

# Surface and Interfacial FTIR Spectroscopic Studies of Latexes. II. Surfactant–Copolymer Compatibility and Mobility of Surfactants

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## SYNOPSIS

Whereas molecular level interactions between sulfonate groups of SDOSS surfactant and COOH groups of EA/MMA copolymer have been discussed in part I of this series, the major focus of this work is to establish the effect of compatibility on the distribution of surfactants at the film–air and the film–substrate interfaces. It is found that the exudation of anionic surfactants is inhibited in neutralized ethyl acrylate/methacrylic acid latex films. On the other hand, nonionic surfactants do not exhibit enrichment at the film interfaces. The inhibited exudation of anionic surfactants is attributed to the increased compatibility resulting from surfactant penetration into the swollen latex particles. This is followed by the formation of solubilized polymer–surfactant complexes through the adsorption of surfactant onto the hydrophobic polymer segments. The effect of neutralization of the carboxylic acid groups on the exudation of anionic surfactants suggests the formation of hydrophobic interactions that overwhelm surface tension effects and prevent surfactant enrichment at either interface.

## INTRODUCTION

Previously,<sup>1</sup> the factors affecting interactions between sodium dioctylsulfosuccinate surfactant in EA/MAA latex films have been established. Although during the course of this work we have become aware of the effect of the surfactant–copolymer compatibility in latex, the issue as to how compatibility may affect mobility of the surfactant molecule was not addressed. After all, it is known that phase separation, such as that observed in polymer blends, often prevents obtaining desirable properties from two different polymer systems, even by a molecular level mixing.

In spite of the fact that polymer blends and latices are dissimilar polymer systems, one can draw an analogy from the standpoint that both are composed of basically two main components: two polymers or copolymers in the case of polymer blends and a

polymer or copolymer with the surfactant in the case of latices. Since in both cases thermodynamic stability will be directly related to compatibility, it is important to determine the effect of compatibility within a given system and how chemical structures composing the network may affect the overall stability. This issue is particularly significant in the latex systems because, under suitable thermodynamic conditions, much smaller surfactant molecules may have a tendency toward greater mobility and may exude, giving rise to undesirable properties.

Typical surfactants used in the emulsion polymerization of latices fall into two major classes: anionic and nonionic. Anionic surfactants are characterized by a long alkyl hydrophobic tail and a hydrophilic head, usually the sodium salt of a sulphate or sulfonate. Nonionic surfactants are composed of a long alkyl hydrophobic tail attached to a long heteroatomic alkyl chain, typically polyethylene oxide with at least 10 repeating units in length, to achieve good hydrophilicity at this end. Such molecular structures impart solution stabilization of latex particles that is achieved by different mechanisms for each class of surfactants. It is believed that anionic

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surfactants stabilize polymer particles through charge repulsion of the ionic double layers between particles in solution, whereas the nonionic surfactants stabilize latex particles through restrictions imposed by loops and trains formed on the particle surface via hydrophobic interactions. Although there are numerous theories of latex stabilization, it is apparent that the chemical differences among surfactants are responsible for different stabilization mechanisms and impose various restrictions on compatibility and solubility within the latex, especially during or after coalescence.

The presence of surfactants, the species necessary for latex polymerization, has been shown to influence the glass transition temperature<sup>2</sup> ( $T_g$ ) of the fully coalesced latex films. This, in turn, will ultimately affect the film formation and other macroscopic properties. Hence, the chemical structures of surfactants become a significant factor in determining such properties as  $T_g$ , hydrolytic stability, and optical properties. Since compatibility is determined not only by the chemical structures, but also by concentration levels involved, the question of how the chemical composition of surfactants may affect mobility within the latex film will be addressed in this part. For that reason, a range of surfactants, both anionic (sodium dioctylsulfosuccinate, SDOSS; sodium dodecylbenzenesulfonate, SDBS; sodium nonylphenol ethylene oxide [2 units] sulfonate, SNP2S; and sodium dodecylsulfate, SDS), and nonionic (nonylphenol ethylene oxide [40 units], NP-40) was used to synthesize the ethyl acrylate/methacrylic acid (EA/MAA) copolymer latices. Since our main concern is the behavior of surfactants after latex coalescence, the film-air and film-substrate interfaces will be monitored using ATR FTIR spectroscopy.

## EXPERIMENTAL

Latex preparation, starting materials, and the related synthetic procedures of acid group neutralization were reported in part I.<sup>1</sup>

### FILM PREPARATION AND SPECTRAL MEASUREMENTS

Latex films were prepared to maintain the film thickness between 100 and 150  $\mu\text{m}$ . Upon deposition, the films were all air-dried for 72 h (unless otherwise specified) at 23°C. The films prepared on other substrates such as polytetrafluoroethylene (PTFE)

were deposited on the PTFE-coated aluminum mold, whereas a purified liquid mercury was used for the films coalesced on that substrate.

The glass transition temperature ( $T_g$ ) of the latex copolymer ( $-5^\circ\text{C}$ ) was determined from the average of three runs on a DuPont Instruments 910 differential scanning calorimeter equipped with a DuPont Thermal Analyzer 2000. The temperature range was from  $-50$  to  $250^\circ\text{C}$  at a heating rate of  $20^\circ\text{C}/\text{min}$ .

Transmission and rectangular ATR FTIR spectral measurements were recorded as previously described.<sup>1</sup> Latex particle diameters were determined by light scattering with a Coulter submicron particle analyzer model N4-SD. Table I lists the latex particle-size diameters of the different EA/MAA copolymer latices used in this study.

## RESULTS AND DISCUSSION

Table II illustrates the chemical structures of the five surfactants chosen in this study. The anionic surfactants (Table II, structures A–D) exhibit high water solubility imparted by the sulfonate and sulfate groups associated with  $\text{Na}^+$  ions. The SDOSS (A) represents an anionic surfactant with two hydrophobic tails and a sulfonate group, whereas the SDBS (B) is an anionic surfactant with one hydrophobic tail and a sulfonate group. This choice will reveal the effect, if any, of increased hydrophobic interactions from the second alkyl tail on the exudation and compatibility of anionic surfactants in latex films. The SDS (D) represents a single hydrophobic tail with a sulfate group, whereas the SNP2S structure (C) bridges the gap between the anionic surfactants and the nonionic NP (E). The latter (E) is less water soluble than are the anionic surfactants, yet it has a hydrophilic end, making it capable of imparting good stability to the system during synthesis where similar nonionic surfactants

**Table I EA/MAA Latex Particle Diameters**

Latex	Surfactant Concentration <sup>a</sup> (wt %)	Average Particle Diameter <sup>b</sup> (nm)
SDOSS	4.0	224
SDBS	4.0	122
SNP2S	4.0	116
SDS	4.0	97
NP-40	6.0	122

<sup>a</sup> Based on a total monomer weight.

