Surface and Interfacial FT–IR Spectroscopic Studies of Latexes. VII. EA/MAA Latex Suspension Stability and Surfactant Migration

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SYNOPSIS

This article, part VII in a series of latex studies, focuses on the effect of ethyl acrylate/methacrylic acid (EA/MAA) latex stability on the exudation of sodium dioctyl sulfosuccinate (SDOSS) surfactant molecules after coalescence. It is found that "aging" of the latex aqueous suspension causes excessive exudation of the surfactant molecules to the film–air interface. Upon exudation to the surface, the surfactant SO_3^- Na^+ hydrophilic heads assemble in preferentially normal-to-the-surface directions, whereas hydrophobic aliphatic tails are randomly burred in the latex surface. ATR FT–IR spectroscopy and a particle size analysis are utilized to elucidate the effects of flocculation and coalescence on the surfactant mobility in latex films. It appears that flocculation, prior to coalescence, enhances exudation and mobility of the surfactant molecules. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The utilization of latex-based polymer systems is undeniably influenced by the presence and ultimate fate of synthetic emulsifiers, along with other low molecular weight additives, which are commonly used in latexes. While their presence in many cases appears to be essential, the ultimate distribution of these species may influence both bulk and interfacial properties. In earlier reports, several polymer/surfactant environments were postulated,[1–4] but were never experimentally investigated in the context of coalescence processes that were responsible for latex film formation. To fill this gap, three extreme situations are considered: (A) the surfactant is incompatible with the copolymer latex and remains as an independent mobile entity at the interfaces between incompletely coalesced latex particles,[1–3] (B) the surfactant is highly compatible with the copolymer latex and dissolves within the polymer particles,[1–3] or (C) the surfactant and polymer may exist in an interpenetrating network, in which there is mutual interdiffusion of the two phases, but still a certain degree of inhomogeneity.[4] While these differences may clearly influence bulk characteristics, possible exudation of the surfactant, and subsequent effects on adhesion and other properties, polymer and surfactant structure, along with their mutual compatibility, are those factors that may influence the nature of the surfactant distribution.[5–10] The effect of external driving forces, such as substrate surface tension and mechanical elongation, have also been identified.[11] It has been established as well that hydrogen bonding between the surfactant and the copolymer acid functionality may play a significant role, and these interactions are often influenced by temperature and water vapor.[12,13]

While these factors may influence surfactant behavior, and the ultimate surfactant distribution within the film and at the film–air (F–A) and film–substrate (F–S) interfaces, it is also important to consider the transient stability of the aqueous suspension of latex particles. For example, issues that have not previously been addressed are the processes prior to latex coalescence, such as flocculation of an aqueous suspension. In view of these considerations and the previously reported data, it is essential to differentiate between surfactant molecules adsorbed

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on the surface of the suspended latex particles and the surfactant excess found in the aqueous phase. The latter is particularly relevant to latex–surfactant compatibility and the way in which these species behave in the latex suspension. In this study, we will examine the changes that occur in ethyl acrylate/methacrylic acid (EA/MAA) latex suspensions and its counterpart in a form of coalesced films.

EXPERIMENTAL

Detailed procedures involving latex synthesis[7-12] and film preparation,[11] along with spectral data acquisition and analysis,[13] were reported previously. Following synthesis, aging of the ethyl acrylate/methacrylic acid/sodium dioctyl sulfosuccinate (EA/MAA/SDOSS) latex suspensions was conducted at room temperature for the storage periods ranging from 3 to 70 days. All films were analyzed spectroscopically, 72 h after deposition on a polytetrafluoroethylene (PTFE) substrate. Characterization of a mean latex particle size was accomplished using a Coulter N4S light scattering instrument (Coulter Electronics). A Specac 12000 IR polarizer was used to obtain polarized ATR FT–IR spectra.

RESULTS AND DISCUSSION

Surfactant Exudation and Latex Suspension Stability

As a starting point, let us first consider ATR FT–IR spectra acquired from coalesced latex films, prepared at various times after latex synthesis. As noted in the experimental section, all films were examined 72 h after deposition and the variable of interest is the time period from the latex synthesis to film deposition. Figure 1 shows the spectra collected from the film–substrate (F–S) interface of EA/MAA. Traces A, B, C, and D are the spectra of films prepared on a PTFE substrate 3, 50, 60, and 70 days after synthesis, respectively. Examination of the previously identified bands at 1046 and 1056 cm^{-1}, assigned to the S–O symmetric modes of the surfactant sulfonate groups,[12] clearly reveals an increased degree of surfactant exudation over a period of time. If one considers the spectra shown in Figure 2, which were recorded at the F–A interface, qualitatively similar but more pronounced changes are revealed. Again, a progressive increase of the degree of surfactant enrichment is observed while proceeding from 3 (trace A) to 70 days (trace D). At both

interfaces, the most significant changes began to occur only after about fifty days of "aging."

