

Cyclic Voltammetric Studies of Serotonin at Sodium Dodecyl Sulfate Modified Carbon Paste Electrode

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Electrochemical oxidation of serotonin has been studied at carbon paste electrode in 0.1M pyrophosphate buffer using cyclic voltammetric (CV) technique. The adsorption of sodium dodecyl sulfate (SDS) at carbon paste electrode was investigated. The results showed that SDS exhibited two types of adsorptive behavior at carbon paste electrode at different concentration ranges viz. i) monomer adsorption at concentration below 3×10^{-3} M and monolayer adsorption at concentrations higher than 3×10^{-5} M SDS onto the surface ii) $5 \mu\text{L}$ monomer adsorption and monolayer adsorption at concentrations higher than $60 \mu\text{L}$ of 3×10^{-5} M SDS into the solution. In the monomer adsorption range the adsorption of SDS could effectively reduce the charge transfer rate. However the surface properties of the carbon paste electrode drastically changed on the formation of a SDS monolayer.

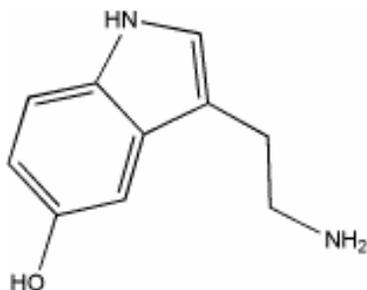
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1. INTRODUCTION

Serotonin (5-hydroxytryptamine, 5-HT) is an important catecholamine neurotransmitter in biological systems. Although the central nervous system contains less than 2% of the total serotonin in the body, serotonin plays a very important role in the range of brain functions. It is synthesized from the amino acid tryptophan. Serotonin regulates mood and sleep and is a major target for pharmaceutical treatments of depression [1]. 5-HT plays a crucial role in an emotional system together with other neurotransmitters [2,3]. [Scheme-1]

Surfactant is a linear molecule with a hydrophilic (attracted to water) head and a hydrophobic (repelled by water) end. Due to its unique molecular structure, surfactant was extensively used in the

fields of electrochemistry and electroanalytical chemistry for various purposes [4-9]. Hu's group [10-13] has introduced surfactants to electroanalytical chemistry to improve the detection limits of some biomolecules. The results showed that the electrochemical responses of these compounds were greatly enhanced in the presence of trace surfactants. They proposed a synergistic adsorption mechanism to interpret these enhancement effects of surfactants; ie; surfactants might combine with the substrate in certain forms and strengthen their adsorption on the electrode surface, which facilitated the electron or the substance transfer between the electrode and the solution. Digua et al.[14.15] mixed the amphiphile hexadecyl sulphonic acid into carbon paste to produce a surfactant modified carbon paste electrode (CPE). Chengguo Hu and Shengshui Hu [16] reported that CTAB formed a compact monolayer on the electrode surface with high density of positive charges. Jianbin Zheng and Xiaoli Zhau [17] reported that SDS formed a monolayer on CPE surface with high density of negative charged end directed outside the electrode. Shen- Ming Chen and Wen- Yan Chzo [18] have studied the simultaneous voltammetric detection of dopamine and ascorbic acid using didodecyl dimethyl ammonium bromide (DDAB) film modified electrodes. The applications of surfactants in the immobilization of biomolecules were also reported [19-21]. Sigal et al. [22] used surface plasmon resonance spectroscopy to measure the association of surfactants with hexadecanethiolate self assembled monolayers (SAMs) on gold. Hu.et al studied the chemical responses of several species at carbon paste electrodes in the presence of surfactants, including diethylstilbestrol [12], thyroxin [23] and dioxygen [24]. The results showed that the addition of trace surfactants to the working solutions could effectively improve the signals of these substances. W. Huang carried out the voltammetric determination of Bisphenol A using a carbon paste electrode based on the enhancement effect of cetyltrimethylammonium bromide [25]. X.L. Wen et al. studied the micellar effects on the electrochemistry of dopamine and its selective detection in the presence of ascorbic acid [26]. S. Corona-Avendano et al. studied the electrochemistry of dopamine in aqueous solution. Part I: The role of [SDS] on the voltammetric behavior of dopamine on a carbon paste electrode [27]. G. Alarcon-Angeles et al. studied the selective determination of dopamine in the presence of ascorbic acid using sodium dodecyl sulphate micelles as a masking agent [28].



