The adsorption behavior of cationic surfactant onto human hair fibers

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ABSTRACT

Quaternary ammonium surfactants are important ingredients that are frequently formulated into hair care products to modify the properties of hair surface. The adsorption kinetics, isotherms and association structures of cationic surfactants on hair surface, however, are not fully understood due to the heterogeneous nature of human hair fibers. In this work, a quaternary ammonium of surfactant, dimethylpabamidopropyl laurdimonium tosylate (DDABDT) was chosen as a probe to investigate the adsorption behavior of cationic surfactant on cuticles of scalp hair. The results reveal that the adsorption kinetics fit to a pseudo-second-order kinetic model and the adsorption isotherms fit to the Freundlich adsorption model. With the increase of DDABDT adsorption, the wettability of hair fibers changes from hydrophobic to hydrophilic. The association structure could be monolayer or bilayer depending on the initial concentration of the surfactant. In the monolayer structure, the 'anchor' surfactant molecules are believed to adsorb vertically on the surface of hair fibers through electrostatic interaction. In the bilayer structure, the second layer molecules may then pile up on top of the first layer with charged groups orienting outward. The thickness of DDABDT film on hair fibers treated with 5×10^{-4} mol/l DDABDT solution is measured to be 5.42 nm on average with a force–distance method. This figure is very close to the two times of the theoretical molecular size of the DDABDT molecule.

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1. Introduction

Human scalp hair takes up a paramount place in human appearance and hair care products have being made a huge cosmetic industry in the world. As natural fibers, hair fibers possess an extremely complex structure. The morphology under microscopy resembles the scales of snake's skin [1]. The cuticles, i.e. scales covering cortex inner, are composed of mostly fatty acid in their flat region and partly protein in their edges.

In hair care products different kinds of cationic surfactants, mainly quaternary ammonium salts, are incorporated with other ingredients to meet a variety of requirements of consumers [1,2]. The functions of the cationic surfactants were generally recognized as conditioner and also as sunscreen to absorb UV light or vehicles for other ingredients. The mechanistic aspects of the effects of cationic surfactants on hair, however, were less frequently addressed in literatures. Robbins et al. proposed that the adsorption of conditioning agents onto hair fibers can be considered as a continuum between a charge-driven and a hydrophobically driven process [3]. Using confocal laser scanning microscopy and fluorescence microscopy, Regismond et al. demonstrated visually

the presence of adsorbed polymer onto hair and also investigated the influence of some factors, such as adsorption time and the presence of cosolutes, on the adsorption process [4]. The adsorption behaviors of lauroylamidobutylguanidine salt (LAG)/1-hexadecanol ($C_{16}OH$) aggregates onto hair were examined with ESR and TOF–SIMS techniques and the results indicated that LAG/$C_{16}OH$ aggregates form a rigid layer on hair fiber and cover the hair surface uniformly [5]. The presence of higher levels of cationic conditioners on the fiber surface of bleached hair relative to that of the undamaged hair was also demonstrated by Harvey et al. by using TOF–SIMS technique [6].

It has been shown that the adsorption of amphiphilic surfactants on solid–liquid interface is affected by many factors such as the nature of the solid surface, the molecular structure of surfactants, temperature and the acidity of the liquid phase [7]. The specific property of hair surface, i.e. heterogeneous in physical and chemical, dictates that the adsorption behavior of cationic surfactants onto hair surface would be more complex than that onto homogeneous solid surfaces. So far the mechanism as how cationic surfactants affect the properties of hair surface is still not clear. Also, little information is available for the orientation of a surfactant molecule on the cuticles and the aggregate structures of surfactants. In this work, a quaternary ammonium surfactant DDABDT was chosen as a probe to characterize the adsorption behavior of cationic surfactants on cuticles of scalp hair.

