

Comparative study on the interaction of DNA with three different kinds of surfactants and the formation of multilayer films

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Abstract

The interactions between double-stranded DNA (dsDNA) and three different kinds of surfactants, i.e., cationic, anionic, and nonionic surfactants, were investigated by cyclic voltammetry, electrochemical impedance spectroscopy and UV–vis spectroscopy. Multilayer films composed of DNA and surfactants were prepared at gold electrode by electrostatic or hydrophobic interactions. It was found that the cationic surfactant, CTAB, can bind to DNA by electrostatic interaction, and the electron transfer resistance of CTAB–DNA complex film increases first and then decreases with CTAB concentration. The anionic surfactant, LAS, can bind to DNA but by hydrophobic interaction, and the electron transfer resistance of the complex film keeps decreasing with LAS concentration. Nonionic surfactants can also directly bind to DNA by hydrophobic interaction. All the three different kinds of surfactants can form multilayer films with DNA on the electrode surface. The chemical structure of DNA keeps unchanged during interacting with these surfactants. The binding modes of DNA with these three different kinds of surfactants were also deduced.

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Keywords: Electrochemical study; Cationic surfactant; Anionic surfactant; Nonionic surfactant; dsDNA; Multilayer film

1. Introduction

Interactions between DNA and surfactants have been studied extensively in recent years [1–5]. It is very important in biotechnological and biomedical applications, particularly for the possibility of using such system for in vivo gene delivery and gene transfer [6,7].

DNA can form tight complex with surfactants through hydrophobic or electrostatic binding [8–10]. Among three different kinds of surfactants, i.e., cationic, anionic and nonionic surfactants, the interaction of cationic surfactant with DNA attracts the most attention. The binding of cationic surfactant to DNA was shown to proceed in two stages [11]. In the first stage, surfactant ions exchange with counterions condensed on the surface of DNA driven by hydrophobic interaction, and the effective charge on DNA does not change. In the second stage, surfactant molecules bind to DNA without exchange of con-

densed counterions, thus the effective charge of DNA changes dramatically, usually followed by phase separation at high surfactant concentration. This feature suggests that DNA–surfactant system have some further applications, such as DNA purification and condensation [12]. Meanwhile, with the increase of cationic surfactant concentration, the conformation of DNA–surfactant complex undergoes a discrete transition from extended coils to collapsed globules, and the two states coexist below a certain critical concentration. This phenomenon has been demonstrated by a number of techniques, e.g., fluorescence microscopy [13], ellipsometry [14], viscosimetry and dynamic light scattering [15]. Notably, the conformation of single-stranded DNA (ssDNA)–surfactant complex differs from that of double-stranded DNA (dsDNA)–surfactant complex, probably due to the difference in chain flexibility between ssDNA and dsDNA. For example, with flexible ssDNA interacting with cetyltrimethylammonium bromide (CTAB), the complex shows a cubic structure while the complex between rigid dsDNA and CTAB prefers a structure of 2D hexagonal close packing of cylinders [16].

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As an anionic polyelectrolyte with a unique double helical rod-like structure, DNA has a potential to be a good candidate for future nanodevices [17] and a good component to fabricate the higher order or hierarchical DNA-based molecular assemblies [18–20]. A lot of methods have been developed for the immobilization of DNA on the electrode surface to prepare novel and sensitive biosensors [21], such as hydrophobic adsorption [22], covalent binding [23], etc. However, fewer reports focus on the characterization of multilayer films formed by DNA and surfactants, especially by anionic and nonionic surfactants. Either, to our knowledge, there has been no systematic study on the interaction of DNA with three different kinds of surfactants.

In this work, the interactions of dsDNA with three different kinds of surfactants, i.e., cationic, anionic, and nonionic surfactants were comparatively studied by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and ultraviolet–visible (UV–vis) spectroscopy. The difference in these interactions was discussed in detail. Through electrochemical methods, it is very easy to investigate the formation of multilayer films by dsDNA and these surfactants. The electrochemical parameters of the films can be simultaneously determined. Moreover, UV–vis spectroscopy offers a simple way for monitoring the interactions of dsDNA with surfactants in aqueous medium. The binding modes of dsDNA with three different kinds of surfactants were also deduced.