Scheme 1.

As a part of our research work on the surfactant modified electrodes at the surface of the electrodes, we extended our work on the modification of carbon paste electrode [29-31]. In this work, the adsorption of SDS at carbon paste electrode was explored by voltammetry, which might be able to

explain the enhancement effects of surfactants in electroanalytical chemistry. The results revealed not only the adsorptive behavior of SDS but also the influences of SDS adsorption on the surface of the electrode interface and the reactions in solution. These results might be able to explain the enhancement effects of surfactants in electroanalytical chemistry.

2. EXPERIMENTAL PART

2.1. Reagents and Chemicals

Serotonin, sodium dodecyl sulphate, tetra-sodium pyrophosphate anhydrous and perchloric acid used were of analytical grade quality from sigma-aldrich and used without further purification. 10mM serotonin stock solution was prepared by adding serotonin to 0.1M perchloric acid. In all the measurements, the supporting electrolyte used was 0.1M sodium pyrophosphate. All the solutions were prepared by using double distilled water.

2.2. Apparatus and Procedure

Cyclic voltammetry (CV) was performed on Model EA-201 Electroanalyser (EA-201, Chemilink System). All the experiments were carried out in a conventional electrochemical cell. The electrode system contained a carbon paste working electrode (3.0mm in diameter), a platinum wire counter electrode and a saturated calomel reference electrode (SCE). The carbon paste electrode was prepared as follows: 70% graphite powder (particle size 50mm and density is 20mg/100ml) 30% silicone oil were mixed by hand to produce a homogeneous carbon paste electrode. The carbon paste was then packed into the cavity of a customized carbon paste electrode and smoothed on a weighing paper.

3. RESULTS AND DISCUSSION

A typical cyclic voltammogram of 1.0×10^{-3} M serotonin in aqueous media using pyrophosphate buffer at pH 7.0 as supporting electrolyte at carbon paste electrode with a scan rate of 50 mVs^{-1} is shown in Fig. 1.

3.1. Effect of concentration

The CV's showed successive enhancement of peak current on increasing serotonin concentration. The plot of peak current (obtained by measuring the peak height) versus the respective concentration of serotonin was found to be linear in the range 0.5 to 3.0mM as shown in Fig. 2 with a correlation coefficient of 0.953 [32,33].

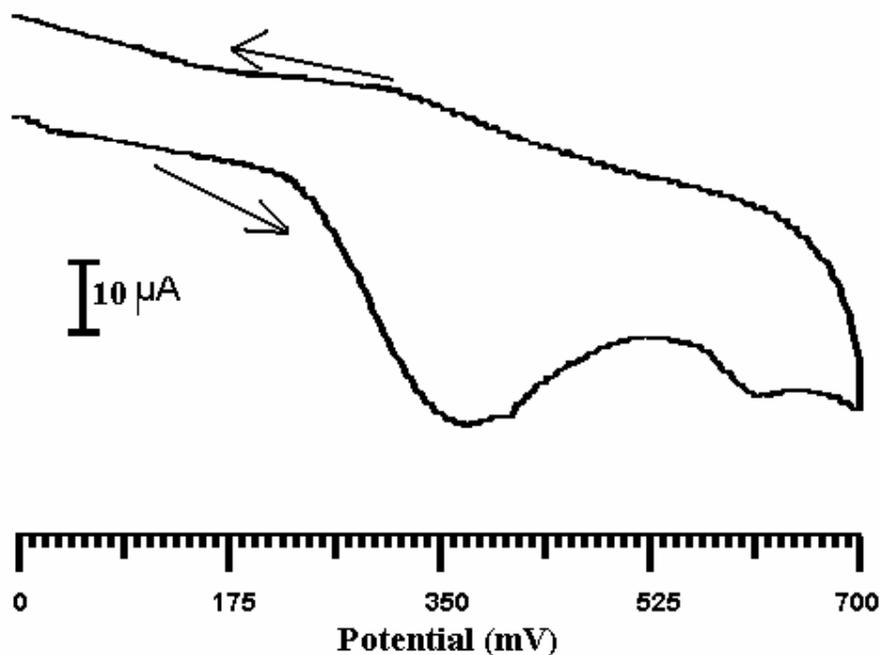


Figure 1. Cyclic voltammogram of $1.0 \times 10^{-3} \text{ M}$ serotonin at carbon paste electrode supporting electrolyte 0.1M Pyrophosphate buffer, pH 7.0 at scan rate 50 mVs^{-1} .