<sup>b</sup> Obtained with Coulter submicron particle analyzer.

**Table II** Chemical Structures of the Surfactants

Sodium dioctylsulfosuccinate		
A	$\begin{array}{c} \text{C}_8\text{H}_{17}-\text{O}-\text{C}(=\text{O})-\text{CH}_2 \\   \\ \text{C}_8\text{H}_{17}-\text{O}-\text{C}(=\text{O})-\text{CH}-\text{SO}_3^-\text{Na}^+ \end{array}$	(SDOSS)
Sodium dodecylbenzenesulfonate		
B	$\text{C}_{12}\text{H}_{25}-\text{C}_6\text{H}_4-\text{SO}_3^-\text{Na}^+$	(SDBS)
Sodium nonylphenol ethylene oxide		
C	$\text{C}_9\text{H}_{19}-\text{C}_6\text{H}_4-\text{O}-\text{CH}_2\text{CH}_2\text{O}-\overset{\text{Sulfonate}}{\text{CH}_2\text{CH}_2-\text{SO}_3^-\text{Na}^+}$	(SNP2S)
Sodium dodecylsulfate		
D	$\text{C}_{12}\text{H}_{25}-\text{O}-\text{SO}_3^-\text{Na}^+$	(SDS)
Nonylphenol ethylene oxide (40 units)		
E	$\text{C}_9\text{H}_{19}-\text{C}_6\text{H}_4-\text{O}-(\text{CH}_2\text{CH}_2\text{O})_{40}-\text{H}$	(NP-40)

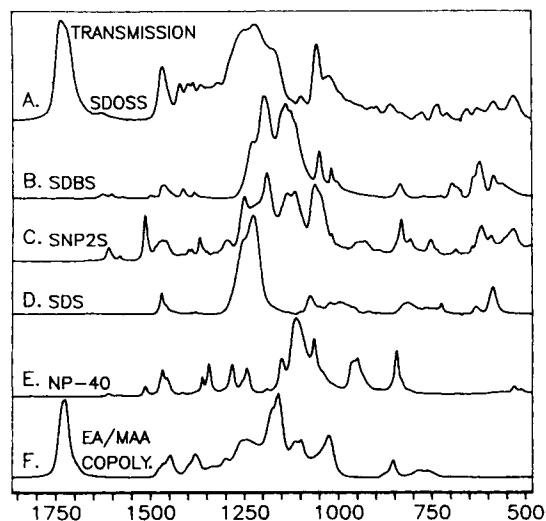
A, sodium dioctylsulfosuccinate (SDOSS); B, sodium dodecylbenzenesulfonate (SDBS); C, sodium sulfonate adduct of nonylphenol ethylene oxide (SNP2S); D, sodium dodecylsulfate (SDS); and E, nonylphenol ethylene oxide (NP).

differing only in fewer ethylene oxide units may be ineffective.

As the first step in an attempt to answer the question concerning about the effect of compatibility on mobility of surfactants in latices, it is necessary to establish the spectral features of the surfactants and the copolymer. Figure 1 illustrates transmission FTIR spectra of the surfactants in the region from the 1800 to 450  $\text{cm}^{-1}$ , and Table III lists the observed bands along with their tentative assignments. Table III also provides the infrared bands with their assignments for the ethyl acrylate/methacrylic acid (EA/MAA) copolymer spectrum obtained by precipitating ethyl acrylate/methacrylic acid copolymer from the latex using a previously described method.<sup>3</sup> A convenient feature of the copolymer spectrum is that there are no absorption bands between 700 and 400  $\text{cm}^{-1}$ . Later on, we will use this spectral region to our advantage and identify the presence of certain functional groups of the surfactants at the latex film interfaces. At this point, however, identification of those spectral regions that may serve as a fingerprint for the surfactant identification in the latex at the film-air or film-substrate interfaces is essential.

Whereas in the case of the anionic surfactants, the hydrophilic groups contribute to the S—O stretching or bending regions of the spectra (1250–1150  $\text{cm}^{-1}$ , S—O asymmetric stretching ( $\nu_{\text{as}}$ ) of the  $\text{SO}_3^-$  group; 1060–1045  $\text{cm}^{-1}$ , S—O symmetric stretching ( $\nu_{\text{s}}$ ) of the  $\text{SO}_3^-$  group; and 700–550  $\text{cm}^{-1}$  region, S—O bending [ $\delta$ ]),<sup>4</sup> the identification of nonionic surfactants can be accomplished by monitoring the polyethylene oxide units of the nonionic surfactant that exhibit a characteristic infrared band at 947  $\text{cm}^{-1}$ . With this in mind, let us focus on the latex spectra obtained at the film-air and film-substrate interfaces.

Figure 2(a) and 2(b) illustrate the film-air and film-substrate interface ATR FTIR spectra of the latex films synthesized with the surfactants listed in Table II. In all cases, the latex films were deposited on a poly(tetrafluoroethylene) (PTFE) substrate. The spectra of the film-air interface [Fig. 2(a)] exhibit the bands characteristic of the respective anionic surfactants except for the sodium nonylphenol ethylene oxide (2 units) sulfonate (SNP2S, trace C) latex spectrum, which essentially represents the spectral features due to the copolymer only. The spectrum of the latex prepared with the use of the nonionic surfactant NP (nonylphenol polyethylene oxide) [Fig. 2(a), E] shows only traces of surfactant at the film-air interface manifested by a weak band at 947  $\text{cm}^{-1}$  and assigned to the —CH<sub>2</sub>—O stretch of the ether linkages of the surfactant.



