rate ( $\nu^{1/2}$ ) with 1 mM bis-phenol A in aqueous solution (0.1 M TEAP supporting electrolyte) at 25 °C. (● : 1st wave, ▼ : 2nd wave)

3, there was no unity between the  $iP_c$  and  $\nu^{1/2}$  values. In addition, there was no approximate linear relationship between the peak current ( $iP_c$ ) and the scan rate ( $\nu^{1/2}$ ). Therefore, it was evident that the electrode reaction of this species of bis-phenol A was not a diffusion controlled reaction<sup>11</sup>. Consequently, the results were mixed reaction current controlled.

#### 4. Conclusions

Two well defined reduction processes were clearly exhibited in cyclic voltammograms of bis-phenol A in a TEAP supporting electrolyte. The 1st couple curve showed a distinct chemical reversibility with a redox peak, whereas the 2nd curve was irreversible. The results were not concentration dependent, thereby implying the presence of both surface and bulk solution processes. The reduction efficiency of the temperature decreased the a gradual increase in

temperature. The effect of temperature on the addition of NaCl, resulted in a complex formation between the magnesium ion in the NaCl and the bis-phenol A in the aqueous solution. In addition, the immobilization of the electro-activity of the added salt was successful. The activity of the  $H^+$  and  $OH^-$  ions in the aqueous solution was found to be relative to the pH. The reversibility of the cathodic peak current with the scan rate was mixed reaction current controlled.

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