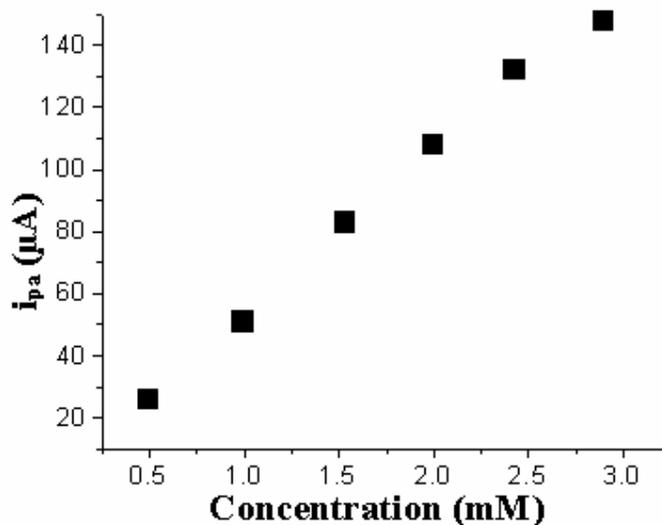


Figure 2. Effect of concentration variation of Serotonin at carbon paste electrode supporting electrolyte 0.1M Pyrophosphate buffer, pH 7.0 at scan rate 50 mVs^{-1} .

3.2. Effect of Scan rate

The effect of varying the potential scan rate on the oxidation peak current of serotonin was studied. The cyclic voltammograms were recorded in 0.1M pyrophosphate buffer of pH 7.0 as a

supporting electrolyte. The oxidation peak current increased linearly with square root of the scan rate over the range 25 to 125 mVs^{-1} with a correlation coefficient of 0.996. The process is diffusion controlled in this region as shown in the Fig. 3. The observed shift in peak potential towards more positive values with increase in scan rate is a typical behavior of an irreversible electron transfer process [32,33].

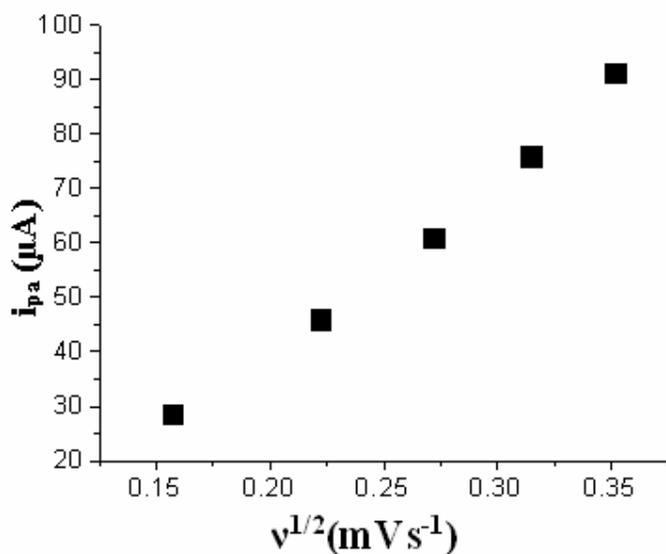


Figure 3. Effect of scan rate variation of $1.0 \times 10^{-3} \text{M}$ serotonin at carbon paste electrode supporting electrolyte 0.1M Pyrophosphate buffer, pH 7.0.