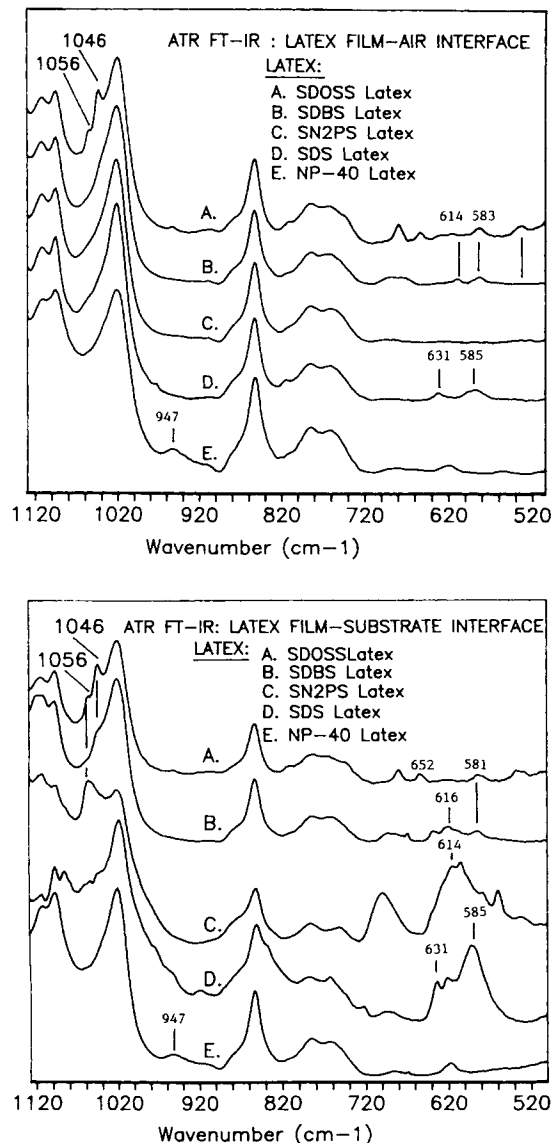
**Figure 1** Transmission FTIR spectra in the 1800 to 500  $\text{cm}^{-1}$  region of the surfactants and EA/MAA copolymer; (A) SDOSS, (B) SDBS, (C) SNP2S, (D) SDS, (E) NP, and (F) EA/MAA copolymer.

**Table III** List of the Observed Bands and Their Tentative Band Assignments

SDOSS	SDBS	SNP2S	SDS	NP	Copolymer	Assignment
—	—	—	—	—	2981	<i>Asym</i> C—H stretch (CH <sub>3</sub> )
2960	2958	2954	2956	2950	2960	<i>Asym</i> C—H stretch (CH <sub>3</sub> )
2934	2925	2930	2919	2930	2934	<i>Asym</i> C—H stretch (CH <sub>2</sub> )
2879	2871	2877	2875	2884	2879	Sym C—H stretch (CH <sub>3</sub> )
1735	—	—	—	—	1735	C=O stretch
—	—	—	—	—	1700	H-bonded—COOH
—	1625	—	—	—	—	Ar—S stretch
—	1603	1611	—	1609	—	<i>p</i> -subst. arom.
—	—	1582	—	1580	—	C=C arom.
—	1493	1513	—	1513	—	C=C arom.
1464	1463	1466	1468	1466	1466	C—H def.
1416	—	—	—	1455	1447	CH <sub>2</sub> scissor
1393	—	1395	—	—	—	HC—S def.
1360	1378	1364	1380	1360	1382	C—(CH <sub>3</sub> ) sym def.
1314	—	1295	—	1279	1299	CH <sub>2</sub> wagging
—	—	—	1248	—	—	S—O stretch (SO <sub>4</sub> )
—	—	—	1221	—	—	
1241	—	1245	—	1241	1252	C—O stretch
1216	1192	1185	—	—	—	<i>Asym</i> S—O stretch (SO <sub>3</sub> )
1175	—	—	—	1146	1173	<i>Asym</i> C—O—C stretch
1094	—	—	—	1108	1098	Sym C—O—C stretch
—	—	—	1071	—	—	Sym S—O stretch (SO <sub>4</sub> )
1050	1046	1056	—	—	—	Sym S—O stretch (SO <sub>3</sub> )
1025	—	—	—	—	1025	C—C—O (ester)
—	1013	1013	—	—	—	=C—H in-plane def.
—	—	942	—	947	—	CH <sub>2</sub> —O (ether)
—	832	828	—	843	—	=C—H out-of-plane
—	—	—	830	—	—	S—O—C stretch
857	—	—	—	—	854	Ester skel. vibr.
729	724	751	722	—	—	—(CH <sub>2</sub> ) <sub>n</sub> — ( <i>n</i> > 3)
—	691	683	—	—	—	CH out-of-plane
652	616	614	—	—	—	S—O bending (SO <sub>3</sub> )
—	—	—	631	—	—	S—O bending (SO <sub>4</sub> )
—	—	—	585	—	—	
581	583	589	—	—	—	SO <sub>2</sub> scissor
529	—	531	—	529	—	Alkyl chain
—	—	—	—	511	—	Skeletal vibrs.

The film–substrate interface ATR FTIR spectra are presented in Figure 2(b). The SDOSS latex spectrum (trace A) exhibits surfactant enrichment at this interface, manifested by the bands at 1056 and 1046 cm<sup>-1</sup>, due to the S—O stretching vibration of the SO<sub>3</sub> groups. In addition, the band at 581 cm<sup>-1</sup> assigned to the scissor vibrations of the sulfonate groups is observed. A comparison of the SDOSS latex film–substrate and film–air spectra indicates that in both cases a similar extent of surfactant exudation is observed. In contrast, the SDBS latex film exhibits greater surfactant enrichment at the film–substrate interface [Fig. 2(b), B], characterized by stronger intensities of the bands at 1046, 616, and 583 cm<sup>-1</sup>

due to the S—O stretching, S—O bending, and scissor vibrations of the sulfonate groups, respectively. The SNP2S latex, which does not exhibit surfactant exudation at the film–air interface, does, however, show exudation at the film–substrate interface (trace C), demonstrated by the appearance of the intense bands at 1056 and 614 cm<sup>-1</sup> assigned to the S—O stretching and S—O bending vibrations of the SO<sub>3</sub> groups, respectively. The presence of high surfactant enrichment at the film–substrate interface is also observed in the case of the SDS latex film [Fig. 2(b), D]. The bands at 631 and 585 cm<sup>-1</sup> assigned to the S—O bending modes of the alkyl sulfonate group indicate increased enrichment at the film–



**Figure 2** (a) ATR FTIR spectra in the 1135 to 500  $\text{cm}^{-1}$  region recorded at the film-air interface of the latex films; (A) SDOSS latex, (B) SDBS latex, (C) SNP2S latex, (D) SDS latex, and (E) NP latex. (b) ATR FTIR spectra in the 1135 to 500  $\text{cm}^{-1}$  region recorded at the film-substrate interface of the latex films; (A) SDOSS latex, (B) SDBS latex, (C) SNP2S latex, (D) SDS, and (E) NP latex.