Before attempting to explain the observed behavior, the results of the ATR FT–IR depth profiling experiments are presented. Figure 3 shows the results acquired at the F–A interface for the latex film aged for 3 days. As the nominal ATR angle is varied from 45 to 60°, a steady increase of the surfactant bands at 1046 and 1056 cm^{-1} is observed. This result indicates that the concentration of surfactant increases near the interface, and it appears that the primary locus for surfactant assembly is at or near the interface. Because similar qualitative behavior is observed for the other latex films, it is believed that the surfactant enrichment observed in these spectra is primarily a surface phenomenon.

The results presented above also indicate that the detected changes within the latex suspension occur over an extended period of time. Because such a stability-related phenomenon is of a great fundamental and practical interest, this behavior is considered in conjunction with experimentally determined particle size analysis, acquired via light scattering. Table I summarizes three mean particle sizes obtained from the EA/MAA/SDOSS latex over the time of study. It is apparent that there is a significant increase of the mean particle size over the examined time period and, although the employed light scat-
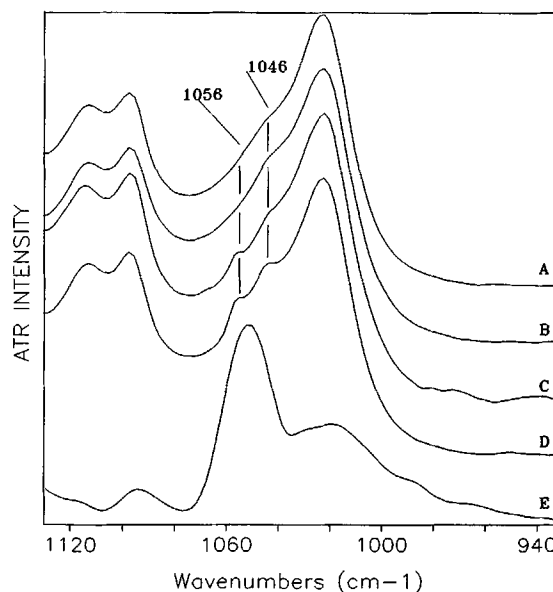

Figure 1 ATR FT–IR spectra in the 930–1130 cm^{-1} region, recorded at the F–S interfaces of latex films, prepared on PTFE after various periods of aging. (A) 3 days, (B) 50 days, (C) 60 days, (D) 70 days, and (E) neat SDOSS surfactant.
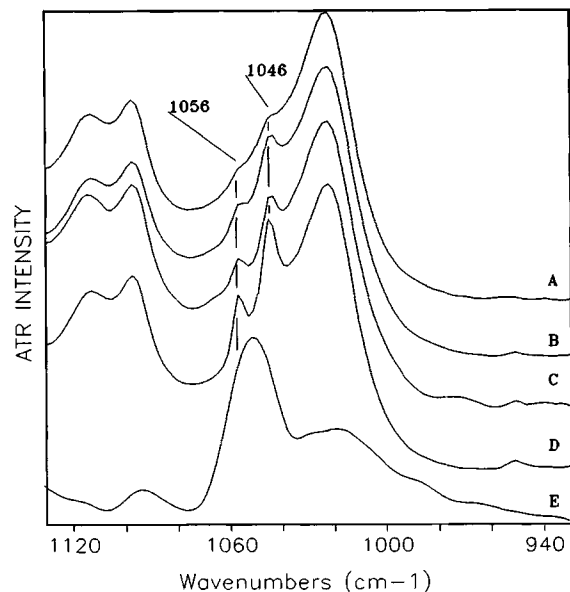
Figure 2 ATR FT–IR spectra in the 930–1130 cm^{-1} region, recorded at the F–A interfaces of latex films, prepared on PTFE after various periods of aging. (A) 3 days, (B) 50 days, (C) 60 days, (D) 70 days, and (E) neat SDOSS surfactant.

