**Desalination and Water Treatment**
www.deswater.com

17 (2010) 127–134
May

doi: 10.5004/dwt.2010.1708

# Introduction of various quaternary ammonium salts as cationic binding sites in partially-hydrolyzed poly(ethylene-co-vinyl acetate) films

Y. Hirata*, T. Kawasumi, K. Hamada

*Division of Chemistry and Materials, Applied Chemistry Course, Shinshu University, Tokida, Ueda-shi. Nagano 386-8567, Japan*
*Tel. +81268215409; Fax +81268215391; email: yhirata@shinshu-u.ac.jp*

Received 1 August 2009; accepted 20 November 2009

## ABSTRACT

Various quaternary ammonium salts as cationic binding sites were introduced to pseudo-bilayer membranes based on partially hydrolyzed poly(ethylene-co-vinyl acetate) (EVA). Three types of quaternary ammonium salts such as bolaform electrolytes, gemini surfactants, and conventional surfactants were used in this study. Gemini surfactants were uptaken more in the membranes than bolaform electrolytes because of the amphiphilicity. The surfactants were dispersed and acted as a binding site for anionic dye in the hydrolyzed membrane under the optimal conditions.

*Keywords:* Poly(ethylene-co-vinyl acetate); Pseudo-bilayer membrane; Bolaform electrolyte; Gemini surfactant; Acid dye; Ionic complexes

## 1. Introduction

Asymmetric structures of polymeric membranes are very important to add some different properties at the same time. We have already reported that the permselectivity ($H_2O/O_2$) of membranes based on EVA containing 70 wt.% of vinyl acetate groups is improved by treating one side of the membrane with solutions of sodium hydroxide dissolved in a mixture of water and methanol [1]. Such a membrane consists of three comonomer units, ethylene, vinyl acetate, and vinyl alcohol, and can be called poly(ethylene-co-vinyl acetate-co-vinyl alcohol). The chemical structure of the modified polymer is shown in Fig. 1. The ratio of the component monomers in the materials can be controlled by the reaction conditions. We consider this type of membrane as a binary A–B laminate system whose layer A is the partially hydrolyzed EVA component, characterized by a gradient of vinyl alcohol and vinyl acetate units throughout its thickness. Layer B is the EVA component (non-modified). In such a structure, one membrane surface is hydrophilic while the other is hydrophobic. There is a gradual variation in the polar natures from the hydrophilic to the hydrophobic side. Consequently, sandwiching the pseudo-bilayer membranes between hydrophilic and hydrophobic films may improve the adhesive properties of the multilayer system. However, both the hydrophilic and hydrophobic layers have no specific affinity with any functional low molecules.

In this study, the pseudo-bilayer membranes were modified by sorption of three types of quaternary ammonium salts as cationic binding sites in order to multifunctionalize the membranes. The chemical structures of quaternary ammonium salts used in this study are shown in Fig. 2 which are classified as conventional surfactant having one charged group, gemini surfactant having two charged groups, and bolaform electrolyte which also has two charged group but do not show surface activity. In the field of disinfection, quaternary ammonium surfactants are well-known

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*Corresponding author

*Presented at the Fifth Conference of the Aseanian Membrane Society Aseania 2009 "Recent Progress in Membrane Science and Technology", 12–14 July 2009, Kobe, Japan.*

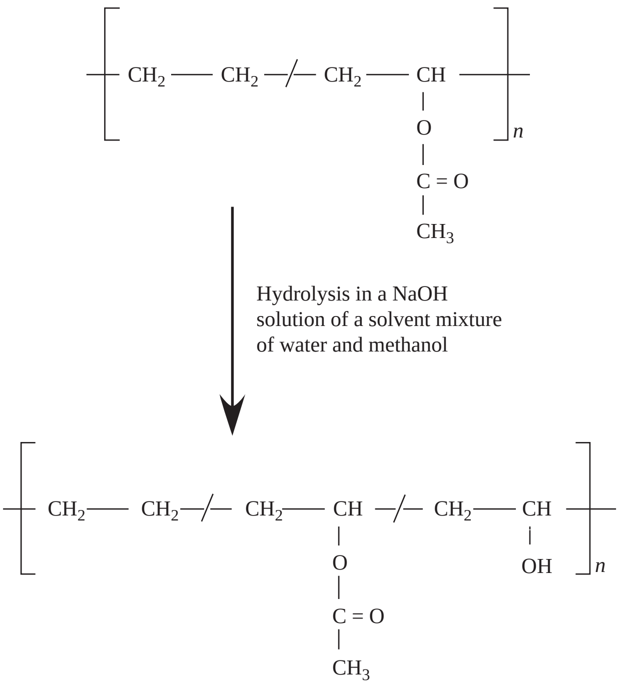

Fig. 1. Partially hydrolysis of PVA.

effective antimicrobial agents and are used in a number of domains such as cosmetics, common antiseptics, sanitizers in hospitals and disinfectants for contact lenses [2].

