

Characterizing the Distribution of Sodium Alkyl Sulfate Surfactant Homologues in Water-Based, Acrylic Pressure-Sensitive Adhesive Films

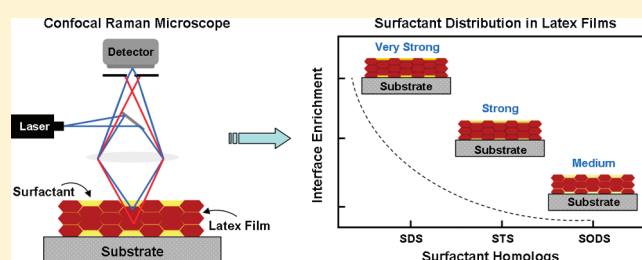
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ABSTRACT: The distributions of three sodium alkyl sulfate surfactants in dry adhesive films cast from water-based latexes were characterized using confocal Raman microscopy (CRM) and contact angle (CA) and tack measurements. Sodium dodecyl sulfate (SDS), sodium tetradecyl sulfate (STS), and sodium octadecyl sulfate (SODS) were added to dialyzed commercial adhesive latex at various concentrations. Uneven distributions were found for all three surfactants along with a tendency to enrich film–air interfaces and, to a much lesser extent, film–glass interfaces. SDS demonstrated the greatest tendency to concentrate near film surfaces followed by STS and SODS. For all three surfactants, water CA values for dried films decreased sharply with increasing concentrations in the latex, but significant differences were observed, with SDS again having the greatest impact followed by STS and SODS. Tack of dried polymer films was also found to decrease with increasing latex surfactant levels, with SDS producing the sharpest drop as well as the lowest plateau values. Results indicate that interfacial enrichment by surfactants is detectable via both CRM and CA measurements, and this enrichment can significantly affect the performance of films. Finally, surface enrichment levels are qualitatively related to measures of the surfactants' affinity for aqueous solutions, as characterized by the logarithm of their 1-octanol–water distribution coefficients (K_{ow}).



INTRODUCTION

The distribution of surfactants in films cast from waterborne latexes is a topic that continues to be of great interest to both scientists and practitioners.¹ Studies on this issue provide insights into the surface and bulk interactions between amphiphilic species and polymer matrixes as well as the transport through polymeric phases in aqueous environments such as that involved in drug transport and membrane separations. The focus of the work presented here is surfactant distribution in films cast from pressure-sensitive adhesive (PSA) acrylic latexes. These types of adhesives are designed to flow under light pressure to wet and form adhesive bonds with a broad variety of surfaces. Intuitively, it can be understood how surfactants may interfere with this function.^{2,3} It is also likely that the distribution of these chemicals is directly related to the level of interaction between cast films and moisture, which impacts appearance as well as performance.

Surfactants are used in acrylic latexes to first provide micelle structures, which house polymerization reactions, and to eventually help stabilize formed polymer particles. Wetting agents are also added to aid in the wetting of low surface energy substrates as is typically necessary during the production of adhesive films. Subsequent to coating, these chemicals are no longer required but remain in the forming film. Over the past decade, several

papers have been published on the adaption of characterization techniques for investigating the distribution of surfactants in adhesive films, more specifically the out-of-plane or *z*-directional distribution. These include X-ray photoelectron spectroscopy (XPS),⁴ Fourier transform infrared (FTIR) spectroscopy, attenuated total reflection (ATR) FTIR,^{5–13} and nuclear magnetic resonance (NMR).^{7,14} For example, Zhao et al.¹⁵ and Kientz et al.¹⁶ combined XPS, secondary ion mass spectrometry (SIMS), and ATR-FTIR to quantify surfactant concentrations within 2 μm thick layers at film interfaces. Zhao et al. showed that enrichment was a function of the surfactant/polymer compatibility and initial surfactant concentrations in the latex.¹⁵ Kientz et al. found that the surfactant concentrations at film interfaces were established primarily during the drying period and subsequently changed little.²⁰

Rutherford backscattering spectroscopy (RBS) is another technique that has been applied to characterize the out-of-plane distribution of surfactant species in dry films.^{17–20} RBS provides quantitative information with regard to the surface concentration