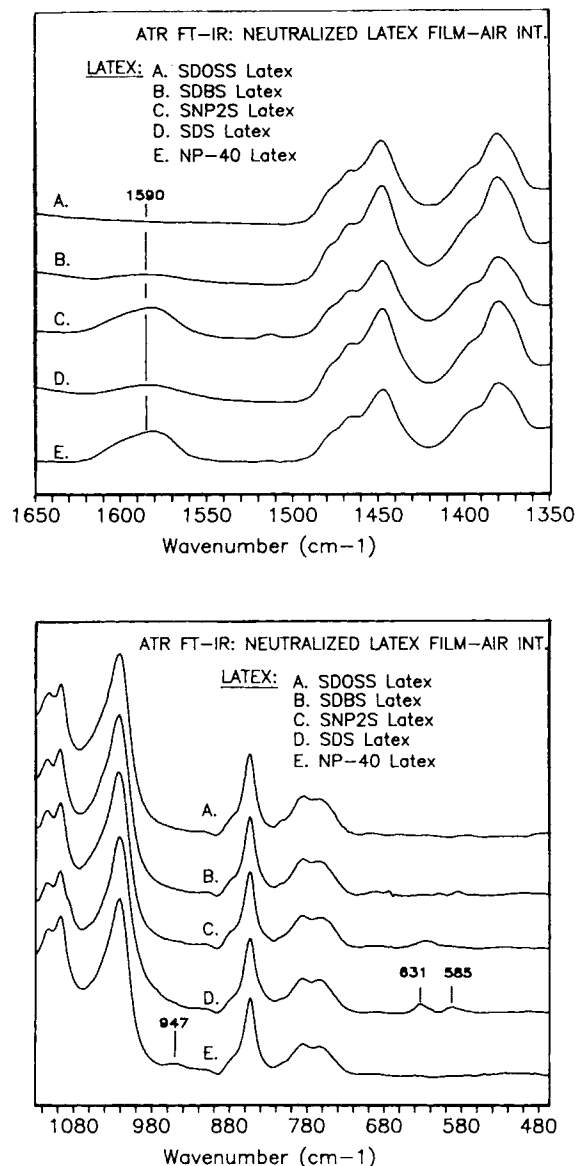
substrate interface relative to the film-air interface [Fig. 2(a), D]. Similarly with the film-air interface, the nonionic surfactant NP latex shows the same spectral features at the film-substrate interface [Fig. 2(b), E], indicating similar surfactant enrichment at both interfaces.

Having established the main features of both interfaces, one would like to address the question of how the structural differences between surfactants

may affect their mobility within the latex and what forces govern their behavior. As has been suggested earlier, the formation of polymer-surfactant complexes<sup>5</sup> may affect the copolymer-surfactant compatibility, and, therefore, a classification of surfactants into penetrating and nonpenetrating types has been identified. Such a division has been furnished for vinyl acetate/vinyl acrylic (PVAc) copolymer latices.<sup>6</sup> In this particular system, the increased polarity of the latex copolymer was achieved with an increased concentration of vinyl acetate, which, in turn, induced the penetration of anionic surfactant into the latex particle. The basis for such assessments had foundation in the increased viscosity of the latex, attributed to the formation of polyelectrolyte-type solubilized polymer-surfactant complexes. It was theorized that for the PVAc latices<sup>7</sup> polymer chains may uncoil and acetyl groups are pushed into the aqueous phase where surfactant readily adsorbs onto the particles through hydrophobic interactions, leading to increased solubility of these segments. The penetration of the surfactant was found to be dependent upon a critical size, charge density at the polymer-surfactant interface and a shape conducive toward penetration. In contrast, the concentration of nonionic surfactants at the polymer-water interface was found to decrease with the increasing polarity, while, at the same time, inhibiting penetration by anionic (penetrating) surfactants in mixed systems.

In view of the above considerations, and considering the spectroscopic results presented in Figure 2(a) and 2(b), one would like to establish how the behavior of various surfactants during coalescence can be modified by altering the polarity of an existing latex particle. The increased polarity of the nonionic surfactant stabilized latex should result in the increased surfactant concentration in the aqueous phase and, subsequently, lead to the increased exudation through the film since, under such circumstances, more surfactant may be displaced from the surface of the latex particle. On the other hand, for anionic surfactant stabilized latices, one would expect a decrease of exudation as a result of the formation of polyelectrolytic-type solubilized polymer-surfactant complexes. Following this approach, one way to modify copolymer/surfactant interactions is to increase the polarity of the latex containing carboxylic acid functionality<sup>8</sup> by the addition of base (NaOH), neutralizing the carboxylic acid groups, and subsequent formation the corresponding carboxylate groups.

The film-air interface infrared spectra of the neutralized latex films are presented in Figure 3(a)



**Figure 3** (a) ATR FTIR spectra in the 1650 to 1350  $\text{cm}^{-1}$  region recorded at the film-air interface of neutralized latex films; (A) SDOSS latex, (B) SDBS latex, (C) SNP2S latex, (D) SDS latex, and (E) NP latex. (b) ATR FTIR spectra in the 1135 to 480  $\text{cm}^{-1}$  region recorded at the film-air interface of neutralized latex films; (A) SDOSS latex, (B) SDBS latex, (C) SNP2S latex, (D) SDS latex, and (E) NP latex.

