Influence of Polyoxyethylene Lauryl Ether on the Binding of Stearyltrimethylammonium Chloride to Human Hair

Toshiharu Sugihara and Naoko Mizuno*

Faculty of Education, Gifu University, Gifu 501-1193, Japan
* Kagamigahara Yogo School, Kagamigahara, Gifu 504-8036, Japan

The influence of polyoxyethylene lauryl ethers on the binding of stearyltrimethylammonium chloride (STAC) to human hair was investigated. The nonionic surfactants decreased the amount of bound STAC to hair. The effect was more prominent with the nonionic surfactant with a longer polyoxyethylene chain. The decreasing effect was correlated to the hydrophilicity of the nonionic surfactant. The binding of the nonionic surfactant of a long polyoxyethylene chain to hair was also decreased by STAC. The analysis of the isotherms of a Langmuir-type binding indicated that the surfactant having a long polyoxyethylene chain reduces both the binding sites in saturation and the binding constant. Thermodynamic study and the surface analysis by FT-IR or X-ray photoelectron spectroscopy (XPS) suggested that the decreasing effect was caused by the interaction of STAC with the nonionic surfactant of a long polyoxyethylene chain in the aqueous phase and on the hair surface.
(Received April 15, 2002; Accepted in revised form January 21, 2003)

Keywords: hair, stearyltrimethylammonium chloride, polyoxyethylene lauryl ether, binding isotherms, FT-IR, interaction.

INTRODUCTION

Cationic surfactants with a long alkyl chain are widely used in daily life, especially as a major component of hair conditioners (Robbins 1994). However, the adsorption of the surfactants or the mechanism of the influence of the chemicals on human hair remains to be clarified. In the previous paper we investigated the binding of stearyltrimethylammonium chloride (STAC) to human hair and clarified that the binding is determined by the ionic strength and pH indicating the importance of both hydrophobic and electrostatic interactions for the binding. The analysis of isotherms of a Langmuir-type binding enabled us to determine the thermodynamic parameters which showed that the former interaction is dominant in the binding (Sugihara and Morikawa 2000).

Cationic surfactants are also an ingredient of a conditioning shampoo, in which they are used in combination with another type of surfactant such as sodium laurylsulfonate or polyoxyethylene lauryl ether. Hence it is important to investigate the binding of cationic surfactants to human hair in the presence of nonionic surfactants or anionic surfactants. In this paper, the binding behavior of STAC to human hair was investigated in the presence of polyoxyethylene lauryl ethers. The effect of the nonionic surfactants on the binding of STAC to human hair was discussed by analyzing the binding isotherm, and FT-IR or X-ray photoelectron spectroscopy (XPS).

MATERIALS AND METHODS

Chemicals

All chemicals are commercially available. STAC was used after recrystallization with acetone.

Hair samples

Hair samples (unaltered, bleached, and permanent-waved hairs) were prepared according to the literature (Ohbu *et al.* 1986). Hairs from males aged 20-22 years which have never been bleached, dyed or permanent-waved for at least 3 years prior to cutting were used. Hair samples were treated as described previously (Sugihara and Morikawa 2000).

Hair samples for the surface measurements were prepared by immersing each hair sample in an STAC solution (5 mM) without or with polyoxyethylene lauryl ether (10 mM) at 40℃ for 24 h. The mixture was filtered, and the remaining solution on the hair surface was absorbed with a filter paper. The hair was then dried *in vacuo*.

Determination of bound surfactant

The amount of bound STAC to hair was determined as follows. A hair sample (1.0 g) was placed in a flask of STAC solution (100 ml, phosphate buffer of pH 7.0) containing a certain amount of polyoxyethylene lauryl ether. The flask was shaken for 24 h. After removing the hair, the STAC solution (5 ml) was acidified to pH 2.6–3.4 with dilute hydrochloric acid. After adding a few drops of 0.1% Methyl Orange solution the solution was titrated with a 1 mM sodium tetraphenylborate solution until the color of the solution changed from yellow to red (Uno *et al.* 1960). A larger amount (20 ml) of the STAC solution was used for the titration of the STAC solution when the initial STAC concentration was below 0.5 mM. The presence of polyoxyethylene lauryl ether did not alter the amount of titration if the concentration of the nonionic surfactant was less than 10 mM. The concentration of free STAC in the solution after the binding was calculated from the amount of a sodium borate solution consumed for the titration.

Determination of the amount of polyoxyethylene lauryl ether bound to human hair was done by the potassium ferrocyanate method (Scheonfeldt 1953) as follows. A hair sample (1.0 g) was placed in a flask of polyoxyethylene lauryl ether solution (10 mM, 100 ml, phosphate buffer of pH 7.0) containing STAC (10 mM). The flask was shaken for 24 h and the hair was removed. To the solution (10 ml) 1 ml of hydrochloric acid and 1.5 g of sodium chloride were added. After shaking the solution vigorously, 1 ml of 0.125 M potassium ferrocyanate solution was added. On standing for 5 min the precipitates produced were removed by filtration. The precipitates were rinsed with 3 ml of water. To the filtrate combined with the washing solution were added 1 ml of 4% ammonium sulfate, a drop of 2% potassium ferricyanate and a drop of 1% diphenylamine as an indicator. The solution was titrated with a 0.075 M zinc sulfonate solution until the color of the solution changed from pale green to deep blue. The presence of STAC did not influence the titration if the concentration of the cationic surfactant was less than 10 mM. The same titration was done for the nonionic solution without hair. The increased amount of the zinc sulfonate solution consumed for the titration on the binding gave the amount of the bound surfactant to hair.

