Effect of Surfactants on Hair Dyeing by Oxidation Dyes and Novel Hair Dyeing by Using Materials of Natural Origin

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1. INTRODUCTION

The hair dyeing using oxidation dye is most frequently employed to dye hair and the population of the people who carry out it increases throughout the world today. The oxidation dye system generally consists of dye precursors oxidized by hydrogen peroxide and dye couplers, which react and give a variety of dyes colouring hair. Surfactants are added to the dyeing system in order to thicken the dye solution for better handling, to help to dissolve dyeing materials and to assist in homogeneous dyeing results. However, the effect of surfactants on the oxidation hair dyeing and its mechanism have not been clarified fully. In the paper, the effect of surfactants on the hair dyeing system and the study of the mechanism are reported.

On the other hand, sensitisation symptoms are in some cases caused by the oxidation hair dyes and some of the components of the dye system are strong allergens. It is very important to invent a novel hair dyeing technique, which is milder and safer for a human body and is environment-friendly, in order to decrease the risks accompanying hair dyeing. Under such the situation, a novel hair dyeing technique by using materials of natural origin and an enzyme was studied. The characteristics and the applicability of the dyeing technique are also reported.

2. EXPERIMENTAL

2. 1. Exp. for Oxidation Dyes and Effect of Surfactants

The oxidation reaction to form hair dyes is started by the mixing of aqueous solution **1**, which contains *p*-aminophenol (PAP, Fig. 1 (a)), 5-amino-*o*-cresol (5AOC, Fig. 1 (b)), ammonia and a surfactant, and solution **2** containing H_2O_2. The anionic surfactants used were sodium hexadecyl sulfate (SHDS). The nonionic surfactant was polyoxyethylene (n=5.5) hexadecyl ether (POE(5.5)HDE). The cationic surfactants were hexadecyltrimethylammonium chloride (HDTAC) and hexadecylpyridinium chloride monohydrate (HDPC). Sample white hair (Matai Japan) was dyed in a dye bath containing the mixture of the solution **1** and **2** under pH=9.91 at 308 K for 2-40 min. The formation of hair dyes in the dye bath was monitored by a spectrophotometer (Hitachi U-2000) from 190-800 nm. The spectroreflectance and colour of dyed hair were measured by a spectrocolourimeter (Konica Minolta CM-2600d) and the resulting colour was expressed in *L*a*b** standard colourimetric system (CIE 1976). The hair dyed by PAP-5AOC system was observed as a non-coated sample by a scanning electron microscope (SEM, Hitachi FE-SEM S-800). For the estimation of the water content of the hair, the amount of water in hair dyed by PAP-5AOC system without or with surfactants at 308 K for 40 min was measured by a halogen moisture analyser (Mettler Toledo HG53).

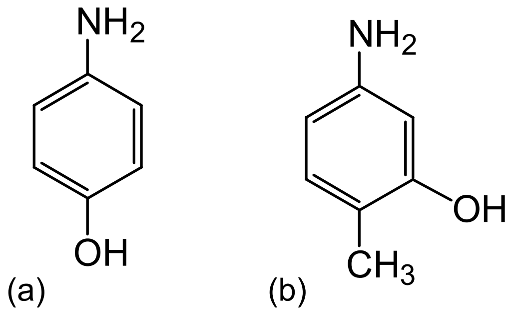

Fig. 1 Chemical structure of
(a) *p*-aminophenol (PAP) and
(b) 5-amino-*o*-cresol (5AOC).

The water content of the hair was calculated by [*Water content*] = ([*Mass of swollen hair*] – [*Mass of dry hair*]) X 100 / [*Mass of dry hair*].

2. 2. Exp. for Novel Hair Dyeing Technique

The oxidation reaction to prepare novel hair dyestuffs is started by adding tyrosinase into Na_2HPO_4-NaH_2PO_4 buffer solution of catechin, or catechin and other natural materials. Sample white hair was dyed in a dye bath containing the above mixture under pH=7 at 303 K for 40min. The spectroreflectance and colour of dyed hair were measured by the spectrocolourimeter. The obtained colour was expressed in *L*a*b** standard colourimetric system. The colourant obtained from catechin was characterised by NMR (Bruker DRX500), MAS (JEOL JMS700) and IR (HORIBA FT-710) measurements. The safety test of the obtained dye was made as acute skin irritation study using three rabbits according to the OECD Guidelines for the testing of chemicals.