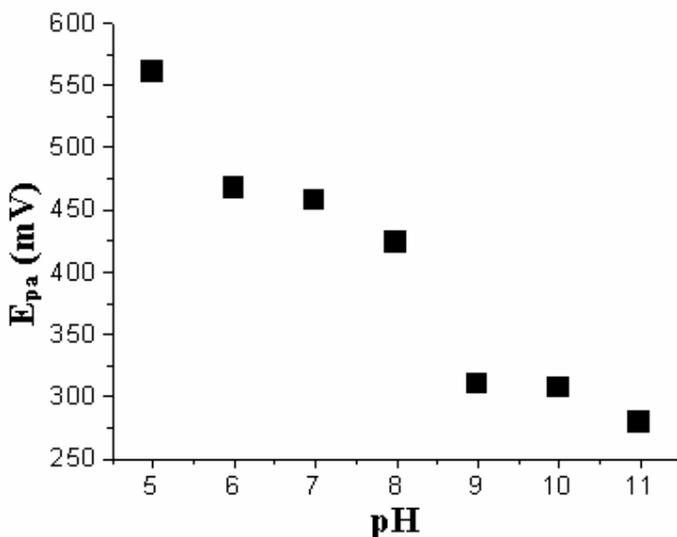


Figure 4. Effect of pH variation of $1.0 \times 10^{-3} \text{M}$ serotonin at carbon paste electrode supporting electrolyte 0.1M Pyrophosphate buffer, pH 7.0 at scan rate 50mVs^{-1} .

3.3. Effect of pH

The electrooxidation of serotonin was studied over pH range from 5.0 to 12.0 using 0.1M pyrophosphate buffer as a supporting electrolyte at a scan rate of 50 mVs^{-1} . The oxidation peak potential of 5-HT decreases with increase in pH indicates that the electro-oxidation process becomes easier at higher pH [34] as shown in Fig .4.

3.4. Electrochemical response of serotonin at carbon paste electrode on to the surface with SDS.

The electrochemical responses of serotonin at carbon paste electrode was shown in Fig.5 with pyrophosphate buffer as a supporting electrolyte at pH 7.0 at a scan rate of 50 mVs^{-1} owing to the complex properties and the roughness of the electrode surface, the cyclic voltammogram of serotonin in the absence of SDS is low signal (solid line). However, the voltammetric response is apparently improved in the presence of $60 \mu\text{L}$ of $3 \times 10^{-5} \text{ M}$ SDS, reflected by the enlargement of anodic peak current (i_{pa}) (dashed line). The probable mechanism is the SDS surfactant molecule diffuses into the carbon paste electrode along with the serotonin results increase in the signal. [29,30]

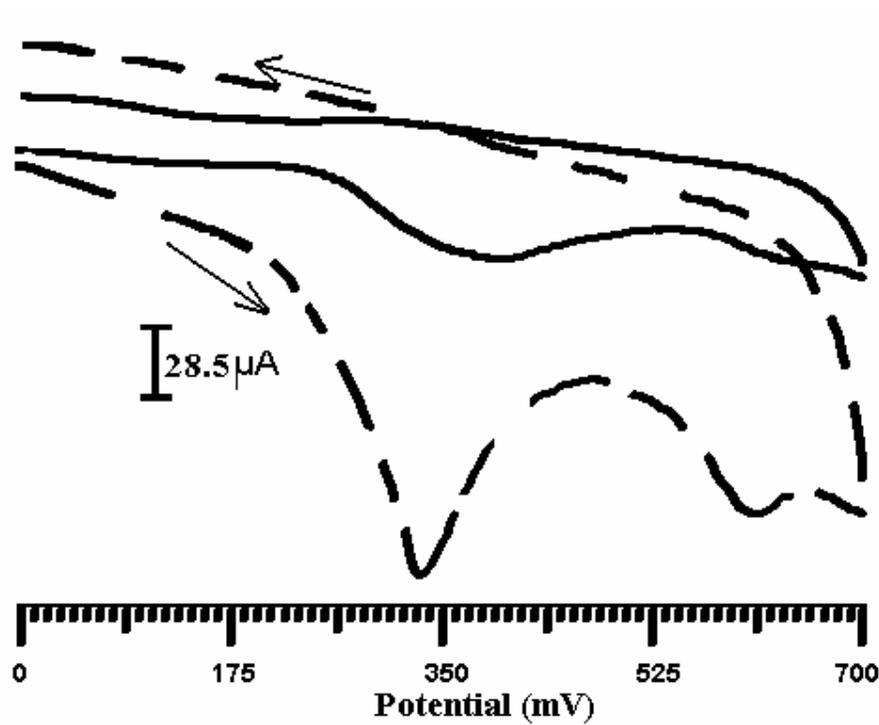


Figure 5. Electrochemical response of $1.0 \times 10^{-3} \text{ M}$ serotonin on to the surface at bare carbon paste electrode (solid line) and (dashed line) at SDS modified carbon paste electrode supporting electrolyte 0.1M Pyrophosphate buffer, pH 7.0 at scan rate 50 mVs^{-1} .