Instrumental analysis

FT-IR spectra were taken on a Perkin-Elmer System 2000 by the ATR method equipped with an MCA detector. FT-IR measurement of a surfactant solution was done with an ATR cell containing 10 mM polyoxyethylene alkyl ether and 50 mM STAC. XPS spectra were recorded on a Shimadzu ESCA-850 equipped with an AlKα radiation source at 1,487 eV and 300 W power at the anode. Nitrogen 1p-core level spectra as well as wide spectra were taken to analyze the hair surface.

RESULTS AND DISCUSSION

Effect of nonionic surfactants on the amount of bound STAC

The binding of STAC to human hair was investigated in the presence of various nonionic surfactants to see the effect of alkyl chain length (m) and degree of polymerization (n) of the polyoxyethylene unit in polyoxyethylene alkyl ethers (C_mE_n) as shown in Figs. 1 and 2. Figure 1 shows the relative amount of bound STAC with the addition of an increasing amount of polyoxyethylene lauryl ethers with various degrees of the polymerization of polyoxyethylene unit. As shown in the figure the amount of bound STAC decreases in the presence of the nonionic surfactants. The rate of decrease in the amount of bound STAC becomes smaller with the increasing concentration of an added nonionic surfactant and finally the amount of bound STAC becomes unchanged with further addition of
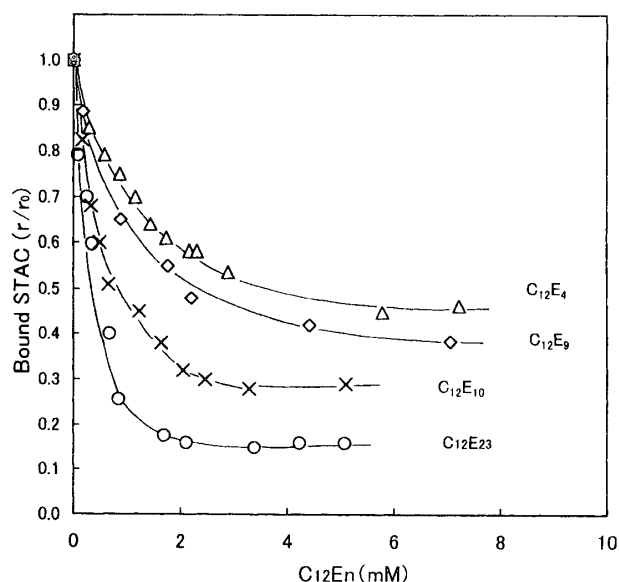

Fig. 1. Binding of STAC to unaltered hair in the presence of polyoxyethylene lauryl ethers (C_mE_n) at initial STAC concentration of 1 mM in phosphate buffer of pH 7.0 at 30℃

The bound STAC is expressed as a relative value (r/r_0) where r is the amount of bound STAC in the presence of C_mE_n and r_0 in the absence of C_mE_n.

Influence of Polyoxyethylene Lauryl Ether on the Binding of Stearyltrimethylammonium Chloride to Human Hair
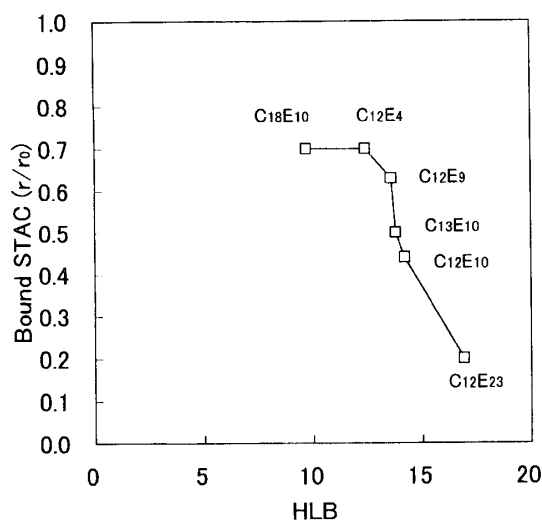

Fig. 2. Relationship between a relative amount of bound STAC and HLB values of polyoxyethylene alkyl ethers (C_mE_n) at the ratio of C_mE_n to STAC, 1.0

The initial STAC concentration was 1 mM.

Fig. 3. XPS N 1p-core spectra of STAC-bound hair samples prepared in the presence (dotted line) or in the absence of $C_{12}E_{23}$ (solid line)

the nonionic surfactant. It should be noted here that the decreasing effect depends on the degree of polymerization of the polyoxyethylene unit; the longer the polyoxyethylene chain, the larger the decreasing effect. Among the surfactants the largest decrease was observed with $C_{12}E_{23}$ and the smallest with $C_{12}E_4$. The surfactant of a long polyoxyethylene chain with low hydrophobicity decreased greatly the binding of STAC to human hair. The effect of polyoxyethylene chain length suggests that the balance of hydrophobicity and hydrophilicity (HLB) of the surfactant is a determinant for the decrease of the binding of STAC to hair.