Not only the binding sites but also functionalization such as antimicrobial property is expected by introduction of quaternary ammonium surfactants into the membranes. The binding capability with anionic molecules was studied about the dyeability of the modified membranes with an acid dye (dye 1). The structure of the acid dye is shown in Fig. 3.

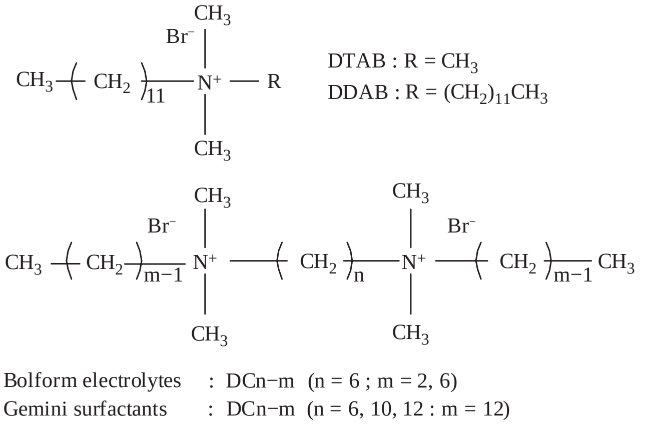

Fig. 2. Chemical structures of quaternary ammonium salts used in this study.

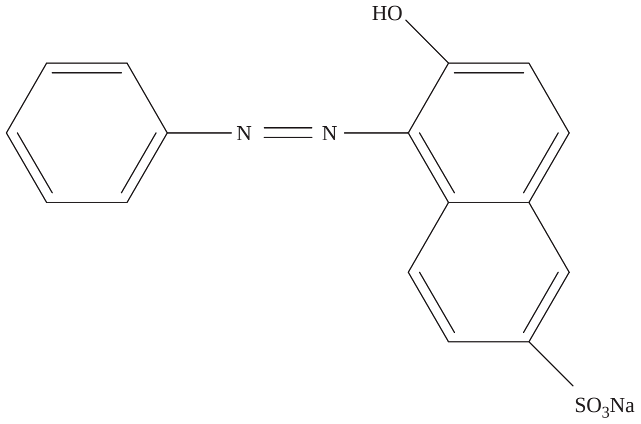

Fig. 3. Chemical structure of dye 1 used in this study.

## 2. Experimental section

### 2.1. Materials

The bis(quaternary ammonium) salts were synthesized by using one of the two following methods [3–7].

*Method a: Reaction of the α,ω-dibromoalkanes with N,N,N-alkyldimethylamine*. The bolaform electrolyte, *N,N′*-bis(ethyldimethyl)-1,6-hexanediammonium dibromide (DC6-2), was prepared as follows. A mixture of 1,6-dibromohexane and *N,N′*-dimethyl-*N*-ethylamine in nitromethane was stirred at room temperature for 6 d. The product was then filtered, purified by repeated precipitation from methanol into acetone and dried at 80°C. For two gemini surfactants such as DC10-12 and DC12-12, A mixed solution of *N,N′*-dimethyldodecylamine and the corresponding 1,*ω*-dibromoalkane [1,10-dibromodecane for DC10-12 and 1,12-dibromododecane for DC12-12] in dry ethanol was stirred at 80°C for 2 d. The products were then filtered, purified by repeated precipitation from acetone into ethyl acetate and dried at 80°C.

*Method b: Reaction of alkandiyl-α,ω- bis(dimethylamine) with 1-bromoalkane*. The bolaform electrolyte such as DC6-6 and the gemini surfactant such as DC6-12 were prepared as follows. A mixture of *N,N,N′,N′*-tetramethyl-1,6-diaminohexane and the corresponding 1-bromoalkane [*n*-hexylbromide for DC6-6 and *n*-dodecylbromide for DC6-12] in nitroethane was stirred at room temperature for 4 d. The products were then filtered, purified by repeated precipitation from ethanol into diethyl ether and dried at 80°C.

