

Full Paper

Electrochemical Studies of Bisphenol-A at Sodium Alpha Olefin Sulfonate Modified Carbon Paste Electrode: A Voltammetric Study

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Abstract- An anionic surfactant sodium alpha olefin sulfonate (SAOS) has been used a modifier for the investigation of Bisphenol-A electrochemically by cyclic voltammetric method. SAOS modified carbon paste electrode was prepared by immobilization technique. This modified electrode shows significant electrochemical response towards Bisphenol-A (BPA) at pH 7.4 with scan rate 50 mVs⁻¹ when compared to bare carbon paste electrode. Effect of concentration and scan rate were studied and resulted linear with oxidation peak current of BPA. Detection limit of BPA found to be 1.46 µM. The modified electrode showed excellent sensitivity and rapid response properties.

Keywords- Bisphenol-A, Cyclic voltammetry, Carbon paste electrode, Voltammetry, Sodium alpha olefin sulphate

1. INTRODUCTION

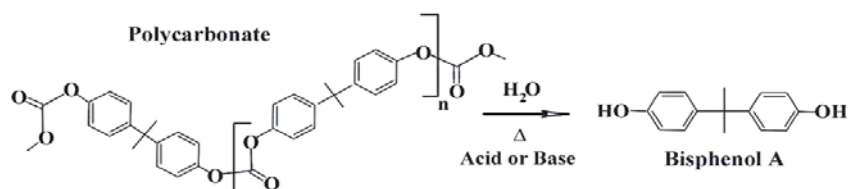
Bisphenol A (2,2-bis (4-hydroxyphenyl) propane, BPA) is a typical endocrine disrupting compound causing abnormal hormone activity and widely used as a major component for the industrial production of polycarbonate and epoxy resins. Polycarbonate and epoxy resins are commonly used to produce plastic food containers, inner surface coating of food and

beverage cans, from which BPA can leach into food and environment [1-3]. BPA exhibits estrogenic activity. Exposure to BPA has resulted human health effects because when BPA molecules are polymerized, they linked by ester bonds that are subjected to hydrolysis (Scheme1). These include reproduction dysfunctions, endometrial hyperplasia, recurrent miscarriages, abnormal karyotypes and polycystic ovarian syndrome [4-6]. Until now, different analytical methods of BPA have been proposed, such as high performance liquid chromatography (HPLC) [7,8], liquid chromatography-mass spectrometry [9], liquid chromatography with fluorescence detection [10], fluorescence [11], gas chromatography [12], gas chromatography-mass spectrometry [13], enzyme-linked immunosorbent assay [14], molecular imprinting technique [15], surface-enhanced Raman scattering technique [16] and electrochemical methods [17,18]. Among these detection techniques, electrochemical methods have attracted more and more because of the advantages of fast response, cheap instrument, low cost, simple operation, time saving, high sensitivity and excellent selectivity [19-21].

The Sodium alpha olefin sulfonate (SAOS) surfactants are produced by the direct reaction of olefins with strong sulfonating agents, such as sulfur trioxide. This leads to the formation of surface active anionic mixtures containing both alkenes sulfonates and hydroxyl alkene sulfonates. These surfactants may be used in place linear alkyl benzene sulfonate in many formulas with resulting improvements in biodegradability, mildness to skin, foaming and detergency. In addition, SAOS surfactants are stable over a much broader pH range than alkyl sulfates alkyl ethers sulfates and esters type surfactants. They also exhibit excellent foaming and detergency in hard water. The INCL name of the primary SAOS of commerce is sodium C14-16 olefin sulfonate. Irritation studies on SAOS have been conducted on the backs of ten human volunteers using the closed patch technique with daily applications of 2.5% aqueous solutions, It was shown that irritation was comparable to that produced by soap. The SAOS surfactants have been used successfully in the formulation of a variety of skin cleaning products including toilet bars and bubbles bath compositions, a suggested liquid bubble bath formulation containing SAOS. The trend in the cosmetic market to use liquid hand cleansers in place of bar soap continues to be strong. As a result of their relative mildness, cleansing efficiency outstanding lathering properties and favorable cost SAOS surfactants have gained popularity for this use [22-25].