2. Experimental section

2.1. Materials

Nonionic surfactants including nonyl phenol polyoxyethylene-10 ether (NP-10), nonyl phenol polyoxyethylene-30 ether (NP-30), and polyoxyethylene coconut-oil fatty acid monoethanolamide ester (SFC-910) were obtained from Shengzhong Ltd. (Shanghai, China). Anionic surfactant linear alkylbenzene sulphonates (LAS) was purchased from Yingpeng Ltd. (Shanghai, China) and cationic surfactant CTAB was from Medicine Group of Chemistry Reagent (Shanghai, China). Methylene blue (MB) was obtained from Beijing Chemical Reagent Company (China) and recrystallized before use. Fish sperm dsDNA was bought from Shanghai Biological Company (China). Other chemicals were all of analytical grade. Double-distilled water was used throughout.

2.2. Apparatus

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed on a CHI 660B electrochemical analyzer (Chenhua Company, China). A conventional three-electrode cell with a gold working electrode (0.2 mm in diameter), a Ag/AgCl reference electrode and a platinum foil counter electrode was employed. DU-800 spectrophotometer (Beckman, America) was used to determine the UV–vis spectra of DNA and the surfactants.

2.3. Preparation of DNA and surfactant–DNA modified electrode

The gold electrode was smoothed with 0.05 μm alumina slurry on a polishing cloth, rinsed with water three times and immersed

in H_2SO_4 solution (0.5 M) for 10 min, then cycled in 0.5 M H_2SO_4 until a stable oxidation/reduction cyclic voltammogram was obtained. After the freshly cleaned electrode was dried under room temperature, 10 μL of 2 mg/mL fish sperm dsDNA solution was dropped onto the electrode surface carefully, followed by air-drying overnight at 4 $^\circ\text{C}$. In this way, the DNA modified electrode (DNA/Au) was prepared. Subsequently, the DNA/Au electrode was dipped in water for 30 min then rinsed with water to remove the redundant DNA that did not bind to the gold electrode. The mass of DNA adsorption on the DNA/Au electrode was about $1.02 \times 10^{-6} \text{ g/cm}^2$, which was estimated by the piezoelectric quartz crystal microbalance (PQCM) method.

The DNA/Au electrode was immersed in surfactant solution of different concentrations and incubated for 30 min, then rinsed with water three times to remove the nonspecifically adsorbed surfactant. In this way, the surfactant–DNA modified electrode (surfactant/DNA/Au) was obtained. The surfactant/DNA/Au electrode was immersed into 2 mg/mL DNA solution for 60 min, and then rinsed with water three times. The resulted electrode was DNA–surfactant–DNA modified electrode (DNA/surfactant/DNA/Au).

2.4. Procedure

Cyclic voltammetry experiment was carried out in 5 mM $\text{K}_3\text{Fe}(\text{CN})_6 + 0.1 \text{ M KCl}$ or 67 mM phosphate buffer solution (PBS, pH 7.0) containing 100 μM MB. In electrochemical impedance measurements, 5 mM $\text{K}_3\text{Fe}(\text{CN})_6 + 5 \text{ mM K}_4\text{Fe}(\text{CN})_6$ was employed as probe and 0.1 M KCl as supporting electrolyte with open potential 0.25 V, amplitude 5.0 mV and frequency range of 0.1 to 10^5 Hz.

A 5 $\mu\text{g/mL}$ DNA solution was incubated with different kinds of surfactants at 37 $^\circ\text{C}$ for 30 min, and then the UV–vis spectra of such mixture were recorded by using water as blank solution. The UV–vis spectra of each surfactant and DNA were also recorded.

3. Results and discussion

3.1. Electrochemical behavior of $\text{K}_3[\text{Fe}(\text{CN})_6]$ at modified electrodes of different kinds

Fig. 1 shows the CVs of $\text{K}_3[\text{Fe}(\text{CN})_6]$ at different surfactant/DNA/Au and DNA/surfactant/DNA/Au electrodes. It can be seen from Fig. 1A–C, the peak current of redox probe (i_p) at bare gold electrode (curve a) is larger than that at DNA/Au electrode (curve b), indicating that the adsorption of negative DNA hinders the negative probe accessing to the electrode surface.