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2. Materials and methods

2.1. Materials

DDABDT ($C_{33}H_{55}N_3SO_4$, with purity of 99%) was obtained from International Special Product (ISP) Company, and was recrystallized three times from acetone to obtain white fine crystalline. The element analysis results (%): N7.232, C67.15, S5.729, H9.328 were agreed well with the calculated data (%): N7.128, C67.23, S5.439, H9.40. The critical micelle concentration (CMC) was determined with Wilhelmy method, and the results obtained at 40 and 50 °C are 0.1745 and 0.1873 mmol/l, respectively (the detailed experimental data are provided in supplementary material 1). The Krafft's points of DDABDT were measured to be 38 °C.

All other reagents used were of analytical grade and ultra-pure water (18 MΩ cm^{-1}) was used throughout the experiments.

Virgin hair samples, i.e. hairs with no chemical and physical damage, were collected from 11 local volunteers aged between 19 and 25. The hair samples were prepared with modified procedures described in the literature [8]. Briefly the hair sample was washed with 3% sodium dodecyl sulphate (SDS) solution to remove the dust and possible contaminants, and then extracted with ether for 8 h to remove grease. Finally the sample was rinsed with water, air-dried and stored for the subsequent experiments.

2.2. Determination of DDABDT adsorption on hair surface

The adsorption amounts of DDABDT on hair surface were determined by depletion method. Hair sample was immersed in DDABDT solution contained in a conical flask with a solid to liquid ratio of 0.8% (w/v). The flasks were shaken in a reciprocating water bath at 60 rpm and a selected temperature. The DDABDT concentration in the solution was online monitored with a home-constructed continue flow system, in which the solution in the conical flask was continuously uptaken by a peristaltic pump via a piece of PTFE tubing (0.8 mm i.d). Upon passing a spectrophotometric flow cell (quartz, 1 cm pathlength), the solution was delivered back to the flask. The absorbance at wavelength of 305 nm (the maximum absorptive wavelength of DDABDT [9]) was registered at predetermined time. The decrease of the DDABDT concentration in respect to its initial value was used to calculate the amount of DDABDT adsorption.

2.3. Determination of dynamic contact angles between hair fibers and water

The dynamic contact angles of hair fibers to water were determined according to the Wilhelmy balance principle with a dynamic contact angles instrument (DCA322, Thermo Cahn). The hair fibers were dispersed in a series of DDABDT solutions of different concentrations, with the hair/liquid ratio fixed at 0.8% (w/v), followed by shaking the mixtures for 1 h at predetermined temperature to reach adsorption equilibrium. Finally the fibers were taken out, air-dried, and the advancing contact angle of water on each fiber was measured to characterize the wettability of hair fibers [10]. For each sample the final result is an average of 20 fibers.

2.4. AFM images and force calibration plot

The morphology of the hair fiber surface was examined with an AFM (CSPM4000, Benyuan, China). Silicon cantilevers obtained from Park Scientific with a nominal spring constant of 0.2 N/m were used to scan specimen surface for obtaining high-resolution images. Hair fibers were fixed on a mini-plate with double-sided adhesive tape so as to ensure good contact with the scanner.
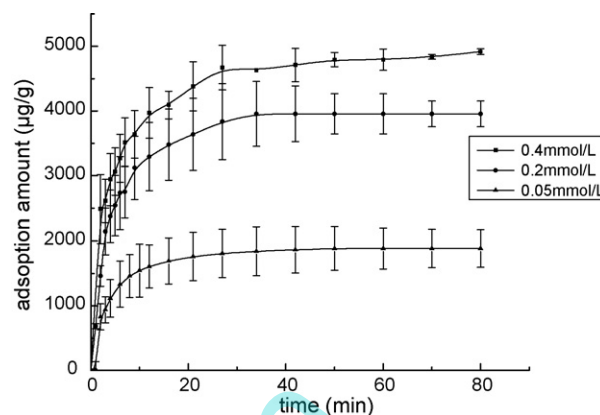

Fig. 1. Kinetic curves of DDABDT adsorption on human hair at different initial concentrations, (▲) 0. 05 mmol/l, (●) 0. 2 mmol/l and (■) 0.4 mmol/l at 50 °C.

