High Selective Determination of Anionic Surfactant Using Its Parallel Catalytic Hydrogen Wave

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A faradaic response of anionic surfactants AS such as linear alkylbenzene sulfonate LAS dodecyl benzene sulfonate and dodecyl sulfate was observed in weak acidic medium. The faradaic response of AS includes 1 a catalytic hydrogen wave of AS in HAc/NaAc buffer that was attributed to the reduction of proton associated with the sulfo-group of AS and 2 a parallel catalytic hydrogen wave of AS in the presence of hydrogen peroxide which was due to the catalysis of the catalytic hydrogen wave of AS by hydroxyl radical · OH electrogenerated in the reduction of hydrogen peroxide. The parallel catalytic hydrogen wave is about 50 times as sensitive as the catalytic hydrogen wave. Based on the parallel catalytic hydrogen wave a high selective method for the determination of AS was developed. In 0.1 mol/L HAc/NaAc pH = 6.2 ± 0.1 /1.0 × 10^{-3} mol/L H$_2$O$_2$ supporting electrolyte the second-order derivative peak current of the parallel catalytic hydrogen wave located at −1.33 V vs. SCE was rectilinear to AS concentration in the range of 3.0 × 10^{-6}—2.5 × 10^{-4} mol/L without the interference of other surfactants. The proposed method was evaluated by quantitative analysis of AS in environmental wastewater.

Keywords　anionic surfactant　linear alkylbenzene sulfonate　hydrogen peroxide　parallel catalytic hydrogen wave

Introduction

Anionic surfactants AS are widely used in household or industrial cleaners cosmetics research laboratories textiles pharmacies *etc*. so large amount of AS released into the environment are causing pollution. Therefore it is necessary to develop a fast simple and cost effective method for the determination of AS. The official methods recommended for the determination of AS are spectrophotometry and potential titration. Spectrophotometric method and its variations are based on the measurement of the colored associates of AS with positive-charged dyes by photometry.[1-4] Although these spectrophotometric methods offer high sensitivity toxic organic solvents such as chloroform are often used for extraction and the procedures are time-consuming. In potential titration [1 5 6] various types of ion-selective electrodes ISE had been used. Because the sensing membrane of ISE consists of an ion-pair association of AS with a positive-charged counter they are sensitive to either the analyte or to the titrant with potentiometric endpoint detection. The relatively poor selectivity by use of ISE is main disadvantage in potential titration method. Since polarographic and voltammetric analysis are simple rapid and inexpensive many polarographic and voltammetric methods for the determination of surface-active substance SAS including AS were preferred and widely used. These polarographic and voltammetric methods had been reviewed in detail [7-9] and can be reduced to four kinds. The first one is established based on measuring the changes of the interfacial tension on mercury drop electrode [10] the second based upon measuring the changes of tensammetric peaks [11] the third measuring the suppression degrees of the voltammetric response of electroactive species such as hexacyanoferrate and parahydroquinone and of polarographic maximum of mercury II and oxygen [12-15] the four measuring the increase of second reduction wave of oxygen.[16 17] In order to improve the sensitivity adsorption stripping voltammetric technique was combined with these polarographic and voltammetric methods. In these methods general property of SAS adsorption of SAS on electrode surface was used. The selected analytical signal just is in the potential domain where various types of SAS have adsorption even maximum adsorption and is function of total concentration of SAS. Therefore these methods can determine total concentration of SAS and had been successfully used to evaluate the pollution of environmental water and seawater by SAS. However the lack of selectivity presents certain limitations. Additionally as adsorption of SAS on electrode surface depends strongly on experimental conditions such parameters as electrolyte type and concentration applied electrode potential adsorption kinetic and others would also significantly influence the obtained results. For this reason the analysis of AS by these methods requires preferably one or more separation process.