To investigate the effect of CTAB concentration on its interaction with DNA, we modified the DNA/Au electrode with CTAB in concentration range from 0.5 to 20 $\mu\text{g/mL}$. The results of two typical concentrations, 1 and 15 $\mu\text{g/mL}$, are shown in Fig. 1A. After DNA/Au electrode is further modified with cationic surfactant CTAB at a low concentration such as 1 $\mu\text{g/mL}$ (curve c), i_p increases to some degree (from 34.9 to 39.1 nA); while CTAB is at a high concentration such as 15 $\mu\text{g/mL}$ (curve d), i_p decreases significantly (from 34.9 to 13.2 nA),

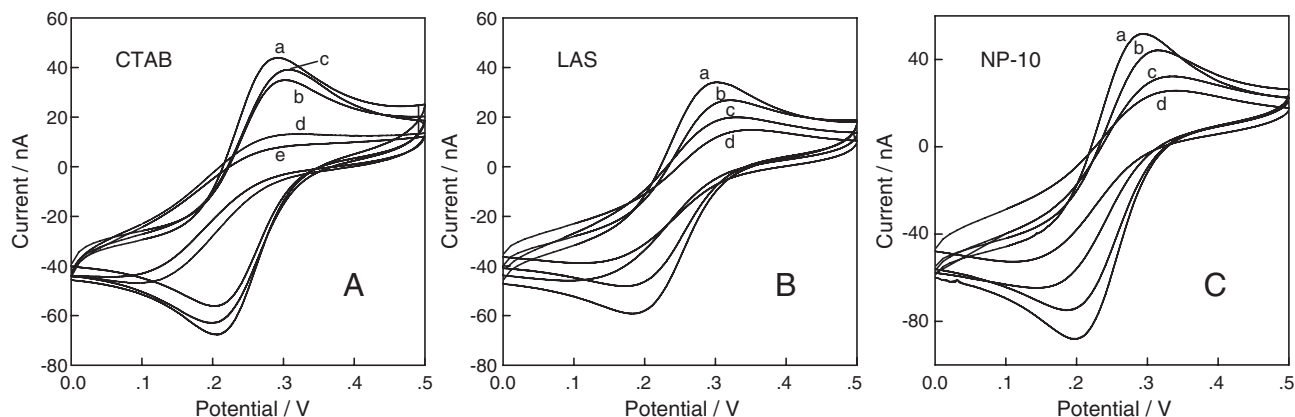


Fig. 1. Cyclic voltammograms of 5 mM $[\text{Fe}(\text{CN})_6]^{3-}$ at different electrodes. (A): (a) bare, (b) DNA/Au, (c) DNA/Au modified with 1 $\mu\text{g/mL}$ CTAB, (d) DNA/Au modified with 15 $\mu\text{g/mL}$ CTAB, and (e) DNA/CTAB/DNA/Au; (B): (a) bare, (b) DNA/Au, (c) DNA/Au modified with 2 mg/mL LAS, and (d) DNA/LAS/DNA/Au; (C): (a) bare, (b) DNA/Au, (c) DNA/Au modified with 2 mg/mL NP-10, and (d) DNA/NP-10/DNA/Au. Scan rate: 50 mV/s.

and the peak potential difference (ΔE_p) increases from 96 to 251 mV. The reasons may be as follows: when at low concentration, cationic surfactant CTAB mainly neutralizes the net negative charges of DNA adsorbed on the electrode surface, which is favorable for the redox of the negative probe. With the CTAB concentration increasing, the adsorption of CTAB can also increase the film density and hinders the electron transfer, which is unfavorable for the redox of probe. Therefore, i_p shows a trend that increase first and then decrease. From the phenomena above, it can be deduced that positive CTAB bound to DNA is mainly related to electrostatic adsorption. When CTAB/DNA/Au electrode is further modified with DNA (curve e), i_p continues to decrease and the reversibility of the redox peaks becomes even worse, indicating that DNA can adsorb on the surface of CTAB/DNA/Au electrode and the multilayer film forms consequently.

