The Adsorption Behavior of Dialkyl Dimethyl Ammonium Chloride—Nonionic Surfactant Binary Systems

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From the practical standpoint of fabric softener formulation, a comparative study was made on adsorption behavior toward fabrics of binary systems consisting of di(hydrogenated tallow) dimethyl ammonium chloride (purified Arquad 2HT) and typical polyoxyethylenated nonionic surfactants which are commonly used as auxiliary agents for softeners.

Soxhlet extraction of treated fabrics and quantitative analysis by high-performance liquid chromatography (HPLC) gave significant results indicating many of these nonionic surfactants, assumed to be inherently unadsorbable in rinse-cycle treatment, were highly adsorbable even at a high bath ratio by being applied with the water-insoluble cationic surfactant. Moreover, it was also disclosed that the hydrophobic structure of nonionic surfactants is another factor, other than hydrophobicity, determining adsorption.

Furthermore, the mechanism of this nonionic adsorption was elucidated on the basis of results of structural analyses of binary dispersions by differential scanning calorimetry (DSC), X-ray diffraction, electron spin resonance spectroscopy (ESR) and transmission electromicroscopy (TEM) in addition to partition measurements of the surfactants into the dispersed and the continuous aqueous phases.

It was concluded that the primary driving force for this nonionic adsorption is an association with the lamellar of Arquad 2HT and that the cationic vesicles act as "anchors" in adsorption.

In the previous paper (1) concerning this topic, the authors reported adsorption behavior toward fabrics and the structure of an aqueous dispersion of Arquad 2HT (2HT), or di(hydrogenated tallow) dimethyl ammonium chloride (DHTDMAC), the most widely used fabric softener base. Meanwhile, a number of papers dealing with the influence of various factors on the adsorption of DHTDMAC in a rinse-cycle treatment have been published, as described previously. However, to the best of our knowledge, only a single study (2) discussing the adsorption of glycerol stearates in the presence of DHTDMAC has been made on the adsorption of nonionic surfactants which are indispensable auxiliary agents for softeners. Therefore, specific effects of nonionic surfactants on adsorption and adsorption structures have remained largely unexplored.

This present paper is a comparative study of the adsorption behavior of binary systems consisting of 2HT-polyoxyethylene (POE) C_{12-18} alkyl ethers or POE nonylphenyl ethers (NPE_n) as a function of the number of ethylene oxide units per molecule (EOP) of nonionic surfactants and alkyl-chain length with the constant molar ratio of 2HT:nonionic surfactant being 3:1. Moreover, to elucidate this adsorption behavior and to estimate adsorption structures of binary systems, structural analyses of aqueous dispersions were made by DSC, X-ray diffraction, the ESR spin probe method and TEM in addition to measurements of partition ratios of surfactants into the dispersed and the aqueous phases in binary systems.

PROCEDURES

Materials. Purified Arquad 2HT® (Lion Akzo Co., Tokyo, Japan) was obtained as described previously (1). Its average molecular weight was calculated to be 566.5 from the amine value of the unquaternized tertiary amine precursor whose main component is di(hydrogenated tallow) methyl amine.

NPE_n, the subscript "n" denoting the EOP in the range of 1-40, were supplied from Lion Chemical Co.

POE alkyl ethers such as POE [3] dodecyl ether, POE [3] tetradecyl ether, POE [3-20] hexadecyl ethers and POE [3-40] octadecyl ethers ($C_{12}E_3$, $C_{14}E_3$, $C_{16}E_n$, $C_{18}E_n$) were obtained from Nihon Emulsion Co.

The average molecular weight of these nonionic surfactants was calculated from the hydroxyl value.

All the polyoxyethylenated nonionic surfactants were of commercial grade and used without further purification, even though impurities such as base catalyst, polyethylene glycol and unethyoxylated free alcohols probably were present (3-6). Hence, in the present study, the EOP is an apparent one which may differ somewhat from the real one.

For the adsorption experiment and the partition measurements, binary dispersions containing 2HT by 4 wt% and the nonionic surfactant, the molar ratio of the former to the latter being 3 to 1, were prepared as mentioned below.

The required amount of 2HT and the nonionic surfactant were melted at ca 60°C with the proper amount of ethylene glycol as a co-solvent and then dispersed in warm water (50°C) containing 0.01 wt% sodium chloride as a viscosity cutter using a high-speed agitator. The dispersion was then cooled to 25°C.

All the water used in the experiments was deionized and distilled except that used for adsorption.

Following thorough pretreatment of detergent-washing at 50°C and repeated rinsing at normal temperature, cotton towels and acrylic jerseys were used as standard substrates for the adsorption experiment.

Methods — The adsorption experiments and measurements of amounts of surfactants adsorbed. The standard conditions employed for the adsorption experiments in which the cotton towel and the acrylic jersey were treated in separate baths using an impeller-type washing machine equipped with a pulsator were as follows: 2HT concentration, 4.7×10^{-5}M (0.00267 wt%); nonionic surfactant concentration, 1.57×10^{-5}M; liquor ratio, 30:1; water hardness, 54 ppm as $CaCO_3$; temperature, 25°C; time, 3 min.

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Following centrifugation for 2 min and static drying at room temperature, the treated fabrics were Soxhlet-extracted with a mixed solvent of 99.5 vol% ethanol (50 vol%) and 95 vol% chloroform (50 vol%) for more than 8 hr. The extractant was dried to release the extract, a mixture of 2HT and nonionic surfactant adsorbed, which was then dissolved with 95 vol% methanol for quantitative analysis using HPLC (7). Two test pieces (about 20 g apiece) for each binary system were randomly sampled for the extraction and HPLC measurements, and the results were averaged.

The HPLC system consisted of a Model LC-5A chromatograph, a RID-2A differential refractometer for 2HT and POE alkyl ethers, a SPD-2A ultraviolet spectrophotometer for NPE_n and a Chromatopac C-RIB data Processor (Shimadzu Seisakusho Co.).