Polarographic catalytic wave as a useful technique has very high sensitivity simplicity in operation and widely practical applications. Besides the parallel catalytic wave

of transition metal ion the catalytic hydrogen wave has been used for the quantitative analysis of proteins alkaloids and many nitrogen- or sulfur- containing substances that can carry the proton diminish the hydrogen overvoltage and accelerate the discharge of hydrogen ion at a more positive potential on the cathode. Recently we observed that the catalytic hydrogen wave of protein HSA and BSA and cationic surfactant tetrabutyl ammonium halide was further catalyzed by various oxidants in ammonium buffer.[18-20] The catalytic hydrogen wave catalyzed is a more sensitive parallel catalytic wave of hydrogen in nature namely parallel catalytic hydrogen wave. The observation is of theoretical significance and of great practical interest. The parallel catalytic hydrogen wave is a new variation of the catalytic wave in polarography. Using it can be further improved analytical sensitivity of these known methods based on the catalytic hydrogen wave. Moreover according to this concept it is possible to find a new pathway for the determination of such substances that their catalytic hydrogen wave is too low sensitive to be neglected in the past.

In this paper a catalytic hydrogen wave of AS in weak acidic medium and its parallel catalytic hydrogen wave in the presence of H_2O_2 are reported and a new polarographic method for the determination of AS with the parallel catalytic hydrogen wave of AS was developed. The proposed method was more simple and convenient and has been successfully used to determine the AS content in environmental wastewater.

Experimental

Apparatus and reagents

The second-order derivative polarograms were recorded with Model JP-303 linear potential scan polarographic analyzer Chengdu Instrumental Factory China . Three-electrode system involved a dropping mercury working electrode DME a platinum wire counter electrode and a saturated calomel reference electrode SCE . Automatic controlled drop time of DME was 7 s and the potential scan rate is 250 mV/s. The cyclic voltammograms were recorded by Model CH660 electrochemical workstation CH Instrument USA . The workstation was equipped with a model 303A static mercury drop electrode system EG&GARA Com. USA that involved a hanging mercury drop working electrode a platinum wire counter electrode and a saturated calomel reference electrode and was controlled by CH660 software under Windows 98 environment.

Sodium linear alkylbenzene sulfonate LAS of average relative molecular mass 344.4 with alkyl carbon number 12 Shanghai Institute of Organic Chemistry China was used as standard of AS according to usual practice. Sodium dodecyl benzene sulfonate SDBS and sodium decyl sulfate SDS are of chemical pure grade content 85% Shanghai Central Chemical Industrial Factory Chi-

na . 1×10^{-3} mol/L standard stock solutions of LAS SDBS and SDS were prepared by dissolving certain amounts of LAS SDBS and SDS with water respectively. The standard working solutions of LAS SDBS and SDS were obtained by diluting the corresponding stock solutions with water. 0.1 mol/L H_2O_2 AR Xi'an Chemical Reagent Factory China solution was standardized by $KMnO_4$ standard solution. Other chemicals used were of analytical reagent grade. Twice-distilled water was used throughout.

Environmental wastewater analysis

Certain amount of LAS standard working solution or wastewater sample solution 0.1 mL of HAc solution 1 mol/L 2.4 mL of NaAc solution 1 mol/L and 0.25 mL of H_2O_2 solution 0.1 mol/L were successively added into 25 mL standard volumetric flask and then diluted to the mark with water. The obtained solution was transferred to a polarographic cell. Second-order derivative polarogram was recorded on JP-303 linear potential sweep polarographic analyzer by scanning cathodically from -1.10 to -1.60 V vs. SCE . The second-order derivative peak current of the parallel catalytic hydrogen wave of LAS at -1.33 V was measured. The calibration curve was constructed by plotting the peak current against LAS concentration. The contents of AS in samples were calculated according to the calibration curve. All experiments were carried out at room temperature.

Results

Voltammetric behavior of LAS

Experiments showed that anionic surfactants such as SDBS and SDS have the voltammeric behavior similar to LAS as standard of AS. Fig. 1 showed cyclic voltammograms of LAS in 0.1 mol/L HAc/NaAc pH = 6.2 buffer after deaeration with free-oxygen nitrogen gas for 10 min. When LAS was present a reduction wave appeared at -1.33 V on cathodic scan no oxidation wave on reverse scan Fig. 1 curve a . The peak current of the reduction wave was small. When H_2O_2 was added into this buffer the peak current of the reduction wave of LAS enhanced greatly and the peak potential remained unchanged at original position Fig. 1 curve b . For convenience the reduction wave enhanced by H_2O_2 was called as the enhanced wave here.