Received: March 23, 2011

Revised: May 17, 2011

Published: May 23, 2011

for the first micrometer or so into a sample. Aramendia et al. used RBS coupled with atomic force microscopy (AFM) to compare films cast from latexes stabilized with sodium dodecyl sulfate, a conventional surfactant, and a reactive surfactant (surfmier), which was grafted to the latex polymer.¹⁷ They observed that the amount of sodium dodecyl sulfate that moved to film surfaces increased with annealing temperature, but that migration of the surfmier (sodium tetradecyl maleate) was only weakly influenced. Using RBS, Tzitzinou et al. found a decrease in the surface-area-to-volume ratio of surfactant with film drying while the surface concentration of surfactant remained constant and speculated that this evolution was driven by a reduction in surface energy.¹⁸ Lee et al. used RBS to compare measured surface enrichments with those predicted by a theoretical model.¹⁹ They found a 30–50 nm thick surface layer rich in surfactant and its presence in the bulk of the film, which partly agrees with their model predictions for the surfactants tested. Although these studies demonstrate the utility of RBS, this technique only provides information with regard to the near-surface region of films and no information with regard to relative concentrations throughout the film structure.

Recently, confocal Raman microscopy (CRM) has been employed to investigate the out-of-plane distribution of surfactants and other small organic molecules in thin films, coatings, membranes, and composites.^{2,3,8,21–23} CRM combines a high-resolution confocal microscope with a sensitive Raman spectroscopy system. Confocal optics provide for the movement of the focal plane in a systematic fashion perpendicular to the film surface over tens of micrometers. This allows for the collection of Raman spectra at various depths. Given that Raman spectroscopy is a quantitative tool for measuring the composition of chemical bonds, CRM is an effective means for the nondestructive depth profiling of various chemical species in PSA films. Belaroui et al.^{8,21} used CRM to characterize the surfactant concentration in waterborne polymer films. From their work, it was concluded that a surfactant enrichment layer forms at the interfaces of latex polymer films. They also showed that the overall distribution was rather heterogeneous. Xu et al.^{2,3} combined CRM and AFM to characterize surfactant distributions of disodium [(nonylphenoxy)polyethoxy]ethyl sulfosuccinate (anionic) and nonylphenoxypoly(ethyleneoxy) ethanol (nonionic). It was shown that the anionic surfactant tended to enrich at the film interfaces, which was attributed to its preference for the aqueous phase and its convective flow during the drying process. The nonionic surfactant on the other hand showed little surface enrichment and a small lateral variability in concentration measurements made via CRM. This was attributed to its greater compatibility with the latex polymer phase.

In this paper, the relationship between surfactant chemical structure and interface enrichment levels is refined. Three anionic surfactants were selected for study: sodium dodecyl sulfate (SDS), sodium tetradecyl sulfate (STS), and sodium octadecyl sulfate (SODS). These homologues differ only in the number of methylene linkages that compose their hydrophobes, which is evident from their solubility and phase distribution behavior, and share identical, sodium sulfate, hydrophiles. Comparisons of aqueous stabilities with measured depth profiles for the homologues provide insight into the processes involved in determining the distribution of anionic surfactant species during film-drying processes. Also presented are contact angle (CA) data, which confirm results from CRM characterization and performance testing showing the negative impact surface enrichment can have on adhesion.

EXPERIMENTAL SECTION

Materials. The water-based PSA latex is a commercial formulation provided by Franklin International (Columbus, OH). The adhesive polymer is composed primarily of the monomer *n*-butyl acrylate. The latex contains ~2 wt % surfactants and has a solids content of 62.8 wt % with a mean latex particle size of 690 nm diameter determined via dynamic light scattering.^{2,3} The glass transition temperature of adhesive films cast from the latex were approximately –34 °C determined via dynamic mechanical analysis.^{2,3} Surfactant was removed from the latex through dialysis. A dialysis tube purchased from Fisher Scientific (Pittsburgh, PA) was filled with the latex, which was then placed in a 2000 mL beaker through which deionized water was allowed to continuously flow for 72 h. Water in the beaker was completely exchanged approximately every 12 h. The removal of surfactant was confirmed via CRM. Surfactant was then added back into the dialyzed latex from aqueous surfactant solutions (5 wt %) at various levels. These samples were stirred for >24 h with magnetic stirring bars. Prior to use, the new latexes were treated for 1 h via sonication in a 40 °C water bath. The surfactants SDS, STS, and SODS were all purchased from Sigma-Aldrich (St. Louis, MO) with purity levels of >95%. The latexes containing the new surfactants were used to cast films on glass substrates, which were dried in a 50 °C oven and stored in a desiccator prior to characterization using CRM.