The adsorption ratios of the surfactants were calculated as follows: Adsorption ratio (%) = (Detected amount/Calculated amount as 100% adsorption) × 100.

The preparatory experiments by the above method showed sufficient extraction efficiency and detection sensitivity, since they gave adsorption ratios of 2HT in good agreement with those determined by titration (1).

Phase transition phenomenon and crystallography. The influence of nonionic surfactants on gel-liquid crystalline transition behavior and the hexagonal crystallographical structure of a hydrated solid of 2HT was examined by DSC and X-ray diffraction, respectively, as described previously. The samples for the measurements were prepared as follows.

The required amounts of 2HT and the nonionic surfactant (3:1 by mol) were melted and thoroughly mixed at ca 120°C. The mixture was thoroughly hydrated by stirring with the required amount of water at ca 90°C for more than 1 hr and then cooled to room temperature to form binary dispersions containing 2HT by 30 wt%.

ESR spectroscopy. ESR spectra of the binary dispersions were obtained with a JOEL JES-FE1X spectrometer, following the spin probe method. In the present study, stearic acid spin- labelled at the 16 position (16NS) was obtained from Syva associates and used as the spin probe. It was dissolved in the binary dispersions as illustrated in Figure 1, and its motion was compared with each of the others.

The concentration of the probe was always 1×10^{-4}M. The sample prepared as shown in Figure 1 was sucked up into a capillary tube of 1 mm i.d. and sealed in the presence of air for ESR measurement. The detailed conditions for this are shown in Figure 1. Due to the poor solubility of the probe in water and high surfactant concentration, the spectra were attributed only to the probe dissolved in the surfactant phases (8).

Generally, the ESR spectra of spin probes in liquid crystals or vesicles are determined primarily by the anisotropic motion of the probes, such as preferential rotation of the molecules around the long molecular axis as illustrated in Figure 1. Rotations perpendicular to this axis are severely hindered, but angular fluctuations of small amplitude occur. It has been found convenient to represent the mean angular fluctuations of a spin probe in terms of order parameter "S" which is dependent on the amplitude of probe motion (9,10). Thus, it was used here as a parameter of anisotropic molecular motion of the probes. That is, it indicates the fluidity of the lamellar structure of binary systems.

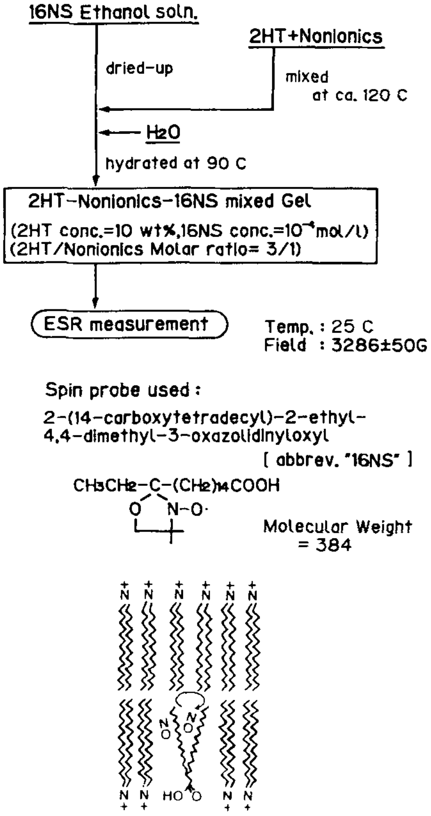

FIG. 1. Procedure for ESR spin probe analysis.

Electronmicroscopy. The structures of the binary dispersions used for the adsorption experiments were observed with a transmission electron microscope (Hitachi Model H-600) applying the freeze-fracture replica technique.

Partition measurement. We reported in the previous paper that ca 90% of 2HT molecules are adsorbed as vesicles with softening treatment using 2HT as a single surfactant in the softener. Therefore, the partition behavior of surfactants in binary dispersions was investigated to see if it had any correlation with the adsorption behavior.

The samples prepared for the adsorption experiment were also used for the measurement. They were maintained at 25°C for 10 to 120 days so as to reach equilibrium. Then they were diluted 100 times with water to a 2HT concentration of 7.06×10^{-4}M. Since this is much higher than the saturated concentration of monomer dispersion, 2HT molecules are considered to maintain their vesicle structure despite dilution if there is no strong interaction with nonionic surfactants. The diluted dispersions were filtered by a membrane filter (Toyo Roshi Co.) of 0.1 μm pore size, and the filtrate was dried and dissolved with 95 vol% methanol of the same volume as that of diluted but unfiltered dispersions additionally diluted with 99.5 vol% methanol to twice the volume, making their solutions clear.

After surfactant concentration in these solutions was determined by HPLC analysis, partition ratios were calculated according to the following two formulae:

1. Partition ratio of 2HT into aqueous phase (%) =

(Conc. in the filtrate/Conc. in the unfiltered and diluted solution) × 100

2. Partition ratio of nonionic surfactant into dispersed phase (%) = [1 - (Conc. in the filtrate/Conc. in the unfiltered and diluted solution)] × 100.

RESULTS AND DISCUSSION

Adsorption behavior of Arquad 2HT — nonionic surfactant binary systems. The initial results are shown in Figure 2 as adsorption ratios of the nonionic surfactants onto the cotton towel in the presence of 2HT as a function of EOP. From these adsorption curves, $C_{16}E_n$ and $C_{18}E_n$ showed better adsorptivity than NPE_n at an equal EOP and all these series exhibited distinct EOP dependence. That is, lower EOP gave higher percentage deposition comparable to that of 2HT. The only exception to this was NPE_1 which was less adsorbable than NPE_3. More specifically, for example, it was quite typical for more than 50% of $C_{18}E_{40}$ to be deposited onto the cotton towel which adsorbed more than 90% of 2HT regardless of the combination, whereas just less than 10% of NPE_{40} was adsorbable.