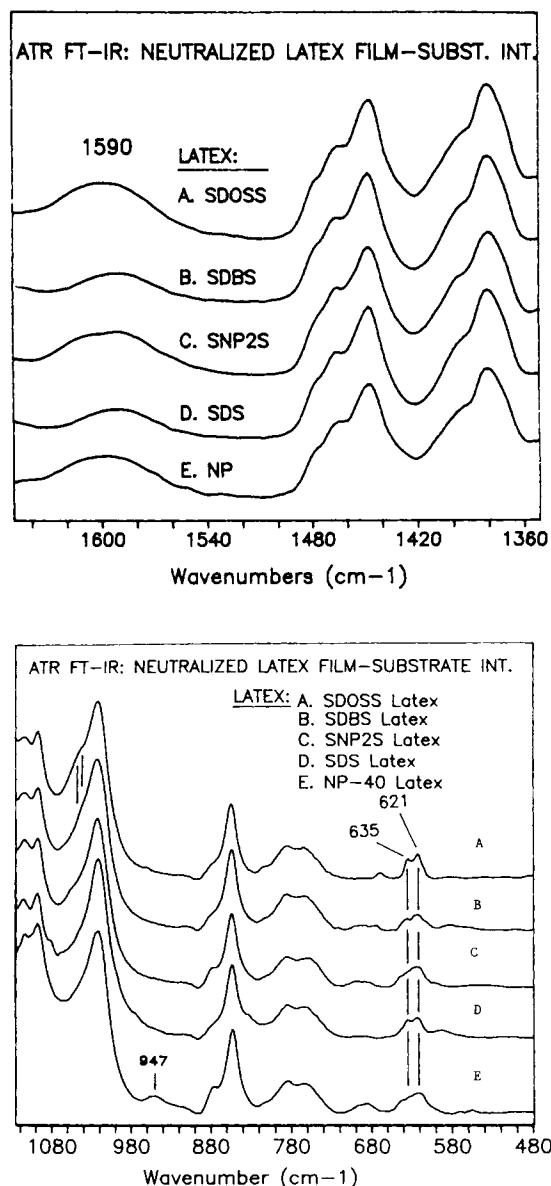
and 3(b). Neutralization of the carboxylic acid groups in the copolymer is verified by the presence of the band at 1590  $\text{cm}^{-1}$ , assigned to the C—O stretching vibrations of carboxylate groups ( $\text{COO}^-$ ). Figure 3(b) illustrates the same film-air interface spectra in the 1140 to 480  $\text{cm}^{-1}$  region. The SDOSS, SDBS, and SNP2S latex film spectra (traces A, B, and C, respectively) do not display the previously

detected [Fig. 2(a) and 2(b)] bands in the 700 to 550  $\text{cm}^{-1}$  region, characteristic of the respective surfactants. However, the neutralized SDS latex spectrum (trace D) exhibits two weak bands at 631 and 585  $\text{cm}^{-1}$ , attributed to the S—O bending mode of the sulfate group. This observation indicates that the exudation to this interface is similar to that of the nonneutralized SDS latex film. This is not surprising in view of the previous studies,<sup>9,10</sup> which pointed out a significantly lower compatibility of SDS in acrylic latex systems. Similarly with the film-air interface of the nonneutralized latex films [Fig. 2(a)], the NP latex spectrum (E) exhibits the band at 947  $\text{cm}^{-1}$  due to the C—O stretch of ethylene oxide groups in the surfactant, indicating the presence of nonionic surfactant at the film-air interface. Apparently, surfactant exudation does not occur in the neutralized latex films.

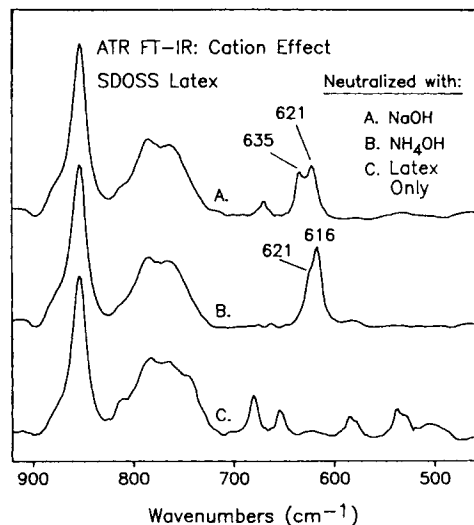
The spectra of the film-substrate interface of the neutralized latices are presented in Figure 4(a) and 4(b). Again, the neutralization of the carboxylic acid groups is verified by the presence of a band at 1590  $\text{cm}^{-1}$ , as shown in Figure 4(a). Figure 4(b) illustrates the same spectra in the 1100 to 480  $\text{cm}^{-1}$  region. Although the bands characteristic of the SDOSS surfactant at 1056, 1046, and 581  $\text{cm}^{-1}$  were detected in the nonneutralized latex spectrum [Fig. 2(b), trace A], their presence is not observed in the neutralized latex film spectrum [Fig. 4(b), A]. Similar results are obtained for all the neutralized anionic surfactant latex films (Fig. 4, B–D). In view of the above results, the mobility of the anionic surfactants changes with neutralization. Surfactant enrichment at either the film-air or film-substrate interfaces is no longer observed, indicating that the surfactant remains dispersed within the polymer network. In contrast, the nonionic surfactant latex spectrum still exhibits the band at 947  $\text{cm}^{-1}$ , assigned to the C—O stretch of the ethylene oxide groups of the surfactant. It should be noted that this band remains intact even after attempts to remove the nonionic surfactant from the film surface, including significant abrasion of the film that resulted in removal of surface layers of polymer.<sup>1</sup> Hence, in this case, the distribution of nonylphenol ethylene oxide is most likely continuous and uniform throughout the film. Such behavior suggests strong hydrophobic interactions between the copolymer and surfactant. Therefore, even with the increased polarity of the copolymer, no detectable concentration differences at either interface are observed.