Characterization of Adhesive Films. CRM characterization of adhesive films was carried out using an Alpha 300R confocal Raman microscope equipped with a UHTS200 spectrometer and a DV401 charge-coupled device (CCD) detector from WITec (Ulm, Germany). An Ar ion laser with a wavelength of 514.5 nm and maximum power of 50 mW was used for excitation. Lateral resolution of the CRM instrument according to the theory of light diffraction is about 250 nm, and the vertical resolution is about 500 nm. Because the sampling volume may be smaller than the average particle size of the latex spheres, measurements were conducted at several random locations on the film to minimize the variation. Raman spectra of film samples were measured (in triplicate) with an integration time of 30 s and laser power of 30 mW. Concentrations were calculated using an approach described in previous papers.^{2,3}

Tack testing was performed using an Instron (Norwood, MA) 5542 single-column testing system equipped with a ~1.15 cm² tip tack probe. Loading and removal speeds of 0.05 and 0.15 mm/s, respectively, and a loading force and dwell time of 5.5 N and 20 s, respectively, were utilized for all testing. CAs were determined using a Krüss (Hamburg, Germany) DSA10-MK2 CA measurement system. Deionized water was used as a probe liquid with droplet volumes of 1 µL. Average CA values were obtained at room temperature by measuring the samples at three different positions.

RESULTS

CRM Depth Profiles. In previous CRM studies, Raman spectral peaks at 1612 and 1735 cm^{–1} for latex films were identified as an aromatic C–C, on-ring stretch mode for the nonylphenol ethoxylate (NPE) surfactants (both the anionic and nonionic forms) and a carbonyl stretch mode of the acrylic polymer, respectively, and ratios of the surfactant peak's area to the polymer peak's area were used to quantify the surfactant concentration (Figure 1).^{2,3} Here, NPE surfactants were removed

from a commercial formulation through dialysis and replaced with various levels of SDS, STS, or SODS. Given that SDS, STS, and SODS are homologues, their Raman spectra are quite similar (Figure 1). For the adhesive film, it can be seen that the peak at 1612 cm^{-1} associated with the NPE surfactants is undetectable following the dialysis process. It was determined that peaks near 600 cm^{-1} , associated with the triply degenerate bending vibration of the SO_4^- group, and 1735 cm^{-1} ,²⁴ associated with the acrylic carbonyl stretch mode on the polymer,^{2,3} were sufficiently isolated and intense for use in quantifying surfactant levels at various depths in polymer films.

Figures 2–4 show the region of the Raman spectra containing the surfactant peak centered near 600 cm^{-1} from measurements at various depths for films cast from dialyzed latexes with the SDS, STS, and SODS surfactants added back. For each surfactant, concentrations in the latex, based on the dialyzed latex solids, of 4, 8, and 16 wt % were investigated. All spectra shown were scaled to keep the acrylate peak at 1735 cm^{-1} fixed at a constant total area; thus, the relative intensities of surfactant peaks indicate their relative concentrations at the indicated depths.

Figure 2a shows the CRM spectra for the 4 wt % SDS sample. It can be seen that the surfactant peak has significant intensity down to a depth of $1.5\text{ }\mu\text{m}$. Beyond this, the surfactant peak is

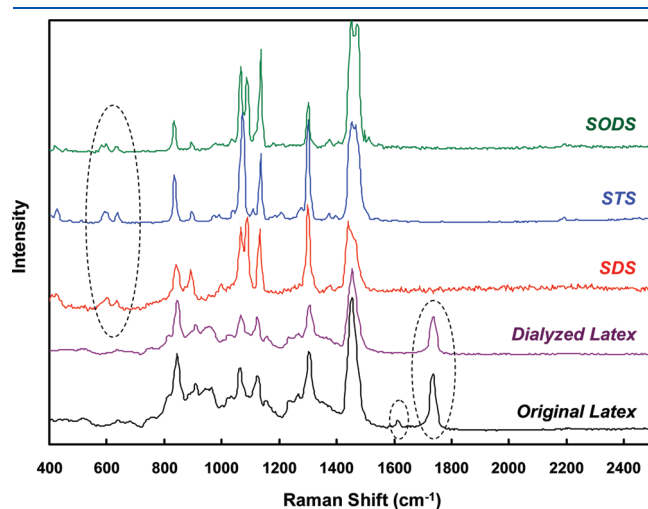


Figure 1. CRM spectra of the original latex polymer, dialyzed latex polymer, and pure SDS, STS, and SODS. Peaks located at 600 cm^{-1} and 1735 cm^{-1} are employed to detect the surfactants and latex polymer, respectively.