To see the contribution of hydrophobicity of nonionic surfactants, the amounts of bound STAC were compared in the presence of polyoxyethylene alkyl ethers (C_mE_n) of various alkyl chain lengths (m) and the degree of polymerization (n) of the polyoxyethylene unit. Figure 2 shows the relationship between the relative amount of the bound STAC and HLB values of the polyoxyethylene alkyl ethers calculated by the weight fraction of hydrophilic groups of a surfactant (Hayano 1964; Kitahara *et al.* 1979; Yoshida *et al.* 1987). It is clearly seen in the figure that the amount of bound STAC decreases as the hydrophobicity decreases. Thus the nonionic surfactant with a longer polyoxyethylene chain and a shorter alkyl chain decreases the bound STAC to hair more.
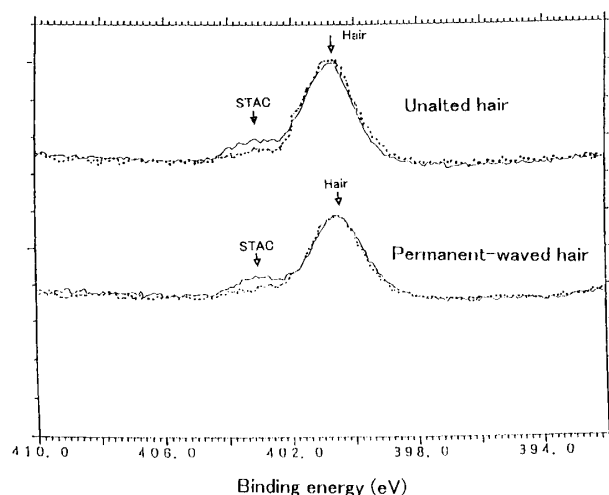
The decrease of the STAC binding by the nonionic surfactant was also indicated by the XPS spectroscopy. Figure 3 shows the N 1p-core level spectra of unaltered and permanent-waved hairs with or without $C_{12}E_{23}$. The peak at 402.7 eV due to nitrogen of STAC bound to hair can be distinguished from that of hair keratin at 400.6 eV. The figure clearly shows that in the spectrum of either unaltered or permanent-waved hair the peak of STAC bound to the hair surface is extremely decreased for the hair sample prepared in the presence of $C_{12}E_{23}$. Because XPS gives information on the surface of a material (Robbins and Blake 1984; Kobunshi Gakkai 1996), the result shows that there is only a little STAC if any on the surface of unaltered or permanent-waved hair when the nonionic surfactant is present.

Binding isotherms and binding characteristics

As shown in Figs. 1 and 2, the STAC binding to hair is decreased with increasing the length of polyoxyethylene chain if the alkyl chain of the nonionic surfactants is the same. Hence it is quite interesting to investigate the distinguished effect of $C_{12}E_{23}$ on the binding of STAC in detail. Figure 4 shows the binding isotherms of STAC for three types of hairs (unaltered, bleached and permanent waved-hairs) at 40℃ in the presence or in the absence of $C_{12}E_{23}$. In all cases the bound STAC increased continuously with the equilibrium concentration of bound STAC in solution and reached a constant value indicating a Langmuir-type binding. The amount of bound STAC was larger at 40 ℃ than at 30℃ for the three types of hairs. The amount of bound STAC to permanent-waved hair was
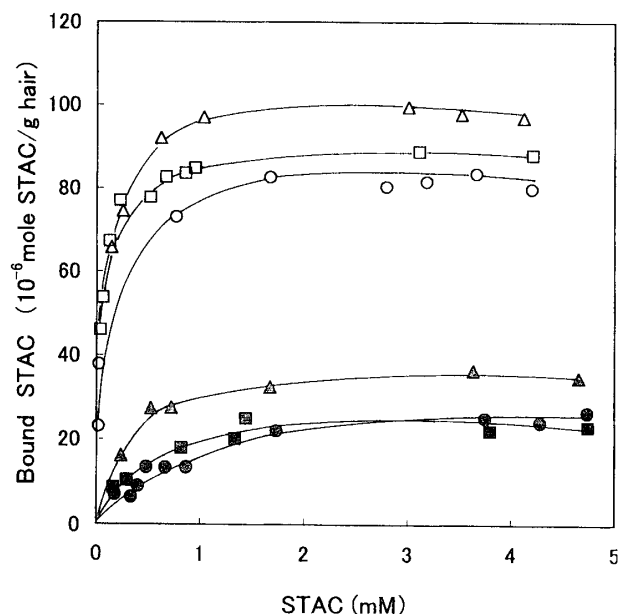
Fig. 4.   Binding isotherms of STAC to unaltered hair ($\bigcirc$, $\bullet$), bleached hair ($\square$, $\blacksquare$) and permanent-waved hair ($\triangle$, $\blacktriangle$) in the presence (5 mM, closed symbol) or in the absence (open symbol) of $C_{12}E_{23}$ in phosphate buffer of pH 7.0 at 40℃

Fig. 5.   Reciprocal plots for the binding isotherms of STAC to unaltered hair ($\bigcirc$, $\bullet$), bleached hair ($\square$, $\blacksquare$) and permanent-waved hair ($\triangle$, $\blacktriangle$) in the presence (5 mM, closed symbol) or in the absence (open symbol) of $C_{12}E_{23}$ in phosphate buffer of pH 7.0 without or with STAC ($C_{12}E_{23}$/STAC = 10) at 40℃

the largest both in the absence and in the presence of the nonionic surfactant. These characteristics of STAC binding in the presence of $C_{12}E_{23}$ are similar to those of the STAC binding to hair in the absence of polyoxyethylene lauryl ether (Sugihara and Morikawa 2000).