tering instrumentation does not provide a highly accurate particle distribution, the data indicate that the degree of particle flocculation increases by about 50% as the suspension is aged from 3 to 70 days.
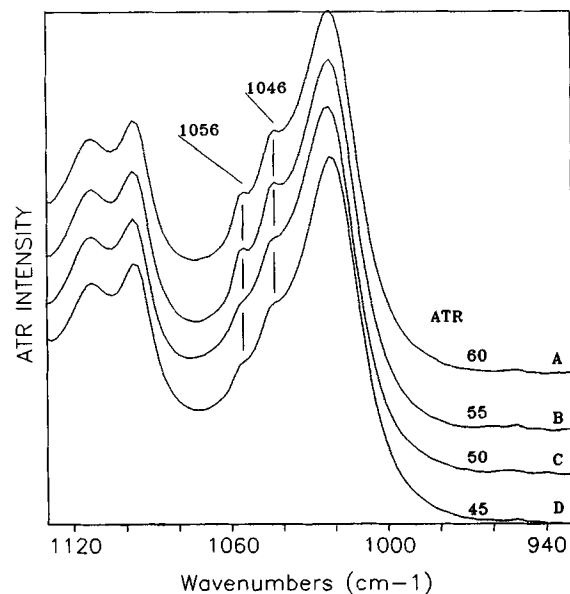

Figure 3 ATR FT–IR spectra in the 930–1130 cm^{-1} region, recorded as a function of nominal ATR angle at the F–A interface of a latex film, prepared on PTFE after 3 days of aging. (A) 60° ATR angle, (B) 55° ATR angle, (C) 50° ATR angle, and (D) 45° ATR angle.
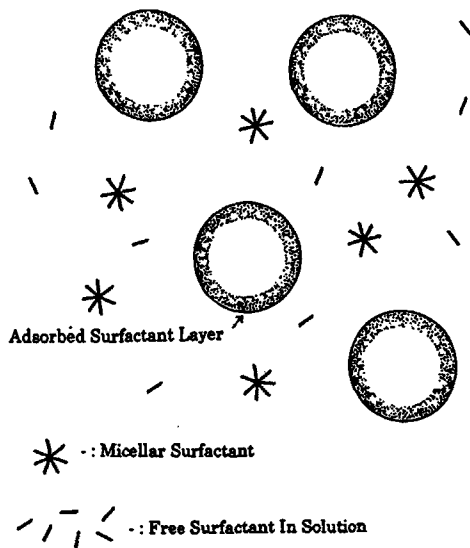
Table I   Results of Mean Particle Size Analysis Performed on the EA/MAA/SDOSS Latex Suspension over a Period of 70 Days Aging[a]

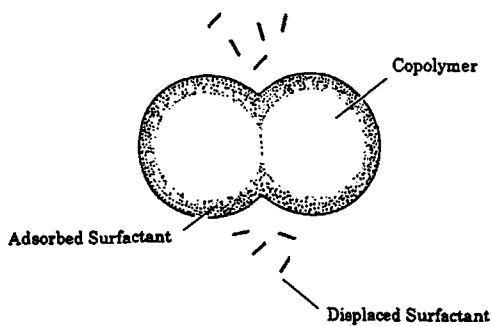| Aging Time (Days)	Mean Particle Size (nm)
3	110
50	130
60	153
70	165

[a] Particle size analysis performed with a Coulter N4S light scattering instrument.