3.5. Dependence of SDS adsorptive behaviour on SDS concentration at carbon paste electrode.

The dependence of the voltammetric responses for $1.0 \times 10^{-3} \text{ M}$ serotonin on SDS concentration as shown in Fig.6. We observed that the addition of trace amount of SDS can effectively promote the peak current signals of serotonin. With the gradual increase in the SDS concentration both the peak current and peak potential varies respectively. As mentioned earlier, SDS might form a monolayer in this concentration range and hence increase in the signal. These results also suggest that completeness of SDS concentration above $3 \times 10^{-5} \text{ M}$ SDS. Over the whole concentration range, the oxidation peak currents (i_{pa}) increases with the increase of SDS concentration and that the increase rate is fast at low SDS concentrations.

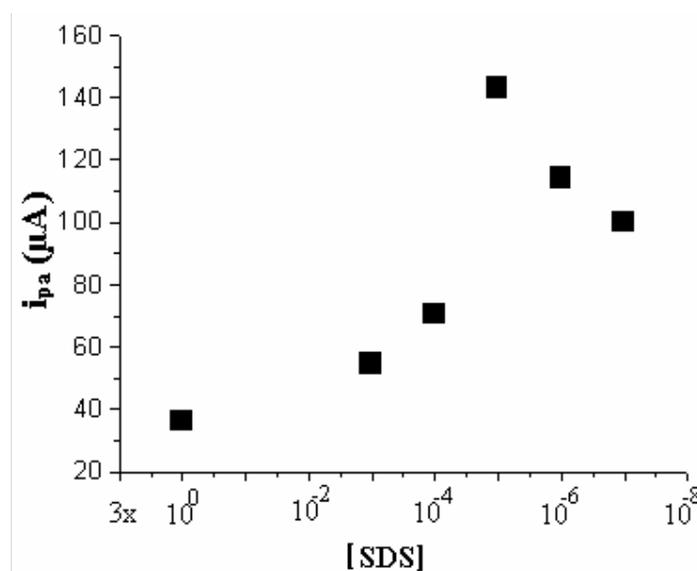


Figure 6. Effect of SDS concentration on to the surface at carbon paste electrode supporting electrolyte 0.1M Pyrophosphate buffer, pH 7.0 at scan rate 50 mVs^{-1} .

3.6. Electrochemical response of serotonin at carbon paste electrode when SDS was added directly into the solution

The electrochemical responses of serotonin at carbon paste electrode was shown in Fig.7 with pyrophosphate buffer as a supporting electrolyte at pH 7.0 at a scan rate of 50 mVs^{-1} owing to the complex properties and the roughness of the electrode surface, the cyclic voltammogram of serotonin in the absence of SDS is low signal (solid line). However, the voltammetric response is apparently improved in the presence of $60 \mu\text{L}$ of $3 \times 10^{-5} \text{ M}$ SDS, reflected by the enlargement of anodic peak current (i_{pa}) (dashed line). The probable mechanism is the SDS surfactant molecule diffuses into the carbon paste electrode along with the serotonin results increase in the signal.