Fig. 1B shows the CVs of probe at LAS–DNA modified electrodes of different kinds. Comparing the DNA/Au electrode (curve b) with the LAS/DNA/Au electrode (curve c), the anodic i_p decreases from 26.9 to 20.0 nA, and ΔE_p increases from 155 to 245 mV. This indicates that although electrostatic repulsion

between negatively charged LAS and DNA may occur, LAS can still bind to DNA by hydrophobic interaction due to its long hydrophobic alkyl chain. Therefore, the net negative charge on the electrode surface increases. This enhances the electrostatic repulsion between the negative probe and the electrode, resulting in i_p decrease. Like CTAB/DNA/Au electrode, LAS/DNA/Au electrode can further adsorb DNA to form multilayer films (curve d).

Fig. 1C shows the CV of the probe after the DNA/Au electrode is modified with nonionic surfactants NP-10. From curve b to c, i_p decreases significantly and the reversibility of the redox peaks becomes bad, for the adsorption of NP-10 increases the film density and hinders the electron transfer. From curve c to d, i_p decrease obviously after NP-10/DNA/Au electrode is further modified with DNA, suggesting that NP-10 has directly bound to DNA; otherwise NP-10 will be washed off with water from the electrode surface (see Section 2.3). Similar experimental phenomena were also observed for NP-30 and SFC-910 (not shown). Therefore, the interaction between DNA and nonionic surfactant may be attributed to hydrophobic binding because nonionic surfactant holds no net charge. Moreover, when the three nonionic

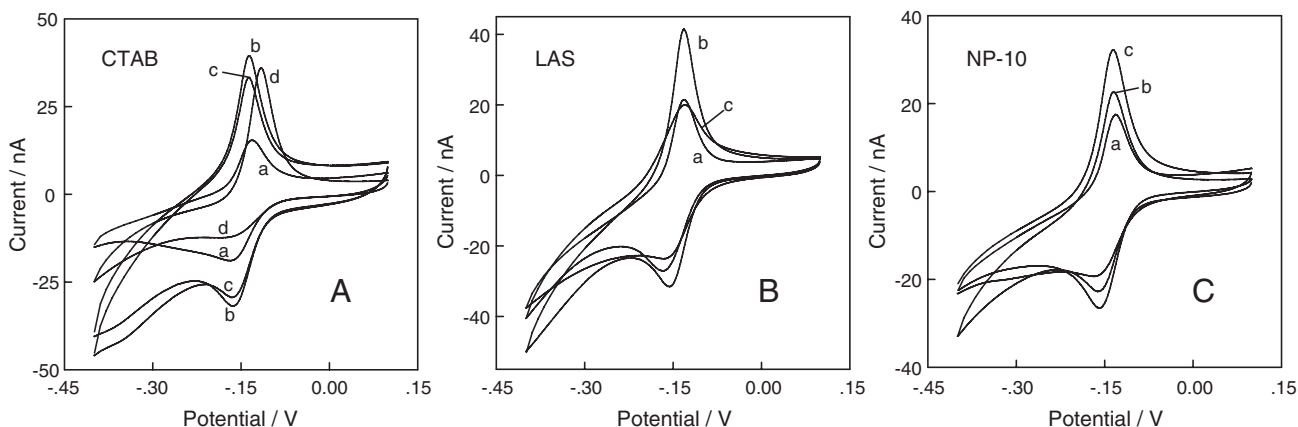


Fig. 2. Cyclic voltammograms of 100 μM MB at different electrodes. (A): (a) bare, (b) DNA/Au, (c) DNA/Au modified with 1 $\mu\text{g/mL}$ CTAB, and (d) with 10 $\mu\text{g/mL}$ CTAB; (B): (a) bare, (b) DNA/Au, and (c) DNA/Au modified with 1 mg/mL LAS; (C): (a) bare, (b) DNA/Au, and (c) DNA/Au modified with 1 mg/mL NP-10. Scan rate: 50 mV/s.