The conventional surfactants, dodecyltrimethylammonium bromide (DTAB) and didodecyldimethylammonium bromide (DDAB) were purchased from Tokyo Kasei Kogyo Co. (Tokyo, Japan) and were used without purification.

An acid dye, sodium 1-phenylazo-2-hydroxy-6-naphthalenesulphonate (dye 1), was synthesized by coupling diazotized aniline with Schaeffer's acid (2-naphthol-6-sulphonic acid) in alkaline conditions. The dye thus obtained was purified by repeated salting-out with NaCl and recrystallization from 80% aqueous ethanol solution.

### 2.2. Partially hydrolyzed membrane preparation

Dense membranes of EVA containing 70 wt.% of vinyl acetate were prepared by casting from dichloroethane (20 wt.%) solutions onto a polyethylene sheet. The EVA membrane obtained was dried for 12 h at atmospheric pressure and room temperature. The EVA film supported with the polyethylene sheet was immersed a NaOH solution containing 75 vol.% of methanol and 25 vol.% of water for hydrolysis. The EVA membrane was hydrolyzed for a determined reaction time. The reaction was terminated by adding a 2.4 M HCl solution. After 60 min, the HCl solution was removed, and then the membrane was soaked in water to remove HCl until the water become neutral. Finally, the membrane was exposed to ambient air for 24 h, and then dried with $P_2O_5$ in desiccators at room temperature under vacuum for 24 h. The membrane thickness was approximately 100 μm.

### 2.3. IR spectroscopy

The IR spectra were obtained by using ATR method (Attenuated total reflection), and by collecting and averaging 32 scans, at a resolution of 4 $cm^{-1}$.

### 2.4. Sorption of quaternary ammonium salts in membranes

Various quaternary ammonium salts were sorbed by soaking the hydrolyzed membrane in pure water and 75 vol.% methanol aqueous solution for 24 h at 25°C. The membrane was dried with $P_2O_5$ and stored in desiccators.

### 2.5. Dyeing with acid dye

The hydrolyzed membranes treated and non-treated in quaternary ammonium salt solution were dyed in a dye solution for 24 h at 25°C. At the end of dyeing, the dyed membranes were removed from the dye bath, rinsed thoroughly in pure water, and dried with $P_2O_5$ in desiccators.

The amount of dye sorbed in the non-treated membrane was determined as follows. The dyed membrane was dissolved in 90 wt.% aqueous pyridine solution and its concentration was determined using JASCO V-530 UV-VIS spectrophotometer.

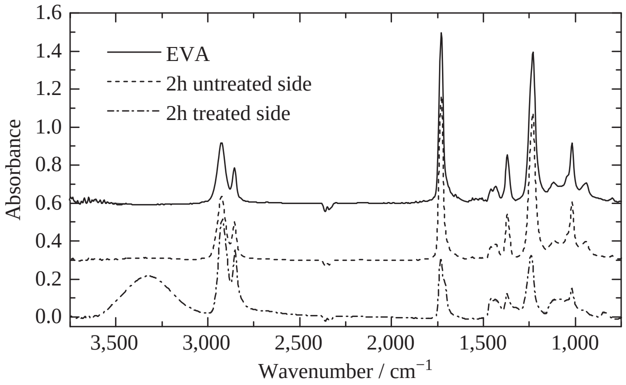

Fig. 4. ATR-mode FT-IR spectra of EVA membrane and both sides of the partially hydrolyzed membrane hydrolyzed for 2 h.

In the case of the membrane treated in quaternary ammonium salt solution, since the 90% aqueous pyridine solution was not enough transparent for the UV-visible spectrometry, sorption of dye 1 in the films was characterized as a degree of transmission by the films of light at the wavelength 360–780 nm, which was measured using the spectrophotometer Konica Minolta CM-3600d. The instrument was first calibrated with a black and white standard and then the whole visible spectrum of the film was recorded at a wavelength interval of 10 nm. Color data were calculated using illuminant D65 (daylight 6,500 K), 10 standard observer. The CIE color parameters used were $L^*$ (Lightness: $L^* = 100$ for white and 0 for black), $a^*$ (redness/greenness axis: positive $a^*$ is red and negative $a^*$ is green), $b^*$ (yellowness/blueness axis: positive $b^*$ is yellow and negative $b^*$ is blue). Total color difference ($\triangle E_{ab}{}^*$) with respect to the amount of dye 1 sorbed in the membranes was determined as given by the following equation:

$$\Delta E_{ab}* = \sqrt{(\Delta a^*)^2 + (\Delta b^*)^2 + (\Delta L^*)^2} \qquad (1)$$

All the tests were performed in triplicate.