Surfactants are substances with molecular structures consisting of a hydrophilic and a hydrophobic part. Considering the charge of the hydrophilic group, surfactants can be divided into four types: anionic, cationic, amphoteric and non-ionic [26]. The applications of surfactants in electrochemistry and electroanalytical chemistry have been widely reported [27,28] because of the enhancement effect and the ability to improve the property of the electrode/solution interface. The using of surfactants as modifiers to improve the electrode quality has been previously reported in Digua et al. [29-31].

In present work SAOS was modified by immobilization technique then it was applied for the voltammetric investigation of BPA at pH 7.4. The SAOS anionic surfactant modified electrode shows increase in the oxidation peak current when compared to bare CPE this is may be adsorption on the surface of the electrode interface and the redox reactions in solution [32]. The proposed work some obvious advantages including high sensitivity, extreme simplicity, rapid response and low cost [33].



Scheme 1. Mechanism of BPA hydrolysis in food and environments

2. EXPERIMENTAL PART

2.1. Reagents and Chemicals

Bisphenol-A and Sodium alpha olefin sulfonate anionic surfactant were obtained from Himedia chemical company, and of analytical grade used without further purification. 25×10^{-4} M Bisphenol-A stock solution was prepared in ethanol, 25×10^{-4} M SAOS was prepared in double-distilled water. Graphite powder of 50 mm size was purchased from Loba, silicon oil was purchased from Himedia. The chemicals for preparation of buffer solution were purchased from Merck and the phosphate buffer (0.2 M pH 7.4) was used as supporting electrolyte.

2.2. Apparatus

Cyclic voltammetry (CV) was performed in a model CHI-660c (CH Instrument-660 electrochemical workstation). All experiments were carried out in a conventional electrochemical cell. The electrode system contained a carbon paste working electrode (3.0 mm in diameter), a platinum wire as counter electrode and saturated calomel as reference electrode for the electrochemical measurements.

2.3. Preparation of bare and modified carbon paste electrode

The carbon paste electrode was prepared by using 70% graphite powder and 30% silicone oil were mixed by hand to produce a homogeneous carbon paste. The paste was then packed into the cavity of a homemade carbon paste electrode and smoothed on a weighing paper. In the same way, the sodium alpha olefin sulfonate modified carbon paste electrode (SAOS

MCPE) was prepared by immobilizing 5 μL of SAOS on the surface of the carbon paste electrode for 5 min and then applied for the electrochemical analysis.

3. RESULTS AND DISCUSSION

3.1. Effect of concentration of SAOS

The Fig. 1 shows the voltammetric response of SAOS concentration from 5 μl to 15 μl in the presence of 20×10^{-6} M BPA at pH 7.4 with scan rate 50 mVs^{-1} .

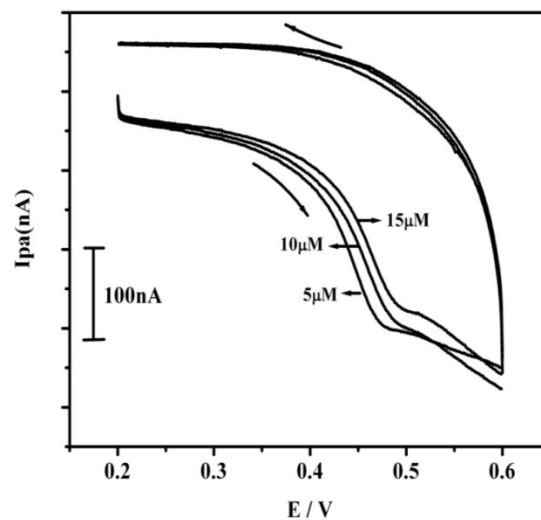


Fig. 1. Cyclic voltammograms of 20×10^{-6} M BPA in pH 7.4 at different concentrations of SAOS/MCPE with scan rate 50 mVs^{-1}