Because the reduction wave of H_2O_2 adjoined the enhanced wave of LAS and was relatively large especially when H_2O_2 concentration was higher the former would overlap the latter. To obtain a good resolution for neighboring polarographic waves the second-order derivative technique was used to record the polarograms. Fig. 2 showed a second-order derivative polarogram. The enhanced wave of LAS was well defined and was well separated from the re-
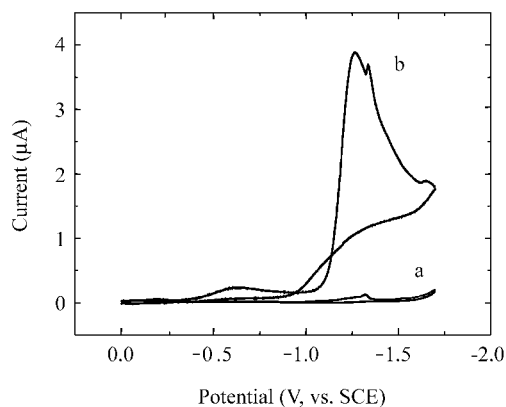
Fig. 1 Cyclic voltammograms of LAS 2.9×10^{-5} mol/L in HAc/NaAc pH = 6.2 0.1 mol/L buffer. a in the absence of H_2O_2 b in the presence of H_2O_2 1.0×10^{-3} mol/L . Starting potential is -0.00 V potential of reversal is -1.60 V potential scan rate = 250 mV/s.
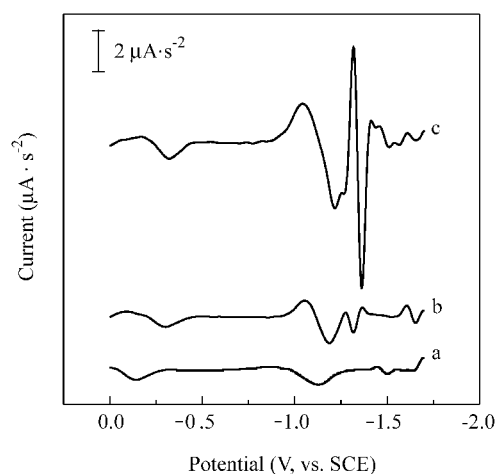

Fig. 2 Second-order derivative polarograms of LAS. a HAc/NaAc pH = 6.2 0.1 mol/L buffer b a + LAS 2.9×10^{-5} mol/L c b + H_2O_2 1.0×10^{-3} mol/L . Starting potential is -0.00 V potential of reversal is -1.60 V potential scan rate = 250 mV/s.

duction wave of H_2O_2.

Effect of pH value

The effect of pH value of HAc/NaAc buffer on second-order derivative peak current $i_{p\ 1}''$ and peak potential E_p of the enhanced wave of LAS was examined in NaAc/HAc/1.0×10^{-3} mol/L H_2O_2 buffer. When the pH value was less than 5.3 the enhanced wave of LAS was close to the reduction wave of H_2O_2 and the two waves could not be distinguished even if the second-order derivative polarogram was recorded. When the pH value was above 7.4 the wave disappeared. Within the pH range of 5.3—7.4 with the pH value increasing the E_p of the enhanced wave of LAS linearly shifted at negative direction the linear regression equation of the E_p-pH relationship was $-E_p = 1.19 + 0.024$pH $r = 0.995$ $n = 8$ Fig. 3 curve b . In the meantime the $i_{p\ 1}''$ of the enhanced wave of LAS

gradually decreased. The $i_{p\ 1}''$ remained a high constant value in the pH range of 6.1—6.3. Thus the NaAc/HAc buffer with pH = 6.2 ± 0.1 was chosen.
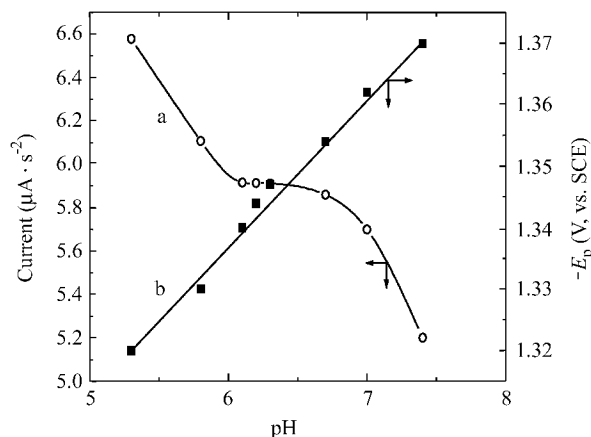