Langmuir-type binding can be described by an Eq. (1) where r, n, K and C are the amount of bound STAC, the amount of binding sites in saturation, a binding constant and the equilibrium concentration of STAC, respectively.

$$1/r = (1/C)\cdot 1/(K\cdot n) + 1/n \qquad (1)$$

The values of n and K are obtained from the plot of $1/r$ versus $1/C$. Figure 5 shows the reciprocal plots. The intercept and slope of the linear plots gave the values of n and K for the binding of STAC to the hair samples. The binding profile is dominated mainly by the number of binding sites and the strength of the binding. These are estimated by n and K in case of Langmuir-type binding.

Table 1 lists those values as well as thermodynamic parameters calculated from the binding constants at 30 and 40℃ for the STAC binding to unaltered or permanent-waved hair in the absence and in the presence of $C_{12}E_{23}$. The large amount of STAC bound to permanent-waved hair comes from the increased
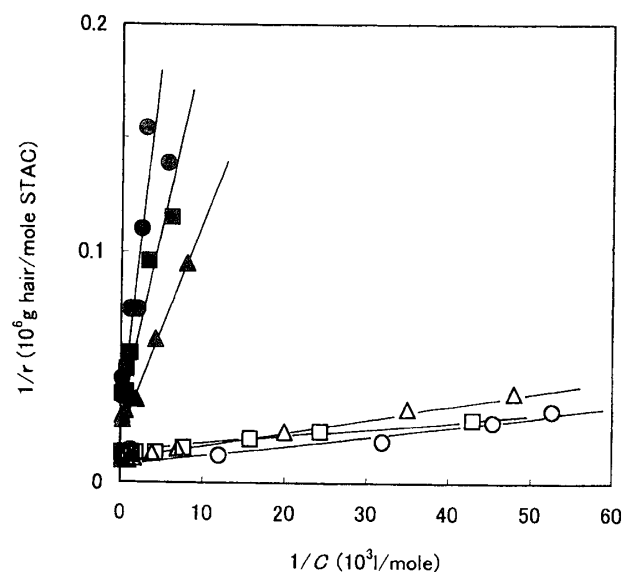
number of binding sites in saturation as clarified in the previous investigation (Sugihara and Morikawa 2000).

It is seen in Table 1 that $C_{12}E_{23}$ reduced both the number of binding sites in saturation and the binding constant in the binding of STAC to unaltered or permanent-waved hair. The nonionic surfactant decreased the number of binding sites by 1/2–1/4, though the number of binding sites of permanent-waved hair is still twice as large as that of unaltered hair. The binding constant also decreased by 1/4–1/10 when $C_{12}E_{23}$ is present.

As to the protein-surfactant interaction, thermodynamic studies have been done on the binding of surfactant with soluble proteins, mainly albumin (Decker and Foster 1967; Tipping *et al.* 1974; Jones *et al.* 1975; Hiramatsu *et al.* 1977; Sukow *et al.* 1980), and with insoluble protein, keratin (Ohbu *et al.* 1986; Nakama and Yamaguchi 1992; Sugihara and Morikawa 2000). In some studies thermodynamic parameters have been drawn by the analysis of binding isotherms or microcalorimetry. In the former analysis binding constants at two different temperatures are usually used for the calculation. The results on soluble protein-surfactant interaction show that the binding enthalpy depends on the surfactant; the

Influence of Polyoxyethylene Lauryl Ether on the Binding of Stearyltrimethylammonium Chloride to Human Hair

Table 1. Amount of binding sites in saturation, binding constant and thermodynamic parameters of STAC binding to human hair

	Temperature ($^\circ$C)	n (10^{-6} mole/g hair)	K (10^3 l/mole)	$-\Delta G$ (kJ/mole)	$-\Delta H$ (kJ/mole)	ΔS (kJ/mole)
Unaltered hair	30	65.5±4.7	16.9±3.1	24.5	−36	200
	40	82.7±0.1	25.9±3.5	26.5		
Unaltered hair with $C_{12}E_{23}$	30	14.0±0.8	2.6±0.3	19.8	29	161
	40	24.5±5.9	1.8±0.3	19.5		
Permanent-waved hair	30	106.4±15.4	6.9±0.2	22.3	−53	249
	40	100.6±7.3	13.6±0.4	24.8		
Permanent-waved hair with $C_{12}E_{23}$	30	34.5±5.9	1.6±0.6	18.6	−48	220
	40	40.1±2.7	3.0±0.3	20.8		

binding of anionic surfactant is exothermic ($\Delta H < 0$) and that of cationic surfactant is endothermic ($\Delta H > 0$), though the cause of the variance has not been clarified. Moreover, the value of ΔH varies largely according to the number of surfactant molecules bound to protein molecule. In spite of the variation of ΔH, the contribution of entropy to the free energy of the binding is larger than enthalpy, indicating that the binding of surfactant is dominant of a hydrophobic nature (Aoki *et al.* 1984).