At this point it is appropriate to correlate the increasing particle size, resulting from latex particle flocculation, with the increased degree of surfactant exudation. This analysis indicates that more extensive exudation is detected for a higher degree of flocculation. Having established this relationship, let us consider implications that the observed phenomenon may have on the mechanisms of film formation and flocculation. As a starting point, let us consider the initial latex suspension and analyze the distribution of the surfactant molecules across the film. As depicted in Figure 4(A), the liquid latex consists of polymer particles suspended in the aqueous phase. A certain fraction of the surfactant molecules is adsorbed on the latex particles to serve as stabilizing agents, suspending them in the aqueous phase via electrostatic repulsions. However, in addition to the adsorbed surfactant molecules, a portion may exist in the aqueous phase, which can be visualized either in the form of micelle-like aggregates or discreet surfactant molecules. Let us now consider the fate of the adsorbed emulsifier when two latex particles come into contact. This situation will occur either during flocculation, as indicated by the particle size analysis data, or during coalescence. First, the behavior of particles forming a contact in aqueous phase will be analyzed. If the surfactant is displaced from the surfaces that form contact between two particles, the surfactant will migrate into the aqueous phase, such as is schematically depicted in Figure 4(B). There is also the possibility that the surfactant molecules may become initially trapped at the particle–particle interface when the particles come into contact. If this is the case, the distribution of latex particles may be envisioned by one of the three schemes referred to as (A), (B), and (C), which were outlined in the introduction. In the case of a highly incompatible polymer/surfactant system, the surfactant may remain as a separate phase, trapped at the interface between the particles,[1-3] such as is shown in Figure 4 (C). The other extreme
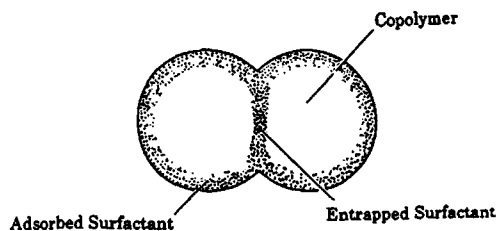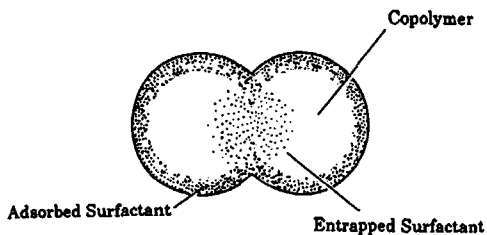
A. Latex Suspension - Surfactant Distribution

Adsorbed Surfactant Layer

✳ - : Micellar Surfactant

╱ ╱⁻╱ ╱ - : Free Surfactant In Solution

B. Flocculation With Surfactant Displacement

Copolymer

Adsorbed Surfactant

Displaced Surfactant

C. Flocculation With Surfactant Entrapment
- Surfactant Remains As Separate Phase

Copolymer

Adsorbed Surfactant

Entrapped Surfactant

D. Flocculation With Surfactant Entrapment
- Complete Interdiffusion of Surfactant

Copolymer

Adsorbed Surfactant

Entrapped Surfactant

E. Flocculation With Surfactant Entrapment
- Partial Interdiffusion of Surfactant

Copolymer

Adsorbed Surfactant
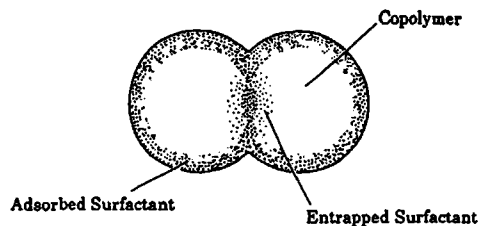
Entrapped Surfactant

Figure 4   Schematic representation of initial surfactant distribution within latex suspension and possible behavior of adsorbed surfactant upon particle collision. (A) Surfactant distribution in the aqueous phase, (B) particle flocculation with surfactant displacement, (C) particle flocculation with surfactant entrapment, surfactant remains as a separate phase, (D) particle flocculation with surfactant entrapment, partial surfactant–polymer interdiffusion.

is represented in Figure 4(D), where the surfactant and copolymer are highly compatible and a high degree of mutual interdiffusion occurs.[1-3] As a result, an essentially homogeneous interfacial region will be formed when two particles are in contact. The intermediate case, in which there is some degree of interdiffusion, may also be envisioned,[4] and this case is schematically depicted in Figure 4(E).

Let us now consider that a flocculated latex suspension is allowed to coalesce. If the flocculation process, prior to coalescence, has any effect on the film formation, and if the behavior of the initially adsorbed surfactant is the same for flocculation and coalescence, one would anticipate that the degree of surfactant exudation to the interfaces of the coalesced film would be essentially the same, regardless of the degree of flocculation occurring prior to the film deposition. For instance, if the surfactant molecules are displaced as a result of two particles coming into contact, one would expect that the amount of surfactant ultimately expelled into the aqueous phase, and thus made available for migration to the interfaces, would be similar, regardless of whether this expulsion occurred as a result of flocculation or coalescence. Similarly, if both processes trap most of the surfactant at the interface, this would also lead to essentially the same concentration of free surfactant at the interface.