Fig. 3 Effect of pH on peak current a and peak potential b of the parallel catalytic hydrogen wave of LAS 2.9×10^{-5} mol/L in HAc/NaAc 0.1 mol/L + H_2O_2 1.0×10^{-3} mol/L buffer.

Effect of buffer concentration

When the total concentration of the HAc/NaAc pH = 6.2 buffer increased from 0.04 to 0.12 mol/L the peak current $i_{p\ 1}''$ of the enhanced wave of LAS increased and the peak potential E_p shifted positively from -1.38 to -1.33 V Table 1 gradually approaching to the reduction wave of H_2O_2. The shift went against the determination of LAS in lower concentration. Thus the total concentration of the HAc/NaAc buffer with pH = 6.2 ± 0.1 used was 0.1 mol/L.

Table 1 Effect of total concentration of HAc/NaAc pH = 6.2 buffer on peak current and peak potential of the parallel catalytic hydrogen wave of LAS 2.9×10^{-5} mol/L in the presence of H_2O_2 1.0×10^{-3} mol/L

	Total concentration of buffer mol/L				
	0.04	0.06	0.08	0.10	0.12
$-E_p$ V vs. SCE	1.382	1.370	1.358	1.344	1.328
$i_{p\ 1}''$ $\mu A\ s^{-2}$	0.984	4.003	6.425	7.479	7.854

Effect of H_2O_2 concentration

As shown in Fig. 4 the second-order derivative peak current $i_{p\ 1}''$ of the enhanced wave of LAS increased gradually with H_2O_2 concentration increasing. When H_2O_2 concentration was 1.0×10^{-3} mol/L the $i_{p\ 1}''$ was 54 times as high as that of the corresponding reduction wave without H_2O_2 for 2.9×10^{-5} mol/L LAS. When H_2O_2 concentration exceeded 1.0×10^{-3} mol/L the reduction wave of H_2O_2 was too large to measure the enhanced wave of LAS in low concentration. Thus the H_2O_2 concentration was 1.0×10^{-3} mol/L.
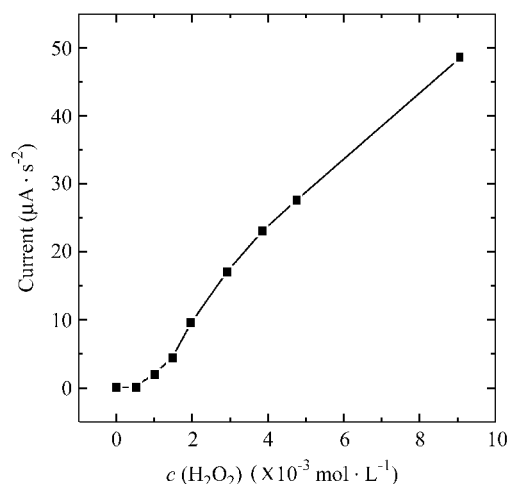
Fig. 4 Effect of H_2O_2 concentration on peak current of the parallel catalytic hydrogen wave of LAS 2.9×10^{-5} mol/L in HAc/NaAc pH = 6.2 0.1 mol/L buffer.

From experimental results mentioned above the optimal supporting electrolyte was 0.1 mol/L HAc/NaAc pH = 6.2 ± 0.1 /1.0 × 10^{-3} mol/L H_2O_2 buffer.