As illustrated in Figure 4(b), all film-substrate spectra of the neutralized latex films exhibit the bands at 635 and 621  $\text{cm}^{-1}$ . Although these bands

may be tentatively assigned to wagging vibrations of the long-chain  $\alpha$ -methyl carboxylic acid salts, in an attempt to verify this assignment, ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) was used as the neutralizing agent. The results for the neutralized SDOSS latex spectra are presented in Figure 5. The NaOH neutralized SDOSS latex film spectrum (trace A) ex-



**Figure 4** (a) ATR FTIR spectra in the 1650 to 1350  $\text{cm}^{-1}$  region recorded at the film-substrate interface of neutralized latex films; (A) SDOSS latex, (B) SDBS latex, (C) SNP2S latex, (D) SDS latex, and (E) NP latex. (b) ATR FTIR spectra in the 1135 to 480  $\text{cm}^{-1}$  region recorded at the film-substrate interface of neutralized latex films; (A) SDOSS latex, (B) SDBS latex, (C) SNP2S latex, (D) SDS latex, and (E) NP latex.

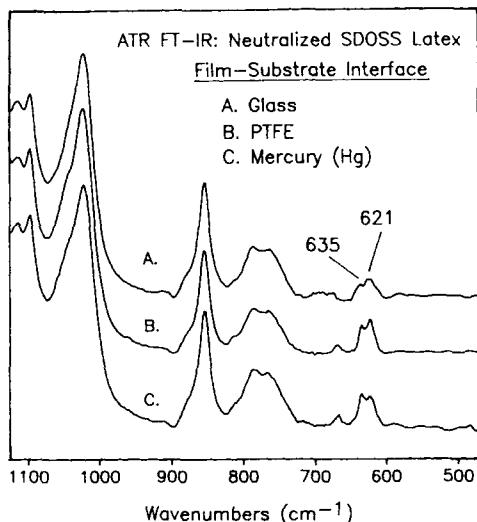


**Figure 5** ATR FTIR spectra in the 920 to 450  $\text{cm}^{-1}$  region of the SDOSS latex films neutralized with NaOH and  $\text{NH}_4\text{OH}$ : (A) NaOH, (B)  $\text{NH}_4\text{OH}$ , and (C) latex.

hibits two bands at 635 and 621  $\text{cm}^{-1}$ , whereas the same latex neutralized with  $\text{NH}_4\text{OH}$  shows two bands but at 621 and 616  $\text{cm}^{-1}$  (trace B). Since the sodium ion has a more localized positive charge than does the  $\text{NH}_4^+$  ion, it is more electropositive and increases the force constant of the carbon-oxygen bond of the carboxylate group, giving rise to higher vibrational frequencies.

To establish the effect of substrate on the exudation process, neutralized latex films were deposited on various substrates. Figure 6 illustrates the neutralized latex spectra of the films prepared on glass, PTFE, and liquid mercury substrates. As seen, all spectra have similar features, indicating that the effect is not substrate related. It should be noted that the presence of carboxylate groups is observed only at the film-substrate interface and, most likely, results from the increased hydrophilicity of the salt groups. It is possible that during coalescence, the increased hydrophilicity of the salt groups provides a driving force to remain in the aqueous phase that exists at the film-substrate interface longer than at the film-air interface because diffusion of water out of the film is slowest at the film-substrate interface.

Since neutralization of the latex modifies the exudation behavior of surfactant, as evidenced by the lack of surfactant enrichment at both the film-air and film-substrate interfaces of the neutralized latex films after coalescence, the neutralization processes may trap the surfactant in latex in the following manner. The neutralization of the copolymer acid functionality causes swelling of the latex particles



**Figure 6** ATR FTIR spectra in the 1135 to 480  $\text{cm}^{-1}$  region recorded at the film-substrate interface of neutralized SDOSS latex films prepared on different substrates; (A) glass, (B) PTFE, and (C) mercury (Hg).

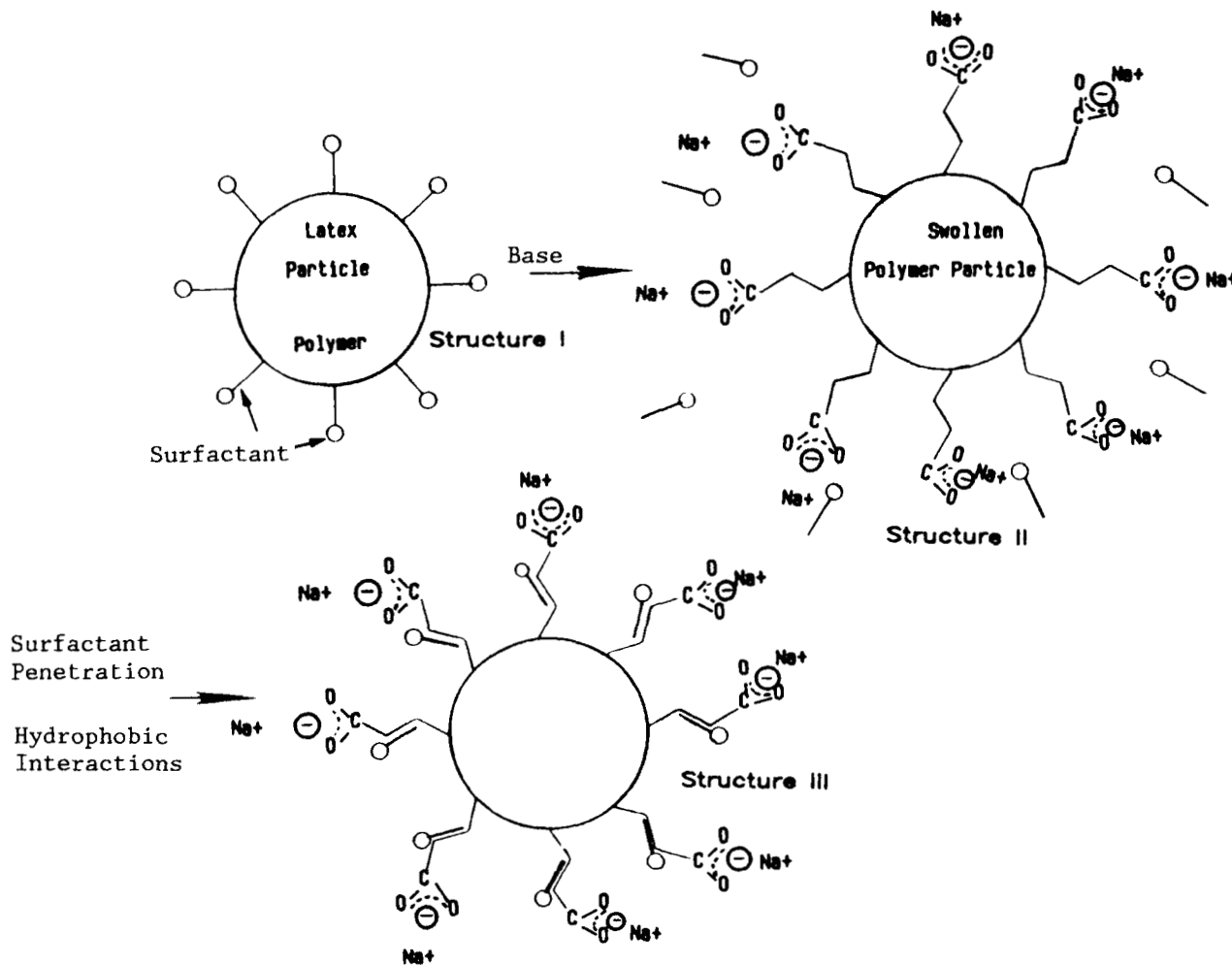
by water due to the increased solubility brought on by the formation of carboxylate groups. The viscosity of the resulting emulsion increases with the increasing pH (8–9)<sup>11</sup> due to the increased hydrodynamic volume of the particles brought on by chain extension.<sup>12</sup> As a result of the chain extension, hydrophobic ethyl groups, pendant on the copolymer chain, will be pushed out into the aqueous phase. At this point, nonadsorbed surfactant in the aqueous phase may adsorb at the polymer-water interface through hydrophobic interactions to form solubilized polymer-surfactant complexes. In contrast, if the neutralization leads to the displacement of surfactant molecules from the particle surface into the aqueous phase, as has been suggested earlier,<sup>13</sup> one could conceive of a higher concentration of surfactant in the aqueous phase of a neutralized latex than that of a nonneutralized latex. Under such circumstances, enhanced surfactant exudation to both interfaces would be observed since the surfactant would be capable of diffusing through the latex film with the water flux out of the film. However, this is not the case, and the exudation of anionic surfactants in neutralized latex films appears to be inhibited. As indicated above, this behavior is opposite to the nonneutralized, anionic surfactant stabilized latex films that exhibit significant surfactant exudation.