3. RESULTS AND DISCUSSION

3. 1. Oxidation Dyes and Effect of Surfactants

The colour of the formed dyes from PAP-5AOC system is orange or reddish brown in acidic solution and in hair. It was revealed by thin-layer chromatography that the dyes consist of four kinds of colour chemicals at least and one of them is majority.

Fig. 2 shows the dependence of the intensity of signal peak (464 nm) in the absorption spectra for the obtained oxidation hair dyes (reaction time: 40 min) in CH_3COOH / CH_3COONa solution (pH=3.7), on the charge of surfactant's hydrophilic part and their concentration.

The results show that the addition of surfactants promotes the formation of the dyes in the dye bath. The promotion by anionic SHDS takes place at lowest concentration and is most effective, while it occurs barely at higher concentration for cationic HDTAC. The critical micelle concentration of SHDS measured by the author is lowest and that of HDTAC is highest. The promotion effect may be concerned with the micelle or aggregate formation of surfactants.

On the other hand, the colour of hair dyed by the PAP-5AOC system with 3.04 X 10^{-2} M of surfactants varies from dark orange to reddish brown according

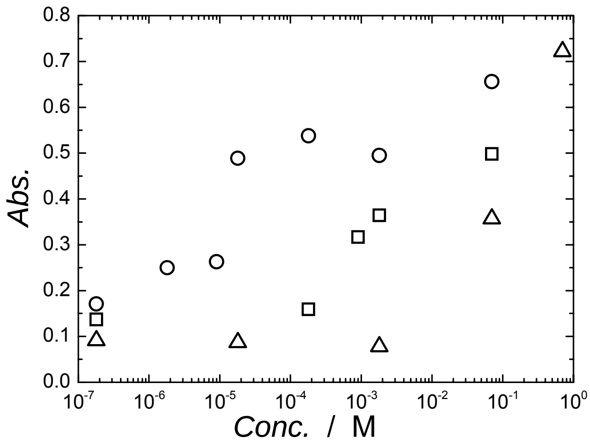

Fig. 2 Dependence of signal peak intensity in absorption spectra for oxidation hair dyes formed in reaction solution, on the concentration of surfactants added to PAP-5AOC system, –: SHDS, □: POE(5.5)HDE, 8: HDTAC. The spectra were measured in CH_3COOH / CH_3COONa solution (pH=3.7).

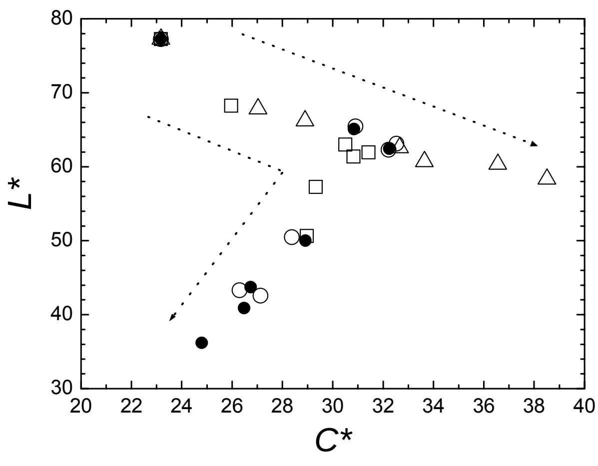

Fig. 3 Time-course of change in colour of hair dyed by PAP-5AOC system expressed in *L*a*b** colourimetry system, ●: without surfactant, –: with 3.04X10^{-2}M SHDS, □: with 3.04X10^{-2}M POE(5.5)HDE, 8: with 3.04X10^{-2}M HDTAC. *L** is the lightness and *C** the chroma.