The ATR FT-IR (Figs. 1-3) and light scattering results (Table I) appear to indicate that, in contrast to the latex particle intractions presented above, there is a significant difference in surfactant behavior when flocculation and coalescence are compared. The process of coalescence does not seem to yield the extent of exudation that is produced by allowing significant flocculation to occur prior to the film deposition. Indeed, the presented data suggest that flocculation leads to a significant degree of surfactant displacement that is not observed during coalescence: the process of flocculation apparently results in a considerable surfactant concentration increase in the aqueous phase, which is able to migrate to the interfaces of the deposited films.

Based on these considerations, we are in a position to address those factors that may distinguish the two processes. One factor that can be readily identified, and that requires further analysis, is the kinetics of the two processes. Flocculation is usually a relatively slow process, with a period of several weeks elapsing between the time of synthesis and the point at which significant macroscopic changes in the behavior of the latex can be detected. Coalescence, on the other hand, is a process measured in terms of hours. It is therefore possible that the slower flocculation process provides enough time for

effective displacement of the interfacial surfactant, whereas the more rapid coalescence results in much of the adsorbed surfactant being trapped in the interfacial regions and the bulk of the film, as the particles are drawn into contact. In addition to the kinetic factors of the two processes, there are also equilibrium adsorption considerations; namely, the adsorption area per surfactant molecule will be affected by the ionic strength of the aqueous phase. In the case of flocculation, the aqueous volume fraction remains essentially constant. In contrast, the evaporation of water, accompanying film formation, causes a significant increase in the total concentration of dissolved aqueous species, which include not only the initial amount of "free" surfactant, but also other ionic species, such as initiator fragments.

Thermodynamics considerations should be also taken into account. During flocculation, surfactant–copolymer compatibility will determine whether the surfactant molecules are more likely to be at the latex particles surface or in the water, such as is shown in Figure 4(A). If $\Delta G_{water-surf} < \Delta G_{copolymer-surf}$, surfactant will be displaced from the latex particle surface and its mobility will be determined by the kinetics of the water flux during coalescence. On the other hand, if $\Delta G_{water-surf} > \Delta G_{copolymer-surf}$, surfactant will not be easily displaced from the latex surface. Entropic and enthalpic factors that may most significantly affect free energy changes ($\Delta G = \Delta H - T\Delta S$). For two or more particles coming into contact during flocculation and coalescence, enthalpy of collision should be independent of environment because a collision of two particles requires the same amount of energy. In contrast, the entropic term may be different because the latex particles are more disordered in an aqueous dispersion, thereby have higher entropy. During coalescence, the entropy of the system is significantly diminished as the particles become packed together when water rapidly evaporates. Therefore, the entropy changes occur much faster, not allowing excessive surfactant exudation and displacement from the surface. In view of the above considerations, the differences of the rate of the entropy changes during flocculation and coalescence appear to have a major effect on the surfactant entrapment at the interfaces.

At this point, it is appropriate to bring our view of surfactant distribution during coalescence into the context of recent studies, which employed small angle neutron scattering to probe latex coalescence. Chevalier et al.[14] have recently shown that monodispersive latex particles, stabilized through the adsorption of ionic surfactants, will coalesce, after packing and deforming into polyhedral cells separated by thin hydrophilic layers or "membranes,"

only after the rupture and displacement of the membrane layers. The conclusion of this neutron scattering work is that "displacement," in this sense, is a necessary precursor to polymer–polymer contact and coalescence. In light of this apparent contradiction with our work, which suggests the possibility of a degree of surfactant entrapment, it is necessary to consider both viewpoints and to reexamine the relevant experimental and terminological differences.

The first issue to consider is the difference between the latex systems examined. In the neutron scattering studies,[14] a 50 : 50 butyl acrylate/styrene (BA/S) system was employed, while the present study is concerned with an EA/MAA system. Additionally, the surfactants employed in the two studies are different. We have previously shown[7-10] that the surfactant–copolymer compatibility, as indicated by the degree of surfactant exudation observed at the film interfaces, can be significantly influenced by copolymer and surfactant structure. Interestingly enough, we have recently examined BA/Sty/MAA/SDOSS latexes[15] and these results indeed indicate a high degree of incompatibility between styrene and the surfactant, which results in considerable exudation of surfactant to the film interfaces, regardless of whether flocculation is a precursor to film preparation or not. A high degree of surfactant–copolymer incompatibility is in agreement with the view that the surfactant present between two latex particles must be largely, if not completely, displaced before significant interdiffusion of the polymeric particle segments may occur.

