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Influence of cationic gemini surfactants on the electrochemical behavior of 2-thiouracil at silver electrodes

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Abstract The voltammetric behavior of 2-thiouracil at a silver electrode is described. 2-Thiouracil can deposit or chemisorb anodically at silver surface; when the potential is made more negative the deposited 2-thiouracil undergoes reductive desorption-process, yielding a cathodic peak at about -1.2 V (vs. SCE) in basic phosphate buffer solution (pH 10.3). In the presence of cationic gemini surfactant $C_4H_8-1,4-(C_{16}H_{33}N^+(CH_3)_2Br^-)_2$ ($C_{16}-C_4-C_{16}$) the deposition of 2-thiouracil is greatly improved and the cathodic peak is enhanced. Meanwhile, the peak shifts to more negative potential. The role of $C_{16}-C_4-C_{16}$ is thought to combine and co-adsorb with 2-thiouracil at silver surface as well as reduce the electrostatic repulse in the deposited film, thus making it more easy to deposit and desorb at more negative potential. With $C_{16}-C_4-C_{16}$ the lateral interaction of deposits reduces, the reductive desorption becomes faster and the cathodic peak becomes sharper. For geminis with different spacer groups and alkyl chains, their influence is mainly determined by their hydrophobicity and adsorbability. It was found that increasing length of alkyl chain was favorable for obtaining a high and sharp desorption peak, whose peak potential is more negative. For comparison, surfactants with single alkyl-chain and double alkyl-chain, such as cetyltrimethyl ammonium bromide and dicyldimethyl ammonium bromide were studied. They made the desorption peak shift less due to their weaker combination with 2-thiouracil.

Keywords 2-Thiouracil · Cationic gemini surfactants · Silver electrode · Voltammetry

Introduction

Thiols and disulfide-containing compounds have been the focus of a great amount of research [1–3]. This is due to their significance in several fields such as biological medicine, chemistry and material protection. Their functions are related to the oxidation–reduction of $-SH$ and $-S-S-$ groups, as well as to their interaction with metals [4–6]. As these compounds generally exhibit electroactivity or cause electrochemical signals partly due to the electrochemical redox of $-S-S-$ and $-SH$ groups, much attention has been paid to their electrochemical study [7, 8]. Among these compounds, thiouracils and thiopurines have attracted special interest. Thiouracils are minor components of transfer RNA and widely used for treatment of hyperthyroidism in man, while thiopurines are usually used in cancer therapy [9–12]. Dryhurst and Wrona et al. have investigated their electrochemical behavior at mercury and some solid electrodes in detail [8, 9, 13]. They exhibited current signals at mercury electrodes, resulting from the reduction of surface films of insoluble thiolate salts (e.g., mercury thiolate) [14–16]. Similarly, they were found to produce cathodic stripping peaks at silver electrodes, but the situation is more complicated [17]. For 2-thiouracil two stripping peaks were observed by Hepels et al. at silver electrodes, and they were attributed to the reduction of microphase and macrophase deposits of 2-thiouracil, respectively [17, 18]. The cathodic stripping peak of microphase deposits could be used for its determination at lower concentration level. 2-Mercaptopyrimidine can also cause two cathodic peaks at silver electrodes, resulting from the reduction of silver thiolate followed by 2-mercaptopyrimidine [19]. Generally, their voltammetric behavior is influenced by many factors at silver electrodes, but the influence of surfactants was seldom elucidated in detail.

Surfactants are extensively used in electrochemical field because they can adsorb onto electrode surface and change electrochemical process. In most cases, their

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adsorption makes the rate of electrode reaction and the current signal decrease. Hence they are usually considered interferences in polarographic and voltammetric studies. However, under some conditions, they show an enhancing effect. Stadlober et al. used cetyltrimethyl ammonium bromide (CTAB) to modify a carbon paste electrode for the determination of titanium and vanadium [20, 21], and a marked improvement in accumulation efficiency and reversibility of the electrode reaction was observed. This was attributed to the formation of an ion-exchanger at the electrode surface caused by the adsorption of CTAB, and to the formation of ion-pairs in solution. In our previous work, cationic surfactants CTAB and cetylpyridium bromide (CPB) were also found to facilitate greatly the deposition and stripping of cysteine and thiopurines at silver electrodes [22–24]. But few similar phenomena were observed with other metal electrodes, including mercury electrodes, although its property is similar to that of silver electrodes. The action of surfactants was closely related to their molecular structure, and only several kinds of surfactants show enhancing effect, such as cationic surfactants bearing $-C_{16}H_{33}$ alkyl-chain. So far, among the surfactants, no gemini surfactants were used for such a study. Geminis are a new type of surfactant that consists of one spacer group, two ionic head groups and two hydrophobic alkyl-chains, and exhibit many unique properties [25–27].

The purpose of this work is to study the influence of cationic gemini surfactants on the electrochemical behavior of 2-thiouracil and compare the characteristics of different surfactants at silver electrode surface.

Experimental

Apparatus

All electrochemical measurements were performed with a CHI 660A electrochemical workstation (CH Instrumental Co., USA). A typical three-electrode system was used for voltammetric determination. It consisted of a platinum wire counter electrode, a saturated calomel reference electrode (SCE) and a silver-disk working electrode (2.0-mm diameter, purity 99.99%, home-made, fixed in a glass tube with epoxy resin). Prior to determination, the silver electrode was polished with 0.3 and 0.05 μm alumina slurry, rinsed with water, then ultrasonicated and washed with water. The pH values were measured using a pHS-3C pH meter (Shanghai, China). ATR-FT-IR spectra were collected on a Nicolet Nexus-670 equipped with an MCT detector and a diamond crystal (45 degree angle) as the attenuated total reflection (ATR) accessory. The spectra were recorded from 4,000 to 650 cm^{-1} . Laser Raman spectra experiments were performed on a Nicolet Nexus-670 Raman meter with an excitation wave number of 1,064 cm^{-1} . The deposition film on silver surface used for recording IR and Raman spectra was obtained by deposition in a

phosphate buffer solution (pH 10.3, 0.05 M) containing 10 μM 2-thiouracil and 20 μM $C_{16}-C_4-C_{16}$.