Calibration curve

Experiments showed that all the tested AS such as LAS SDBS and SDS had the analogous relationship of the peak current with their concentration in the optimal supporting electrolyte. The linear regression equations were listed in Table 2. The second-order derivative peak current $i_{p\,1}''$ of the enhanced wave of both LAS and SDBS with a sulfo-group was rectilinear to their concentration in the range of 3.0×10^{-6}—2.5×10^{-4} mol/L 1.0 and 86.1 mg/L . For SDS with a sulfate group the linear range was over 4.7×10^{-5}—3.3×10^{-4} mol/L. The difference of both LAS and SDBS with SDS in analytical sensitivity must originate from the difference between sulfo-group and sulfate group in chemical properties. Compared with those known tensammtric and polarographic adsorption methods for the determination of AS [7 8] the proposed method improved the sensitivity by about two orders of magnitude. Additionally the enhanced wave showed good-stability and reproducibility. The peak current of the enhanced wave was unchanged at least within 8 h. The RSD observed for 30 repetitive measurements of 2.9×10^{-5} mol/L LAS was 2.4%.

Interference test

The effect of some inorganic ions and cationic surfactants usually present in wastewater was tested by analyzing a standard solution of 2.0×10^{-5} mol/L LAS containing the various amounts of interfering compounds. When the variation was at ± 5% level the tolerable concentration ratios with respect to 2.0×10^{-5} mol/L LAS were more than 1000 for Cl^- NH^{4+} Pb^{2+} Ca^{2+} Mg^{2+} Ag^+ 500 for NO_3^- 100 for Cu^{2+} NO_2^- 50 for SO_4^{2-} and 5 for Co^{2+} Fe^{3+} Zn^{2+} tetrabutyl ammonium bromide tetramethyl ammonium chloride hexadecyl trimethyl ammonium bromide. The tolerable amounts of these substances were generally more than their normal ones in environmental water.

Determination of the AS in wastewater

To evaluate the proposed method after wastewater sample was properly diluted with water the AS in wastewater was directly determined by the proposed method without any pre-separation. The obtained results were summarized in Table 3. These results were in good agreement with those obtained by spectrophotometric method using methylene blue.[1] Recovery tests were performed by adding different amount of LAS standard solution to a sample solution. The recoveries obtained were listed in Table 4.

Discussion

Fig. 5 curve a showed an alternating current voltammogramm. A pair of tensammetric wave of LAS appeared at − 0.20 and − 1.30 V respectively. The result was consistent with that obtained by Kalvoda [11] Szymanski and his coworkers.[21] Experiment showed that the peak potential of the pair of tensammetric wave was function of LAS concentration and the current value of the pair of tensammetric wave was neither increased nor decreased after adding H_2O_2 Fig. 5 curve b . These differences between the tensammetric wave and the reduction wave of LAS in polarographic behavior indicated that the observed reduction wave at − 1.33 V was not tensammetric one. In addition under the condition of this work the presence of LAS would make the reduction wave of H_2O_2 shift slowly to negative direction.[16] When LAS concentration was 2.9×10^{-5} mol/L the peak potential of the reduction wave of H_2O_2 was near to − 1.20 V. Therefore the observed re-

Table 2 Calibration curves

Compound	Concentration range mol/L	Linear regression equation		
		Intercept μA	$10^4 \times$ slope μA L/mol	r $n = 7$
LAS	3.0×10^{-6}— $- 2.5 \times 10^{-4}$	− 0.41	11.3	0.999
SDBS	3.2×10^{-6}— $- 2.4 \times 10^{-4}$	− 0.41	11.3	0.998
SDS	4.7×10^{-5}— $- 3.3 \times 10^{-4}$	− 0.38	6.80	0.997

Table 3   AS content in environmental wastewater

Wastewater sample	Proposed method			Methylene blue spectrophotometric method mg L^{-1}
	AS content mg L^{-1}	Average mg L^{-1}	RSD %	
1$^{\#}$	2.51 2.54 2.53 2.58 2.51 2.59	2.54	3.4	2.56
2$^{\#}$	2.45 2.46 2.43 2.49 2.40 2.39	2.44	3.7	2.41