In the case of the binding of surfactant to insoluble protein (hair keratin), the binding of anionic surfactant is endothermic, while ΔH of the binding of cationic surfactant is positive (Sugihara and Morikawa 2000) or nearly zero (Ohbu *et al.* 1986). In the binding of surfactant to hair the entropy factor is also dominant for the binding.

As mentioned above a large entropy change has been reported in the binding of ionic surfactants to proteins, which is associated with the hydrophobic interactions (Tanford 1979). This is true in the binding of STAC to hair showing that the hydrophobic interactions are dominant (Sugihara and Morikawa 2000) and also in the binding of STAC in the presence of $C_{12}E_{23}$ in the present investigation.

In this investigation it is shown that $C_{12}E_{23}$ decreased ΔS and increased $-\Delta H$. This indicates that $C_{12}E_{23}$ made entropy change (ΔS) unfavorable but enthalpy change ($-\Delta H$) favorable for the binding of STAC to human hair, suggesting that the nonionic surfactant brought less hydrophobic interactions in spite of the increased electrostatic interactions in the binding of STAC to hair.

The decrease of n and K in the presence of $C_{12}E_{23}$ suggests that $C_{12}E_{23}$ not only competes for the binding site with STAC but also influences the

Table 2. Amount of polyoxyethylene lauryl ether bound to permanent-waved hair[a]

	$C_{12}E_{23}$ (10^{-5} mole/g hair)	$C_{12}E_4$ (10^{-5} mole/g hair)
Without STAC	2.1	12.0
With STAC[b]	0.2	11.8

[a] In phosphate buffer of pH 7.0; initial $C_{12}E_n$ concentration, 10 mM. [b] [STAC]/[$C_{12}E_n$] = 1.

interaction of STAC with hair.

Interaction of surfactants in the aqueous medium

In order to clarify the mechanism of the decreasing effect of polyoxyethylene lauryl ethers, $C_{12}E_4$ and $C_{12}E_{23}$, were compared, since the latter decreased the binding of STAC the most while the former the least. First, an experiment was carried out to determine if the binding of polyoxyethylene lauryl ether to human hair is influenced by STAC. Table 2 lists the amounts of bound $C_{12}E_{23}$ or $C_{12}E_4$ to human hair in the presence of STAC. From the table it is apparent that in the presence of the cationic surfactant, the binding of $C_{12}E_{23}$ was decreased by 1/10 while the binding of $C_{12}E_4$ was hardly affected. This is well related to the decrease of STAC binding to hair by polyoxyethylene lauryl ethers; the decreasing effect of $C_{12}E_{23}$ is much larger than that of $C_{12}E_4$. These results suggest that STAC competes for the binding site on human hair with $C_{12}E_{23}$ but not with $C_{12}E_4$, and/or STAC interacts strongly with $C_{12}E_{23}$ but less strongly with $C_{12}E_4$, in the aqueous phase. Thus the binding of $C_{12}E_{23}$ and STAC to human hair will be reduced.

The competition of STAC and $C_{12}E_{23}$ for the binding site is likely because the number of the binding sites in saturation (n) of STAC was decreased in the presence of $C_{12}E_{23}$ as seen in Table 1.
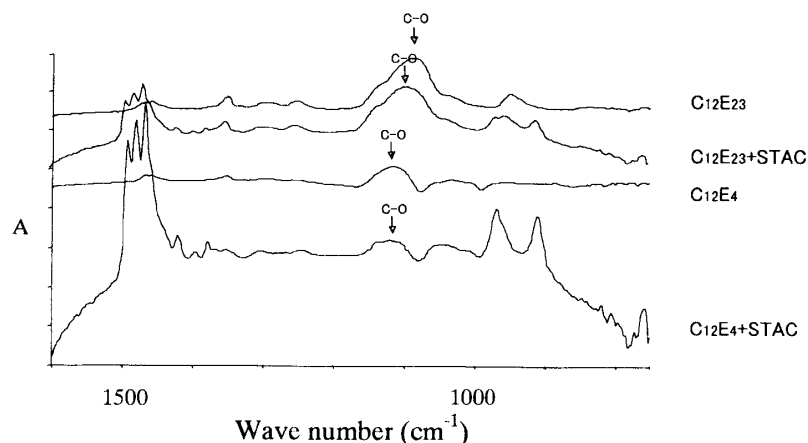
Fig. 6. FT-IR spectra of $C_{12}E_{23}$ and $C_{12}E_4$ in phosphate buffer of pH 7.0 (1,000 scans)

Table 3. Effect of STAC on FT-IR absorption of $C_{12}E_{23}$ and $C_{12}E_4$ in phosphate buffer of pH 7.0

Absorption	$C_{12}E_{23}$		$C_{12}E_4$	
	Without STAC (cm^{-1})	With STAC[a] (cm^{-1})	Without STAC (cm^{-1})	With STAC[a] (cm^{-1})
CH_2 sciss	1,457	1,467	1,466	1,467
CH_2 twist	1,295	1,300	1,351	1,351
C-O stretch	1,085	1,093	1,115	1,113
CH_2 rock, C-C stretch	948	953		

[a] $[C_{12}E_n]/[STAC] = 1/10$.