Reagents

2-Thiouracil (97%) was purchased from Aldrich and used as received. Its stock solution (0.01 M) was prepared with diluted sodium hydroxide solution and water. Gemini surfactants, $C_4H_8-1,4-(C_{16}H_{33}N^+(CH_3)_2Br^-)_2 (C_{16}-C_4-C_{16})$, $C_{12}H_{24}-1,12-(C_{16}H_{33}N^+(CH_3)_2Br^-)_2 (C_{16}-C_{12}-C_{16})$, $C_{12}H_{24}-1,12-(C_{12}H_{25}N^+(CH_3)_2Br^-)_2 (C_{12}-C_{12}-C_{12})$ and $CH_2CHOH(CH_2)_2-1,4-(C_{16}H_{33}N^+(CH_3)_2Br^-)_2 (C_{16}-C_4OH-C_{16})$ etc. were synthesized and purified according to the method reported in the reference [28]. Their stock solutions were prepared with alcohol and water. All stock solutions were stored in a refrigerator and prepared periodically. Other chemicals used were of reagent or analytical grade. Solutions of lower concentration were obtained by diluting the stock solutions with sodium phosphate buffer (pH 10.3) and water. Water used was double distilled.

Experimental procedure

Ten milliliter of 0.05 M sodium phosphate buffer solution (pH 10.3) and proper amount of surfactants and 2-thiouracil were added into a conventional single cell, then the electrode system was mounted in it. After a deposition process at proper potential cyclic voltammograms (CVs) were recorded from 0.05 V to -1.50 V. During the deposition process the working solutions were stirred with a Teflon coated stirring rod. In general, the stirring rate was unchanged. The solutions were deaerated as needed for at least 5 min by bubbling nitrogen gas. All experiments were performed at room temperature.

Results and discussion

Voltammograms of 2-thiouracil

In alkaline solutions, 2-thiouracil of high concentration (e.g., 100 μM) can exhibit a small cathodic peak at about -1.2 V at silver electrodes after an anodic accumulation step (Fig. 1b). This peak is somewhat symmetric, indicating that the reduction of the deposits is random [19]. Without anodic accumulation, no discernible peak was observed under this condition, so it was thought that the adsorption or deposition of 2-thiouracil was quite slow and the 2-thiouracil diffusing from bulk solution could not directly generate this peak. On the other hand, a very small cathodic peak occurred at this potential after the silver electrode was immersed in a 0.01 M 2-thiouracil solution for 1 h. Therefore, the cathodic peak should be ascribed to the reduction of the deposited or adsorbed 2-thiouracil. As the peak appears

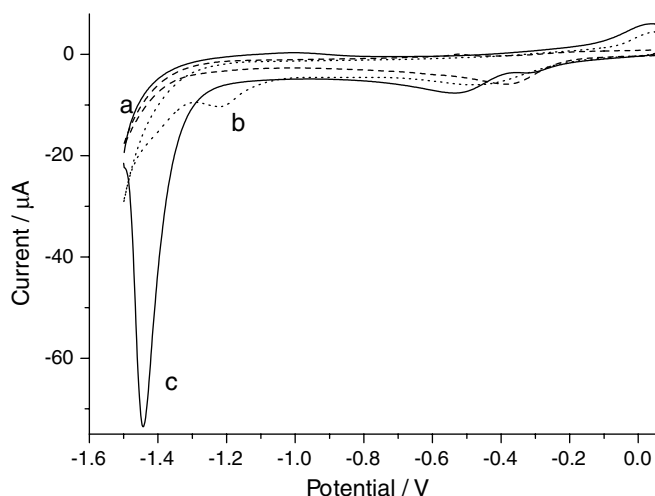


Fig. 1 CVs of a silver electrode in: *a* 0.05 M sodium phosphate buffer (PBS, pH 10.3), *b* a + 100 μM 2-thiouracil, *c* b + 200 μM $\text{C}_{16}\text{-C}_4\text{-C}_{16}$. Scan rate 100 mV/s; deposition potential 0.05 V; deposition time 120 s

at quite negative potential, it was thought not to result from the reduction of silver ion in complexes concerning 2-thiouracil but from the reductive desorption of chemisorbed 2-thiouracil as reported in literatures about thiocholine at silver electrodes and alkanethiols at gold electrodes [29–31]. Thus the electrode reaction can be described as: $\text{Ag(s)} + \text{TUH}_2(\text{aq}) = \text{Ag(s)-TUH} + \text{H}^+ + \text{e}^-$ ($\text{TUH}_2 = 2\text{-thiouracil}$). The deposition efficiency of 2-thiouracil is quite low, for there was no cathodic peak visible when its concentration decreases to 10 μM . However, when some cationic gemini surfactants such as $\text{C}_{16}\text{-C}_4\text{-C}_{16}$ are present, the deposition process is improved significantly and a sharp cathodic peak occurs (Fig. 1c). While the peak becomes higher, the peak shifts to more negative potentials (e.g., shifts for about 200 mV in the presence of 200 μM $\text{C}_{16}\text{-C}_4\text{-C}_{16}$, in comparison to that without geminis). As no

