Electrochemical behavior of Bisphenol A (4,4'-Isopropylidenediphenol) in the Presence of Fe(III) Species

Eriko Shimada, Michiko Ohya, Ysuro Ikuma, Tsuneo Watanabe*, and Koji Tachibana**

Dept. of Applied Chemistry, Kanagawa Institute of Technology, 1030 Shimo-ogino, Atsugi, Kanagawa 243-0292, Japan
Fax: +81-46-242-8760, e-mail: shimada@chem.kanagawa-it.ac.jp
*Dept. of Electrical Engineering, Grad. School of Engineering, Tokyo Metropolitan University,
Minamiosawa, Hachioji, Tokyo 192-0397, Japan
Fax: +81-426-77-2737, e-mail: *tsuneo@eei.metro-u.ac.jp*
**Dept. of Chemistry, Faculty of Science, Science University of Tokyo, 1-3 Kagurazaka, Shinjuku Tokyo 162-0825, Japan
Fax: +81-3-3235-2214, e-mail: ktachiba@ch.kagu.sut.ac.jp

We examined using bisphenol A (4,4'-isopropylidenediphenol), which is well-known to be suspected one of endocrine disruptors. By means of cyclic voltammetry, oxidation kinetics were analyzed of free bispenol A and adsorbing bisphenol A to Fe(III)colloidal species at pH =1.3. The electrochemical oxidation reaction was irreversible. The kinetics of oxidation of adsorbing bisphenol A to Fe(III)colloidal species were estimated as kinetic parameters of the transfer coefficient and the number of electrons for the rate determining step, comparing free bisphenol A. The results suggested the electron transfer rate of bisphenol A became slower by adsorption onto Fe(III)colloidal particle.

Key words: colloid, bisphenol A, endocrine disruptor, kinetic parameter, cyclic voltammetry

1. INTRODUCTION

Recently, an effective method has been developed to purify filthy water from reclamation lands, which has electrolysis preprocesses using Fe electrodes and strong magnetic separation processes [1]. The electrolysis preprocesses are expected to create paramagnetic or ferromagnetic colloidal particles adsorbed with organic compounds, however, the actual reactions have not been analyzed in detail. It is necessary to clarify actual electrode reactions, their current efficiencies, and factors altering an amount of adsorption, such as size and surface potential of adsorbent colloid, functional group of organic compound (adsorbate), pH and so on.

In this work, we studied using Fe(III) colloidal species (ferric hydroxide sol) with controlled particle size and bisphenol A (4,4'-isopropylidenediphenol), which is suspected to be one of endocrine disruptors, under controlled pH. Our purpose in this paper is to analyze kinetically the difference in the electrochemical behavior of free bisphenol A from adsorbing bisphenol A to Fe(III) colloidal species.

2. EXERIMENTAL

Fe(III) colloidal species, ferric hydroxide sol solution was prepared by means of the usual hydrolysis method [2]. Boiling deionized water and dense $FeCl_3$ aqueous solution ($FeCl_3 \cdot 6H_2O$, Kanto Chemical Co., reagent grade) were used for the preparation of the Fe(III) colloid solution. Bisphenol A used was also

reagent grade. The electrochemical measurement was carried out using Potentio/galvanostat NP-G1002ED and Potential scanner ES-512A (Nichia Keisoku Kogyo). The potential scan rates were in the range of 0.01 ～0.5 mV/sec. Cyclic voltammetry was performed at room temperature around 25°C and under N_2 atmosphere. A saturated KCl-Ag/AgCl electrode was used as reference electrode. Pt disk electrode of our own making (2mm in diameter), which was polished with Al_3O_2 fine particles (0.05 μ m particle size) before every experiment, was used as working electrode. Pt coil electrode with sufficient surface area was used as counter electrode. Clark-Lubs buffer solution (the mixture of an appropriate proportion of 0.2mol/dm³ KCl and 0.2mol/dm³ HCl) was prepared and applied to keep the pH of experimental solution at 1.3, as same as the Fe(III) colloidal species solution. Taking into account of the pKa for phenol (pKa=9.98), both of the two phenolic hydroxyl groups in bisphenol A molecule are considered not to dissociate at such pH. In addition, the buffer solution was also acted as supporting electrolyte solution.
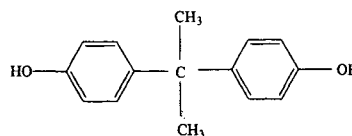
The structure of bisphenol A
(4,4'-isopropylidenediphenol)