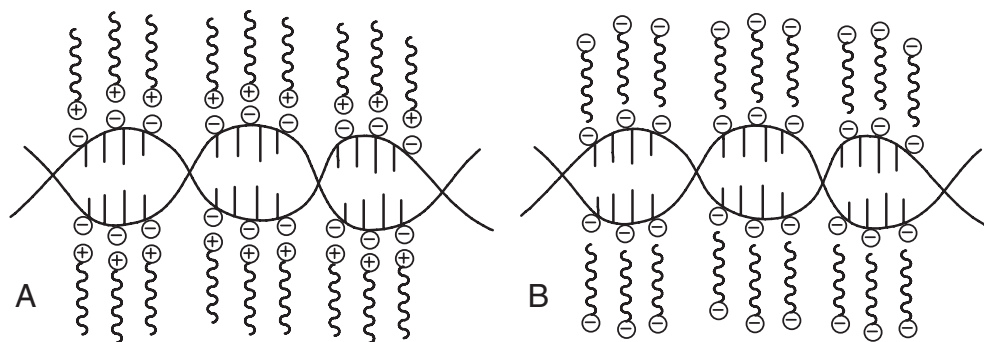


Fig. 3. Schematic representation for the supposed binding mode of DNA–CTAB complex (A) and DNA–LAS complex (B).

surfactant/DNA/Au electrodes were further modified with DNA, the anodic i_p changed most greatly for NP-30; while the cathodic i_p changed most greatly for SFC-910. This indicates that the difference in structure of the nonionic surfactants can affect their binding to DNA.

3.2. Electrochemical behavior of MB at modified electrodes of different kinds

Oxidized MB holds one positive charge and reduced MB holds no net charges, so using MB as redox probe we can further compare the interactions of DNA with the different kinds

of surfactants. As shown in Fig. 2A–C, i_p of DNA/Au electrode (curve b) is much larger than that of bare gold electrode (curve a). MB cannot only adsorb to DNA by electrostatic attraction [24], but also specifically binds to the G bases of DNA strands [25]. Therefore, more MB is accumulated at the surface of DNA/Au electrode than bare gold electrode.

We investigated the CVs of MB after DNA/Au electrode was modified with CTAB in concentration range of 0.5–20 $\mu\text{g/mL}$. Fig. 2A shows the results of two typical concentrations, 1 and 10 $\mu\text{g/mL}$. After DNA/Au electrode (curve b) is modified with 1 $\mu\text{g/mL}$ of cationic surfactant CTAB (curve c), i_p decreases to some extent; while the CTAB concentration increases by 10