cathodic peak belonging to $\text{C}_{16}\text{-C}_4\text{-C}_{16}$ and bromide ion was observed in the potential range, the enhancing action should be ascribed to the influence of $\text{C}_{16}\text{-C}_4\text{-C}_{16}$ on the deposition and reductive desorption behavior of 2-thiouracil. It is well known that surface-active species easily accumulate at electrode-solution interface and change the electrode-surface property and interface-potential distribution, then altering the active energy of the interface reaction. Here, the action of $\text{C}_{16}\text{-C}_4\text{-C}_{16}$ was thought to combine with 2-thiouracil at silver surface in addition to those, thus the resultant deposition film was different from that without $\text{C}_{16}\text{-C}_4\text{-C}_{16}$. In the presence of $\text{C}_{16}\text{-C}_4\text{-C}_{16}$ the electrode reaction can be proposed as: $n\text{Surf} + \text{TUH}_2(\text{aq}) + \text{Ag(s)} = \text{Ag(s)-TUH}(\text{Surf})_n + \text{e}^- + \text{H}^+$ (where $\text{Surf} = \text{C}_{16}\text{-C}_4\text{-C}_{16}$). Besides the desorption peak, a broad peak at about -0.4 V is observable. This peak is related to the reduction of dissolved oxygen. When the solutions were deaerated by bubbling nitrogen gas the peak decreased. The addition of 2-thiouracil and surfactant make it change a little due to their influence on the electrode surface.

Characterization with IR and Raman spectra

Figure 2 shows the IR and Raman spectra of the deposition film. As can be seen, the deposition film exhibits strong absorption bands at 2,925 and 2,851 cm^{-1} , which correspond to the asymmetric and symmetric stretching vibration of plentiful methylene groups in $\text{C}_{16}\text{-C}_4\text{-C}_{16}$. Meanwhile, the plane swaying vibration of methylene is observed at 726 cm^{-1} . The weak band appearing at 1,376 cm^{-1} is ascribed to the bending vibration of methyl groups in $\text{C}_{16}\text{-C}_4\text{-C}_{16}$. As shown in Fig. 2b, $\text{C}_{16}\text{-C}_4\text{-C}_{16}$ exhibits no discernible absorption peaks over the frequency range of 2,000–1,490 cm^{-1} and 1,370–1,050 cm^{-1} , thus the absorption peaks of deposition films in this range must be caused by 2-thiouracil in the film as there is no other component

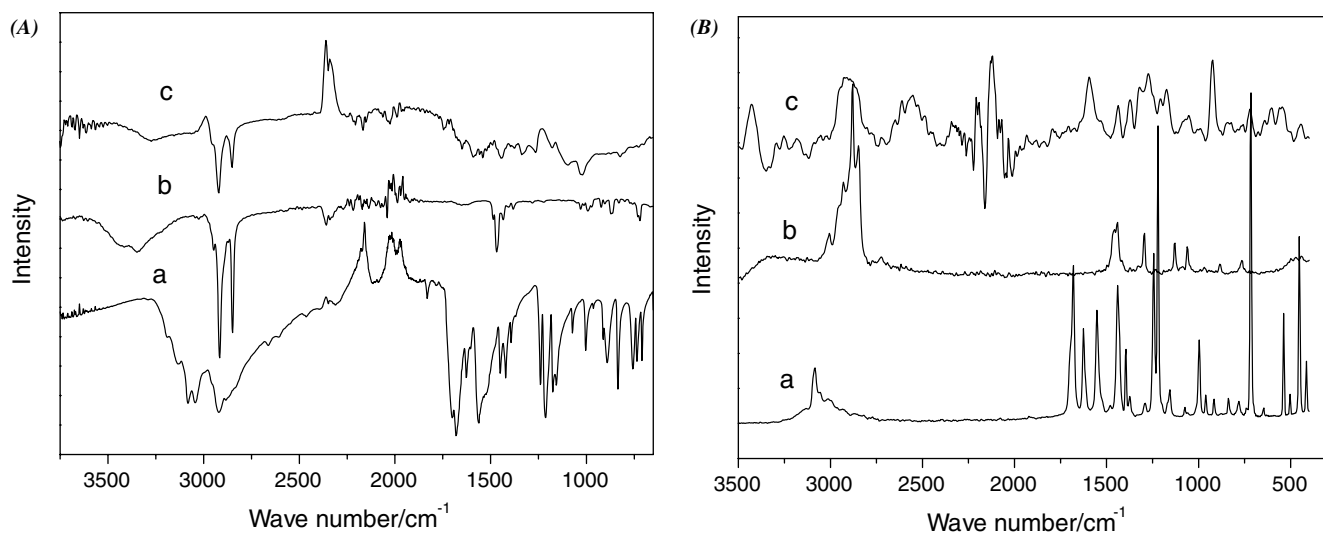


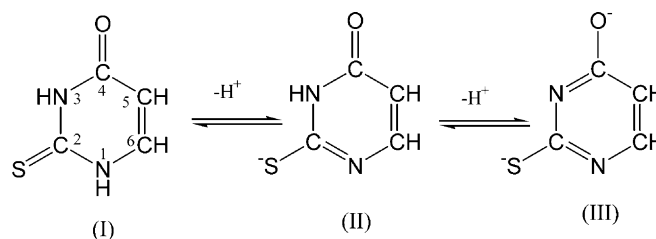
Fig. 2 IR (A) and Raman spectra (B). (a) 2-thiouracil, (b) $\text{C}_{16}\text{-C}_4\text{-C}_{16}$, (c) deposition film of 2-thiouracil with $\text{C}_{16}\text{-C}_4\text{-C}_{16}$

contained in it. Owing to the interaction of 2-thiouracil with Ag electrode and $C_{16}\text{-C}_4\text{-C}_{16}$, the absorption bands shift to some degree, and part of its bands disappear, compared with pure 2-thiouracil. For example, the vibration frequency of $C=O$ shifts from $1,681\text{ cm}^{-1}$ to $1,650\text{ cm}^{-1}$ due to the formation of silver thiolate or Ag-SR bond. The formation of silver thiolate also can be deduced from the disappearance of the band at $1,157\text{ cm}^{-1}$, which belongs to stretching vibration of $C=S$ [32]. The corresponding Raman spectra of the deposition film also shows a little trace of 2-thiouracil and $C_{16}\text{-C}_4\text{-C}_{16}$, but the signal is relative weak. Therefore, the deposition film contained both 2-thiouracil and $C_{16}\text{-C}_4\text{-C}_{16}$, but some change occurred with them due to the interaction.