The mixture of Fe(III) colloidal species and bisphenol A was prepared not to leave free bisphenol A, that is, the concentration of bisphenol A was $5 \times 10^{-5} \sim 2 \times 10^{-4}$ mol/dm^3 against 1×10^{-2} mol/dm^3 of concentration as Fe atom. Other chemicals used were reagent grade(Kanto Chemical, Co.).

The colloidal particle sizes were measured with light scattering method using Beckman Coulter, DELSA 440SX.

3. RESULTS AND DISCUSSION

3.1 Colloidal particle sizes

The particle sizes of only Fe(III) colloidal species solution and the mixture of bisphenol A and Fe(III) colloid solution were shown in Fig.1. The Fe(III) colloid was relatively uniform around 270nm particle size. The colloid size of mixed solution of Fe(III) colloid and same concentration of bisphenol A was larger than that of only Fe(III) colloid. Though this ratio of bisphenol A in the mixture was larger than that used in electrochemical experiments, it was found that bisphenol A and Fe(III) colloid particles attached each other and the particle size became larger.
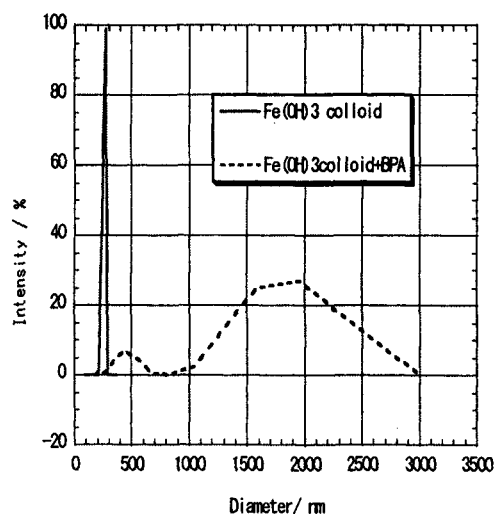

Fig. 1   Collodal particles sizes of free Fe(III) colloid and Fe (III) colloid adsorbed with bisphenol A. 'Fe(OH)3 colloid' is Fe (III) colloid, 'BPA' is bisphenol A.

3.2 Cyclic voltammetry

Some examples of the cyclic voltammograms of bisphenol A solution, Fe(III) colloid solution, and mixture of Fe(III) colloid and bisphenol A solution were illustrated in Figs.2a-c. In Fig.2a, for the first scanning an oxidation peak around 900mV(vs. saturated KCl - Ag/AgCl reference electrode) of the free bisphenol A was observed irreversibly. In Fig.2c, the cyclic voltammogram of the mixture of Fe(III) colloid and

bisphenol A showed a similar peak for the first scanning. The voltammogram of only Fe(III) colloidal species had no peak around 900mV (Fig.2b).
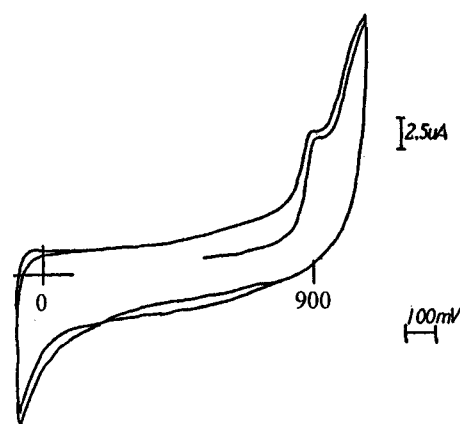