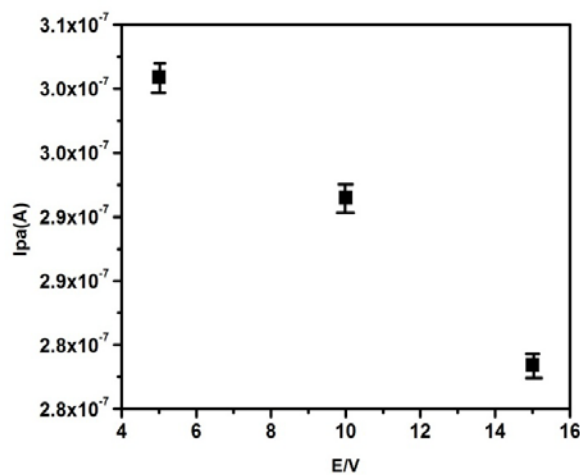


Fig. 2. Graph of I_{pa} versus potential for 20×10^{-6} M BPA at 5, 10 & 15 μL SAOS/MCPE

By increasing the concentration of SAOS (E_{pa}) oxidation peak potential shifts positive side. In 5 μl shows (Fig. 2) high sensitivity in the presence of 20×10^{-6} M BPA after there is

decrease in the current, this is may be SAOS surfactant molecule form a monolayer on the surface of the electrode and subsequently electrostatic interaction between adsorbed substrate.

3.2. Electrochemical response of potassium ferrocyanide at sodium alpha olefin sulfonate modified carbon paste electrode

To evaluate performance of modified carbon paste electrode potassium ferrocyanide was chosen for the electrochemical study. Fig. 3 shows electrochemical response of 1 mM $K_4Fe(CN)_6$ bare (dashed line) and SAOS/MCPE (solid line) in supporting electrolyte 1 M KCl at the scan rate 50 mVs^{-1} . The background current is significantly enlarged at modified carbon paste electrode compared to that of bare carbon paste electrode. This indicates that surface property of modified electrode has been significantly changed.

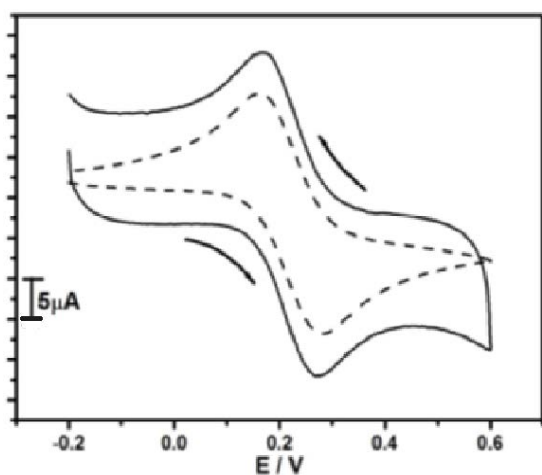


Fig. 3. Cyclic voltammograms of 1 mM potassium ferrocyanide ($K_4Fe(CN)_6$) in 1 M KCl for bare (dashed line) and SAOS/MCPE (solid line) at scan rate 50 mVs^{-1}

3.3. Electrochemical behavior of Bisphenol-A (BPA) at Sodium alpha olefin sulfonate modified carbon paste electrode (SAOSMCPE)

The Fig. 4 shows that electrochemical behavior of $20 \times 10^{-6}\text{ M}$ of BPA at bare carbon paste electrode (solid line) and SAOS/MCPE (dashed line) at 7.4 pH with scan rate 50 mVs^{-1} . At bare carbon paste electrode BPA shows oxidation peak potential at 500 mV with less background current. However at Sodium alpha olefin sulfonate modified carbon paste shows high enhancement in anodic peak current when compared to bare carbon paste electrode. This result indicates the electron transfer process will take place when the electro active species approaches the vicinity of the electrode surface.