Similar results were obtained with the acrylic jersey as shown in Figure 3, though each nonionic surfactant showed poorer adsorptivity than that toward the cotton towel with the maximum deposition being in the range of 40-50%.

This coincides with the lower adsorptivity of 2HT toward the acrylic jersey than the cotton towel as shown in Figure 4 in which the alkyl-chain length of POE alkyl ethers was considered another factor at constant EOP(=3). These adsorption data on 2HT toward cotton and acrylonitrile agree by and large with those reported by H.W. Bücking *et al.* (11) and K. Bräuer *et al.* (12), *though they conducted adsorption experiments under* slightly different conditions in regard to the starting concentration of DHTDMAC, temperature, bath ratio and treatment period. It is obvious from Figure 4 that the longer alkyl-chain gave better adsorptivity to POE alkyl ethers while 2HT was almost constantly adsorbed regardless of the combination, showing single dependence on the kind of fabric. This independence of 2HT adsorption from the simultaneous presence of nonionic surfactants indicates a discrepancy with the results of K. Bräuer *et al.* who observed the higher weight ratios of POE [7] alkyl($C_{14,15}$) ether to DHTDMAC to give lower saturation values of DHTDMAC adsorption (12). This discrepancy may be due to our lower starting concentration of 2HT and lower weight ratios of nonionic surfactants to 2HT in the present study.

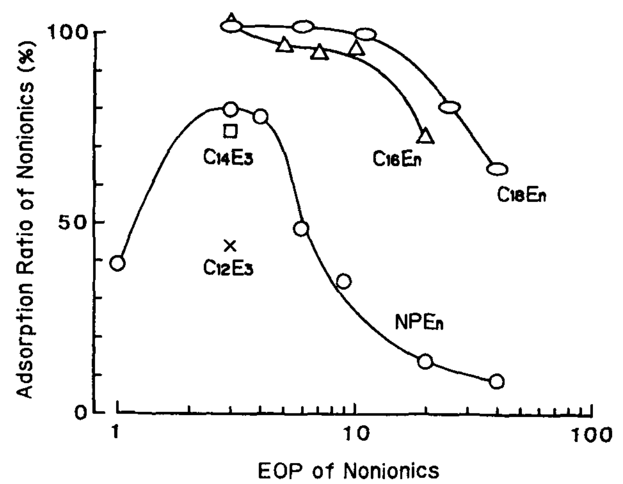

FIG. 2. EOP dependence of nonionic adsorption onto the cotton towel in the presence of Arquad 2HT at a 3:1 molar ratio of 2HT:nonionic surfactant.

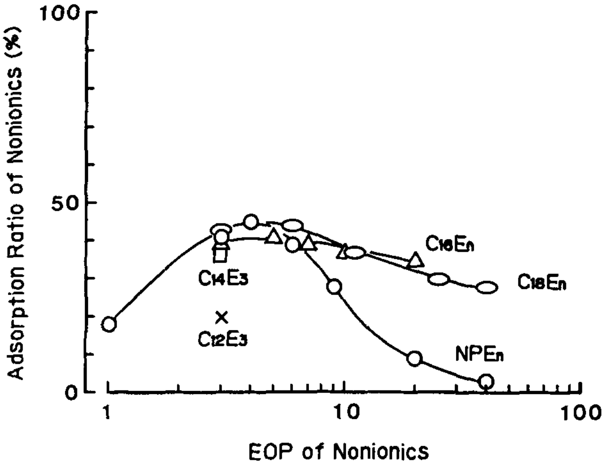

FIG. 3. EOP dependence of nonionic adsorption onto the acrylic jersey in the presence of Arquad 2HT at a 3:1 molar ratio of 2HT:nonionic.

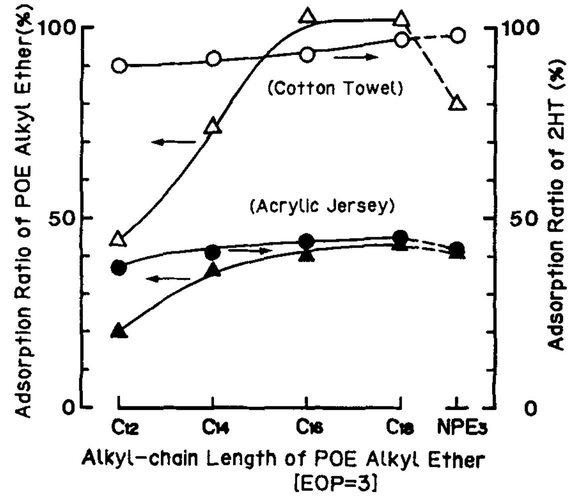

FIG. 4. Alkyl-chain length of POE(3) alkyl ether vs adsorption ratio of 2HT and of POE alkyl ether.

Since 2HT adsorption occurred constantly as mentioned above, it is only natural that the EOP vs molar ratio of adsorbed nonionic surfactant/2HT curves in Figure 5 should be similar to that in Figure 2.

The above mentioned adsorption data indicate two findings. First, it is quite significant that many nonionic surfactants assumed to be inherently unadsorbable toward fabrics in water become highly adsorbable when used with the water-insoluble cationic surfactant even at a high bath ratio of 30:1, even though a control run was not done to verify this assumption.