Based on the spectroscopic changes depicted in Figures 3(b) and 4(b), the neutralization of the latex acid functionality leads to the increased compatibility of anionic surfactants with the copolymer

latex films. Since it is conceivable that the surfactant is not displaced from the particle surface as a result of neutralization of the acid functionality, such behavior would result in the lower surfactant concentration in the aqueous phase. However, another possibility is that as carboxylic acid groups are neutralized and the latex particles are swelled by the aqueous phase then the water soluble surfactant is desorbed and resides in the aqueous phase. At this point, chain extension proceeds further, and water diffuses into the polymeric network. The surfactant, being in the aqueous phase, penetrates into the particle and forms the previously discussed polymer/surfactant complexes that become buried in the latex film during coalescence. Figure 7 illustrates the proposed mechanism of anionic surfactant penetration in the neutralized latices. Structure I represents the nonneutralized latex particle in solution and stabilized by adsorbed anionic surfactant at the polymer-water interface. Structure II depicts the particle upon neutralization with the surfactant being initially displaced from the particle surface as the solubilized polymer chains extend into solution. Structure III illustrates the adsorption of surfactant onto the hydrophobic segments of the polymer. This mechanism explains the lack of surfactant enrichment observed at the film-air and film-substrate interfaces of the neutralized latex films. The compatibility of the surfactant may be enhanced by the presence of sodium carboxylate groups that increases the polarity of the copolymer and thus facilitates the proposed ionic associations.<sup>14</sup> These associations may be further increased by the presence of bound water that has been shown to play a significant role in the sodium and potassium salts of poly(acrylic acids).<sup>15</sup>

At this point, it is appropriate to bring the proposed mechanism of compatibility into perspective. Let us first note that, according to Vijayendran et al.,<sup>6</sup> SDS, SDBS, SDOSS, and SNP2S surfactants can be classified as penetrating the latex network because of their relatively low molecular weights (< 500) as compared with the molecular weights of some nonpenetrating anionic surfactants (> 1500) including the nonionic NP. If these surfactants are able to penetrate the latex particles, they will maintain or most likely will exhibit lower concentration levels in the aqueous phase. Second, it should be noted that the penetration of latex particles by anionic surfactants in the nonneutralized films cannot be precisely determined due to the high degree of exudation occurring in the latex films. As will be shown later on,<sup>16</sup> elongation studies indicate that the surfactant is trapped within the polymer film





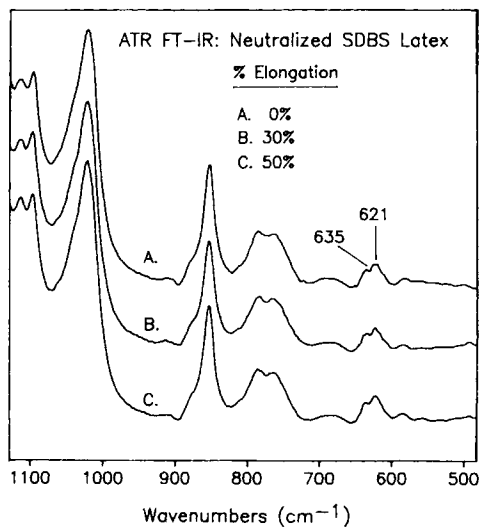
**Figure 7** Schematic representation illustrating a latex particle (Structure I), neutralization of the latex particle (Structure II), and surfactant penetration into the neutralized latex particle (Structure III).

matrix and can be easily forced to either the film-air or film-substrate interfaces by elongating the film. Although this observation indicates some degree of incompatibility, this is not the case for the neutralized latex films. As illustrated in Figure 8, the intensities of the bands at 635 and 621  $\text{cm}^{-1}$ , previously assigned to the presence of  $\alpha$ -methyl carboxylate groups, are not affected by elongation of the film by 30% and 50%, indicating no surfactant enrichment at the surface. Similar results were obtained for all other surfactants. Based on these experiments, it is apparent that the neutralization process inhibits exudation of the surfactants due to increased compatibility with the copolymer.