Table 4   Recovery results in samples

| Amount added mg L^{-1}	Amount found mg L^{-1}	Recovery %	Average recovery %
8.0	8.09 7.74	101.1 96.8	
10.0	9.65 10.32	96.5 103.2	99.4
12.0	11.48 11.94	99.3 99.5	
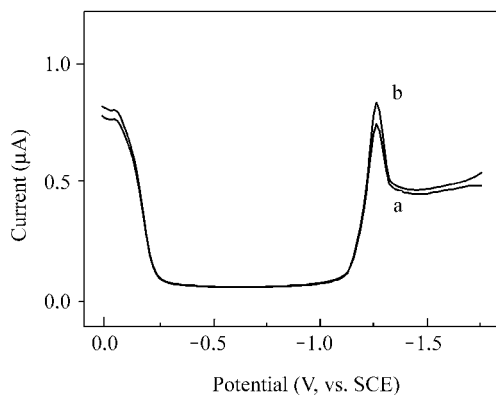
Fig. 5   Alternating current voltammograms of LAS 2.9 × 10^{-5} mol/L in a HAc/NaAc pH = 6.2 0.1 mol/L buffer b HAc/NaAc + H$_2$O$_2$ 1.0 × 10^{-3} mol/L increment potential 15 mV amplitude 30 mV frequency 100 Hz. Starting potential is − 0.00 V potential of reversal is − 1.60 V.

duction wave at − 1.33 V was not the reduction wave of H$_2$O$_2$ shifted negatively by LAS too.

Except the irreversibility of the reduction wave was proved with cyclic voltammetry as shown in Fig. 1 curve a the dependence of both peak current and peak potential of the reduction wave on both pH value and the total concentration of the HAc/NaAc buffer was also examined. With the pH value of the buffer increasing the peak current i_p'' decreased and the curve of the i_p''-pH relationship showed a trend similar to that of the partition ratio of hydrogen ion on strong-acid anion-exchanger with the pH value increasing. The peak potential E_p linearly shifted to negative direction. The linear regression equation of the E_p-pH relationship was $− E_p = 1.14 + 0.031\text{pH}$ $r = 0.998$ $n = 8$. Moreover with the increase of the total concentration of the buffer the i_p'' increased gradually and the E_p shifted slowly to positive direction. These charac-

teristics of the reduction wave of LAS were in accord with that of the catalytic hydrogen wave presented by Koutecky.[22] Therefore the reduction wave was the catalytic hydrogen one.

Because LAS possess no reducible group the catalytic hydrogen wave must result from the reduction of some variants of LAS. Despite of strong-acid sulfonic acid with pK_a value of approximately − 0.5 the sulfo-group anion of LAS can partially form ion-association specie RSO$_3$ H by electrostatic attraction of the negative-charged sulfo-group anion of LAS with positive-charged hydrogen ion in acidic and weak acidic solution. It was the reduction of the hydrogen ion that was carried on RSO$_3$ H led to the production of the catalytic hydrogen wave of AS. The production process of the catalytic hydrogen wave of LAS was proposed as follows

$$RSO_3^- + H^+ \rightarrow RSO_3\ H$$

$$RSO_3\ H + e^- \rightarrow RSO_3\ H^*$$

$$2\ RSO_3\ H^* \rightarrow 2\ RSO_3^- + H_2 \uparrow$$
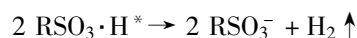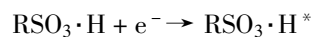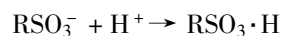
where R presented alkylbenzene part of LAS RSO$_3$ H* was an intermediate product of the reduction of the ion-dissociation specie RSO$_3$ H of LAS.

As mentioned above when H$_2$O$_2$ was present the peak potential of the catalytic hydrogen wave at − 1.33 V remained unchanged and the peak current increased greatly. And the peak current of the catalytic hydrogen wave of LAS increased gradually with H$_2$O$_2$ concentration increasing. The ratio of the peak current $i_{p\ 1}$ of the enhanced wave with the peak current i_p of the catalytic hydrogen wave was linear with the square root of H$_2$O$_2$ concentration in the range of 1.0×10^{-3}—9.0×10^{-3} mol/L. The linear regression equation $i_{p\ 1}/i_p$ was $77.4\ c_{H_2O_2}^{1/2}$ $r = 0.998$ $n = 7$. These characters demonstrated that the catalytic hydrogen wave of LAS was further catalyzed by H$_2$O$_2$ producing the parallel catalytic hydrogen wave.