To verify the strong interaction of STAC and $C_{12}E_{23}$ in the aqueous medium, an FT-IR study of the surfactants was done. Figure 6 shows the FT-IR spectra of $C_{12}E_{23}$ and $C_{12}E_4$ in the absence or the presence of STAC in the aqueous medium and the data are summarized in Table 3. The assignment of the absorption of the polyoxyethylene unit was done according to the literature (Vasanthan *et al.* 1996; Binder and Klose 1998). The absorption at 1,085 cm^{-1} due to C-O stretching mode of $C_{12}E_{23}$ shifted to 1,093 cm^{-1} when STAC is present while little shift was observed in the absorption of $C_{12}E_4$ with the addition of STAC. The absorption of $C_{12}E_{23}$ at 1,457 cm^{-1} due to CH_2 scissoring mode and at 1,295 cm^{-1} due to CH_2 twisting mode also shifted to 1,467 cm^{-1}, 1,300 cm^{-1}, respectively with the addition of STAC. On the other hand, little shift was observed in these absorption bands of $C_{12}E_4$ with the addition of STAC. A fairly large shift in the absorption bands of C-O and CH_2 of the polyoxyethylene unit of $C_{12}E_{23}$ with STAC indicates that STAC interacts strongly with $C_{12}E_{23}$, probably through the interaction between cationic nitrogen of STAC and electronegative oxygen atoms

of $C_{12}E_{23}$, while minimal shift in the FT-IR spectrum of $C_{12}E_4$ with STAC indicates that STAC hardly interacts with $C_{12}E_4$.

Thus the FT-IR study suggested that the interaction between STAC and $C_{12}E_{23}$ is stronger than that between STAC and $C_{12}E_4$ in the aqueous phase. The interaction might be the cause of the decreasing effect, retaining a larger amount of free STAC in the aqueous phase.

Thermodynamically the strong interaction of STAC with $C_{12}E_{23}$ in the aqueous medium could contribute to lower the potential energy of the original state in the reaction coordinate where no STAC molecules are bound to hair. As shown below, STAC interacts with $C_{12}E_{23}$ on the hair surface as well, which also lowers the potential energy of the bound state. The free energy change of the binding reaction is the difference of potential energies of the original state and the bound state. Though $C_{12}E_{23}$ could lower the potential energies of both states, if the fall of the potential energy of the original state with the addition of the nonionic surfactant is larger than that of the bound state, the strong interaction in the aqueous

12

Influence of Polyoxyethylene Lauryl Ether on the Binding of Stearyltrimethylammonium Chloride to Human Hair

medium then might have brought about the decrease of the free energy change ($-\Delta G$) of the binding of STAC to hair, resulting in the decrease of the binding constant (K).

Interaction of surfactants on hair surface

FT-IR (ATR) of STAC-bound hair was investigated to see if there is an interaction between the surfactants on the hair surface. The experiment was done on the permanent-waved hair-$C_m E_n$ system because the amount of bound STAC to permanent-waved hair was the largest among the three types of

hair samples, unaltered, bleached, and permanent-waved hairs, which could make it easy to detect a small shift of FT-IR absorption of each component of the hair-$C_m E_n$ system. A stronger interaction between $C_{12}E_{23}$ and STAC was also detected on the hair surface. The spectra are shown in Figs. 7 and 8. The shift of the absorption bands of polyoxyethylene lauryl ether with STAC on the hair surface was not as large as that in the aqueous phase as seen in Figs. 6-8. But a distinctive shift was observed for the C-O stretching band of the nonionic surfactant. The absorption at
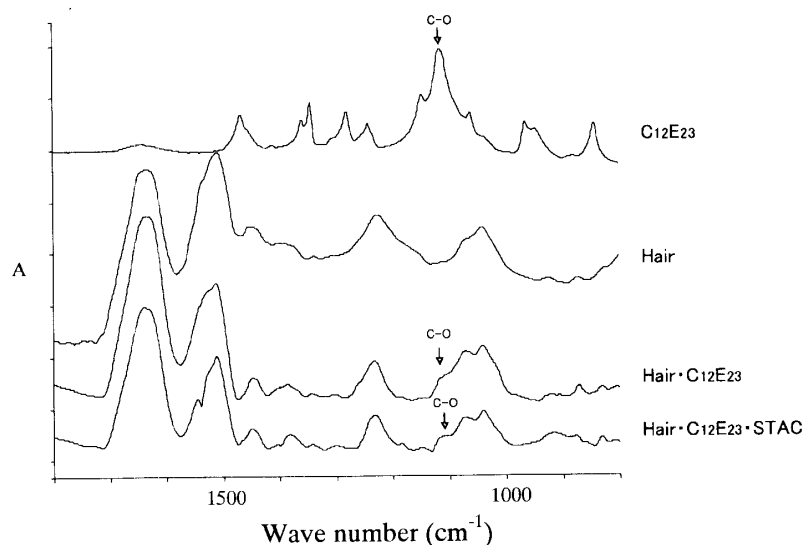