3.4. Effect of concentration of BPA

The relationship between the oxidation peak current of BPA and its concentration was studied by using cyclic voltammetric method. Fig. 5 shows different concentration of BPA varied from 20 μM to 60 μM at SAOS/MCPE. Peak current goes on increase with the increase in the concentration of BPA with the negligible shift. The graph of anodic peak current versus concentration of BPA (Fig. 6) showing linear increase in the anodic peak current with the increase in concentration. This indicates that modified carbon paste electrode shows diffusion controlled process. The detection limit was found to be 1.46 μM and it is calculated by using equation (1) the proposed methods for determination of BPA are compared [34-39] with the analytical data in Table 1.

$$\text{LOD}=3S/M \quad (1)$$

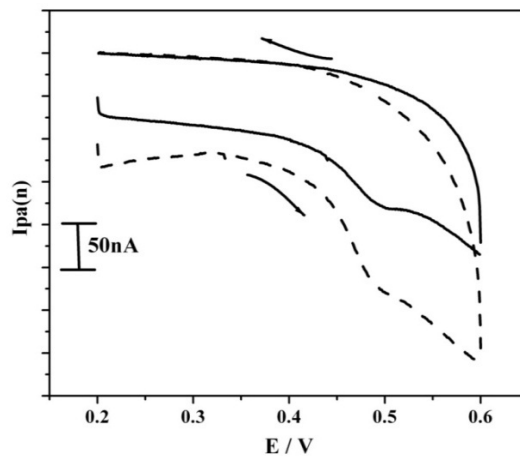


Fig. 4. Cyclic voltammograms of $20 \times 10^{-6} \text{ M}$ BPA at bare carbon paste electrode (solid line) and SAOS/MCPE (dashed line) at 7.4 pH with scan rate 50 mVs^{-1}

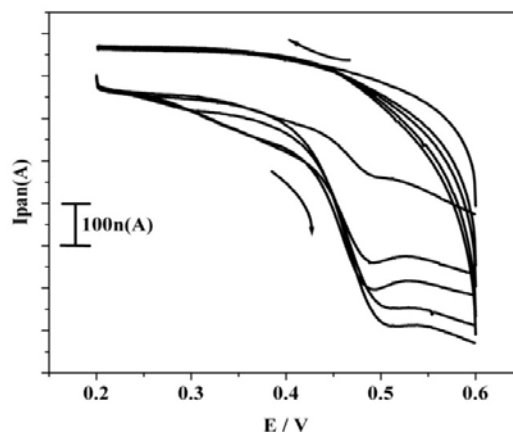


Fig. 5. Cyclic voltammograms at different concentration 20-60 μM of BPA at SAOS/MCPE (from top) in 7.4 pH

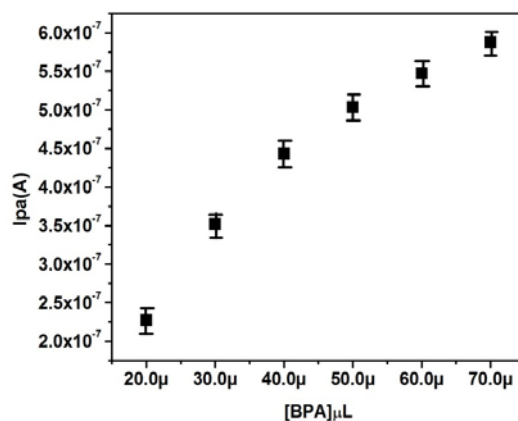


Fig. 6. Graph of I_{pa} versus concentration of BPA at SAOS/MCPE in 7.4 pH

Table 1. Comparison of detection limit of this work and literature reported ones

Electrode	Linear Range (μM)	Detection limit (μM)	Ref.
HDS/SDS/CPE	0.01 - 100	0.018	[34]
PAMAM-AuNPs-SF/GCE	0.001–1.33	0.0005	[35]
Tyrosinase- CPE	1-20	0.15	[36]
MCM-41/ CPE	0.088–0.22	0.038	[37]
CoPc-CPE	0.0875–12.5	0.01	[38]
dsDNA/Au	0.01–1	0.01	[39]
SAOS/MCPE	20-60	1.4	This work

3.5. Effect of scan rate variation

Effect of scan rate was carried out in order to know the kinetics of the electrode reactions and to verify whether process is diffusion or adsorption. The graph of anodic peak current versus scan rate was plotted (Fig. 7). The obtained graph shows good linearity between scan rate and anodic peak current, ranging from 20 to 100 mVs⁻¹ and the obtained correlation coefficient was 0.98557, which indicates that the electron transfer reaction was diffusion-controlled.