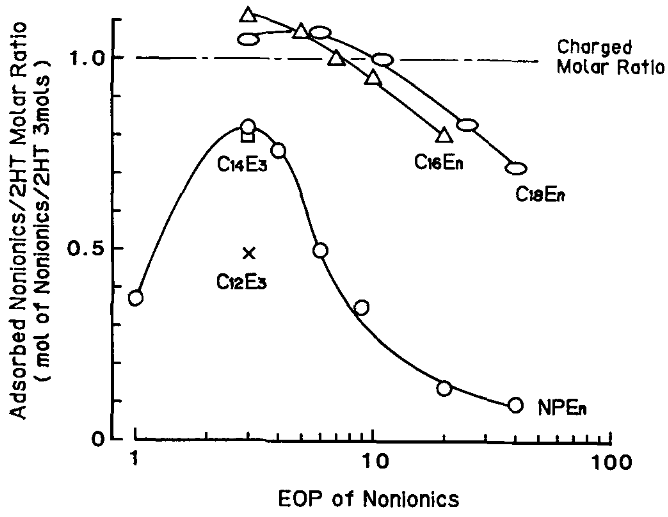

FIG. 5. EOP of nonionic surfactant vs molar ratio of nonionic surfactant/2HT adsorbed.

Moreover, it is also noteworthy that the structure of the hydrophobic part of nonionic sufactants is another deciding factor of their adsorption besides hydrophobicity.

Then, what is the driving force for the adsorption of these nonionic surfactants? To answer this question, structural analyses of these binary systems are essential.

Structures of Arquad 2HT — nonionic surfactant binary aqueuos dispersions — phase transition phenomenon. The gel-liquid crystalline phase transition phenomenom gives useful information as a first step for determining the structures of mixed systems containing amphiphilic compounds such as DHTDMAC and lipids which form the hydrated solid phase (13-15).

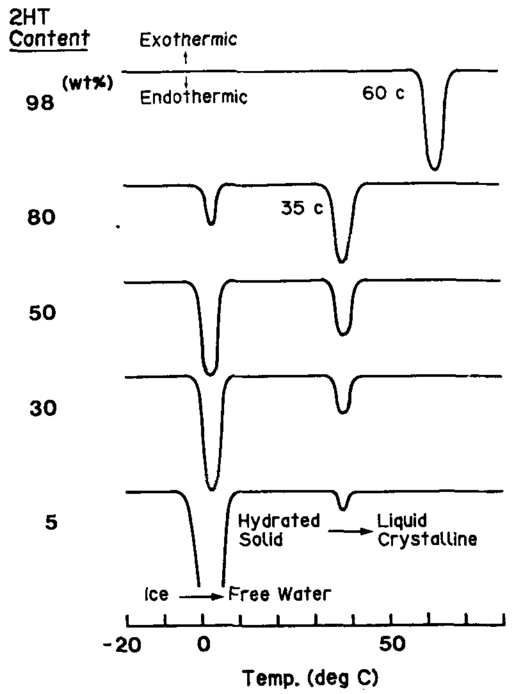

FIG. 6. DSC heat transition curves and Tc of hydrated 2HT.

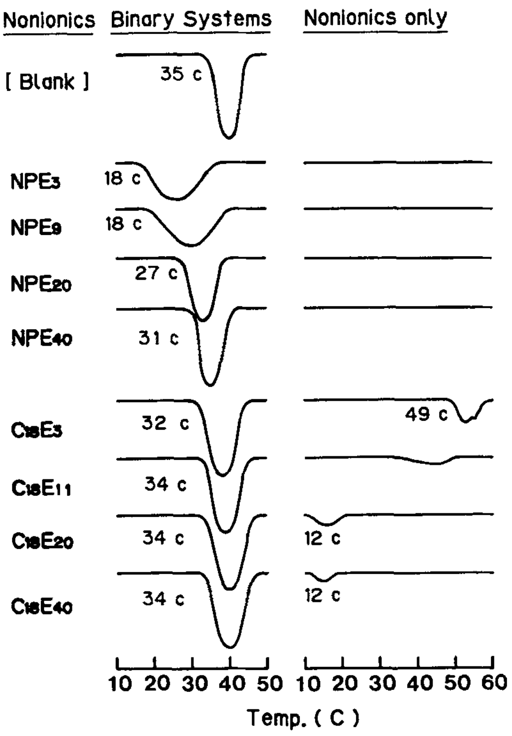

FIG. 7. DSC curves and Tc of 2HT - NPE_n or $-C_{18}E_n$ mixed gel.

Before discussing the binary systems, the DSC heat transition behavior of hydrated 2HT should be reviewed as shown in Figure 6. The gel-liquid crystalline transition temperature (Tc) determined from the intersection of the base line and the extrapolated onset of the endothermic peak was written in addition to the respective DSC curves in the present paper. Figure 6 shows that recrystallized 2HT powder containing water by ca 2 wt% at room temperature causes the phase transition at 60°C, whereas the thoroughly-hydrated 2HT gel containing water by more than ca 20 wt% has a definite Tc at 35°C. This is the Krafft point at which the alkyl-chains of 2HT molecules melt to form the liquid crystalline phase (16-18).

As the first results obtained for the binary systems, the effects by NPE_n and $C_{18}E_n$ on this transition behavior are comparatively shown in Figure 7, in which the lower EOP for NPE_n gives lower Tc in addition to broader peaks whereas $C_{18}E_n$ give little effect regardless of their EOP. From these results, the following hypothesis seems to offer a reasonable explanation about how these nonionic surfactants exist in binary aqueous dispersions with 2HT.