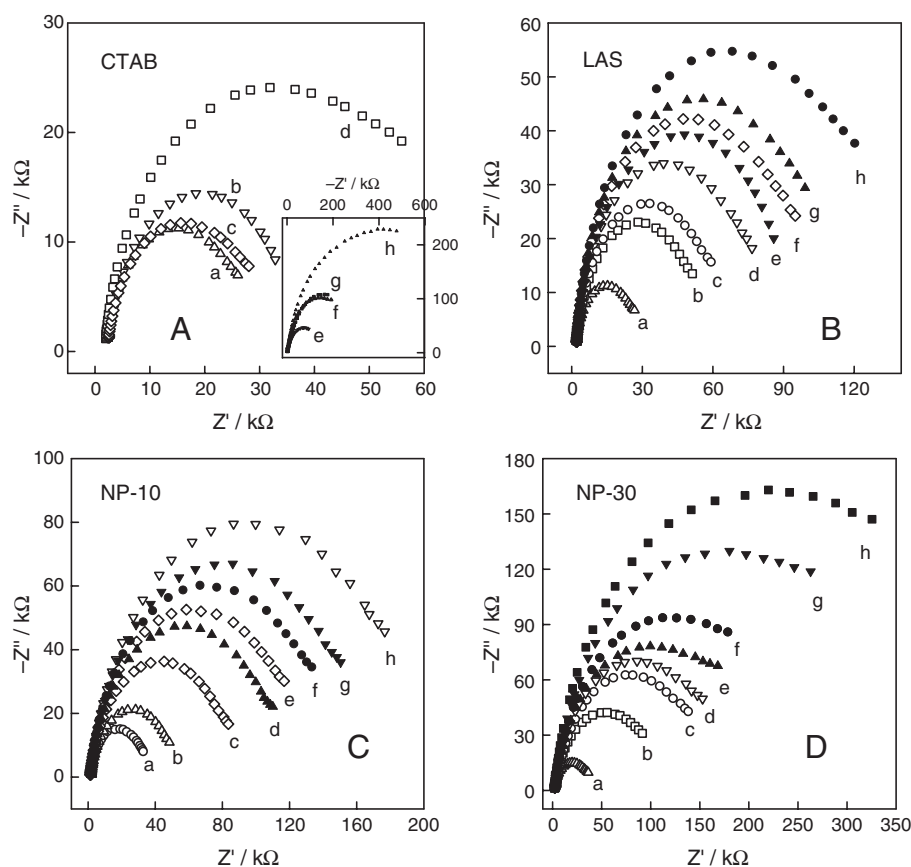


Fig. 4. Electrochemical impedance spectra of 5 mM $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ at: (a) bare Au, (b) DNA/Au, (c–g) surfactant/DNA/Au and (h) DNA/surfactant/DNA/Au. (A): (c) 1 $\mu\text{g/mL}$, (d) 5 $\mu\text{g/mL}$, (e) 10 $\mu\text{g/mL}$, (f) 15 $\mu\text{g/mL}$, (g) 20 $\mu\text{g/mL}$ CTAB; (B): (c) 0.1 mg/mL, (d) 0.2 mg/mL, (e) 0.5 mg/mL, (f) 1 mg/mL, (g) 2 mg/mL LAS; (C): (c) 0.1 mg/mL, (d) 0.2 mg/mL, (e) 0.5 mg/mL, (f) 1 mg/mL, (g) 2 mg/mL NP-10; (D): (c) 0.1 mg/mL, (d) 0.2 mg/mL, (e) 0.5 mg/mL, (f) 1 mg/mL, (g) 2 mg/mL NP-30.

fold (curve d), the cathodic peak tends to disappear, and the anodic peak potential shifts positively. That may be because when CTAB is at low concentration, the binding of CTAB mainly weakens the interaction between MB and DNA, thus less MB is accumulated at the electrode surface; while CTAB concentration is relatively high, the binding of CTAB mainly increases the film density, thus the activation energy of the electrode reaction of MB rises. Furthermore, the increase of the film hydrophobicity is favorable for the adsorption of neutral reduced MB but unfavorable for that of positive oxidized MB, so the anodic peak remains but the cathodic peak declines in curve d. From the discussion above, we can infer the binding mode of CTAB–DNA complex: as shown in Fig. 3A, the positive groups of CTAB bind with the negative phosphate groups of DNA by electrostatic attraction, and the hydrophobic groups of CTAB extend outside the DNA structure.

Fig. 2B shows the CVs of MB on DNA/Au and LAS/DNA/Au electrodes. Obviously, i_p of LAS/DNA/Au electrode (curve c) is smaller than that of DNA/Au electrode (curve b) due to the increase of film density. It is worth noting that the anodic i_p decreases more rapidly than the cathodic i_p , indicating that the increase of net negative charges on the electrode surface greatly hinders the binding of hydrophobic reduced MB. Therefore, the binding mode of LAS–DNA complex can be inferred as Fig. 3B: the negative groups of LAS face the bulk solution, and the hydrophobic chains of LAS face DNA.

Fig. 2C shows the CVs of NP-10–DNA modified electrode. After DNA/Au electrode (curve b) is modified with NP-10 (curve c), i_p increases to some extent, and ΔE_p almost remains unchanged. This indicates that the adsorption of NP-10 cannot greatly affect the electrode reaction of MB. Similar phenomena were also observed for NP-30 and SFC-910 (not shown). However, as concluded in Section 3.1 (Fig. 1C), the nonionic surfactants can directly bind to DNA through hydrophobic interaction. Therefore, it can be concluded that the interaction of DNA with nonionic surfactant has no effect on the net negative charge of DNA, and the electrode reaction of MB still goes on. Moreover, due to the increase of the film hydrophobicity, anodic i_p increases more rapidly than the cathodic i_p .