The scanning was performed in contact mode AFM and the scanning range was set at an area of about $5 \times 5\ \mu m$. All images were obtained at ambient conditions. Film thickness is measured by a force–distance method [11], and more detailed discussions of the measurement are given in Section 3.4. The theoretical size of the DDABDT molecule is measured on the molecule structure by using AM1 method, as it was proved to be suitable for such estimation [20].

3. Results and discussion

3.1. Adsorption kinetics of DDABDT on human hair surface

The experiments for adsorption kinetics of DDABDT were carried out with initial concentrations of DDABDT at 0.05, 0.2 or 0.4 mmol/l and the temperature at 40 or 50 °C. The temperature above the Krafft's point of DDABDT was chosen so as to allow the surfactant to have good solubility. Also it is in the temperature range that the hair care products are more likely used by consumers. The adsorption kinetics curves of DDABDT at various initial concentrations at 50 °C on human hair are presented in Fig. 1. The data obtained at 40 °C are very similar to that obtained at 50 °C, therefore following discussions will be focused only to the results obtained at 50 °C.

At beginning of the process, the adsorption of DDABDT is very rapid. It was also noted that the larger the initial concentration, the higher the rate of adsorption. Cationic quaternary ammonium is positively charged in solution, while the hair surface is negative charged due to the presence of ammonia acidic residue [1]. Thereby, when DDABDT molecules diffuse to the surfaces of hair fibers, the electrostatic interaction would take place immediately and the substantive adsorption of DDABDT onto hair fibers occur. The initial rate of adsorption mainly depends on the diffusion rate of surfactant molecules [12]. The adsorption reaches equilibrium at about 1 h in our experiment. At this stage, it can be seen from Fig. 1 that for $c_0 >$ CMC the amount of surfactant adsorption is significantly greater than that for $c_0 <$ CMC. But the amounts of surfactant adsorptions are not linearly proportional to their initial concentrations.

The first-order and pseudo-second-order adsorption kinetics can be expressed as Eqs. (1) and (2), respectively:

$$\ln(\Gamma_e - \Gamma_t) = \ln \Gamma_e - k_1 t \tag{1}$$

$$\frac{t}{\Gamma_t} = \frac{1}{k_2 \Gamma_e^2} + \frac{t}{\Gamma_e} \tag{2}$$

where k_1 and k_2 are the rate constants of adsorption for the first-order and pseudo-second-order, respectively; Γ_e and Γ_t are the

Table 1
Comparison of the kinetics models of DDABDT adsorption.

C_0 (mol/l)	Rate constants of pseudo-second order (k_2)	Correlation coefficients (R^2)	Rate constants of first order (k_1)	Correlation coefficients (R^2)
0.5×10^{-4}	1.88E−4	0.9999	0.0884	0.9044
2×10^{-4}	4.20E−5	0.9986	0.0458	0.9749
4×10^{-4}	6.89E−5	0.9997	0.0516	0.9734

amounts of DDABDT adsorbed on dry hair at equilibrium and time t, respectively.

The rate constants for first-order and pseudo-second-order along with the correlation coefficients were derived (Table 1) by fitting the experimental data to Eqs. (1) and (2), respectively. It was found that the experimental data are better fitted to the pseudo-second-order kinetics model than to the first-order kinetics model.

3.2. The adsorption isotherms of DDABDT onto hair surface

The adsorption isotherms were obtained in the presence of 0.8% (w/v) fibers dispersed in a series of DDABDT solutions. The mixtures were shaken for 1 h at 40 or 50 °C to reach equilibrium of adsorption. The amounts of DDABDT adsorptions are plotted against equilibrium concentration as shown in Fig. 2.

To construct relationship between the amount of adsorptions and the equilibrium concentrations, two most frequently used models are selected in this study, namely, the Langmuir and Freundlich isotherms [13].

The Langmuir model is usually expressed as

$$\Gamma_e = \frac{\Gamma_0 b C_e}{(1 + b C_e)} \tag{3}$$

which can be transformed to the following linear form

$$\frac{C_e}{\Gamma_e} = \frac{1}{\Gamma_0} b + \frac{C_e}{\Gamma_0} \tag{4}$$

where Γ_e is the equilibrium adsorption amount at an equilibrium concentration C_e, and Γ_0 and b are the saturated adsorption and Langmuir constant related to adsorption free energy, respectively, which can be obtained from the slope and intercept of linear Eq. (4).