NPE_n of EOP lower than 20 decrease Tc to a considerable degree possibly by association with the bimolecular lamellar of 2HT so that they can be fairly adsorbed with 2HT as if 2HT vesicles act as "anchors" in the adsorption. In contrast, most NPE_{20} and NPE_{40} molecules are presumably excluded from the lamellar only to dissolve into the aqueous medium as micelles, because of the large difference in their hydrophobicity compared to that of 2HT molecules. This seems to be the reason for their weak effect on Tc and poor adsorptivity. On the other hand, the minimal effect by $C_{18}E_n$ on this transition behavior implies the possibility that their high adsorptivity resulted from their orderly association with the lamellar; their straight hydrophobic chains having similar length to

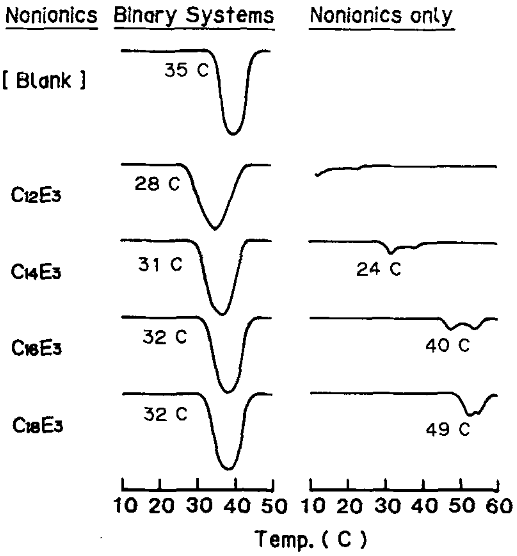

FIG. 8. Alkyl-chain length of POE(3) alkyl ether vs DSC curve and Tc of mixed gel with 2HT.

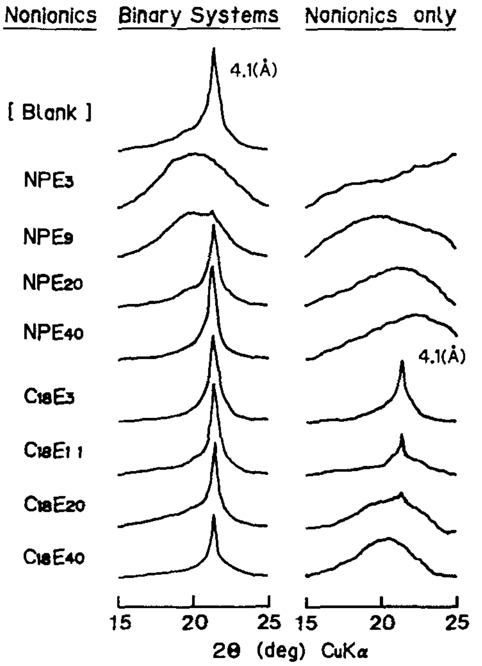

FIG. 9. the effect by the addition of NPE_n or $C_{18}E_n$ upon X-ray short spacing of hydrated 2HT.

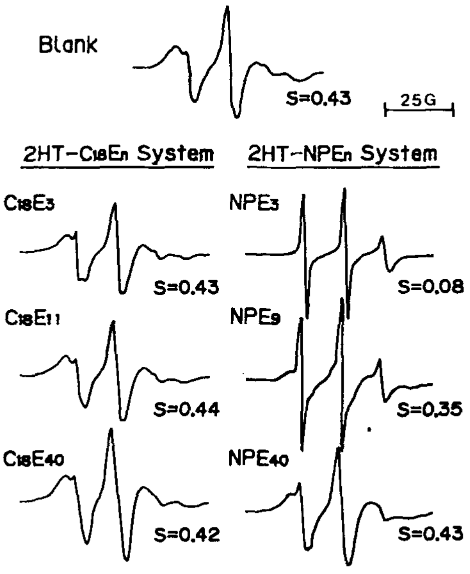

FIG. 10. EOP of nonionic surfactant vs ESR spectrum and order parameter 'S' of the binary system.

those of 2HT unlike that of NPE_n might contribute to this orderly association. Another result to support this possibility is that the endothermic peaks attributed to the hydrated $C_{18}E_n$ of equivalent concentration to that in the binary systems were undetectable in the binary dispersions.

The second series of the DSC curves for the binary systems is shown in Figure 8 in which the alkyl-chain length of POE [3] alkyl ethers is considered another factor as in Figure 4. Apparently, the shorter alkyl-chain gave the lower Tc as well as broader peaks. It thus appears that $C_{12}E_3$, the least-adsorbed among POE [3] alkyl ethers, gives the severest disorder to the lamellar despite its least association. From this, it follows that the higher EOP for $C_{12}E_n$ and $C_{14}E_n$ may possibly cause their exclusion from 2HT vesicles and make them less adsorbable as in the case of NPE_n.

Crystallography. X-ray diffraction analysis was conducted to substantiate the hypothesis in the previous section. As in the previous section, the crystallography of hydrated 2HT should be reviewed before going into a discussion on effects due to the addition of nonionic surfactants.

We previously reported that recrystallized 2HT powder which contains water by ca 2 wt% is triclinic in terms of crystallography, whereas the crystal system of the thoroughly-hydrated 2HT gel whose water content is more than ca 20 wt% is hexagonal, as indicated characteristically by the X-ray diffraction peak at 4.1 Å (1). Since this hexagonal 2HT should be discussed here in relation to adsorption behavior, attention should be directed to how this peak at 4.1 Å may be affected by the addition of nonionic surfactants.

A striking change in this peak was brought about as evident from its complete disappearance by NPE_3 or NPE_9 as shown in Figure 9. This supports the aforementioned hypothesis that both NPE_3 and NPE_9 impart irregularity to the arrangement of the alkyl-chains of 2HT and convert the structure into that of low energy by association with the lamellar. The crystallinity of the lamellar, however, is restored by NPE_n of EOP exceeding 9. Again, this supports the assumption that most NPE_{20} and NPE_{40} molecules are excluded from the lamellar to the aqueous medium. On the other hand, $C_{18}E_n$, whose own crystallinity was also detected in the case of lower EOP and high concentration as in Figure 9, had little effect on the crystallinity of the lamellar regardless of EOP. This is also consistent with their transition behavior.