Influence of solution pH

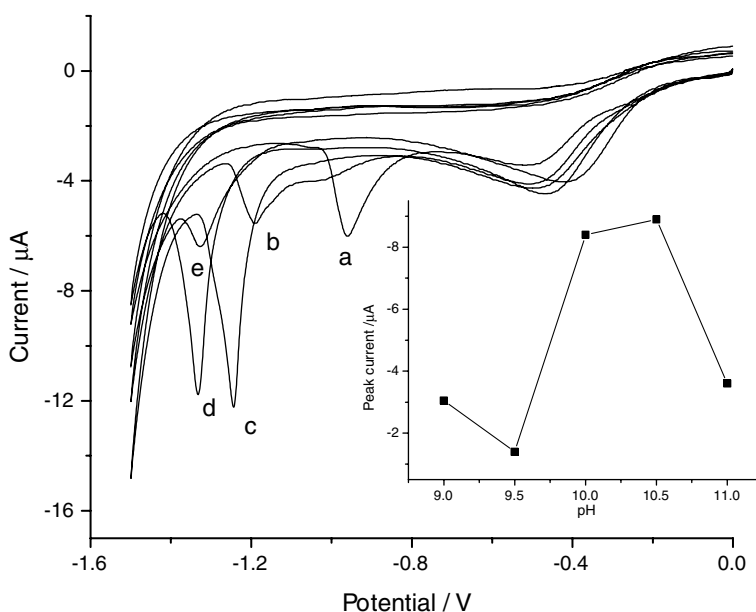
Solution pH has pronounced influence on the peak shape and peak potential (Fig. 3). In acidic, neutral and weakly basic phosphate buffer, there is no discernible cathodic peak observed for $20\text{ }\mu\text{M}$ 2-thiouracil even in the presence of $C_{16}\text{-C}_4\text{-C}_{16}$. However, a sharp cathodic peak occurs in alkaline media. This peak increases with rising pH and reaches a maximum at about pH 10, and then decreases. The change of peak current is partly related to the dissociation of 2-thiouracil. It is known that the first dissociation constant of 2-thiouracil (K_{a1}) is $10^{-7.75}$ and the second is about $10^{-12.7}$ [33]. That is to say, 2-thiouracil can turn to 4-keto-2-thione (I, H_2TU), enolized (II, HTU^-) or di-enolic structure (III, TU^{2-}) with changes in solution pH (Scheme 1). Thus it exhibits different reaction and adsorption activity under different conditions due to the change in structure and charge number. In acidic solutions, the deposition of 2-thiouracil is relative difficult because of the influence of

plentiful protons. In alkaline solutions, the deposition of 2-thiouracil as $AgHTU$ or $AgTU^-$ is easier because it turns into anion and easily adsorbs at positively charged silver electrode surface. But in strong alkaline solutions (e.g., $pH \geq 11.0$), the formation of silver hydroxide dominates at the deposition potential, which suppresses the deposition of 2-thiouracil. Additionally, further dissociation of HTU^- gives rise to the electrostatic repulsion among 2-thiouracils. Hence, an alkaline solution with pH values of 10–11 is favorable for the formation of silver thiolate film. Taking into account the change of optimum deposition potential with solution pH, following experiment was performed to examine the influence of pH on the reductive desorption-process. The deposited 2-thiouracil was reduced in solutions with different pH after it was deposited under the same conditions. As a result, the peak was sharper when it was reduced in solution with pH 10–11, indicating that the pH range was also favorable for the reductive desorption-process. As expected, the peak potentials were similar to those of Fig. 3. It should be pointed out, the influence of solution pH associates with the change in the enhancing action of surfactants. In alkaline solutions, cationic surfactant $C_{16}\text{-C}_4\text{-C}_{16}$ combines with 2-thiouracil more strongly due to increase in electrostatic attraction, making the deposition easier.



Sch. 1 Dissociation equilibrium of 2-thiouracil

Fig. 3 CVs of $20\text{ }\mu\text{M}$ 2-thiouracil in the presence of $33\text{ }\mu\text{M}$ $C_{16}\text{-C}_4\text{-C}_{16}$ at a silver electrode. Solution pH 9.0 (a), 9.5 (b), 10.0 (c), 10.5 (d) and 11.0 (e); supporting electrolyte: 0.05 M sodium phosphate buffer; scan rate 50 mV/s ; deposition potential 0 V ; deposition time 120 s



The peak moves in negative direction with rising pH. It is due to the protons taking part in the electrode reaction. However, the change of peak potential is greater than expected. The combination of C₁₆-C₄-C₁₆ with 2-thiouracil should account for this in addition to the change of ohm drop caused by the film. The combination must become stronger when solution pH increases, since the structure and charge number of 2-thiouracil change. Hence more change of peak potential than that caused only by pH variation is observed.