From the production process of the catalytic hydrogen wave of LAS the intermediate product RSO$_3$ H* in the reduction of the ion-dissociation specie RSO$_3$ H of LAS was a particle that carried a reactive atomic hydrogen. If the intermediate product RSO$_3$ H* were in the chemical environment in the presence of oxidant a chemical reaction specific for the atomic hydrogen would take place. The chemical reactions of atomic hydrogen that was produced by radiolysis or photolysis of water with inorganic oxidant had been studied.[23,24] The results showed that the reaction of atomic hydrogen with H$_2$O$_2$ molecule is a hydrogen abstraction resulting in the formal oxidation of H$_2$O$_2$ to HO$_2$ but this is a much slower process. However the reaction of atomic hydrogen with hydroxyl radical ·OH as an intermediate of H$_2$O$_2$ reduction is very fast with a rate constant of ~ 10^{10} L/ mol s .[23] It is known that H$_2$O$_2$ is reduced via a hydroxyl radical ·OH in two successive one-

electron addition steps.[25] In the case of this work the reduction wave of H_2O_2 appeared at more positive potential than where the catalytic hydrogen wave of LAS did. Therefore at more negative potential domain than the appearance of the reduction wave of H_2O_2 there was the hydroxyl radical ·OH generated in H_2O_2 reduction on electrode surface. When the atomic hydrogen carried by the intermediate product $RSO_3 H^*$ met with the hydroxyl radical ·OH from H_2O_2 reduction on electrode surface the former was oxidized by the latter to reproduce the original reactant proton that was subsequently reduced again producing the parallel catalytic wave of hydrogen of LAS in nature namely parallel catalytic hydrogen wave of LAS. The oxidation process of the atomic hydrogen of the intermediate product $RSO_3 H^*$ by the electrogenerated hydroxyl radical ·OH was proposed as follows

$$RSO_3 H^* + \cdot OH \rightarrow RSO_3 H + OH^-$$
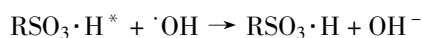
In order to prove that the hydroxyl radical ·OH from H_2O_2 reduction participated in the oxidation reaction ferrous salt solution was added into the HAc/NaAc buffer containing H_2O_2. The peak current of the parallel catalytic hydrogen wave of LAS further increased with ferrous salt concentration increasing. This was due to that the Fenton's reaction of ferrous ion with H_2O_2 produced more amount of hydroxyl radical ·OH.

The production mechanism of the parallel catalytic hydrogen wave of SDBS and SDS should be the same as that of LAS. Thus the catalytic cycle for the parallel catalytic hydrogen wave of AS was presented as follows

$$RSO_3^- + H^+ \rightarrow RSO_3 H$$

$$RSO_3 H + e^- \rightarrow RSO_3 H^*$$

$$RSO_3 H^* + \cdot OH \rightarrow RSO_3 H + OH^-$$
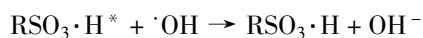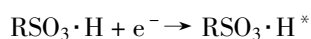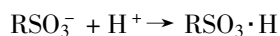
Conclusion

A catalytic hydrogen wave of electroinactive AS in weak acidic medium was first reported in this paper. The catalytic hydrogen wave of AS was catalyzed by hydroxyl radical ·OH from H_2O_2 reduction producing a parallel catalytic hydrogen wave.

With the parallel catalytic hydrogen wave of AS the new and high selective method for the determination of AS in environmental sample was proposed. The main advantages of the proposed method are 1 All the AS such as LAS SDBS and SDS have the same polarographic behavior and linear range similar to LAS as standard. The total concentration of AS can be conveniently determined. 2 The certain amounts of other surfactants are tolerated and do not interfere with the determination. The selectivity is good. 3 The sensitivity for the determination of AS has been improved by about two orders of magnitude compared with the known tensammetry and polarographic adsorption

analysis methods. 4 The proposed method is more simple and convenient as it only requires the addition of suitable electrolyte and the use of current linear potential scan polarograph.

Acknowledgement

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