## 3. Results and discussion

### 3.1. Preparation of partially hydrolyzed membranes

The ATR spectrum reflects the average surface structure of the materials in limited depth (1–4 μm). The ATR method permits the comparison between the treated and the untreated surface structures of the membranes. The IR spectra of surface of the EVA membranes before and after hydrolysis are shown in Fig. 4. In the EVA membranes, the 1,731 $cm^{-1}$ band was attributed to the carbonyl group due to the vinyl

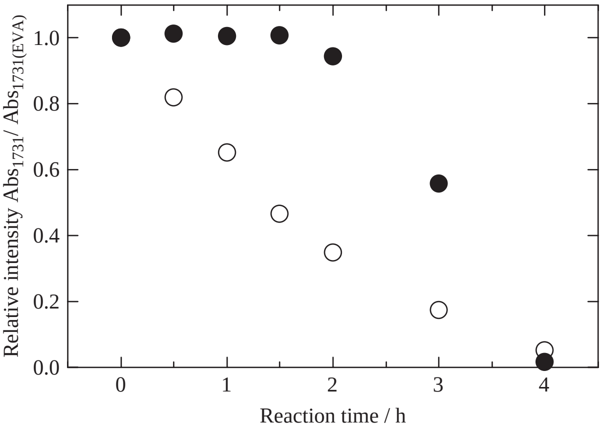

Fig. 5. Hydrolysis degree of surface vs. reaction time from ATR-mode FT-IR spectra; ○ hydrolyzed and ● non-treated surfaces.

acetate structure. In the case of a partially hydrolyzed membrane treated for 2 h, the peak intensity of the carbonyl peak for its treated side was smaller than that of its untreated side. The 3,300 cm$^{-1}$ band referred to the hydroxyl group was appeared at the treated side of the partially hydrolyzed membrane, which is produced by hydrolysis of the ester bond of vinyl acetate unit.

Fig. 5. shows the hydrolysis degree of the hydrolyzed and untreated surface layers of the membranes. The relative intensities of carbonyl group normalized with the peak intensity of the carbonyl group of the EVA membrane, $Abs_{1731}/Abs_{1731}(EVA)$ are plotted. It can be observed that for the treated surfaces of the membranes, the relative intensity decreases as the reaction time increases while, for the untreated surfaces, the relative intensity is not changed up to 1.5 h of the reaction time, after which, it decreases. In the case of the hydrolysis time more than 1.5 h, the untreated side of membranes was also partially hydrolyzed and the membranes had a gradient of hydrolysis degree in all thickness. In the case of the membranes of 3 h or more of the hydrolysis time, the membrane was separated from the polyethylene sheet of a support medium after a hydrolysis treatment. When the hydrolysis time was 2 h, the hydrolysis reaction had reached to the untreated side of the membrane but the membrane surface was maintaining the adhesive property of the EVA membrane. Therefore, the effect of quaternary ammonium salts on the dyeability with the acid dye was examined for the membrane hydrolyzed for 2 h.

### 3.2. *Influence of hydrolysis time on dyeability of partially hydrolyzed membranes*

In color measurement with spectrophotometer, the color difference ($\triangle E_{ab}^*$) calculated from the CIE $L^*a^*b^*$ values of the dyed membranes using Eq. (1) may reflect the concentration of the dye molecule in the membrane. An increase of dye uptake in a membrane would increase a color difference relatively. In this study, the partially hydrolyzed membranes after dyeing became more or less an orange transparently while the EVA membrane was still clear and colorless. Fig. 6 shows the color difference of the hydrolyzed film with the different hydrolysis time. The increase in the value of $\triangle E_{ab}^*$ shows that the orange of the membranes becomes deeper. The hydrophilic layer in the membranes becomes thicker with increasing the reaction time of hydrolysis as mentioned above, which absorbs the water molecules and is swollen in the dye bath during the dyeing process. The cross section of the partially hydrolyzed membrane was observed by optical microscope to study the depth profile of the dyed layers. It confirmed that the layers dyed by dye 1 extended from the treated side toward the center of membrane. Consequently, the dye molecules could penetrate into the hydrophilic layer in the case of the partially hydrolyzed membranes since the acid dye such as Dye 1 is hydrophilic and hydrated in water. On the other hand, the dye molecules were not able to diffuse into the EVA membrane, which is hydrophobic material and is not swollen in water. It is suggested that the sorption of dye in the EVA membrane was improved by hydrolysis.