almost undetectable, indicating little or no surfactant exists in the bulk region of the latex polymer. However, the surfactant peak does reappear near the film–substrate interface but with less intensity than that found at the film–air interface. Similar results are observed for the 8 and 16 wt % SDS samples as well, parts b and c, respectively, of Figure 2. From these data, it can be seen that SDS has a strong tendency to collect at the interfaces of the adhesive films and little if any remains in the bulk subsequent to film drying. It is also apparent that significantly more surfactant collects at the film–air interface than at the film–substrate interface.

Figure 3 shows the region of the Raman spectra containing the surfactant peak for CRM analysis of films cast from the STS/dialyzed latex samples. Concentrations of 4, 8, and 16 wt % are shown in parts a–c, respectively, of Figure 3. As with the samples containing SDS, there is little or no STS found in the bulk regions of the films and there exists significant enrichment near the film–air interface. For these samples, it appears that the enrichment layer is larger, extending to a depth of $4\text{ }\mu\text{m}$ into the film at the film–air interface and enrichment occurs to a lesser extent than with the SDS/dialyzed latex sample. It also appears that the concentration of surfactant at the film–substrate interface is significantly lower relative to that at the film–air interface.

Figure 4 shows results for films cast from the SODS/dialyzed latex films at various depths. Results for SODS concentrations of 4, 8, and 16 wt % are shown in parts a–c, respectively, of Figure 4. For all three concentrations, the SODS peaks are relatively intense at the film–air interface and decrease gradually with depth. In contrast to the results for SDS and STS, peaks associated with SODS are clearly detectable throughout the entire film. However, for depths beyond $5\text{ }\mu\text{m}$, their intensities are decreased significantly. Near the film–substrate interface, the SODS surfactant peak intensities increase again, but not nearly to the levels observed at the film–air interface. In general, the SODS appears to be more evenly distributed in the films than SDS and STS.

A more quantitative comparison of depth profiles in cast latex films between SDS, STS, and SODS is shown in Figure 5.^{2,3} Values for areas under the curves were determined by integrating the areas of peaks above the baseline. It can be seen that all three surfactants preferentially enrich the interfaces of dried films, with higher concentrations being found at the film–air interface as compared to the film–substrate interface. Among the three surfactants, SDS provides the greatest enrichment levels at both the film–air and film–substrate interfaces followed in order by STS and SODS, which both have significantly lower interfacial

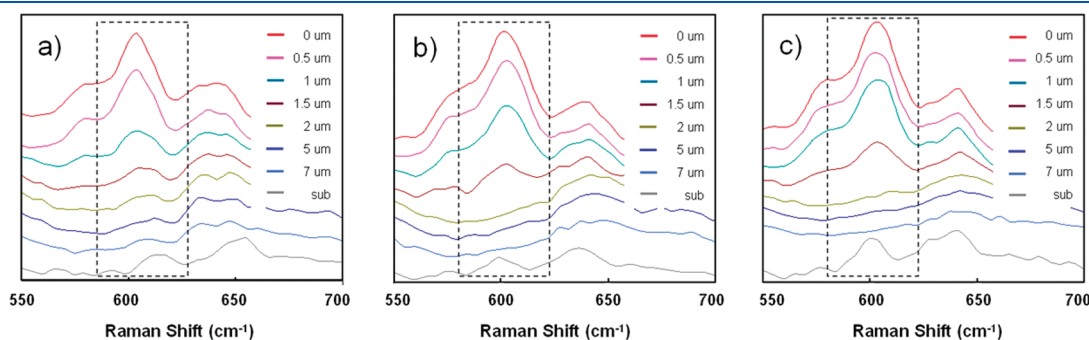


Figure 2. CRM spectra of SDS/dialyzed latex films from the film surface to film-substrate interface: (a) 4 wt % SDS; (b) 8 wt % SDS; (c) 16 wt % SDS.