The Freundlich adsorption model is shown in the following equation:

$$\Gamma_e = k_f \times C e^{1/n} \tag{5}$$
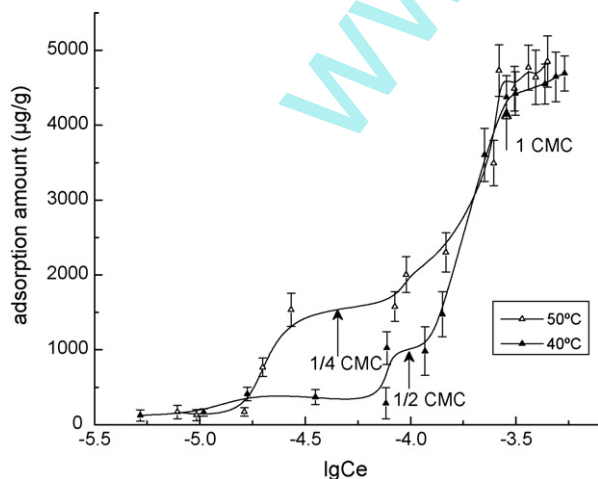
Fig. 2. DDABDT adsorption isotherms. Adsorption isotherms for DDABDT on human hair at (▲) 40 °C and (△) 50 °C.

where k_f and n are the Freundlich constants. Eq. (5) can also be transformed into linear form

$$\ln \Gamma_e = \ln k_f + \frac{1}{n} \ln C_e \tag{6}$$

and both parameters can be obtained from the slope and the intercept. The derived equations by fitting the experimental data along with the correlation coefficients (R^2) are presented in Table 2.

The results show that the adsorption isotherm of DDABDT on hair surface are better fitted to the Freundlich model at both temperatures, which indicates the presence of surfactant association in the adsorption layers. It is also noted from Fig. 2 that the adsorption isotherms are noticeably influenced by temperature. The first plateau is more readily reached at 50 °C than at 40 °C, which implies that the adsorption is more likely to be an endothermic process. This kind of adsorption isotherms are usually observed in the adsorption on porous absorbents [14].

In a physical adsorption system, especially the adsorption of ionic surfactants onto oppositely charged solid surface, electrostatic interactions play a governing role in beginning of adsorption process [12]. When the concentrations of surfactants are increased to a threshold value, analogous to aggregation in the bulk, lateral interactions between hydrocarbon chains would take place and lead to an abrupt increase in adsorption density [12,13].

In Fig. 2 the adsorption isotherm can be divided into five regions. The adsorption amount of DDABDT increases slowly with the increase of the equilibrium concentration in the first region, in which the adsorption is believed to take place principally through electrostatic interaction between the negative charges of the hair surface and the ammonium ions of the surfactant. However, due to the relatively low charge density of hair surface, the adsorption amount in this region is also relatively low. In the second region, with increased concentration the adsorption amount begin to rise accordingly. This could be related to the onset of the lateral hydrophobic interactions among the hydrocarbon chains of surfactants. Thus surfactant molecules start to aggregate at the solid–liquid interface and form monolayer/hemi-micelle. When the concentration is increased to about 1/4CMC at 50 °C and 1/2CMC at 40 °C, the adsorption amount become constant and the isotherm curves reach their first plateau. It is suggested that the surfactant molecules associate on the hair surface in hemi-micelle in this region [11]. With the further increase of concentration, the adsorption amount increases rapidly again (the fourth region). When the DDABDT concentration is increased to about 1CMC in bulk solution, the second plateau (the fifth region) is reached at the isotherm curve. This phenomenon can be explained by the transition of the association structure of surfactant molecules from hemi-micelle to bilayer/admicelle. Therefore more compact aggregation of DDABDT on hair surface is produced by the lateral hydrophobic interactions of adjacent hydrocarbon chains, leading to the formation of a bilayer structure of DDABDT molecules on the hair surface.