A second issue to be considered is the matter of terminology with respect to the interpretation of the experimental results. For the purposes of the present study, the terms "displacement" or "expulsion" of surfactant, during processes involving particle–particle contact, indicates migration of the surfactant to a mobile aqueous phase, which facilitates exudation to the film interfaces. For the latter, undeniable experimental data exists.[7-12] Similarly, we have outlined "entrapment" as any process that results in the surfactant being buried within the bulk of the film, regardless of the degree of polymer–surfactant interdiffusion. On the other hand, the cited studies[15] focused on particle–particle interfaces. They accordingly defined "expulsion" as displacement of surfactant from the locus of particle–particle interdiffusion, regardless of whether such "expelled" surfactant is exuded to the film interfaces or remains within the film as an inhomogeneous phase. Indeed, the use of the term "displacement," from the polymer–polymer interfaces, resulting in the migration

of surfactant into inhomogeneous interstices within the bulk of the film, is entirely consistent with one of our proposed "entrapment" mechanisms, understood such that there is little or no polymer–surfactant interdiffusion and that the surfactant remains essentially segregated as separate domains, which are surrounded by a coalesced polymer network. In light of the conflicting terminology, this behavior is perhaps most accurately characterized as microscopic displacement, defined as the displacement from the actual interface of polymer–polymer contact, which results in macroscopic entrapment, that is, segregation of the surfactant into a separate bulk phase.

Considering the more detailed nature of the surfactant distribution within the coalesced films, it is appropriate to address the effect of "entrapment" that is observed within the bulk of EA/MAA/SDOSS latex films. The issue is whether the non-exuded surfactant can interdiffuse within the copolymer matrix, leading to a highly homogeneous film or, if this surfactant is indeed present in the form of a separate phase, with regions of surfactant trapped between incompletely coalesced latex particles. Our previous studies have shown that elongation of the films, prepared from latexes synthesized with SDOSS and other anionic surfactants, can lead to an appreciable increase in the degree of interfacial surfactant enrichment.[10] This behavior would seem to be consistent with the view that the surfactant does indeed reside in nonhomogeneous interstices within the bulk of the film. However, such ready mobility would not be anticipated if there were a high degree of mutual surfactant–copolymer interdiffusion. Despite these observations, it can not be explicitly determined that the microscopic surfactant displacement, that is, the displacement from the actual interfaces between two particles in contact, is a mandatory prerequisite to polymer–polymer interdiffusion. In fact, our elongation studies[11] have shown that a more compatible nonionic surfactant, a nonylphenol ethylene oxide adduct with 40 ethylene oxide units, would not exude to the film interfaces. This behavior suggests a greater degree of surfactant–polymer interdiffusion, resulting from higher compatibility, due to a more negative $\Delta G_{copolymer-surf}$.

Orientation of Interfacial Surfactant

Although we have assessed the assembly of surfactant at the interfaces of latex films and have focused on how the magnitude of assembly may be influenced

by suspension stability and other factors, a remaining issue is the nature of the interfacial assembly of surfactant. Specifically, whether or not the surfactant may adopt a particular orientation with respect to the film interfaces will be examined. We have previously identified the significant orientation of acid dimeric species assembled at the F–S interface of EA/MAA latex films prepared on mercury,[15] and, at this point, it is appropriate to determine whether polarized ATR FT–IR experiments can provide the orientation information for the surfactant molecules as well.

To begin this analysis, let us temporarily return to Figure 1 of Part VI of these series and consider the basic polarized ATR FT–IR setup, as shown in Figure 1.[16] While the pertinent experimental considerations and limitations have been discussed previously,[16] it is appropriate to note that the two mutually perpendicular polarizations have their electrical vector parallel to the film plane for TE polarization, and perpendicular to this plane in the case of TM polarization. The spatial direction of the two polarizations thus allows us to distinguish between the dipole moment changes, lying in the film plane, and those oriented perpendicular to the plane.