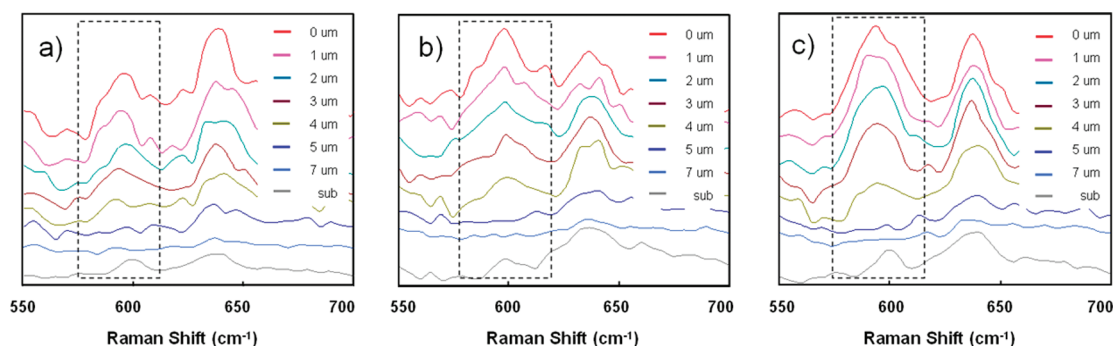


Figure 3. CRM spectra of STS/dialyzed latex films from the film surface to film-substrate interface: (a) 4 wt % STS; (b) 8 wt % STS; (c) 16 wt % STS.

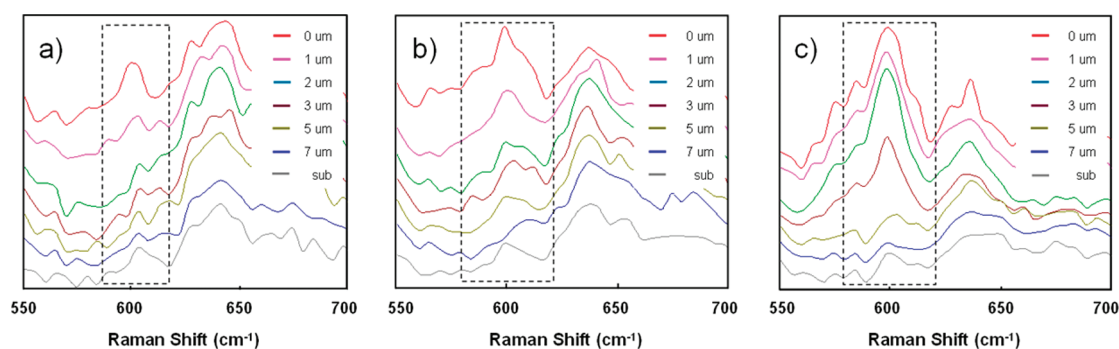


Figure 4. CRM spectra of SODS/dialyzed latex films from the film surface to film-substrate interface: (a) 4 wt % SODS; (b) 8 wt % SODS; (c) 16 wt % SODS.

concentrations. For example, for latex-cast films containing 4 wt % surfactant, the concentration at the film–air interface of the film containing SDS is about 28 wt %, much higher than the concentrations for both the STS (~ 12 wt %) and SODS (~ 8.5 wt %) containing films (Figure 5a). When surfactant concentrations are increased to 8 wt %, the film–air interfacial surfactant concentration of SDS increases to ~ 40 wt %, which again is higher than the film–air concentrations of films containing either STS (~ 21 wt %) or SODS (~ 15 wt %) (Figure 5b). For the highest surfactant concentrations, i.e., 16 wt %, the film–air surfactant concentration of films containing SDS is ~ 90 wt %, much higher than that found for films containing STS (~ 31 wt %) and SODS (~ 24 wt %) (Figure 5c).

Film CAs. Figure 6 summarizes water CA measurements made on films cast from the latex samples containing the various surfactants. The CA is a simple but effective measurement for gauging the hydrophilic–hydrophobic balance of film surfaces. Films cast from the dialyzed latex films with most of the surfactant removed are hydrophobic and have an average CA with water of $111 \pm 1.4^\circ$. It was shown previously that when surfactants locate at the surfaces of acrylic films, they tend to orient in such a way as to increase the surface energy and lower the CA for water.²⁵ Figure 6 shows plots of CAs for films cast from latexes containing SDS, STS, and SODS at various concentrations. From Figure 6, it is evident that the films containing SDS are significantly more hydrophilic than the films containing the other surfactants, resulting in the lowest CAs. Even for the lowest SDS concentration of 4 wt %, a water CA on the dried film surface is less than 15° , which is much lower than that on the dialyzed latex film surface of $\sim 111^\circ$. When the surfactant concentration is increased to 8 and 16 wt %, the CA of the dried films decreases to below 10° .