to the reaction time and the type of surfactants added. The hair dyed with HDTAC shows most vivid. Fig. 3 shows the time-course (0, 2, 5, 10, 15, 25 and 40 min following the arrows) of the change in colour of hair dyed by the system. The colour is expressed in the lightness (L^*) - chroma (C^*) colour system. The results show the chroma of hair dyed without surfactants, with anionic SHDS or nonionic POE(5.5)HDE increases and decreases with dyeing time and its lightness decreases, whereas the chroma of hair dyed with cationic HDTAC increases monotonously with dyeing time and its lightness decreases gradually. It can be said from the results that the only the cationic surfactant changes the colour of hair dyed by oxidation dye in the colouring process. From the fact that while the concentration of dyes formed in the reaction solution for non-surfactant and cationic surfactant system is low and that for anionic surfactant system is highest, only the cationic surfactant is remarkable for the effect on change in colour of dyed hair and anionic and nonionic surfactants don't give effect, such the colouring effect is thought not to be caused by the action of surfactants to the oxidation reaction but to be caused by the interaction between the surfactant and hair.

Fig. 4 shows the SEM photographs of hair dyed without surfactants and with HDTAC. The surface of hair dyed without surfactants is smooth. The same results were obtained in the case of the hair dyed with SHDS and POE(5.5)HDE. In contrast, the surface of hair dyed with HDTAC shows rough. The cationic HDPC gives the same results as HDTAC. This indicates that the hair shrunk by the cationic surfactant during dyeing. In fact it was revealed by the measurements of the water content in hair as shown in Fig. 5. The water content of the hair dyed with HDPC as the cationic surfactant instead of HDTAC is shown in Fig. 5.

Moreover, it was also found that cationic surfactants ab/adsorb in/onto hair remarkably whereas anionic surfactants ab/adsorb in/onto hair a little. Therefore, the surface of hair should be covered with cationic surfactants and/or the hair network should shrink. These restrain the diffusion of PAP, 5AOC or oxidants into/in hair network. Then the amount of dyes formed in hair decreases by cationic surfactants and the distribution of the dyes in hair may also be different from that of the dyes in hair dyed without surfactants, with anionic surfactants or with nonionic surfactants.

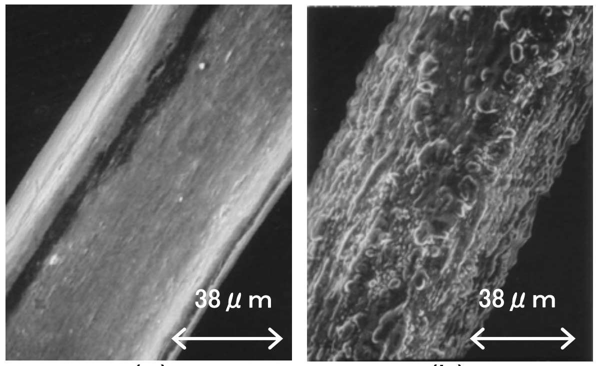

Fig. 4 SEM photographs of hair dyed by PAP-5AOC system, (a) without surfactants and (b) with HDTAC.

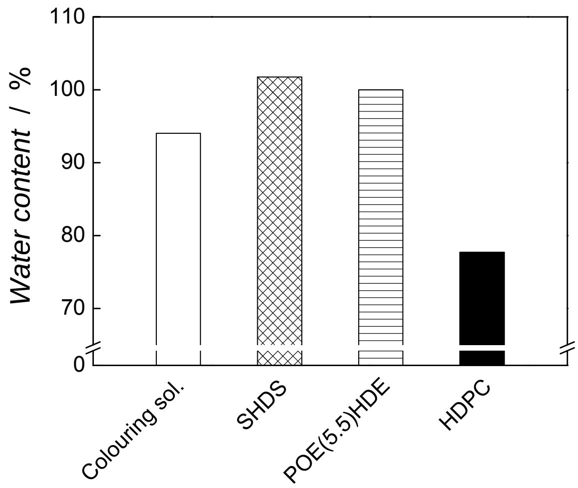

Fig. 5 Water content (≡ ([Mass of swollen hair] – [Mass of dry hair]) X 100 / [Mass of dry hair]) for hair dyed by PAP-5AOC system, □ : without surfactant, ⊠ : with $3.04X10^{-2}$M SHDS, ▤ : with $3.04X10^{-2}$M POE(5.5)HDE, ■ : with $3.04X10^{-2}$M HDPC.