Let us consider the F–A latex spectra that were recorded at various time intervals from synthesis to coalescence using polarized light. Figure 5 compares the TE and TM polarized ATR FT–IR spectra (traces A and B, respectively), acquired from the
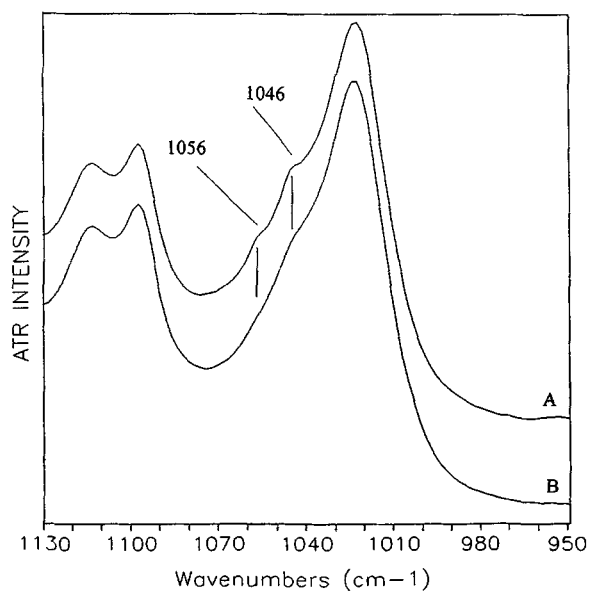
Figure 6   ATR FT–IR spectra in the 930–1130 cm^{-1} region, recorded as a function IR polarization at the F–A interface of a film, prepared on PTFE after 70 days of aging. (A) TE polarization and (B) TM polarization.
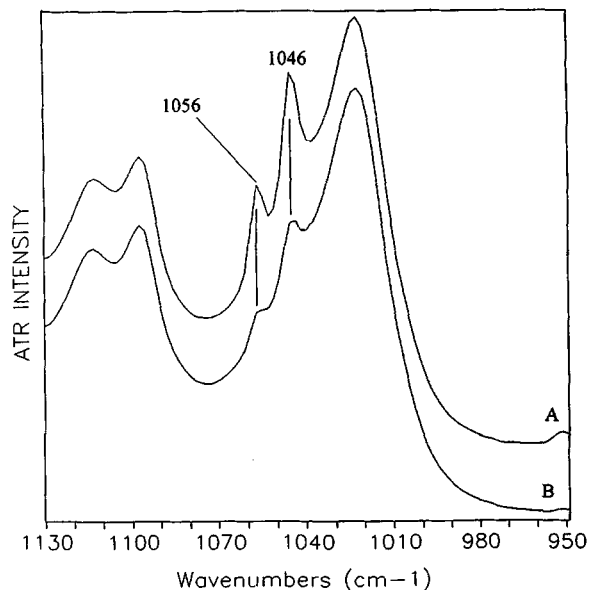
F–A interface of films prepared after three days of aging. As was seen previously, the degree of enrichment observed for the "freshly" synthesized latex is marginal, but a detectable enhancement of both the 1046 and 1056 cm^{-1} bands is indeed observed in the TE-polarized spectrum (trace A).

The next question is whether or not a significant degree of orientation is maintained as the degree of surfactant assembly at the interface is increased. Figure 6 shows the corresponding ATR FT–IR spectra for a latex aged 70 days prior to film preparation. Again, a pronounced orientation dependance, with considerable enhancement of both surfactant bands, is detected with TE-polarizated light (trace A), thus indicating that SDOSS does maintain an appreciable degree of orientation upon assembly at the F–A interface, even when the interfacial surfactant concentration becomes high.

The presented polarized ATR FT–IR data enable us to obtain more detailed information about the interfacial surfactant assembly. If the F–A interface is a reference point, there are three possible ways in which the hydrophilic sulfonate groups may be assembled. These possibilities are depicted in Figure 7(A), (B), and (C). Based on the polarized ATR FT–IR data, case A (no particular preferential orientation) may be eliminated because the intensities of the 1056 and 1046 cm^{-1} bands decrease very substantially while progressing from TE to TM polarization. Thus, two possible arrangements, in which

Figure 5   ATR FT–IR spectra in the 930–1130 cm^{-1} region, recorded as a function IR polarization at the F–A interface of a film, prepared on PTFE after 3 days of aging. (A) TE polarization and (B) TM polarization.