For films containing the surfactant STS, the CAs indicate partial wetting for water, as is the case for SDS, but the angles are significantly greater. For a concentration of 4 wt %, the CA is $\sim 68.0 \pm 2.5^\circ$; increasing the surfactant concentrations to 8 and 16 wt % decreases the CAs to $52.6 \pm 1.4^\circ$ and $40.1 \pm 2.1^\circ$, respectively. CA results for water on films cast from latexes containing SODS show nonwetting behavior for the lowest surfactant concentration of 4 wt % on latex solids; that is, the CA is above 90° , and thus, the surface is hydrophobic. Although partial wetting occurs at 8 wt %, with the CA decreasing to $76.6 \pm 1.8^\circ$, it is still high relative to that of samples produced with the other surfactants. Even at 16 wt % on latex solids, the CA of the dry, cast film containing SODS is still relatively high at $60.6 \pm 2.3^\circ$.

Tack Testing. Tack measures the ability of an adhesive to rapidly wet a surface to form an adhesive bond, which is an important process in determining PSA performance. As such, this test is a key parameter in gauging the performance of PSAs. In practice, tack measurements gauge the force or energy necessary to separate two surfaces that are brought together at low pressure for a short period of time, usually just a few seconds. By varying the test conditions and materials, information on the dependency of tack on the initial application pressure, dwell time, and material properties can be obtained.

Figure 7 shows the results of probe tack tests run according to the method described in the Experimental Section. In the figure, the maximum force experienced during the removal of the probe from the adhesive film surface is plotted against the concentration of the surfactant in the latex. The trends are clear. The tack force for cast films decreases sharply with increasing surfactant content. The decrease in tack is most significant for samples containing

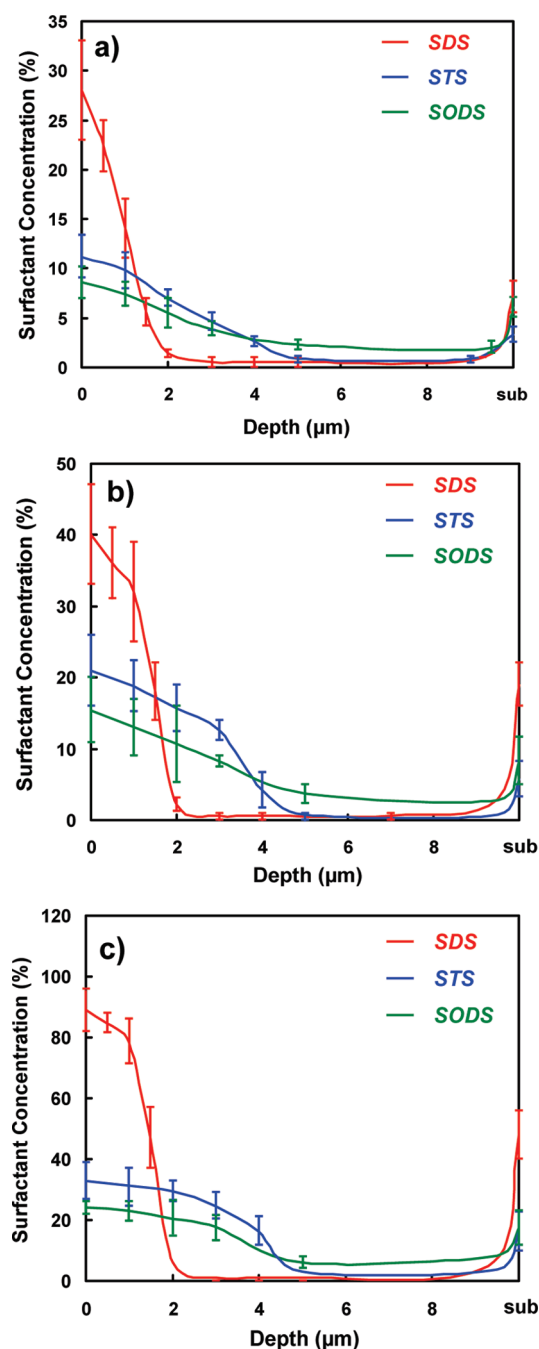


Figure 5. Calculated surfactant concentrations at different film depths based on CRM spectra for the (a) 4 wt %, (b) 8 wt %, and (c) 16 wt % samples.