3. 2. Novel Hair Dyeing Technique

The colour of the formed colourant in dyeing solution from the catechin - tyrosinase system is orange. The colourant works as a dye and can dye hair orange and reddish orange as shown in Fig. 6 (printed in a B/W photograph in the paper).

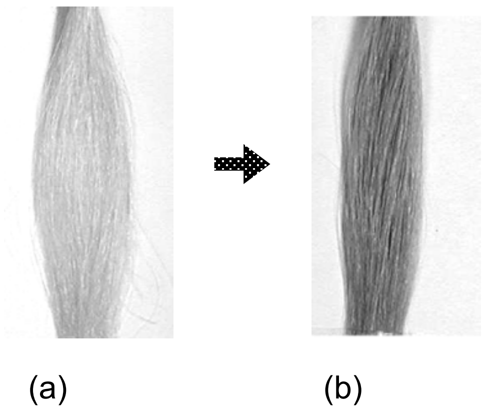

Fig. 6 Change in colour of hair dyed by catechin - tyrosinase system, (a) initial hair and (b) dyed hair (reddish orange).

The resulting change in colour of hair, which is expressed in *L*a*b** standard colourimetric system, is from L^*: 78, a^*: 4.4, b^*: 21, C^*: 21 (initial hair) to L^*: 61, a^*: 15, b^*: 58, C^*: 60 (dyed hair). On the other hand, although catechin reacts with H_2O_2 to give deep dark red colourant, hair is not dyed by the coloured solution. The results show that the enzymatic treatment of catechin is applicable to obtain the hair dyestuff.

It was revealed by thin-layer chromatography that the dye mainly consists of one kind of pigment molecule. The pigment molecule obtained is reddish powder and soluble in water and ethanol. The chemical structure of the pigment was determined as shown in Fig. 7 by NMR, MAS and IR measurements. The characterised pigment, 4-(3, 4-dihydro-3α, 5, 7-trihydroxy- 2H-1- benzopyran-2α-yl) 1, 2-benzoquinone), was named catechinone by the author. It was also found that white hair is dyed orange in the neutral catechinone aqueous solution prepared from its powder.

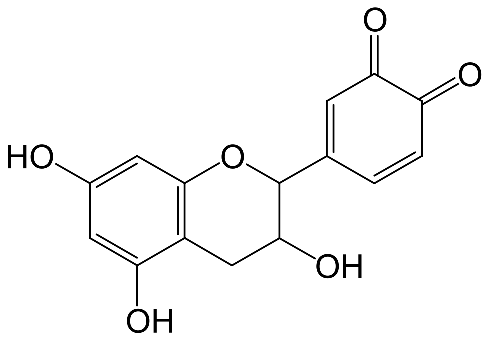

Fig. 7 Chemical structure of catechinone (4-(3,4-dihydro-3α, 5, 7-trihydroxy-2H-1-benzopyran-2α-yl) 1, 2-benzoquinone).

The results of the acute skin irritation test for catechinone according to the OECD Guidelines are shown in Table 1. No reactions on skin such as erythema or oedema are found as seen from Table 1. It can be said that catechinone obtained from catechin does not cause terrible acute skin irritation.

Table 1 Results of the acute skin irritation test for catechinone according to the OECD Guidelines.

Animal No.	Reactions	Results			
		Time after patch removal / h			
		1	24	48	72
1	Erythema	-	-	-	-
	Oedema	-	-	-	-
	Other findings	-	-	-	-
2	Erythema	-	-	-	-
	Oedema	-	-	-	-
	Other findings	-	-	-	-
3	Erythema	-	-	-	-
	Oedema	-	-	-	-
	Other findings	-	-	-	-

The control of the colour of dyed hair is important and it was attempted by using materials of natural origin as colour-control additives. Hair was dyed with catechin and the natural materials treated by tyrosinase. As a result, a variety of colours of hair are obtained as light brown for cysteine, yellowish brown for tyrosine, dark brown for L-dopa, yellow for naringenin and lac, light orange for tamarind, deep orange for hematoxylin, reddish orange for kaoliang, yellowish green for gardenia blue, and reddish violet for red cabbage used with catechin. When hair is dyed only with the additive, the resulting colour is different from that of hair dyed with catechin and the additive. The results of the measurement of the colour for dyed hair, which are expressed in chromaticity (a^* - b^*), are shown in Fig. 8. The a^* and b^* values are widely distributed in the figure. The colour of hair dyed by the technique can be controlled by using materials of natural origin.