Surfactant adsorptions on solid–liquid interfaces are often described by the Somasundaran–Fuerestenau isotherm, which can be divided into 3 or 4 regions [13]. In the region 1, the adsorptions of surfactants take place due to electrostatic interactions and the slope of the log–log adsorption isotherm is about unity. In the region 2, the adsorbed ions begin to associate as hemi-

Table 2
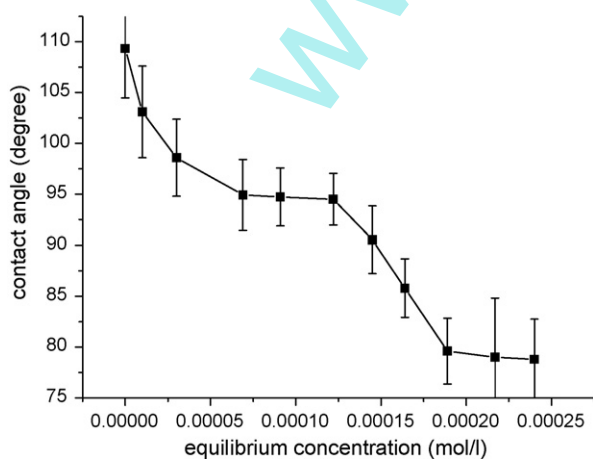The comparison of the two adsorption models.

	Langmuir adsorption model	R^2	Freundlich adsorption model	R^2
50 °C	$C_e/\Gamma_e = 0.00008C_e + 5E{-}08$	0.275	$\ln\Gamma_e = 0.864\ln C_e + 15.39$	0.894
40 °C	$C_e/\Gamma_e = 0.00007C_e + 7E{-}08$	0.283	$\ln\Gamma_e = 0.851\ln C_e + 15.02$	0.962

micelles due to, in addition to the electrostatic interaction, the lateral interaction between hydrocarbon chains, and the adsorption isotherm shows a sharp increase in the slope. In region 3, the adsorption takes place mainly due to lateral interaction and the slope of adsorption isotherm reduces and gradually reaches a constant. In the last region, the surface of solid is saturated with the aggregated surfactant molecules arranged in bilayer-organized structures.

So far most of the published works were focused on the oxide or mineral surfaces with high density of charges, so the transition from hemi-micelle to admicelle may not exist or be too quick to be observed [15,16]. The adsorptions of surfactants onto the surfaces of bio-materials are more complex due to the heterogeneous nature of surface in both physical and chemical terms. The sparse distribution of chemical residual conferring electrostatic charge would result in a retardation in the transition [13]. Therefore the isotherms obtained in the current work are not fully in accordance with that of the Somasundaran–Fuerestenau isotherm, but are in agree with the theoretical model proposed by Łajtar et al. [16] and Li and Ruckenstein [17]. In this model, the different aggregates, including monomer, hemimicelle or admicelle, coexist. With the increase of surfactant concentrations, the combined effects of electrostatic and dispersive interactions cause the aggregates changing from monomer, monolayer to bilayer, as being reflected on the regions of isotherm curves.
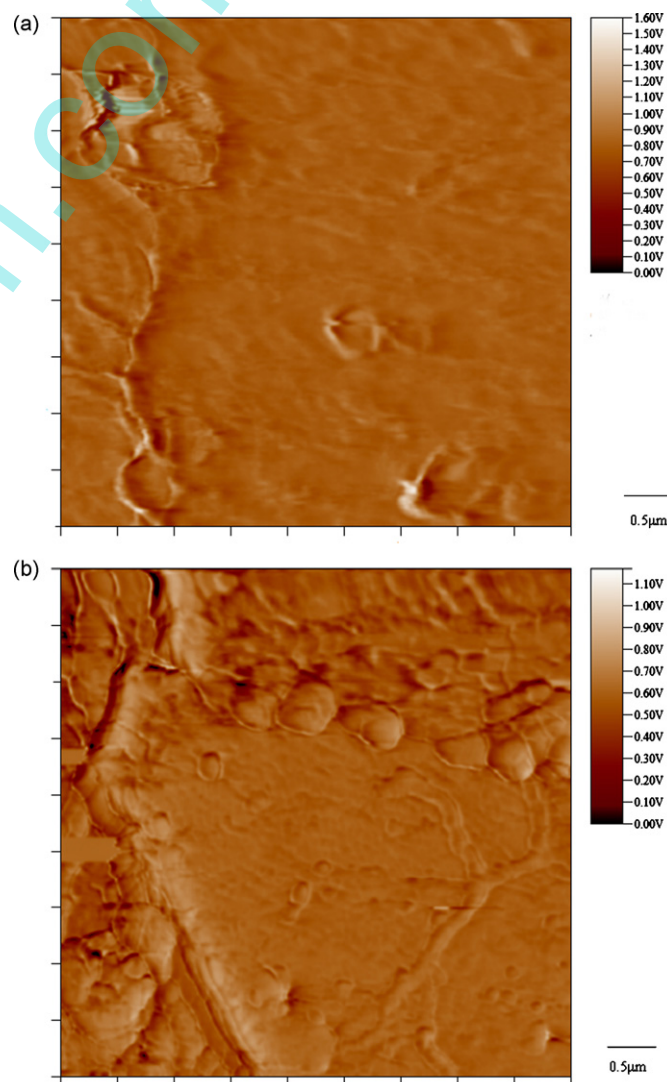
3.3. The effect of DDABDT adsorption on wettability of hair fibers