SDS. At its highest concentration, i.e., 16 wt %, the film is no longer tacky to the touch and its tack force is reduced by 96% compared with that of the films cast from the dialyzed latex. Similar results were found for films cast from latexes containing STS. For latexes containing SODS, the drop is not as sharp, but the induced decrease is substantial.

DISCUSSION

Bindshaedler et al.²⁶ and Kientz and Holl⁵ have previously studied and discussed the fate of surfactants in latex films. From

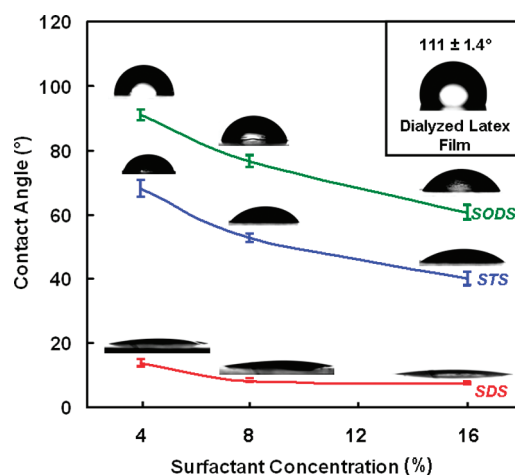


Figure 6. Water CAs on SDS/latex, STS/latex, and SODS/latex film surfaces for different surfactant concentrations. Inset: a water droplet placed on a dried latex-cast film from the dialyzed sample.

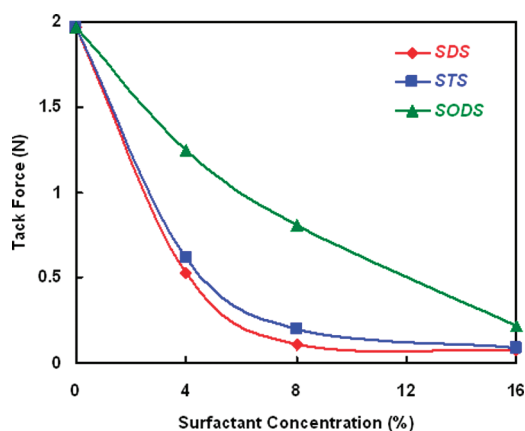


Figure 7. Tack force of latex films with different surfactant concentrations.

their work, it can be concluded that surfactants that are highly compatible with the latex polymer tend to distribute evenly throughout the film while surfactants that are highly incompatible tend to concentrate at or enrich film interfaces. Our previous papers in this area compared the enrichment tendency of two NPE analogues having similar chemical structures and molecular weights. It was demonstrated that the anionic form of the NPE tended to enrich film surfaces while the nonionic version prefers to distribute uniformly, possibly throughout the latex polymer.^{2,3} It was speculated that the difference was due to the strong acid functionality of the anionic surfactant, which would provide it with significant water solubility, favoring its distribution into the aqueous phase and removal from the film during drying. In other words, the distribution has less to do with affinity for polymer surfaces and is more governed by surfactant activity in the aqueous phase. It is well established that the extent to which aqueous organic acids sorb to materials such as soils, sediments, and wood and their elution volumes in reversed-phase high-performance liquid chromatography (RP-HPLC) often correlate with measures of their tendency to partition out of water. It is also commonly found that sorption and elution volumes are substantially lower for the conjugate base form of aqueous organic acids.^{27,28}

Table 1. Physical Parameters for SDS, STS, and SODS

surfactant	SDS	STS	SODS
chemical structure	C ₁₂ H ₂₅ SO ₄ Na	C ₁₄ H ₂₉ SO ₄ Na	C ₁₈ H ₃₇ SO ₄ Na
molecular weight (<i>M_w</i>)	288.38	316.44	372.54
cmc (wt %)	2.4 × 10 ^{−1}	6.6 × 10 ^{−2}	6.3 × 10 ^{−3}
log <i>K_{ow}</i>	1.6	2.1	3.3
surface enrichment degree	very strong	strong	medium

The purpose of this study is to further refine the role the stability of surfactants in water plays in determining their distribution behavior in forming latex films. The surfactants chosen for this study are sodium alkyl sulfate homologues. All three possess the sodium salt of a strong acid functional group and are ionized during the latex drying process. The differences that exist in their hydrophobes, specifically two methylene linkages between SDS and STS and four methylene linkages between STS and SODS, provide clear differences in their tendency to partition out of an aqueous solution and into adjacent phases. It is the study of surfactant species such as these, which have a moderate affinity for the latex polymer, that likely holds important insights into the mechanism and properties controlling surfactant distribution.