The colour fastness of hair dyed by catechinone or catechinone + red cabbage to washing was examined. Almost no change in colour of the dyed hair is observed by the naked eye after 30 times of washing with a surfactant. Fig. 9 shows the change in colour of dyed hair, which is expressed as L^*, a^* and b^*, as a function of number of washing. The change in colour of hair dyed by PAP+5AOC is also shown in Fig. 9 as a reference. Only a little change in L^*, a^* and b^* is found for the hair dyed by catechinone or catechinone + red cabbage as same as the hair dyed by the general oxidation hair dye. The results show that the hair coloured by the dyestuff of natural origin has enough colour fastness to washing. It was also found that the hair coloured by the same dyestuff has enough colour fastness to fluorescent light.

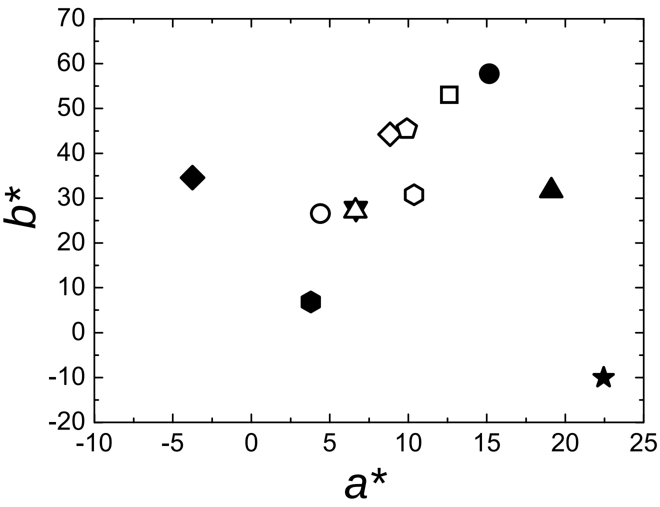

Fig. 8 Chromaticity (a^* - b^*) of hair dyed with catechin and materials of natural origin treated by tyrosinase. ○: initial, ●: catechin only, ▼: with cysteine, □: with tyrosine, ⬢ : with L-dopa, ◇: with naringenin, ⬠ : with lac, ⬡ : with tamarind, △: with hematoxylin, ▲: with kaoliang, ◆: with gardenia blue, ★: with red cabbage.

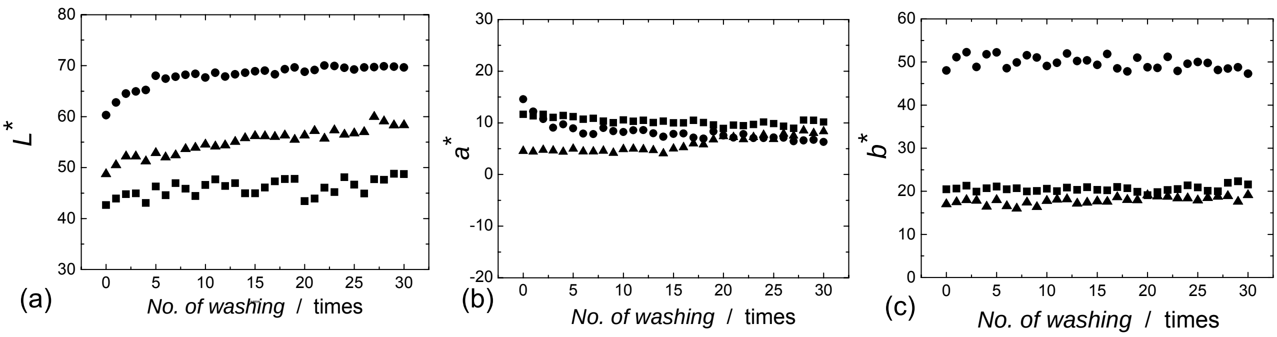

Fig. 9 Change in colour of hair dyed by catechinone (●), catechinone + red cabbage (▲) and PAP+5AOC (■) as a function of number of washing, (a): L^*, (b): a^* and (c): b^*.

4. REFERENCES

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