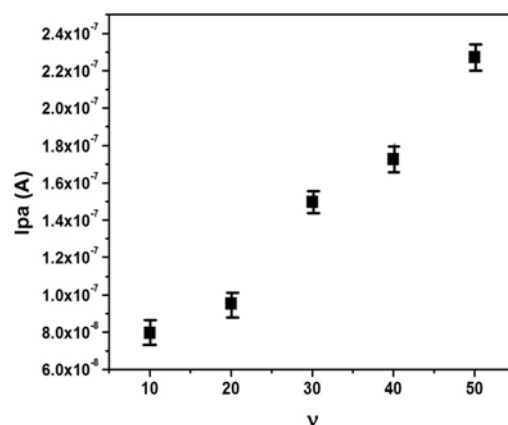


Fig. 7. Graph of I_{pa} versus scan rate for 20×10^{-6} M BPA at SAOS/MCPE

4. CONCLUSION

A simple immobilization technique was used for the investigation of BPA at pH 7.4. The SAOS modified electrode showed high oxidation peak current when compared to bare along with this the additional parameters were studied such as effect of scan rate and concentration of BPA. Overall result shows that our modified electrode undergoes diffusion controlled process and the detection limit was found to be $1.46 \mu\text{M}$. The modified electrode showed good sensitivity, selectivity, simple and lower cost.

REFERENCES

- [1] J. Fan, H. Guo, G. Liu, and P. Peng, *Anal. Chim. Acta* 585 (2007) 134.
- [2] B. Kun Kim, J. Y. Kim, D. H. Kim, H. N. Choi, and W. Y. Lee, *Bull. Korean Chem. Soc.* 34 (2013) 1065.
- [3] Y. Hideyuki, H. Hajime, N. Hitoshi, and Y. Masatoshi, *Anal. Chim. Acta* 488 (2003) 211.
- [4] B. Ntsendwana, B. B. Mamba, S. Sampath, and O. A. Arotiba, *Int. J. Electrochem. Sci.* 7 (2012) 3501.
- [5] H. Yin, Y. Zhou, J. Xu, S. Ai, L. Cui, and L. Zhu, *Anal. Chim. Acta* 659 (2010) 144.
- [6] H. S. Yin, H. Y. L. Zhou, and S. Y. Ai, *J. Electroanal. Chem.* 626 (2009) 80.
- [7] J. Lou, W. Wang, L. Yanb, C. Ruan, X. Sun, W. Sun, and P. Li, *Int. J. Environ. Anal. Chem.* 95 (2015) 911.
- [8] Y. Wen, B. S. Zhou, Y. Xu, S. W. Jin, and Y. Q. Feng, *J. Chromatogr. A* 1133 (2006) 21.
- [9] R. S. Zhao, X. Wang, and J. P. Yuan, *J. Sep. Sci.* 33 (2010) 1652.