Table 1 provides properties for the three surfactant species, including their log *K_{ow}* values.²⁹ The logarithm of 1-octanol–water distribution coefficients for organic species is a well-accepted gauge of their tendency to partition out of water and into contacting organic phases. log *K_{ow}* values are often used in single-parameter linear free energy relationships (LFERs) for predicting partition constants or partitioning coefficients in various two-phase systems. This parameter is also an effective parameter for modeling relative elution volumes of organic species in RP-HPLC, which was the analogy drawn previously for the movement of nonylphenol ethoxylates out of drying latex films. It is instructive to show how the relatively minor structural differences between the chemical homologues influence their tendency to partition out of water. *K_{ow}* values are related to the free energy of transfer between the two phases, Δ*G_{ow}*, by

$$K_{ow} = \frac{\bar{V}_w}{\bar{V}_o} \exp\left(\frac{-\Delta G_{ow}}{RT}\right) \quad (1)$$

where \bar{V}_o and \bar{V}_w are the molar volumes for the octanol and water phases, respectively, *R* is the gas law constant, and *T* is the absolute temperature. A plot of $-RT \ln K_{ow}$ versus the number of methylene linkages in the surfactant hydrophobe produces a straight line (*r*² > 0.99) with a slope of -1.63 kJ/mol. The slope here is the Gibbs free energy change associated with the transfer of a single methylene out of an aqueous solution and into the 1-octanol phase. This value is consistent with values reported previously for the transfer of methylene linkages out of aqueous solutions;³⁰ thus, the difference in free energy for the transfer of the different homologues is significant.

As reported above, the CA for water on the dialyzed latex film is about 111°, which indicates that the latex particles are relatively hydrophobic. For a surfactant being carried with the aqueous solution through a drying latex film, it is likely that SODS will have the greatest tendency to partition to the latex particles while SDS will have the least, which is consistent with the distribution profiles determined via CRM. SDS, for the most part, is exuded from the drying film and settles primarily on the film surface. STS is also exuded but concentrates more within the interfacial region. In contrast, SODS, which has six more methylene

linkages than SDS and four more than STS, is found throughout the film, but concentrates to its highest levels near the interfaces. The differences in enrichment between the film–air and film–substrate interfaces are also consistent with a connection to partitioning. The film–air interface is a free surface where water has significant contact with the surrounding atmosphere, increasing its rate of evaporation. The film–substrate interface on the other hand would limit evaporation rates. This simple analysis would indicate that more of the water is evaporated from the film–air interface and, if water is carrying the surfactant, more surfactant should be found at this interface subsequent to drying.

Also listed in Table 1 are critical micelle concentrations (cmc's) for the three surfactants. As might be expected from the discussion above, there exist significant differences between their cmc values. A higher relative cmc value indicates that the surfactant stays in a monomer state in aqueous solution to higher concentrations. cmc values decrease in the order SDS > STS > SODS. The relative magnitudes of the cmc's provide further evidence for the role of hydrophobe size in determining the level of enrichment at the interface, but it also raises an important issue in that the aggregated state of the surfactants must be considered when the partitioning of the surfactant between the aqueous phase and the latex polymer surface is being studied. Given the differences observed in interfacial enrichment for latexes containing the different surfactants, it seems that their transport is governed to a large extent by their monomer form. However, more evidence is required to confirm this, which is the focus of current research.

CONCLUSIONS

CRM measurements indicate that sodium alkyl sulfate surfactants tend to be concentrated at the air–film interface of PSA films. In addition to confirming surface enrichment of surfactant species, CA and tack data indicate that this behavior can significantly impact the performance of coatings and materials cast from latex systems. As expected, as one moves to longer alkyl chain lengths and thus greater hydrophobic character, the tendency for surfactants to collect at film interfaces is less significant. It is proposed that the observed enrichment levels of the three homologues are due to differences in their affinity for the aqueous solution over latex particles (surfaces and bulk), and it appears that 1-octanol–water distribution coefficient (*K_{ow}*) values may provide a means for predicting interfacial enrichment by surfactant species.

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ACKNOWLEDGMENT

This research is financially supported by a grant from the U.S. Postal Service, Stamp Acquisition and Distribution.

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