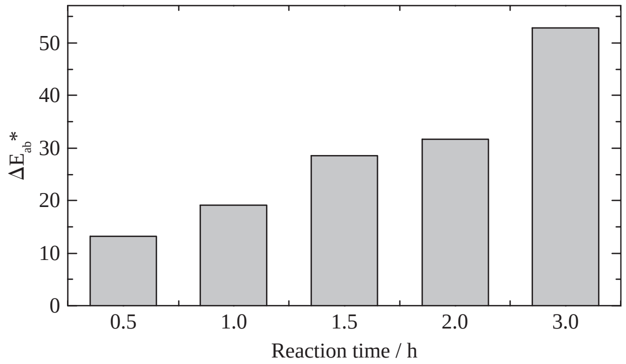

Fig. 6. Influence of hydrolysis time on color difference of partially hydrolyzed membranes dyed in 5.0 × 10$^{-3}$ mol dm$^{-3}$.

A series of the hydrolyzed membranes were soluble to the 90% pyridine aqueous solution and their solutions were transparent enough to the UV-visible spectroscopic measurement. When the membrane was dissolved into the 90% pyridine aqueous solution, the amount of dye 1 sorbed in the membrane ($C_{polym.}$: mol g$^{-1}$) can be calculated by the dye concentration in the solution. We checked the relationship between $\triangle E_{ab}^*$ and the sorption of dye 1 in the partially hydrolyzed membranes as shown in Fig. 7. The linearity was

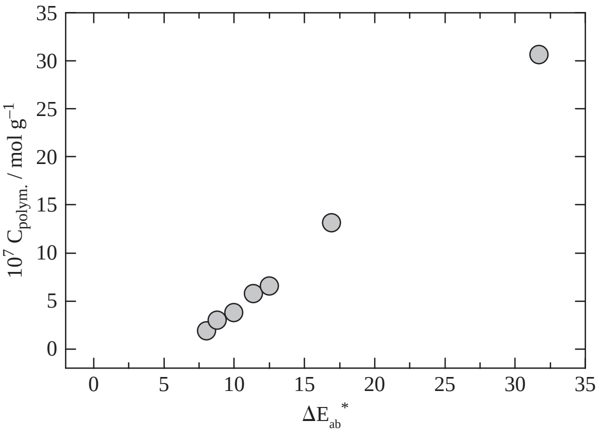

Fig. 7. Relationship between color difference ($\triangle E_{ab}^*$) and the amount of Dye 1 in partially hydrolyzed membranes dyed in $5.0 \times 10^{-3}$ mol $dm^{-3}$ of Dye 1 solution for 24 h at 25°C.

observed by the correlation of $\triangle E_{ab}^*$ and $C_{polym}$. It is indicated that the dyeing behavior of the membranes used in this study can be described by using colorimetry. Therefore, the dyeability of the membranes treated in the quaternary ammonium salt aqueous solutions is discussed using the color difference ($\triangle E_{ab}^*$) instead of the concentration of dye 1 in the membrane in next section because of the problem of the membrane solubility as mentioned in the experiment section.

### 3.3. *Effect of DC6-12 surfactant on dyeability of the hydrolyzed membrane*

Prior to dyeing, the EVA membrane hydrolyzed for 2 h was soaked in $4.0 \times 10^{-4}$ mol $dm^{-3}$ of DC6-12 surfactant solution to introduce the surfactant into the membrane. Isotherms of the color difference ($\triangle E_{ab}^*$) of dye 1 by the partially hydrolyzed membrane were compared with the membrane sorbing the DC6-12 surfactant in Fig. 8. In the presence of the DC6-12 surfactant, the value of $\triangle E_{ab}^*$ increased rapidly in a low-concentration region and then approached a constant value in the high dye concentration region. The isotherms showed like a bimodal sorption including the partition- and Langmurir-type sorption. On the other hand, in the absence of the DC6-12 surfactant, the isotherms of $\triangle E_{ab}^*$ became linear defined as the partition-type sorption.