Possible Sulfonate Group Orientation

A. Random:

B. S-O Bonds Predominantly In-Plane:
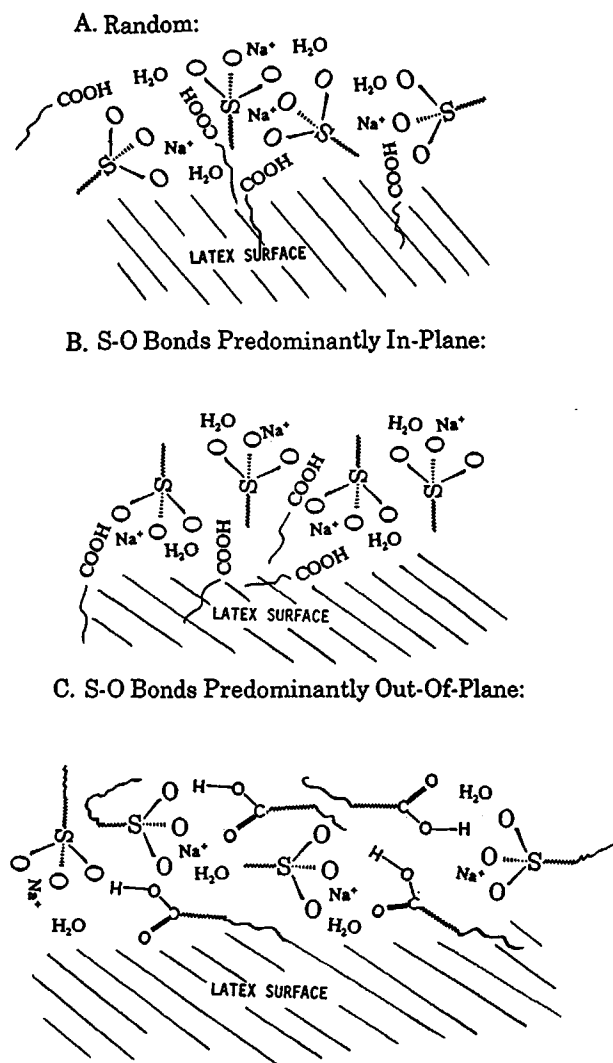

C. S-O Bonds Predominantly Out-Of-Plane:

Figure 7 Schematic depiction of possible orientations of surfactant sulfonate groups at the film interfaces. (A) Random orientation, (B) orientation with S — O bonds lying predominantly in-plane, and (C) orientation with S — O bonds lying predominantly out-of-plane.

the sulfonate groups may be preferentially assembled, are possible, and are depicted in Figure 7(B) and (C). They represent the conditions where the vibrating S — O dipoles lie predominantly in-plane and out-of-plane, respectively. Polarization data shows enhancement of the S — O stretching bands at 1046 and 1056 cm^{-1} when the IR electric vector lies parallel to the plane of the film (TE polarization; trace A), which may indicate that the configuration B, depicted in Figure 7, may be possible. However,

simple geometrical considerations and projections of the S — O bond, with respect to the incoming polarized beam and the surface of the film, indicate that the orientations B and C of Figure 7 will yield similar band intensity changes with polarization changes. Therefore, both orientations may occur, but the preferential one is depicted in Figure 7(C), because, as we recall, the orientation of the dimer acid groups in the films deposited on a high surface tension substrate, the acid dimers take preferentially out-of-plane orientation, thus favoring structure C.

In contrast to the behavior observed for the hydrophilic sulfonate groups, examination of the C — H stretching region of these spectra (not shown) reveals no detectable polarization dependence of the bands, characteristic of the surfactant hydrophobic segments, regardless of the magnitude of interfacial surfactant assembly. Based on these data, we are in a position to deduce the nature of surfactant assembly. The hydrophilic sulfonate "heads" assemble in a uniform, ordered manner, while the hydrophobic alkyl "tails" remain as an amorphous, unordered phase. This scenerio is reasonable, not only because the hydrophobic segments are long and flexible, and thus able to adopt numerous configurations with minimum energy, but also because these segments do not contain any functionalities that may participate in strong intermolecular interactions, such as hydrogen bonding, ion–dipole, and dipole–dipole associations. This is, however, not the case for the charged sulfonate groups with polar S — O bonds. These groups not only exhibit strong ionic interactions with the sodium counter cation, but are capable of forming hydrogen bonds with both the latex acid functionality and with residual water. This issue was addressed in our previous studies and here is demonstrated again by a splitting of the S — O band at 1050 cm^{-1} in the pure SDOSS surfactant spectrum to two bands at 1046 and 1046 cm^{-1}, when the SO$_3^-$ Na$^+$ hydrophilic ends are surrounded by COOH and H$_2$O.[12,13] The presence of these molecular interactions may serve as one of the factors that causes the sulfonate groups to be "locked" into a preferred "parallel-to-the-surface" configuration.

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