3.3. Electrochemical impedance characteristics of modified electrodes of different kinds

It is well known that EIS is a useful tool for studying the interface properties of the modified electrode [26]. The typical impedance spectra of the three different kinds of surfactant–DNA modified electrodes are shown in Fig. 4. The semicircle diameter in the impedance spectrum equals to the electron transfer resistance, R_{et} , which is related to the electron-transfer kinetics of the redox probe at the electrode surface. As shown in Fig. 4A, with the increase of CTAB concentration (from curve b to g), R_{et} decreases first and then increases; while in Fig. 4B–D,

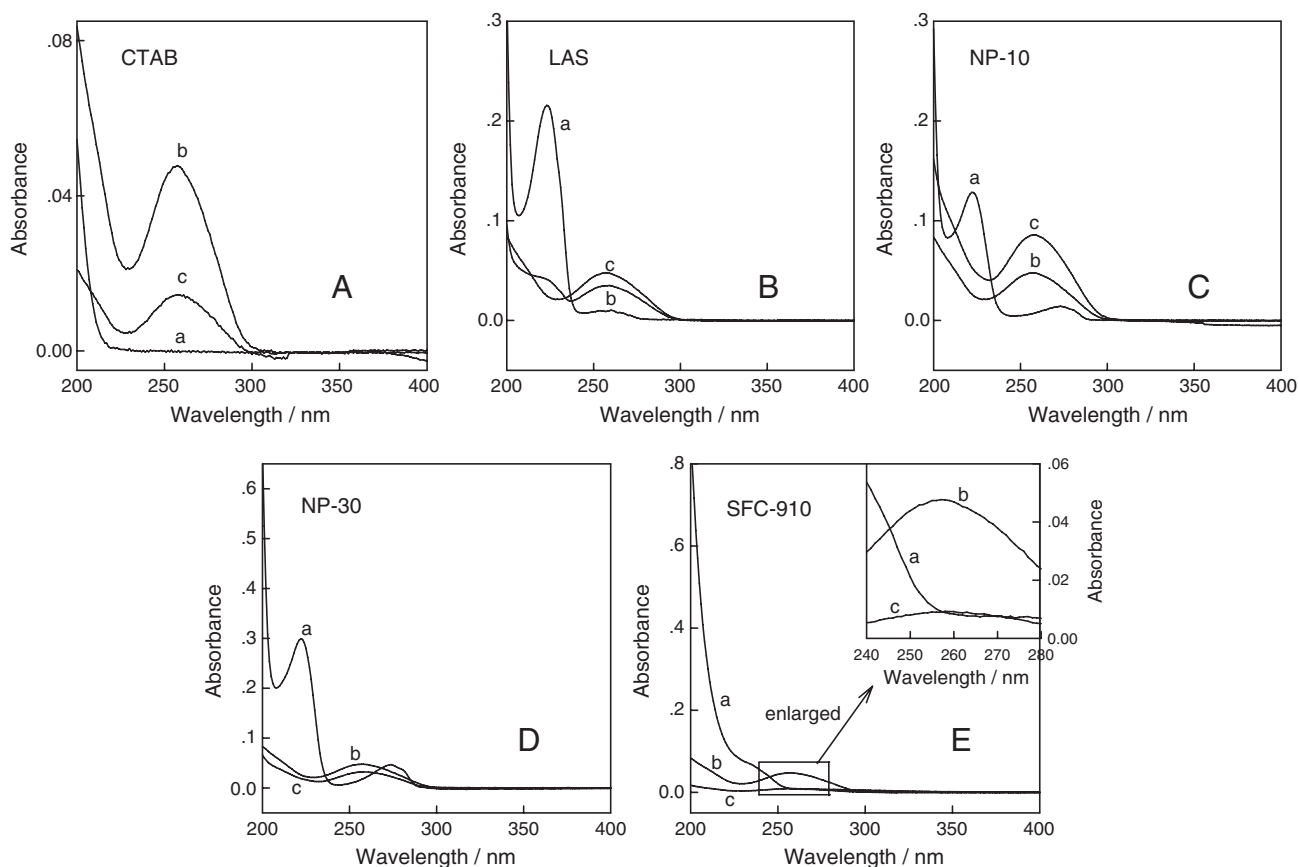


Fig. 5. UV spectra of DNA and surfactants. (A): (a) 1 µg/mL CTAB, (b) 5 µg/mL DNA, and (c) 5 µg/mL DNA + 1 µg/mL CTAB; (B): (a) 5 µg/mL LAS, (b) 5 µg/mL DNA, and (c) 5 µg/mL LAS + 5 µg/mL DNA; (C): (a) 5 µg/mL NP-10, (b) 5 µg/mL DNA, and (c) 5 µg/mL NP-10 + 5 µg/mL DNA; (D): (a) 5 µg/mL NP-30, (b) 5 µg/mL DNA, and (c) 5 µg/mL NP-30 + 5 µg/mL DNA; (E): (a) 5 µg/mL SFC-910, (b) 5 µg/mL DNA, and (c) 5 µg/mL SFC-910 + 5 µg/mL DNA.