ESR spectroscopy. The above hypothesis is also supported by results obtained by the ESR spin probe method, as shown in Figures 10 and 11. In Figure 10, NPE_{40} and

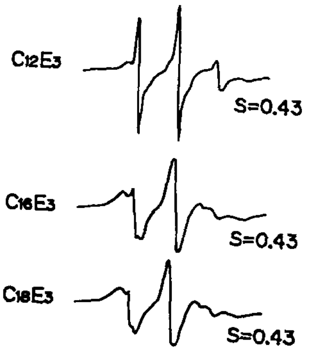

FIG. 11. Alkyl-chain length of POE(3) alkyl ether vs ESR spectrum and order parameter of mixed gel with 2HT.

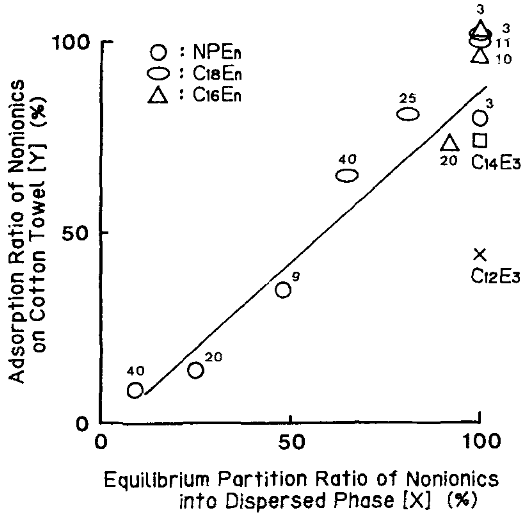

FIG. 12. The correlation between the equilibrium partition ratio of nonionic surfactant into the dispersed phase of binary dispersion and nonionic adsorption ratio onto the cotton towel; the arabic number indicates EOP of NPE$_n$, C$_{18}$E$_n$ and C$_{16}$E$_n$, respectively.

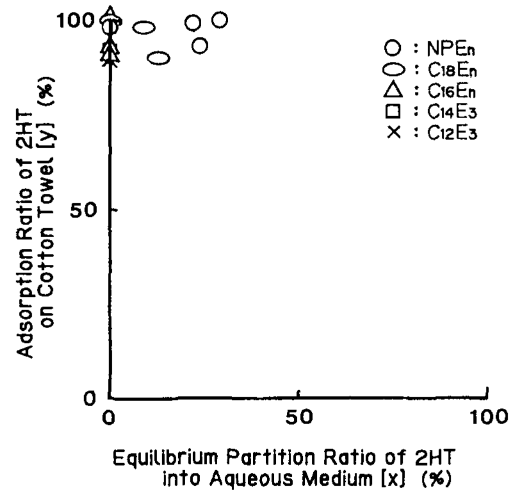

FIG. 13. The equilibrium partitioned ratio of 2HT into the aqueous phase of binary dispersion vs 2HT adsorption on cotton towel.

each $C_{18}E_n$ had little effect on the spectra and the order parameter "S". This indicates that they have little adverse effect on the orderly arrangement of hydrophobic chains in the lamellar.

In contrast, the sharp decrease in "S" by NPE_3 supports again the hypothesis that NPE_3 damages the lamellar to a great degree, since S=0 means that a completely isotropic rotation is possible for probes in the environment (9).

A similar interpretation of the spectra is possible for local parts of the two systems containing NPE_9 or $C_{12}E_3$ by their sharp resonance lines attributable to the isotropic motion of the probes (9), though the value of "S" is maintained for the latter. This appears to support their medium level adsorptivity.

Partition behavior. Direct and quantitative evidence for our hypothesis of the mechanism of nonionic adsorption was obtained from partition measurements. Namely, as described in the experimental section, the partition behavior of nonionic surfactants into the dispersed phase and that of 2HT into the continuous aqueous phase in the respective systems were examined to detect possible correlation with the adsorption behavior of binary systems. The results are shown in Figures 12 and 13, respectively.

It is immediately apparent from Figure 12 that the equilibrium partition ratios of nonionic surfactants into the dispersed phase are closely correlated with their adsorption ratios onto the cotton towel. The regression analysis, which gave the regression line in Figure 12, indicates this correlation to be highly significant with a 99% level of significance and the correlation coefficient of 0.866 which increases to 0.952 without the data of $C_{12}E_3$. This evidence proves that many nonionic surfactants become highly adsorbable by association with the 2HT lamellar, as if 2HT vesicles act as "anchors" in adsorption, and others less adsorbable by being driven out of the vesicles into the aqueous medium. This appears due to preferential fractionation of their lower EOP portions into the lamellar which even higher EOP nonionic surfactants such as NPE_{20} or NPE_{40} can partition into the dispersed phase by as much as 25% or 9%, respectively, owing to their polydispersed composition (19).

It is quite apparent from Figure 13 that 2HT adsorption is completely independent of partition behavior in the present study, though a small portion of 2HT dissolves in the aqueous medium by several coexisting nonionic surfactants. This solubilization of 2HT may be promoted by greater amounts of nonionic surfactants than those in this study, and may possibly result in the deterioration of 2HT adsorption as reported by K. Bräuer *et al.* (12).

Electronmicroscopy. The authors have already reported that 2HT maintains the spherical structure of vesicles even when present at low concentration in practical softening baths. Vesicles can be regarded as a lamellar mesophase bent into a globular structure, in which amphiphilic molecules are arranged in coherent double layers of molecules separated from each other. The polar groups are in contact with water, while the nonpolar tails form the hydrocarbon core of the bimolecular layer. Therefore, to provide additional evidence for the above conclusion, it is necessary to determine if 2HT actually maintains the vesicle structure in the presence of nonionic surfactants.