The contact angles between hair fibers and water are plotted against equilibrium concentration of DDABDT in Fig. 3. The figure shows that hair fibers are hydrophobic (the contact angle more than 90°) in the absence of DDABDT on the surface of hair fibers. With the increase of the equilibrium concentration of DDABDT, the contact angles begin to decrease and become constant when the equilibrium concentration is close to 0.05 mmol/l (1/4CMC). When the equilibrium concentrations are between 0.05 (1/4CMC) and 0.1 mmol/l (1/2CMC), in accordance with the adsorp-

tion isotherm, the curve reaches the first plateau. When the surfactant concentration reaches to 0.1 mmol/l, the hydrophobic property of the hair fibre may attribute to the monolayer associate of DDABDT molecules, as the hydrophilic group of the DDABDT is anchored on hair surface with its long alkyl chain orientated outward. With the further increase of the concentrations, the contact angles decrease sharply. When the concentration of the surfactant molecule is greater than 0.15 mmol/l, the wettability changes from hydrophobic to hydrophilic. Similar to the adsorption isotherm, the curve of contact angles reaches the second plateau when the surfactant concentration approaches its CMC. Bilayer associates of DDABDT molecules may be formed at this stage, and which is accountable for the improvement of the wettability of hair fibers.

Fig. 3. The effects of DDABDT concentration on the contact angles between hair fibers and water.

Fig. 4. The morphology of hair surface for samples (a) initial hair, (b) hair treated with 0.1 mmol/l DDABDT (about 1/2CMC), (c) hair treated with 0.5 mmol/l DDABDT (about 5/2CMC).
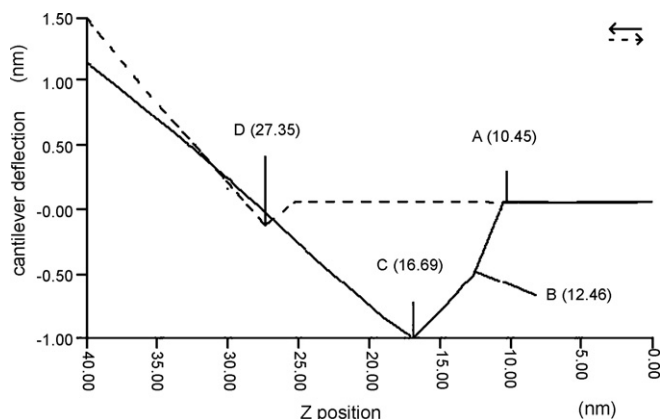
Fig. 5. The force calibration plot obtained from DDABDT-treated hair fiber.