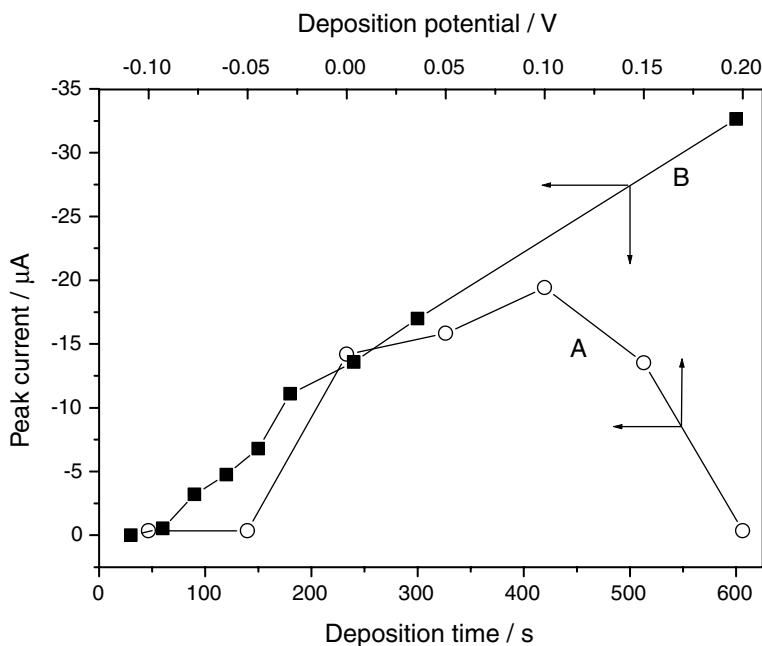
Influence of deposition potential and time

As the formation of silver thiolate associates with the oxidation of silver or the HS-group in 2-thiouracil, the deposition potential is an important factor to influence the deposition efficiency as reported for alkanethiols on gold [34]. It can be seen in Fig. 4, when the deposition potential changes, the peak current varies. At a potential below 0 V, the peak is smaller or invisible, indicating little 2-thiouracil deposits. At potential above 0.2 V, however, the peak is also very small or invisible, due to the formation of silver oxide or silver hydroxide. In this case, a new peak at about -0.1 V can be observed, which belongs to the reduction of silver oxide or silver hydroxide. Accordingly, the potential range of 0.0–0.15 V is preferable for deposition when solution pH is around 10.3. On the other hand, when the potential exceeds the optimum value, the number of silver ions formed increases; a poorly soluble compound is formed in the bulk solution to an increasing extent. This compound is not adsorbed on the electrode surface, so the peak current decreases [35]. When C₁₆-C₄-C₁₆ was absent, the optimum deposition potential was a little

smaller, indicating C₁₆-C₄-C₁₆ shows some influence on the reaction active energy of 2-thiouracil with silver.

The peak current keeps growing with deposition time increasing in the time scope studied, a deposition time longer than 10 min has not been studied further. This indicates that the deposition film is a dense one or includes multi-layer. Film thickness was estimated under the assumption that the change corresponding to a monolayer is not very different from those of other pyrimidine derivatives, which were determined from capacitance data obtained on mercury electrodes [36]. The value for uracil, which is quite similar in structure and size to 2-thiouracil. The area occupied by one uracil molecule is about 0.63 nm². According to the difference of intercept of $Q-t^{1/2}$ plots corresponding to both blank and 2-thiouracil solutions (Fig. 5), the charge corresponding to deposits can be known (i.e., 1.6 μC). Thus the thickness of the deposited film is estimated to be about one monolayers for 10 μM 2-thiouracil with 50 μM C₁₆-C₄-C₁₆ after a 2 min deposition (assuming the roughness ratio of silver electrode surface is 2.0). When the deposition time was prolonged the deposited amount increased further. The deposition film seems to turn to multi-layer, which is partly related to the imprecise estimation-method used. The orientation of 2-thiouracil on silver surface generally is not flat, thus it occupies smaller area. On the other hand, it is possible for 2-thiouracil to form not only a silver thiolate monolayer as silver can turn to ion more easily at a positive deposition-potential. Meanwhile, the peak shifts slightly in negative direction probably due to the ohm drop increase. It is worth noting that the film structure was complicated by the surfactant in this case, hence the film thickness estimated was not accurate enough. As shown in Fig. 5, the Q increases more rapidly within

Fig. 4 Dependence of cathodic peak current on deposition potential (A) and deposition time (B). Concentration of 2-thiouracil 10 (A) or 5 μM (B); C₁₆-C₄-C₁₆ concentration 20 μM (A) or 10 μM (B); other conditions as in Fig. 1



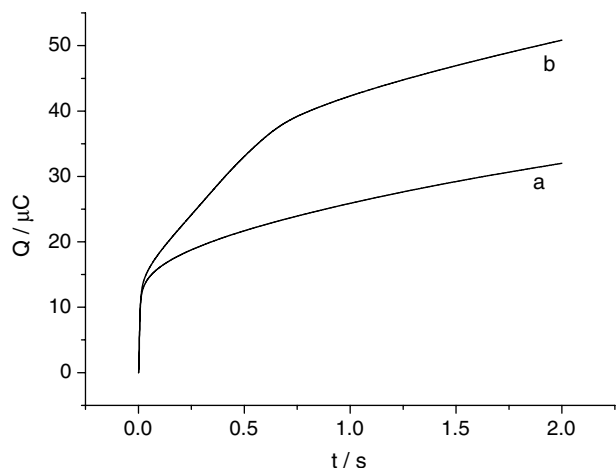
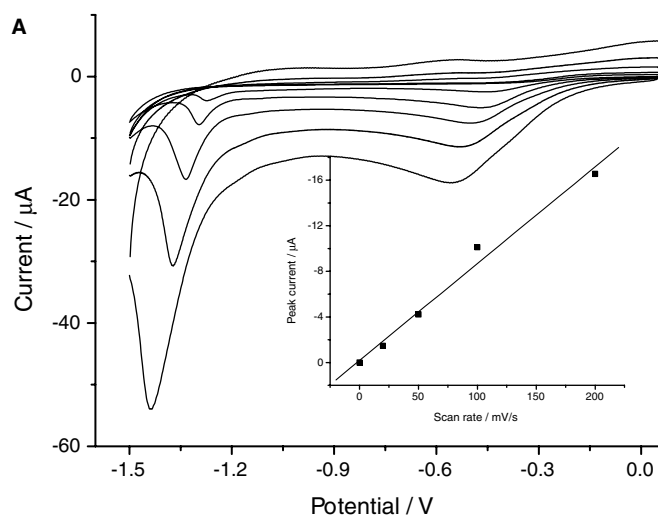


Fig. 5 $Q-t$ plots. (a) 0.05 M phosphate buffer + 50 μM $\text{C}_{16}\text{-C}_4\text{-C}_{16}$; (b) (a) + 10 μM 2-thiouracil; $E_d=0.05$ V; $t_d=120$ s; $E=-1.4$ V

0.7 s and then slows down, meaning that the reductive desorption of the deposits was completed in about 0.7 s.