In contrast to anionic surfactants, the neutralized nonionic surfactant films exhibit no changes in the surfactant behavior. In all cases, irrespective of the interface or neutralization, similar amounts of sur-

factant are present at both interfaces. This is most likely attributed to the high propensity for favorable interactions of hydrophobic groups with the copolymer because of the high concentration (96%) of ethyl acrylate monomer in the system. The absence of ionic hydrophilic groups in the nonionic surfactant along with its relatively high molecular weight ( $\text{MW} = 1980$ ) inhibit its penetration into the latex copolymer matrix and, ultimately, prevents the formation of solubilized polymer-surfactant complexes. Therefore, the surfactant remains adsorbed on the latex particle surface or dispersed in the aqueous phase where later on it may re-adsorb on the polymer/water interface during coalescence.

Based upon these results, it is apparent that favorable interactions between hydrophobic groups of the surfactant and the copolymer influence surfactant exudation in the latex film. Although the non-



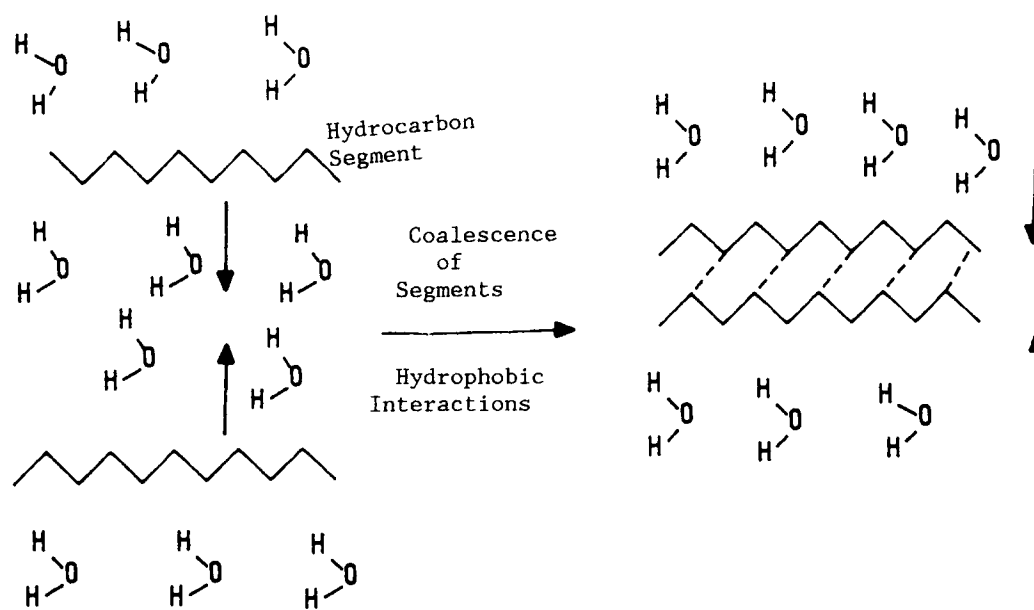
**Figure 8** ATR FTIR spectra in the 1135 to 480  $\text{cm}^{-1}$  region for the film-substrate interface of the neutralized SDBS latex film as a function of elongation; (A) 0% elongation, (B) 30% elongation, and (C) 50% elongation.

neutralized latex films exhibit exudation of surfactant since free surfactant is present in the aqueous phase or can be expelled from the latex particle surface during coalescence, some degree of interaction between the surfactant and the copolymer at the copolymer particle interface cannot be ruled out. However, neutralization of the carboxylic acid groups in the copolymer forces hydrophobic polymer

segments into the aqueous phase, which further increases the opportunity for favorable interactions along with the formation of polymer-surfactant complexes, ultimately inhibiting surfactant exudation.

Since interactions between hydrophobic groups influence the mobility of the surfactants under different coalescence conditions, it is important to realize the factors governing such interactions. Adamson<sup>17</sup> has pointed out the importance of long-range forces between particles in colloidal solutions. For example, two hydrocarbon segments placed far apart in an aqueous phase, each possessing a water-hydrocarbon interfacial surface free energy,  $\gamma$ , will have  $2\gamma$  surface energy. If these segments come into contact such as illustrated in Figure 9, the  $2(\gamma)$  interfacial surface free energy is lost. This is translated into a gain of  $2\gamma$ , driving the segments together. Once the particles become sufficiently close, van der Waals and London dispersion forces induce additional interactions that lead to the increased compatibility.

It is now appropriate to address the issue of the effect of the chemical structure of the surfactants on the exudation behavior in EA/MAA latex films. As opposed to nonionic surfactants, and in the absence of neutralization, the anionic surfactants with ionic hydrophilic groups exhibit significant exudation during latex coalescence. This is attributed to the relatively low molecular weight (size), which



**Figure 9** Schematic representation illustrating hydrophobic interactions between hydrocarbon segments.

provides greater mobility and high water solubility due to the ionic groups allowing the surfactant to diffuse through the aqueous phase. The nonionic surfactants, however, have lower water solubility than do the anionic surfactants, and, therefore, a greater driving force exists for favorable interactions between alkyl groups as well as ether functional groups. These groups are capable of interacting with carboxylic acid groups to form hydrogen bonds that increase the surfactant tendency to adsorb on the polymer particle surface. Since there is no significant difference in mobility between the SDOSS and SDBS in the neutralized latex films, it seems that the number of hydrophobic alkyl tails is not a dominating factor in the latex particle penetration. However, further studies are needed to establish the effect of increasing the number of hydrophobic tails in anionic surfactants on the exudation in latex films.

## CONCLUSIONS

The exudation of anionic surfactants in the ethyl acrylate/methacrylic acid copolymer latex films is inhibited in neutralized latex films. This behavior is attributed to the increased compatibility as a result of surfactant penetration into the swollen latex particle followed by the formation of solubilized polymer-surfactant complexes through adsorption of surfactant onto the hydrophobic polymer segments. In contrast, the nonionic surfactant latex does not exhibit surfactant enrichment at either interface, regardless of the conditions employed. The effect of neutralization of the carboxylic acid groups in the EA/MAA latices on the exudation of anionic surfactants in the EA/MAA latex films suggests the formation of hydrophobic interactions that preclude

surface tension effects in the coalescing films and prevent surfactant enrichment at either interface.

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