3.4. The morphology of hair surface and the thickness of adsorbed DDABDT

It is well known that the outer surface of hair fibers, the epicuticle, is essentially made of fatty substances, while the edge of scale is composed of keratin. The presence of carboxylic anion of amino acid residue impart negatively charged hair surface [1]. When spare DDABDT molecules diffuses to hair fibers, the positive head groups of surfactants would interact with the carboxylic anion electrostatically, meanwhile, the long hydrophobic chains in the surfactant molecules are extended outward and hydrophobic interaction between chains leads to the formation of monolayered aggregates. The presence of hemi-micelles has been proved with the images obtained from AFM techniques [18,19]. Therefore, in this work the AFM technique was selected to obtain the nano-scale images in order to assess the effects of DDABDT adsorptions on the hair surfaces.

The typical images of morphology of hair fibers observed with AFM are presented in Fig. 4. The three-dimensional images clearly reveal the morphology of hair surface. For the control sample (Fig. 4a), a flat cuticle surface with a little accident edge of scale is displayed. After treatment with 0.5 mmol/l DDABDT solution (the equilibrium concentration of DDABDT exceeds its CMC), as can be seen in Fig. 4b that some thicker ridges along the edge of the scale are emerged. The differences between the Fig. 4b and the Fig. 4a can be attributed to the adsorptions of cationic surfactants on hair surface.

To further elucidate the adsorption behavior, a force calibration plot for surfactant-treated hair fiber is presented in Fig. 5. The measurement starts at large separation where there are no interaction between hair surface and the tip ended in silicon cantilever, i.e. no deflection of cantilever for point A. When the tip approaches the surfactant film, the interaction occurs and a meniscus around the tip is formed. Accordingly, a sudden mechanical change appears in the plot from point A to point B. As the tip approaches more closely to the hair fiber, the deflection of the cantilever increases while the tip travels in the surfactant film. When the tip eventually contacts the hard surface at point C, the change in deflection of cantilever is proportional to the deformation of the hair fiber. So the difference between point C and point B along Z axis should represent the thickness of surfactant film. Considering the unavoidable history of shampooing for hair samples and a 2 nm thickness offset to actual film thickness with AFM technique [11], the thickness of DDABDT film in this paper can be estimated by the apparent thickness subtracting control thickness and the value of 2 nm. The distances of BC along Z axis in the Fig. 5 were shown on

Table 3
The distances of BC along Z axis extracted from Fig. 5.

Samples	Distance of BC along Z axis (nm)	Average (nm)
Control	6.48, 3.99, 4.23, 6.05, 4.28	5.01 ± 1.16
Treated	11.58, 10.74, 12.26, 14.81, 12.76	12.43 ± 1.36

the Table 3. The thickness of DDABDT film for hair fibers treated with 0.5 mmol/L DDABDT is therefore calculated to be 5.42 nm (12.43 nm − 5.01 nm − 2 nm), which is close to the two times of the theoretical size of DDABDT molecule (supplementary material 2). Furthermore it is suggested that the surfactant molecules are arranged with their head groups outward in the bilayer structure of adsorption, leading to the increase of hair wettability, which is therefore accountable for the function of cationic surfactant as conditioner in hair care products [21].

4. Conclusion

The adsorption behavior of cationic surfactant DDABDT onto hair surface revealed complex characteristics. It is found that the adsorption kinetics fit to pseudo-second-order kinetics model and the adsorption isotherm fit to Freundlich adsorption model. The adsorption isotherm can be divided into five regions. The structure of association of DDABDT molecules on hair surface is suggested to be monolayer or bilayer depending on the initial concentration of the surfactant. For the structure of bilayer, the 'anchor' surfactant molecules adsorbed vertically on the surface of hair through electrostatic interaction, and the top layer molecules, with charged groups oriented outside, were attracted to the 'anchor' molecules with lateral hydrophobic interaction.

The equilibrium adsorption amount relates with initial concentration of surfactant but is not linearly proportional to it. The effect of temperature on the adsorption of DDABDT onto hair surface tends to suggest that the whole process is an endothermic one.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.colsurfb.2008.09.024.

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