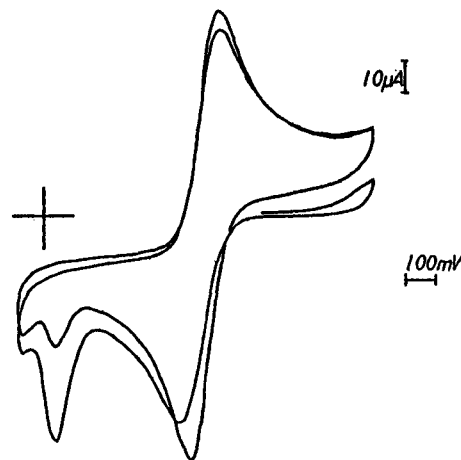Fig. 2a Cyclic voltammogram of of free bisphenol A at pH 1.3. scan rate:0.4V/sec.

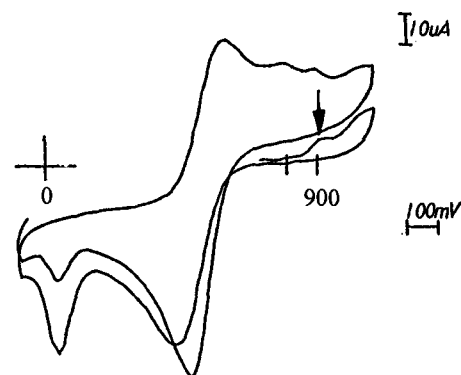Fig. 2b Cyclic voltammogram of of Fe (III) colloid at pH 1.3. scan rate: 0.4V/sec.

Fig. 2c Cyclic voltammogram of of Fe (III) colloid and bisphenol A at pH 1.3. scan rate: 0.4V/sec.

The oxidation peak around 900mV in Fig.2c was considered to show the oxidation of adsorbing bisphenol A to Fe(III) colloidal particle. In the mixture solution all the bisphenol A were considered to adsorb to Fe(III) colloidal particle because the peak current i_p was not changed with increasing the concentration of bisphenol A to $2x10^{-4}$ from $1x10^{-4}$ mol/dm^3 and was decreased with decreasing bisphenol A to $5x10^{-5}$mol/dm^3. If there were not only adsorbing bisphnol A to Fe(III) coloid but also free bisphenol A in the mixture solution, the i_p should increase simply. This result suggested that the Fe (III) colloid adsorbed with bisphenol A of a certain surface concentration on the particle might grow keeping adsorbate surface concentration. The bulk concentration of bisphenol A giving such a certain surface concentration on the particle was considered around $1x10^{-4}$mol/dm^3 in our experimental condition. It is noteworthy that the cyclic voltammogram for mixture of Fe(III) colloid and bisphenol A has a small oxidation wave at lower potential than free bisphenol A(Fig 2c).

The electrochemical oxidation of bisphenol A were analyzed by using the following equations (25℃)[3][4][5] for general irreversible electrochemical reaction.