Fig. 7. FT-IR spectra of $C_{12}E_{23}$ (neat), permanent-waved hair, permanent-waved hair with $C_{12}E_{23}$, and permanent-waved hair with $C_{12}E_{23}$ and STAC (2,000 scans)
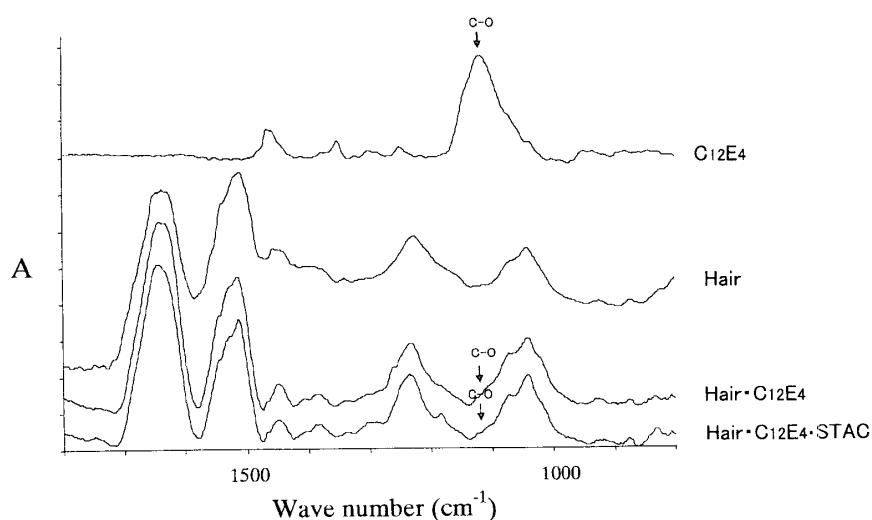

Fig. 8. FT-IR spectra of $C_{12}E_4$ (neat), permanent-waved hair, permanent-waved hair with $C_{12}E_4$, and permanent-waved hair with $C_{12}E_4$ and STAC (2,000 scans)

$1,115$ cm^{-1} of neat $C_{12}E_{23}$ due to C-O stretching mode shifted to $1,109$ cm^{-1} for the $C_{12}E_{23}$-STAC-bound hair while the C-O absorption of $C_{12}E_{23}$-bound hair appeared at $1,115$ cm^{-1} (Fig. 7). On the other hand the absorption of $C_{12}E_4$ exhibited no shift upon binding to hair with or without STAC. The C-O stretching bands of the polyoxyethylene unit of neat $C_{12}E_4$, $C_{12}E_4$-bound hair and $C_{12}E_4$-STAC-bound hair all appeared at $1,119$ cm^{-1} (Fig. 8). Thus the stronger interaction of STAC with $C_{12}E_{23}$ than with $C_{12}E_4$ was also indicated on the hair surface.

The stronger interaction of STAC with $C_{12}E_{23}$ on the hair surface was also suggested by XPS. The N 1p-core peak of STAC appeared at 402.7 eV when it was free, and at 403.1 eV when bound to hair. It appeared at 403.4 eV for the STAC-bound hair prepared with $C_{12}E_{23}$. On the other hand, the peak of STAC at 403.1 eV remained unchanged for the STAC-bound hair prepared with $C_{12}E_4$.

The stronger interaction of STAC with $C_{12}E_{23}$ on the hair surface could explain the features seen in the Langmuir-type binding of STAC to hair. As indicated in Table 1, the number of binding sites in saturation is greatly decreased in the presence of $C_{12}E_{23}$. Because of the interaction between STAC and $C_{12}E_{23}$ the binding of STAC to hair could accompany the binding of $C_{12}E_{23}$ to hair as well, which might mean the binding of STAC-$C_{12}E_{23}$ complex to hair. For the binding site of ionic surfactants a hole on the hair surface to be occupied by each surfactant is proposed (Ohbu *et al.* 1986). If the proposed mechanism of the surfactant binding is applicable to the binding in this investigation, the number of the binding sites would then be decreased because the complex would be too large for the site.

The influence of $C_{12}E_{23}$ on the thermodynamic parameters in Table 1 can also be interpreted by the interaction between STAC and $C_{12}E_{23}$. The nonionic surfactant reduced the free energy change, and hence the binding constant. Both the enthalpy change and the entropy change contribute to the free energy change. The nonionic surfactant affected the two thermodynamic parameters in the opposite direction. The enthalpy change became favorable for the STAC binding in the presence of $C_{12}E_{23}$. This might be because $C_{12}E_{23}$ facilitates the binding of STAC to hair on the hair surface through the electrostatic interactions with electronegative oxygen atoms of the polyoxyethylene unit of $C_{12}E_{23}$. The interaction of $C_{12}E_4$ would be weaker as the degree of polymerization of the polyoxyethylene unit is smaller. However,

the favorable electrostatic interaction was overwhelmed by the large entropy change unfavorable for the STAC binding, which might accompany a large conformational change of the surfactant molecules on the binding to the hair surface. Thus the overall effect of $C_{12}E_{23}$ was disadvantageous for the interaction.

Finally, it should be noted that the inner structure of hair remains to be clarified. The change of the structure with the addition of the nonionic surfactant could be related to the influence of the surfactant on the binding of STAC to human hair, and hence the change of thermodynamic parameters.

CONCLUSION

The binding of a cationic surfactant, STAC, to human hair was investigated in the presence of nonionic surfactants, polyoxyethylene lauryl ethers. The nonionic surfactants decreased the STAC binding by decreasing both the number of binding sites in saturation and the binding constant. The effect was larger with a nonionic surfactant of a longer polyoxyethylene chain. It was suggested that the decrease was brought about by the interaction of STAC with the nonionic surfactant in the aqueous phase and on the hair surface.