with the increase of surfactant concentration, R_{ct} keeps increasing. The results of SFC-910 were similar with that of NP-10 and NP-30, thus not shown. This indicates that with the increase of the cationic surfactant concentration, the electron-transfer rate of the redox probe at surfactant/DNA/Au electrode increases first and then decreases; while for the other two kinds of surfactants, the electron-transfer rate of the probe at surfactant/DNA/Au electrode surface keeps decreasing. This is in consistence with the experimental results obtained in the CV measurements. It can be seen that R_{ct} in Fig. 4A increases most rapidly, indicating that the interaction of cationic surfactant with DNA is the strongest among the three kinds of surfactants.

As shown in Fig. 4C and D, R_{ct} increases more rapidly in the latter than that in the former. Considering that NP-10 and NP-30 have the similar structure, it may be concluded that the longer alkyl chain the nonionic surfactant has, the more rapid the R_{ct} increases. This means that the NP-30–DNA complex film is denser than the NP-10–DNA complex film. Meanwhile, after the surfactant/DNA/Au modified electrode is further modified with DNA (curve h in Fig. 4A–D), R_{ct} increases obviously, indicating the formation of DNA/surfactant/DNA multilayer films.

3.4. UV–vis spectroscopy for characterization of the interactions of DNA with surfactants

The UV absorption of DNA is an important property for determining whether π – π stacking of nucleobases occurs. The dsDNA in aqueous solution has a specific absorption λ_{max} at 260 nm. Fig. 5 shows the UV spectra of surfactants (curve a), DNA (curve b) and surfactant–DNA mixtures (curve c). There are peaks at about 220 nm in curve a (Fig. 5B–D), which is assigned to the absorption of the hydrophobic groups of LAS, NP-10 and NP-30. All the three kinds of surfactant–DNA mixtures have an absorption λ_{max} at 260 nm, which is assigned as the characteristic absorption of the nucleobases in DNA. These mixtures have the same absorption λ_{max} as that of DNA, indicating that the chemical structure of DNA in these mixtures is identical with that of DNA in solution [27].

However, the absorbance for all the three kinds of surfactant–DNA mixtures changed significantly compared with that of DNA aqueous solution. After DNA incubating with CTAB, NP-30 and SFC-910, the absorbance of DNA decreases; while it increases with LAS and NP-10. It indicates that the π – π stacking structure of the DNA strands changes to some extent [27]. Probably, the interaction of DNA with surfactant changes the equivalent absorption area of DNA. How it varies is determined by the surfactant structure and concentration. Additionally, it is worth noting that after interacting with DNA, the peaks at about 220 nm of LAS, NP-10 and NP-30 disappear. It may suggest that the structure of hydrophobic groups in LAS, NP-10 and NP-30 is greatly affected due to the interaction with DNA.

4. Conclusion

The interactions between dsDNA and three different kinds of surfactants, i.e., cationic, anionic and nonionic surfactant, have been investigated by CV, EIS and UV–vis spectroscopy. The

results show that the cationic surfactant CTAB can bind to DNA mainly by electrostatic interaction. With the CTAB concentration increasing, the electron transfer resistance of CTAB–DNA complex film increases first and then decreases. The anionic surfactant LAS can also bind to DNA but by hydrophobic interaction. The nonionic surfactants tested can interact with DNA directly through the hydrophobic binding as the anionic surfactant. The UV spectra of the surfactant–DNA mixtures show that the chemical structure of DNA keeps unchanged during the interaction with the surfactants, indicating that these surfactants can be used for DNA purification, protection, separation and fabricating DNA complex film materials.

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