- [10] A. G. Prieto, M. L. Lunar, S. Rubio, and D. Perez-Bendito, *Anal. Chim. Acta* 630 (2008) 19.
- [11] X. Wang, H. Zeng, L. Zhao, and J. M. Lin, *Anal. Chim. Acta* 556 (2006) 313.
- [12] H. S. Shin, C. Park, S. J. Park, and H. Pyo, *J. Chromatogr. A* 912 (2001) 119.
- [13] X. Wang, C. P. Diao, and R. S. Zhao, *J. Sep. Sci.* 32 (2009) 154.
- [14] B. D. Meulenaer, K. Baert, H. Lanckriet, V. V. Hoed, and A. Huyghebert, *J. Agric. Food. Chem.* 50 (2002) 5273.
- [15] W. Zhao, N. Sheng, R. Zhu, F. Wei, Z. Cai, M. Zhai, S. Du, and Q. Hu, *J. Hazard. Mater.* 179 (2010) 223.
- [16] J. Q. Xue, D. W. Li, L. L. Qu, and Y. T. Long, *Anal. Chim. Acta* 777 (2013) 57.
- [17] F. Brugnera, M. A. G. Trindade, and M. V. B. Zanoni, *Anal. Lett.* 43 (2010) 2823.
- [18] H. S. Yin, Y. L. Zhou, J. Xu, S. Y. Ai, L. Cui, and L. S. Zhu, *Anal. Chim. Acta* 659 (2010) 144.
- [19] T. V. Sathisha, B. E. Kumara Swamy, C. C. Vishwanath, M. Kumara, T. S. Anvekar, and B. Eswarappa, *Chem. Sensors* 4 (2014) 1.
- [20] H. Yin, Y. Zhou, S. Ai, R. Han, T. Tang, and L. Zhu, *Microchim. Acta* 170 (2010) 99.
- [21] U. Chandra, B. E. K. Swamy, O. Gilbert, and B. S. Sherigara, *Anal. Methods* 3 (2011) 2068.
- [22] M. M. Rieger, and L. D. Rhein, *Surfactants in cosmetics* 2nd ed, Marcel Dekker, Inc, NewYork 68 (1977).
- [23] Bioterge Alpha olefin Sulfonate Bulletin Stepan Chemical Co., Northfield, IL 800 (2012) 745.
- [24] B. Rouge, La., Communique, Toxicity Studies on Sodium Alpha Olefin Sulfonate, Ethyl Corporation. 24 (1979).
- [25] G. Barker, *Cosmetic Formulation of Skin Care products* 90 (1975) 70.
- [26] X. Hao, J. L. Lei, N. B. Li, and H. Q. Luo, *Anal. Chim. Acta* 852 (2014) 63.
- [27] C. Hu, X. Dang, and S. Hu *J. Electro. Anal. Chem.* 572 (2004) 161.
- [28] J. F. Rusling, *Acc. Chem. Res.* 24 (1991) 75.
- [29] C. Hu, S. Hu, *Electrochim. Acta* 49 (2004) 405.
- [30] K. Digua, J. M. Kauffmann, and J. L. Delplancke, *Electroanalysis* 6 (1994) 451.
- [31] K. Digua, J. M. Kauffmann, J. L. Delplancke, *Electroanalysis* 6 (1994) 459.
- [32] S. S. Shankar, B. E. Kumara Swamy, and B. N. Chandrashekar, *J. Mol. Liq.* 168 (2012) 80.
- [33] J. G. Manjunath, B. E. Kumara Swamy, G. P. Mamatha, S. S. Shankar, O. Gilbert, B. N. Chandrashekar, and B. S. Sherigara, *Int. J. Electrochem. Sci.* 4 (2009) 1469.
- [34] T. V. Sathisha, B. E. Kumara Swamy, C. C. Vishwanatha, Mohan Kumara, Tushar S. Anvekar, and B. Eswarappac, *Chem. Sensors* 4 (2014) 1.
- [35] H. Yin, Y. Zhou, S. Ai, R. Han, T. Tang, and L. Zhu, *Microchim. Acta* 170 (2010) 99.

- [36] S. Andreescu, and O. A. Sadik *Anal. Chem.* 76 (2004) 552.
- [37] F. Wang, J. Yang, K. Wu, *Anal. Chim. Acta* 638 (2009) 23.
- [38] H. Yin, Y. Zhou, and S. Ai, *J. Electroanal. Chem.* 626 (2009) 80.
- [39] F. Yan, and O. Sadik, *Anal. Chem.* 73 (2001) 5272.