REFERENCES

Aoki, K., Takagi, T., and Terada, H. (1984) *Serum Albumin* (in Japanese), Kodansha, Tokyo, 91–111

Binder, M. H., and Klose, G. (1998) Compound Complex Formation in Phospholipid Membranes Induced by a Nonionic Surfactant of the Oligo(ethylene oxide)-Alkyl Ether Type: A Comparative DSC and FTIR Study, *J. Colloid Interface Sci.*, **202**, 124–138

Decker, B. V., and Foster, F. (1967) Amphoteric Behavior of Bovine Plasma Albumin and Its Detergent Complexes, *J. Biol. Chem.*, **242**, 1526–1532

Hayano, S. (1964) A Trial to Elucidate the Structure of Griffin's HLB-System, *Yukagaku*, **13**, 220–223

Hiramatsu, K., Ueda, C., Iwata, K., Akihara, K., and Aoki, K. (1977) The Interaction of Bovine Plasma Albumin with Cationic Detergent. Studies by Binding Isotherm, Optical Rotation and Difference Spectrum, *Bull. Chem. Soc. Jpn.*, **50**, 368–372

Jones, M. N., Skinner, H. A., and Tipping, E. (1975) The Interaction between Bovine Serum Albumin and Surfactants, *Biochem. J.*, **147**, 229–234

Kitahara, F., Tamai, Y., Hayano, S., and Hara, I. (1979) *Surfactants* (in Japanese), Kodansha, Tokyo, 24–29

Kobunshi Gakkai (1996) *Polymer Structure (3) Molecular Spectroscopy* (in Japanese), Kyoritsu Shuppan, Tokyo, 380

Influence of Polyoxyethylene Lauryl Ether on the Binding of Stearyltrimethylammonium Chloride to Human Hair

Nakama, Y., and Yamaguchi, M. (1992) Adsorption of Cationic Surfactants to Keratin Powder, *Yukagaku*, **41**, 336-340

Ohbu, K., Tamura, T., Mizushima, N., and Fukuda, M. (1986) Binding Characteristics of Ionic Surfactants with Human Hair, *Colloid Polym. Sci.*, **264**, 798-802

Robbins, C. R. (1994) *Chemical and Physical Behavior of Human Hair*, Springer-Verlag, New York, 153-232

Robbins, C. R., and Blake, M. K. (1984) Analysis of Hairs by Electron Spectroscopy for Chemical Analysis, *J. Soc. Cosmet. Chem.*, **35**, 379-390

Scheonfeldt, N. (1953) Quantitative Determination of Ethylene Oxide Products in Aqueous Solutions or Dispersions, *Nature*, **172**, 820

Sugihara, T., and Morikawa, M. (2000) Binding of Stearyltrimethylammonium Chloride to Human Hair, *Nihon Kasei Gakkaishi (J. Home Econ. Jpn.)*, **51**, 717-724

Sukow, W. W., Sandberg, H. E., Lewis, A. E., Eatough, D. J., and Hansen, L. D. (1980) Binding of the Triton X Series of Nonionic Surfactants to Bovine Serum Albumin, *Biochemistry*, **19**, 912-917

Tanford, C. (1979) *The Hydrophobic Effect*, Wiley-Interscience Publication, New York, 1-50

Tipping, E., Jones, M. N., and Skinner, H. A. (1974) Enthalpy of Interaction between Some Globular Proteins and Sodium *n*-Dodecyl Sulfate in Aqueous Solution, *J. Chem. Soc., Faraday 1*, **70**, 1306-1315

Uno, T., Miyajima, K., and Tsukatani, H. (1960) Determination of Quaternary Ammonium Salts by Sodium Tetraphenylborate, *Yakugaku Zasshi*, **80**, 153-155

Vasanthan, N., Shin, I. D., and Tonelli, A. E. (1996) Structure, Conformation, and Motions of Poly(ethylene oxide) and Poly(ethylene glycol) in Their Urea Inclusion Complexes, *Macromolecules*, **29**, 263-267

Yoshida, T., Shindo, S., Ogaki, T., and Yamanaka, K. (1987) *Handbook of Surfactants* (in Japanese), Kogakutosho Shuppan, Tokyo, 234-240

毛髪への塩化ステアリルトリメチルアンモニウムの結合に対するポリオキシエチレンラウリルエーテルの影響

杉原利治, 水野奈緒子*

(岐阜大学教育学部, * 各務原養護学校)

陽イオン界面活性剤, 塩化ステアリルトリメチルアンモニウムの毛髪への吸着結合に対する非イオン界面活性剤, ポリオキシエチレンラウリルエーテルの影響を研究した. 非イオン界面活性剤は, 陽イオン界面活性剤の結合を阻害し, その効果は, ポリオキシエチレン鎖の長い, 親水性の非イオン界面活性剤で顕著であった. また, 非イオン界面活性剤の毛髪への結合も, 陽イオン界面活性剤によって阻害された. 非イオン界面活性剤は, 陽イオン界面活性剤の結合サイトと結合定数の両方を減少させた. 熱力学研究と FT-IR, XPS による分析から, この阻害効果は, 水中や毛髪表面上における非イオン界面活性剤と陽イオン界面活性剤との相互作用によるものであることが示唆された.

キーワード：毛髪, 塩化ステアリルトリメチルアンモニウム, ポリオキシエチレンラウリルエーテル, 結合等温線, FT-IR, 相互作用.