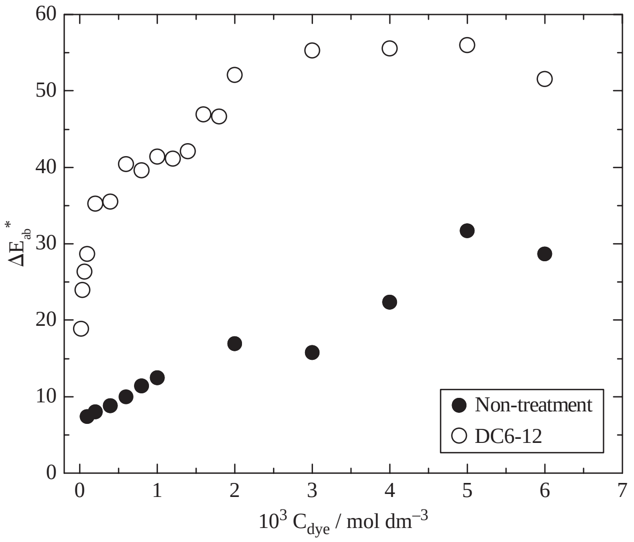

Fig. 8. Isotherms of color difference of dye 1 by partially hydrolyzed membrane at 25°C in the absence and presence of DC6-12 gemini surfactant.

The Langmuir type sorption may be associated with the presence of the DC6-12 surfactant in the membrane. It is reported that anionic dyes and cationic quaternary ammonium salts can form ion complexes by electrostatic interaction [8]. In the case of silk fiber, cationic quaternary ammonium salts already sorbed by the fiber might itself enhance the uptake of dye [5]. In order to confirm the strong interaction of dye 1 and DC6-12 surfactant, the membranes after dyeing in $5.0 \times 10^{-3}$ mol $dm^{-3}$ of dye 1 solution were washed by soxhlet extractor with pure water. In the case of the membrane soaking in the DC6-12 surfactant solution, the value of $\triangle E_{ab}^*$ was slightly changed from 56 to 41 before and after extraction while the value of $\triangle E_{ab}^*$ in the non-treated membrane was greatly decreased from 32 to 9 before and after extraction. It means that the DC6-12 surfactant sorbed in the membrane is operated as a binding site for dye 1, and the ion complexes (DC6-12 surfactant / dye 1) is an insoluble and was fixed by the membrane.

As shown in Fig. 9, the dyeability of the partially hydrolyzed membrane was dependent on the DC6-12 surfactant concentration. The value of $\triangle E_{ab}^*$ increased with the increase in a surfactant

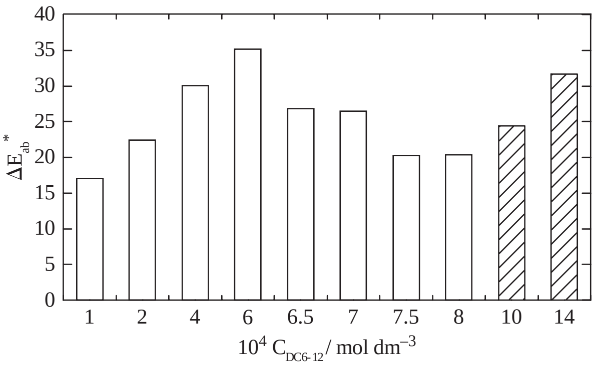

Fig. 9. Concentration dependence of DC6-12 solution on dyeability of partially hydrolyzed membranes.

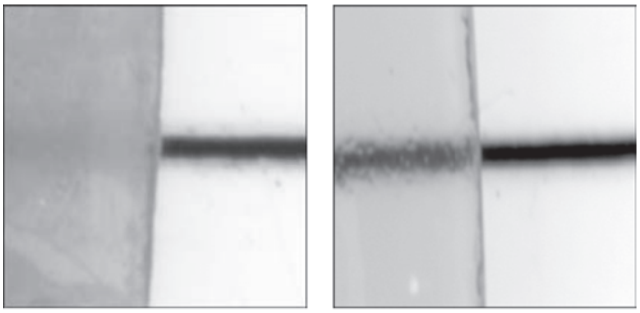
(a) $C_{DC6\text{-}12} = 4.0 \times 10^{-3}$ mol dm$^{-3}$ (b) $C_{DC6\text{-}12} = 4.0 \times 10^{-4}$ mol dm$^{-3}$

Fig. 10. Photo images of dyed membranes soaked in the surfactant solutions below and above the critical micelle concentration. (a) opaque membrane, (b) transparent membrane. (a) $C_{DC6\text{-}12} = 4.0 \times 10^{-3}$ mol dm$^{-3}$ (b) $C_{DC6\text{-}12} = 4.0 \times 10^{-4}$ mol dm$^{-3}$.