In order to clarify whether the reduction process is complicated by adsorption-desorption of the electroactive species, consecutive experiments were carried out with progressively increasing deposition times followed by progressively decreasing deposition times. Reduction is carried out after each deposition, and the electrode is not physically cleaned between runs. If no accumulation occurs, plots of the cathodic peak current versus the deposition time should be straight line in certain time scope. In this case, a curve for decreasing deposition time lies above the forward line (the figure was ignored). This indicates the desorption rate of the reduced products, i.e., 2-thiouracil, is slower [18, 19].



Dependence of peak current on scan rate

Figure 6 shows the dependence of cathodic peak current on scan rate. As can be seen, the peak current is linear to the scan rate, the regression equation is $i_{pc} (\mu\text{A}) = -0.18 - 0.085 v (\text{mV/s})$ with a correlative coefficient of 0.993. This indicates that the electrochemical process is surface-reaction controlled, which is in accordance with the electrode reaction mechanism mentioned above. Meanwhile, the peak moves to more negative potential with rising scan rate, meaning that the electron-transfer rate is not very fast or/and the ohm drop is increasing. Without $\text{C}_{16}\text{-C}_4\text{-C}_{16}$, the peak current also changes linearly with scan rate, and the peak potential shifts simultaneously.

Influence of $\text{C}_{16}\text{-C}_4\text{-C}_{16}$ on deposition and reductive desorption-process

The influence of $\text{C}_{16}\text{-C}_4\text{-C}_{16}$ concentration on the peak current is shown in Fig. 7. The peak current keeps increasing until the $\text{C}_{16}\text{-C}_4\text{-C}_{16}$ concentration reaches 100 μM for a 10 μM 2-thiouracil solution. As the $\text{C}_{16}\text{-C}_4\text{-C}_{16}$ concentration increases, its adsorption amount increases, thus the deposited amount of 2-thiouracil also grows. The peak moves in negative direction slightly, resulting from the increase in ohm drop and combination strength.

Figure 8 shows the influence of $\text{C}_{16}\text{-C}_4\text{-C}_{16}$ on the deposition and reduction-process of 2-thiouracil. It can be seen that a sharp peak occurs after deposition in a solution containing 10 μM 2-thiouracil and 50 μM $\text{C}_{16}\text{-C}_4\text{-C}_{16}$, while a small or no discernible peak is observed after deposition in a solution without $\text{C}_{16}\text{-C}_4\text{-C}_{16}$. These indicate that $\text{C}_{16}\text{-C}_4\text{-C}_{16}$ has heavy influence on the

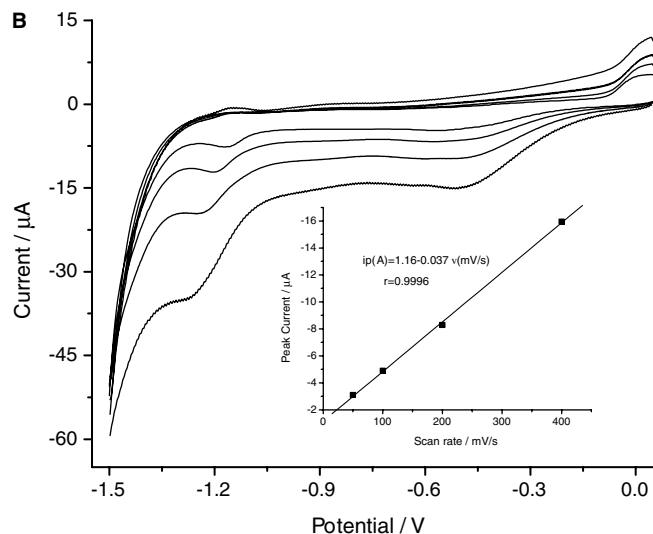
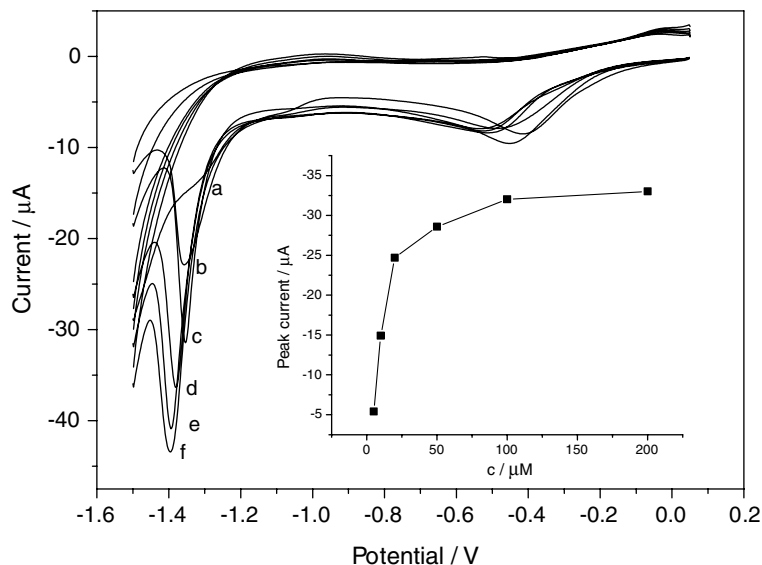