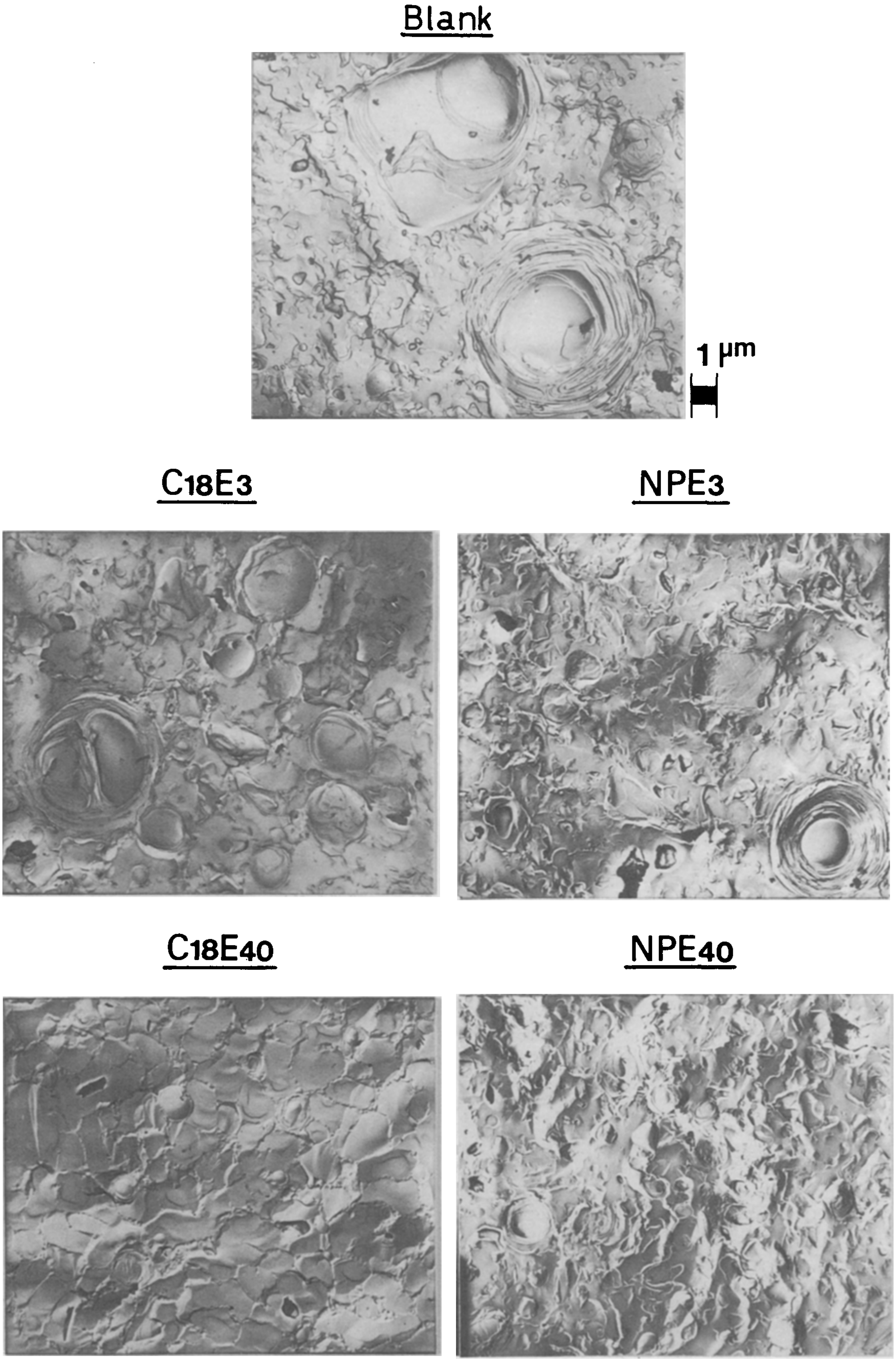

FIG. 14. TEM micrographs of 2HT - NPE$_n$ or -C$_{18}$E$_n$ binary dispersions by freeze-fracture replica technique.