concentration, and the concentration showed the maximum by $6.0 \times 10^{-4}$ mol dm$^{-3}$ and changed it to the increase again from the concentration $1.0 \times 10^{-3}$ mol dm$^{-3}$. The concentration range of the surfactant solution used for this study includes the critical micelle concentration ($1.1 \times 10^{-3}$ mol dm$^{-3}$) evaluated from the electroconductivity of the surfactant solution with different concentrations. The decrease of the dyeability of the hydrolyzed membrane is associated with the premicellar region. Penetrate of the surfactant molecules to the membrane might be obstructed by a premicellar association of monomeric surfactant ions. Since the dyed membrane became opaque, the value of $\triangle E_{ab}{}^{*}$ increased above the critical micelle concentration. The photo images of the dyed membranes soaked in the surfactant solutions below and above the critical micelle concentration are shown in Fig. 10. In the case of the membranes soaked in the surfactant solution above the critical micelle concentration, orange particles were observed on the surface of the membranes. When the surface of the membrane was rubbed, orange particles fell. It seems that the anionic dye/cationic surfactant ion complexes precipitated on the surface of the membrane. To uniformly distribute the ion complexes inside the membrane, the concentration of the surfactant solution is limited below the premicellar region when surfactant is dissolved in water without co-solvent such as lower alcohols.

### *3.4. Effect of co-solvent on dyeability of hydrolyzed membrane*

Fig. 11 shows the concentration dependence of the DC6-12 surfactant on the dyeability of the membrane using a mixture of water and methanol as a solvent. Methanol was added into the surfactant aqueous solution to control the formation of surfactant micelle. The concentration of methanol in the methanol aqueous solution was 75 vol%. The value of $\triangle E_{ab}{}^{*}$ continuously increased in the concentration range beyond the critical micelle concentration of the surfactant in water, without producing particles of the ionic complexes, maintaining transparency of the dyed membrane. When the hydrolyzed membrane was immersed in the methanol aqueous solution with concentration of the surfactant four times larger than the critical micelle concentration of the surfactant in water, the value of $\triangle E_{ab}{}^{*}$ was higher than the best value of the membrane soaked using water as a solvent.

### *3.5. Effect of various quaternary ammonium salts on dyeability of the hydrolyzed membrane*

Fig. 12 shows the Influence of chemical structure of various quaternary ammonium salts on the color difference of the membrane. The concentration of the quaternary ammonium salts in the methanol aqueous solution was $8.0 \times 10^{-3}$ mol dm$^{-3}$ except for DC12-12, DDAB, and DTAB. With respect to DC12-12 and DDAB, even if the solvent mixture was used, the membrane immersed in $8.0 \times 10^{-3}$ mol dm$^{-3}$ of the surfactant solution became opaque after dyeing. The surfactant concentration for the two quaternary ammonium salts was used $8.0 \times 10^{-4}$ mol dm$^{-3}$. Since the number of the charged group of DTAB was a half of gemini surfactant having two charged groups, The concentration of the DTAB solution was two times larger than that of the gemini surfactant solution to

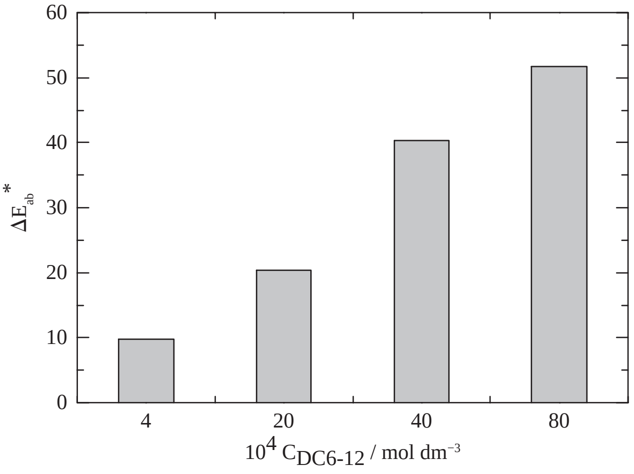

Fig. 11. Effect of 75 vol% MeOH aqueous solution of DC6-12 surfactant on the dyeability of the partially hydrolyzed EVA films.