Fig. 6 Dependence of cathodic peak current on scan rate. **a** 5 μM 2-thiouracil in the presence of 10 μM $\text{C}_{16}\text{-C}_4\text{-C}_{16}$; **b** 100 μM 2-thiouracil without surfactants; scan rate 20, 50, 100, 200 and 400 mV/s (from inner to outer); other conditions as in Fig. 1; inset is the i_p vs. v plot

Fig. 7 Influence of $C_{16}-C_4-C_{16}$ concentration on the CVs of $10 \mu\text{M}$ 2-thiouracil at a silver electrode. $C_{16}-C_4-C_{16}$ concentrations: 5 (a), 10 (b), 20 (c); 50 (d), 100 (e) and $200 \mu\text{M}$ (f); other conditions are same as in Fig. 1



deposition process of 2-thiouracil at a silver electrode. Anionic surfactant sodium dodecanethyl sulfate (SDS) and non-ionic surfactant Triton X-100 do not exhibit such action. Interestingly, cationic surfactants with shorter alkyl chain also do not have such a behavior, probably because they cannot reduce the repulse among deposits effectively or show enough strong hydrophobicity.

Besides its influence on the deposition of 2-thiouracil, $C_{16}-C_4-C_{16}$ also can improve the desorption-process. As shown in Fig. 8, without $C_{16}-C_4-C_{16}$ the peak is almost invisible (Fig. 8 curve c). However, a small peak is observable when the solution contains $C_{16}-C_4-C_{16}$ for reductive desorption. Therefore it was thought that $C_{16}-C_4-C_{16}$ could reduce the repulse among deposits and

accelerate the electron transfer, since the peak becomes sharp and high. As the peak changes less for both deposits in solution containing $C_{16}-C_4-C_{16}$ (Fig. 8a, b), it can be inferred that $C_{16}-C_4-C_{16}$ must have adsorbed at the silver electrode and combined with 2-thiouracil during the deposition process, which shows facilitating action during the stripping process. Thus the deposition film is virtually a mixed one of AgHTU and $\text{Ag}C_{16}-C_4-C_{16}$ or a composite one such as $\text{AgHTU}-C_{16}-C_4-C_{16}$.

Comparison of different surfactants

In order to understand the influence of different surfactants, several surfactants with different structure have

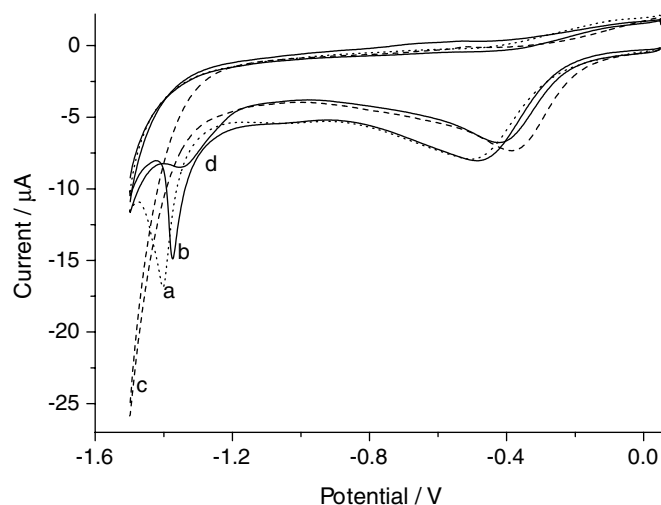


Fig. 8 CVs of a silver electrode in a 0.05 M pH 10.2 phosphate buffer solution (PBS) containing $50 \mu\text{M}$ $C_{16}-C_4-C_{16}$ (a, d), 0 M $C_{16}-C_4-C_{16}$ (b, c) after deposition for 2 min in 0.05 M PBS + $50 \mu\text{M}$ $C_{16}-C_4-C_{16}$ + $10 \mu\text{M}$ 2-thiouracil (a, b) or 0.05 M PBS + $10 \mu\text{M}$ 2-thiouracil (c, d). Other conditions as in Fig. 1

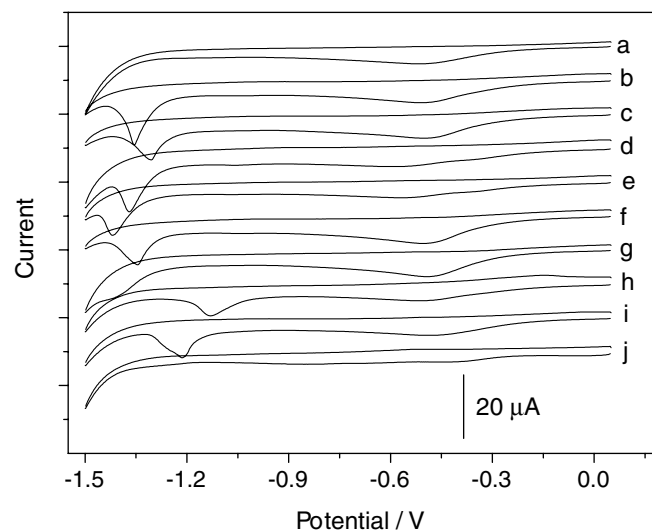


Fig. 9 CVs of a silver electrode in $10 \mu\text{M}$ 2-thiouracil solution containing $20 \mu\text{M}$ surfactant. Scan rate 50 mV/s ; surfactants: (a) $C_8-C_4-C_8$, (b) $C_{12}-C_4-C_{12}$, (c) $C_{12}-C_{12}-C_{12}$, (d) $C_{16}-C_4-C_{16}$, (e) $C_{16}-C_4\text{OH}-C_{16}$, (f) $C_{16}-C_{12}-C_{16}$, (g) $C_{16}-\text{Ph}-C_{16}$, (h) CPB, (i) CTAB, (j) DCAB; other conditions as in Fig. 1