$$i_p = 0.227x10^{-3}nFACk \exp[\alpha n_a F/RT(E_p-E_{1/2})]   (1)$$

where k is a rate constant of an electrode reaction, E_p is a peak potential, $E_{1/2}$ is a formal potential, A is an electrode surface area, C is a concentration of a reactant in bulk, α is a transfer coefficient, n_a is a number of electrons for a rate determining step, n is a total number of electrons for a reaction, F is Faraday's constant, R is the gas constant and T is a temperature.
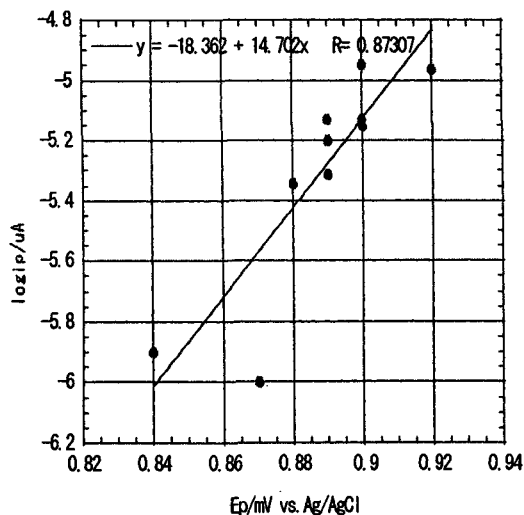
Kinetic comparison of free bisphenol A and adsorbing bisphenol A to Fe(III) colloidal particle was performed as estimation of the parameter αn_a. The slope of the plots of log i_p vs. E_p gives αn_a. In this study, the peaks around 900mV for the solutions containing $5x10^{-5}\sim 1x10^{-4}$ mol/dm^3 bisphenol A were used for analysis of the oxidation kinetics of bisphenol A. Figures 3 and 4 show the plots of free bisphenol A and adsorbing bisphenol A to Fe(III) colloidal particle, respectively. The slope for adsorbing bisphenol A to Fe(III) colloidal particle was 1.6 times larger than that for free bisphenol A. It shows that the αn_a for adsorbing bisphenol A to Fe(III) colloidal particle was 1.6 times larger than free bisphenol A. That is, the electron transfer from bisphenol A at rate determining step changed slower by adsorbing to Fe(III) colloidal particle. This result was corresponding to the appearance of small oxidation wave described above. It is possible to explain that the two phenolic hydroxyl groups of bisphenol A molecule did not become equivalent by adsorbing to Fe(III) particle.
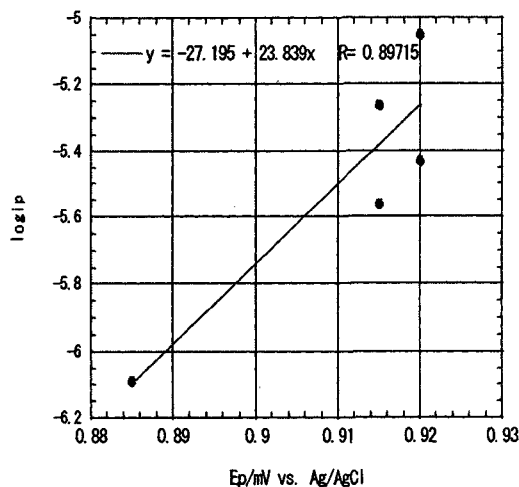

Fig.4   Plots of log i_p vs. E_p for adsorbing bisphenol A to Fe(III) colloid at pH1.3.

Fig.3 Plots of log i_p vs. E_p for bisphenol A at pH1.3 .

4 Conclusion

We studied kinetically the electrochemical behavior of free bisphenol A and adsorbing bisphenol A to Fe(III) colloidal species (ferric hydroxide sol) with colloidal particle size. To analyze the kinetics, cyclic voltammetry was performed using aqueous solutions of controlled pH 1.3 containing bisphnol A and/or Fe(III) colloid. The oxidation peak of bisphnol A was observed around 900mV (vs. saturated KCl -Ag/AgCl reference electrode) irreversibly. The parameter of αn_a (α : transfer coefficient, n_a: number of electrons for the rate determinating step) for adsotbing bisphenol A to

Fe(III) colloidal particle was larger than free bisphenol A. It was suggested that the electron transfer rate of bisphenol A became slower by adsorbing to Fe(III) colloidal particle.

References
[1] T. Watanabe, Abstract of Workshop on Superconducting Magnetic Separation, 25(2000).
[2] M. Nakagaki, " Modern physical chemistry course 9-Surface and colloid states", Vol. 1, p. 246, Tokyo Kagaku-dojin, Co., Tokyo (1968).
[3] A. Fujishima, M.Aizawa and T. Inoue, "Electrochemical Methods", Vol.1, 160, Giho-do, Co., Tokyo (1991).
[4] H. Matsuda, Y. Ayabe, Z. *Elektrochem.*, **58**, 494 (1995).
[5] E. Shimada, K. Goto, Y. Ikuma and K. Tachibana, *Transactions of Materials Research Society of Japan*, **24**,485(1999).