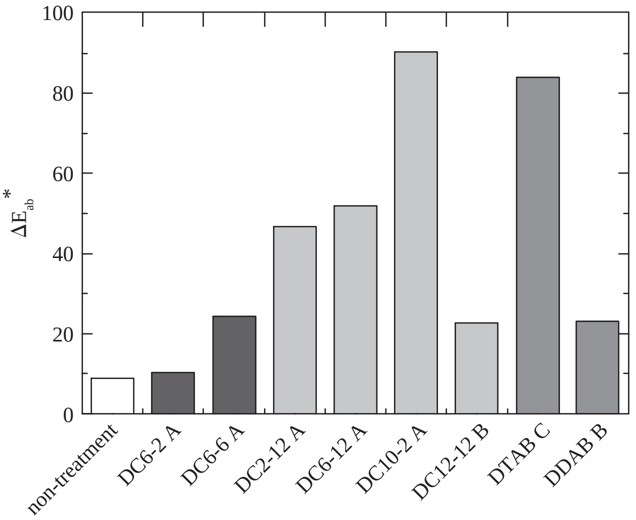

Fig. 12. Influence of chemical structure of various quaternary ammonium salts on color difference. ''A'' is $8.0\times10^{-3}$ mol dm$^{-3}$, ''B'' is $8.0 \times 10^{-4}$ mol dm$^{-3}$, ''C'' is $1.6 \times 10^{-2}$ mol dm$^{-3}$.

maintain the same concentration of charged groups which is $1.6 \times 10^{-2}$ mol dm$^{-3}$.

The treatment of all the quaternary ammonium salt solution improved more or less the dyeability of the hydrolyzed membrane. The quaternary ammonium salts used in this study are classified at least as three types such as conventional surfactant having one charged group, gemini surfactant having two charged groups, and bolaform electrolyte which also has two charged group but don't show surface activity. The characteristics of three type of quaternary ammonium salt affected the dyeability of the hydrolyzed membrane.

The effect of the bolaform electrolytes such as DC6-2 and DC6-6 to the dyeability of the hydrolyzed membrane was the lowest in these three types of quaternary ammonium salts, which may be related with the bolaform electrolyte not showing surface activity. Between the solvent phase and the membrane phase, the electrolytes are distributed more to the phase having strong affinity. It suggests that the affinity of two types of surfactants have stronger interaction with the hydrophobic domain in the hydrolyzed membrane such as ethylene unit compared to the bolaform electrolytes because of the hydrophobic long alkyl chain of the tail group in the surfactant.

The dyeability of the hydrolyzed membrane depended on the length of alkyl spacer in gemini surfactants. The hydrophilic and hydrophobic balance of gemini surfactants modulates the solution properties such as surface activity, critical micelle concentration, solubilization of organic compounds [3,6,9]. We considered that the DC10-12 surfactant was more effective for the dyeability of the hydrolyzed membrane than the DC6-12 because the alkyl spacer of the former was longer and more hydrophobic than the latter. Moreover, the dyeability of the hydrolyzed membrane immersed in the DC10-12 solution was comparable to that of the DTAB as a conventional surfactant though the concentration of the DC10-12 solution was a half of that of the DTAB solution.

## 4. Conclusions

The dyeability of the pseudo-bilayer membranes based on partially hydrolyzed EVA with the different time of hydrolysis was higher as a hydrophilic layer was thicker. The fastness to water washing was enhanced immersing the hydrolyzed membrane in the quaternary ammonium electrolytes. Various quaternary ammonium salts as cationic binding sites were introduced to the hydrolyzed membrane. The acid dye/cationic quaternary ammonium salt complexes could be dispersed in the hydrophilic layer of the hydrolyzed membrane. Water–methanol mixture was more effective as a pretreatment solvent at high surfactant concentration than pure water. Gemini surfactants were uptaken more in the membranes than bolaform electrolytes because of the amphiphilicity and were effectively bound acid dyes. Moreover, the dyeability of the hydrolyzed membrane immersed in the DC10-12 solution was comparable to that of the DTAB as a conventional surfactant though the concentration of the DC10-12 solution was a half of that of the DTAB solution.

## Acknowledgement

This work was supported by Grant-in-Aid for Global COE Program by the Ministry of Education, Culture, Sport, Science, and Technology.

## Symbols

| | |
|---|---|
| $C_{\mathrm{poym.}}$ | Amount of Dye 1 in the membrane, mol g$^{-1}$ |
| $C_{\mathrm{dye}}$ | Concentration of Dye 1 in the dye bath, mol dm$^{-3}$ |
| $C_{\mathrm{DC6\text{-}12}}$ | Concentration of the DC6-12 surfactant in aqueous solution, mol dm$^{-3}$ |

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