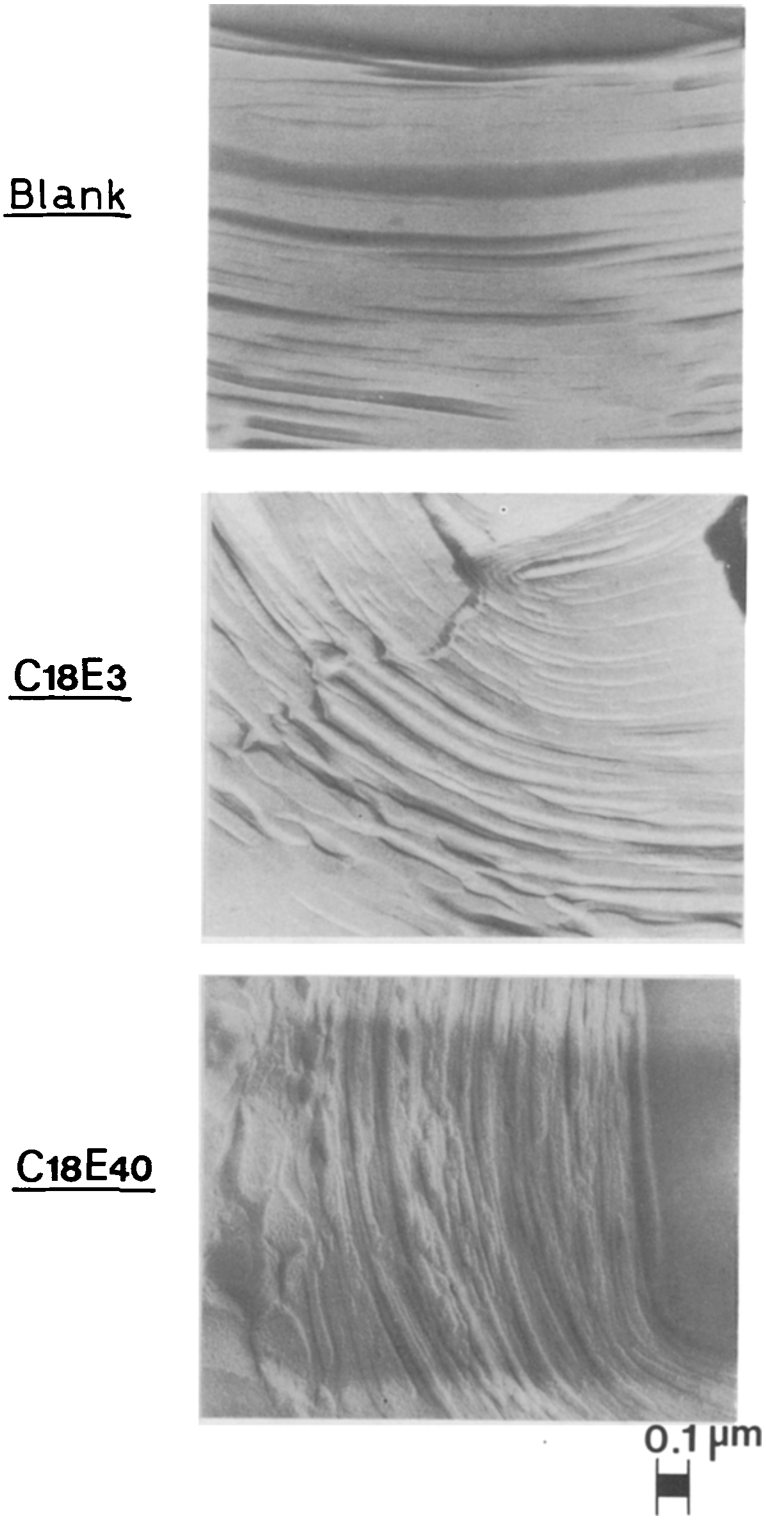

FIG. 15. Lamellar structure of 2HT - $C_{18}E_n$ binary vesicles.

As shown in the TEM pictures of Figure 14, vesicles were found in all binary dispersions of the 2HT-NPE_n or -$C_{18}E_n$ systems. And, they were also formed in the presence of $C_{16}E_n$, $C_{14}E_3$ or $C_{12}E_3$.

This supports the conclusions in the previous section. Moreover, a comparison of three TEM pictures in Figure 15 should give some indication as to how these nonionic surfactants associate with the lamellar. That is, the multi-

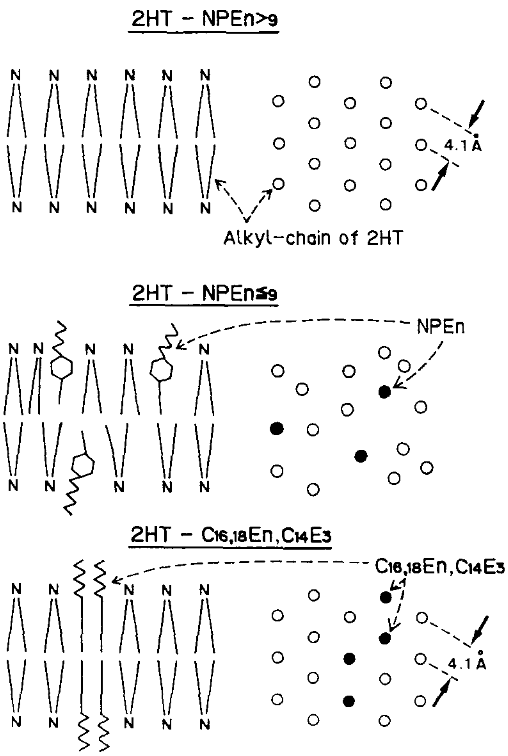

FIG. 16. The proposed bimolecular lamellar models of 2HT — nonionic surfactant binary systems.

layered biomolecular lamellar observable as the regularly-striped pattern in the 2HT vesicles was partially disordered in the binary systems, this possibly being due to the nonionic surfactants incorporated with the 2HT lamellar. However, since it is yet uncertain whether the nonionic molecular arrangement in the lamellar is homogenous or heterogenous, the molecular level structure of binary vesicles should be clarified through additional experiments.

Lamellar models of the binary systems. Based upon the evidence presented above, the lamellar models illustrated in Figure 16 appear reasonable for the 2HT — nonionic surfactant binary systems at the molar ratio of the former to the latter being 3 to 1.

First, a greater portion of the 2HT lamellar is considered to maintain its original structure even by the addition of NPE_n of EOP exceeding 9, since these nonionic surfactants are mostly driven out of the lamellar into the aqueous medium mainly by the driving force of their own great difference in hydrophobicity with that of 2HT molecules. This exclusion makes them less adsorbable.

Secondly, due to essentially the same hydrophobicity as that of 2HT, NPE_n of EOP lower than 9 can remain in the lamellar so as to be fairly adsorbed with 2HT. Because of the incorporation of molecules consisting of bulky hydrophobic parts with the lamellar, however, considerable disorder is given to the arrangement of the alkyl-chains of 2HT so that the mixed surfactant phases can barely maintain the vesicle structure which exists as the liquid crystalline at normal temperature.

Thirdly, the orderly arrangement in the lamellar, whether homogenous or heterogenous on the molecular level, seems possible for POE alkyl(C_{14},C_{16},C_{18}) ethers, particularly for those of lower EOP. Their straight hydrophobic chains with essentially the same length as those of 2HT may contribute to this orderly arrangement.

For $C_{12}E_3$, the mixed image of the first and the third looks natural.

Although these models may facilitate an understanding as to why these nonionic surfactants are highly or less adsorbable and how they affect the vesicle structure, they are not sufficiently accurate, since it remains to be clarified whether the nonionic arrangement in the lamellar is homogenous to a certain degree or completely heterogenous on the molecular level and how some 2HT molecules are solubilized in the aqueous medium by various coexisting nonionic surfactants. Further study should be conducted on binary aqueous dispersions for clarification of these points.

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