been studied. As can be seen in Fig. 9, except for DCAB and $C_8-C_4-C_8$, other surfactants examined can make the peak increase. Namely, they can facilitate the deposition and reduction of 2-thiouracil at a silver electrode. But their promoting action is different, stemming from the difference in their molecular structures and hydrophobicity. According to the figure, for geminis with same spacer group, their influence increases with increase in alkyl-chain length, such as $C_8-C_4-C_8 < C_{12}-C_4-C_{12} < C_{16}-C_4-C_{16}$. For geminis with same alkyl chain, the peak current seems to decrease with increase in spacer length. It is clear that the peak potentials are also different. For geminis with the same alkyl chain, it seems that the peak potential shifts positively with the increase in the length of spacer group, e.g., the peak potentials for surfactants bearing- $C_{16}H_{33}$ tail group follow such order as $C_{16}-C_4OH-C_{16} \approx C_{16}-ph-C_{16} < C_{16}-C_4-C_{16} < C_{16}-C_{12}-C_{16} < (CTAB) < (CPB)$. However, for gemini surfactants bearing same spacer group, the longer the alkyl chain, the more negative the peak potential, such as E_p (for $C_8-C_4-C_8$) $> E_p$ (for $C_{12}-C_4-C_{12}$) $> E_p$ (for $C_{16}-C_4-C_{16}$). This is related to their interaction with 2-thiouracil and hydrophobicity.

For CTAB and CPB, the peak potentials are more positive than those for geminis, even though their concentrations are two times of geminis. This should be ascribed to the weaker combination of these with 2-thiouracil. As known, geminis bear two long alkyl chains and two ionic head groups, they must have interacted with 2-thiouracil simultaneously, making the combination stronger. When the length of spacer group in a gemini increases, the gemini surfactant becomes more similar to normal surfactant in molecular structure, thus shows similar behavior to that of normal surfactant as shown above. It should be pointed out, in the presence of DCAB, no visible peak appears probably due to its poor solubility and adsorbability at silver electrodes,

though it also bears two alkyl chains. Increasing the surfactant concentrations, the peak increases and reaches maximum values at concentration of about 2–5 folds of 2-thiouracil concentration. When their concentrations exceed certain values, the peaks almost remain unchanged or decrease slowly due to congregation of surfactants in solution.

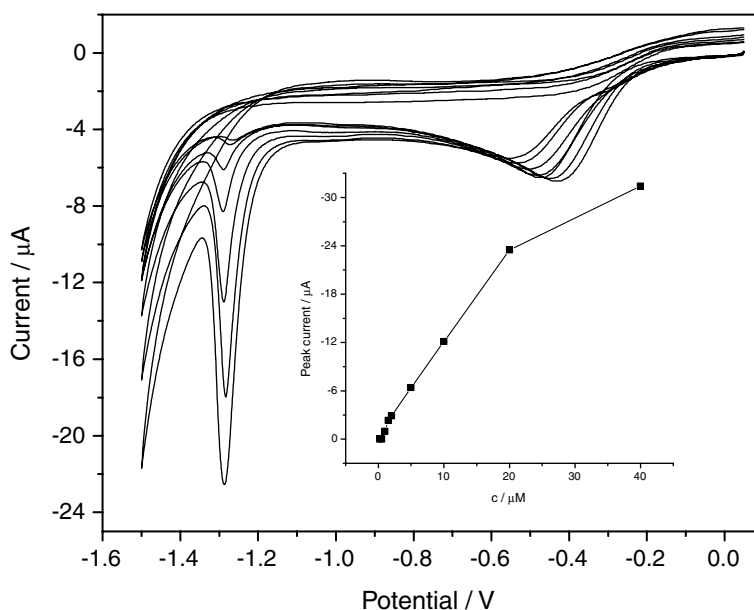
Dependence of peak current on 2-thiouracil concentration

When the concentration of $C_{16}-C_4-C_{16}$ is fixed, the cathodic peak current increases with 2-thiouracil concentration (Fig. 10). Over a certain range, the peak current is linear to 2-thiouracil concentration. As expected, the peak current leaves off the plot when its concentration exceeds certain value, indicating that the deposition efficiency reduces gradually at higher concentration. It was reported that the orientation of deposits might change with concentration, which affects the deposition efficiency [18]. In addition, there are other factors accounting for this, such as the reducing opportunity for each 2-thiouracil to contact silver surface, the weakening adherence of the deposits, the reducing electrical conductivity of the film. The peak potential almost remains unchanged in this case; this can be ascribed to the smaller deposition amount. When the concentration was further increased the peak would move in negative direction.

Conclusion

2-Thiouracil can deposit at silver electrodes and exhibit a cathodic peak at about -1.2 V (vs. SCE) in basic solutions when the potential moves negatively. In the

Fig. 10 Variation of peak current with 2-thiouracil concentration in the presence of $20 \mu\text{M}$ $C_{16}-C_4-C_{16}$. Other conditions as in Fig. 1



presence of cationic geminis the deposition and reductive desorption-process can be improved and the peak increases greatly. This associates with the combination of gemini surfactants and the adsorbed 2-thiouracil, which makes the electrostatic repulse weaker in deposited 2-thiouracil film, thus more 2-thiouracil could be deposited. Geminis show greater influence in comparison with single-chain surfactant with same alkyl chain because of their stronger combination. Different geminis show different promoting action. The enhancing effect is mainly determined by their molecular structure. In general, strong hydrophilicity of the spacer group and long tail-chain were favorable to obtaining a high and sharp reductive desorption peak whose peak potential was more negative.

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