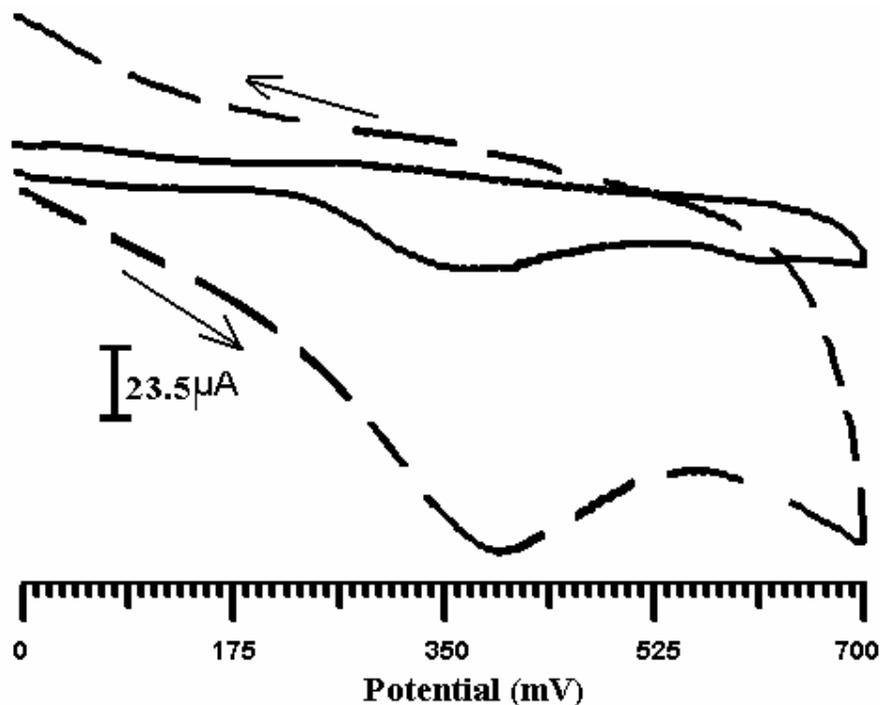


Figure 7. Electrochemical response of 1mM Serotonin directly in to the solution at bare carbon paste electrode (solid line) and (dashed line) at SDS modified carbon paste electrode supporting electrolyte 0.1M Pyrophosphate buffer, pH 7.0 at scan rate 50 mVs^{-1} .

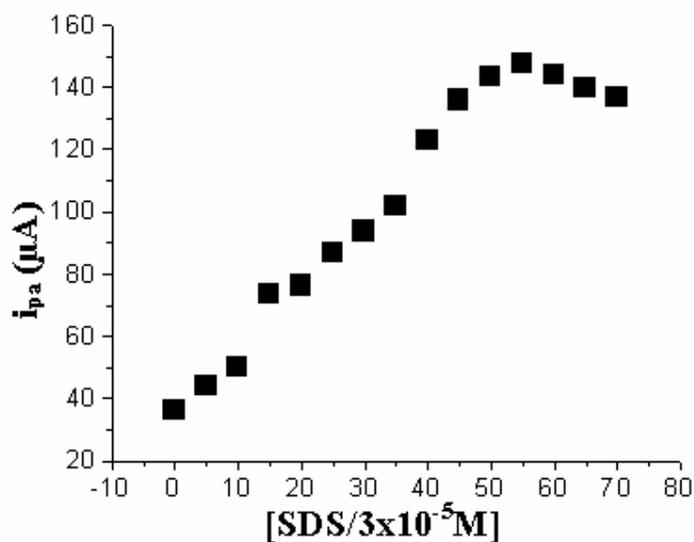


Figure 8. Effect of SDS concentration in to the solution at carbon paste electrode supporting electrolyte 0.1M Pyrophosphate buffer, pH 7.0 at scan rate 50 mVs^{-1} .

3.7. Dependence of SDS adsorptive behavior on SDS concentration at carbon paste electrode.

The dependence of the voltammetric responses for $1.0 \times 10^{-3} \text{ M}$ serotonin on SDS concentration as shown in Fig.8. Obviously, the addition of SDS can effectively promote the signals of serotonin, as

shown in even for a trace amount of (SDS). With the increase of SDS concentration, the peak current varies respectively. As mentioned above, SDS might form a monolayer in this concentration range and hence increase in the signal. These results also suggest that completeness of SDS concentration above 60 μ L of 3×10^{-5} M SDS. Over the whole concentration range, the oxidation peak currents (i_{pa}) increases with the increase of SDS concentration and that the increase rate is fast at low SDS concentrations.

4. CONCLUSIONS

The adsorption of SDS on a hydrophobic carbon paste electrode surface was investigated by cyclic voltammetry. The results showed that SDS exhibited different types of adsorptive behavior at carbon paste electrode at different SDS concentrations. Below 3×10^{-3} M, the adsorption of SDS as the monomer and could effectively affect the charge transfer rate instead of the surface properties of the carbon paste electrode. When the SDS concentration was higher than 3×10^{-5} M, SDS formed a monolayer on the electrode surface. Whereas in the case of SDS directly in to the solution, we observed same type of 5 μ L monomer and monolayer adsorption at concentrations higher than 60 μ L of 3×10^{-5} M SDS. From this data we can conclude that the surface adsorption of SDS onto the surface is more feasible compare to the same as in the case of into the solution.

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