Surface and Interfacial FTIR Spectroscopic Studies of Latexes. IV. The Effect of Surfactant Structure on the Copolymer–Surfactant Interactions

TIMOTHY A. THORSTENSON and MAREK W. URBAN*

Department of Polymers and Coatings, North Dakota State University, Fargo, North Dakota 58105

SYNOPSIS

The interactions between sodium dodecylbenzene sulfonate (SDBS) and the components of an ethyl acrylate/methacrylic acid (EA/MAA) copolymer latex were examined and the influences of using D_2O as the synthetic suspension medium were investigated. Whereas it is found that D_2O has no detectable influence on the fully coalesced latex films, the film coalescence conditions are shown to significantly affect the nature of surfactant interactions within the film matrix. When films are prepared and stored under controllable low atmospheric water-vapor concentrations, hydrogen-bonding interactions between the surfactant $SO_3^-Na^+$ groups and the copolymer acid functionality dominate. However, coalescence and storage of the films under higher relative humidity conditions results in a displacement of these interactions in favor of the hydrated form of the surfactant. It is also shown that the presence of an aromatic ring adjacent to the surfactant sulfonate group exerts an influence on the nature of the $SO_3^- \cdots HOOC$ interactions within the copolymer matrix. Relative to sodium dioctyl sulfosuccinate (SDOSS), the aromatic group near hydrophilic end of SDBS increases the strength of the $S{-}O$ bond in the presence of acid interactions.

INTRODUCTION

It is well established that low molecular weight surfactants are extensively used in latex synthesis and formulation. However, because of high mobility, surface activity, and potential incompatibility with the latex polymer matrices, these species may migrate. If such migration is stimulated by external or internal sources, certain regions of the latex films may exhibit excessive local concentration of surfactant. If these regions are the film–air (F–A) or film–substrate (F–S) interfaces, they, in turn, may lead to optical defects, premature degradation, or a loss of adhesion. In contrast, however, one may take advantage of the enhanced mobility and design latex systems with surfactant structures that may improve adhesion or other properties.

Despite previous efforts in determining the sources of surfactant mobility, only limited studies have addressed the issue of molecular level interactions that occur between surfactants and latex components.[1,2] It is these interactions that may ultimately govern surfactant behavior during or after latex coalescence, and understanding of these phenomena is essential to the prediction of surfactant behavior within polymer matrices.

Recently, we[3,4] studied the behavior of a variety of surfactants in ethyl acrylate/methacrylic acid (EA/MAA) latexes using ATR FTIR spectroscopy. These studies have shown that factors such as neutralization, film elongation, substrate surface tension, and the nature of the surfactant may significantly influence surfactant behavior.

Interactions between sodium dioctyl sulfosuccinate (SDOSS) surfactant and the components of the EA/MAA latex system were also extensively examined.[5] It was shown that the polar sulfonate groups of the surfactant can interact with the acid functionality of the copolymer and these interactions

---

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 47, 1381–1386 (1993)
CCC 0021-8995/93/081381-06

are affected by residual water present in the film after coalescence. Apparently, the presence of these species disturbs the symmetry of the $SO_3^-Na^+$ environment such that a splitting of the 1050 cm^{-1} band due to the S—O symmetric stretching mode of the surfactant sulfonate group into two bands at 1046 and 1056 cm^{-1} occurs.

In this study, we will further examine the nature of surfactant–copolymer interactions, specifically the influence of an adjacent aromatic ring on the behavior of the sulfonate group in sodium dodecylbenzene sulfonate (SDBS). In an effort to assess the effects of the suspension medium on the coalesced latex film properties, the latex polymers were synthesized in H_2O and D_2O.

EXPERIMENTAL

Synthesis of H_2O-based latexes, film preparation, and acquisition and analysis of ATR FTIR spectra were performed following previously published methodologies.[5] To control coalescence conditions, film preparation under dry conditions was accomplished by preparing the films in a dry box containing anhydrous $CaSO_4$.

Synthesis of the D_2O latex was performed in the same general manner as that used for the H_2O latexes, with the exception that doubly deionized water was replaced by an equal volume of D_2O (Aldrich, 99.9% D). All weighing and measuring operations involving the D_2O were performed in a glove box maintained under a dry-air purge.

Preparation of films of the D_2O latexes under conditions of higher atmospheric D_2O vapor concentration was accomplished by deposition of the films on a substrate placed in a chamber containing D_2O-saturated $CaCl_2$. These conditions will maintain a controlled relative humidity of approximately 40%.[6]

RESULTS AND DISCUSSION

In the synthesis of latexes, H_2O is typically employed as the suspension medium. In an effort to further examine the nature of the surfactant/latex interactions, EA/MAA latex was prepared using SDBS surfactant. However, instead of H_2O as a suspension medium, D_2O was employed. Examination of the ATR FTIR spectra of the F-A and F-S interfaces of latex films prepared from both H_2O and D_2O latexes reveal essentially the same spectral features. Figure 1 shows the 1080–950 cm^{-1} region of the spectra with the S—O symmetric stretching mode of the surfactant sulfonate group located at 1046 cm^{-1} in the spectrum of pure surfactant (trace A), which appears to shift; in the case of both the latexes prepared from H_2O and D_2O (traces B and C, respectively), this band is detected at 1056 cm^{-1}.

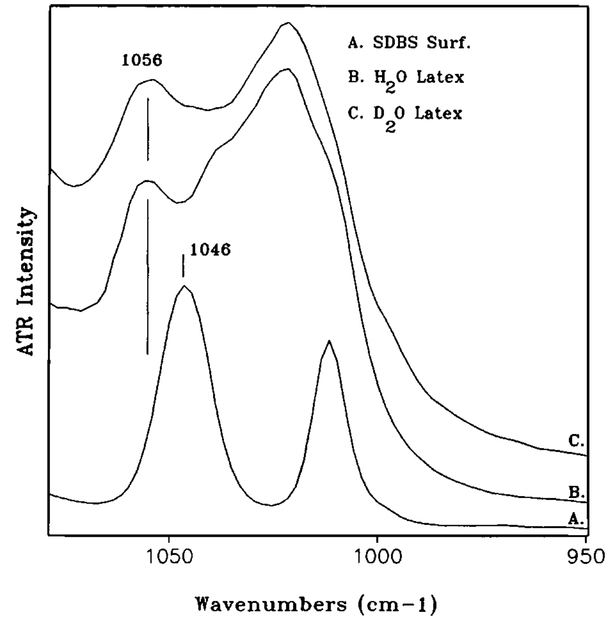

Figure 1 ATR FTIR spectra in the 1080–950 cm^{-1} region recorded at the film–substrate interfaces of the H_2O and D_2O latex films prepared with SDBS under dry-box conditions: (A) SDBS surfactant; (B) H_2O latex; (C) D_2O latex.

However, it is important to realize that the atmospheric relative humidity during the coalescence process may have a significant effect on the acid/surfactant interactions. For that reason, let us consider the conditions employed in film formation while keeping in mind the behavior previously reported for the SDOSS surfactant.[5] In the preparation of films for ATR FTIR measurements, the D_2O latex was prepared under dry-box conditions to avoid possible D_2O/H_2O exchange. Because residual water[5] left in the film after coalescence may influence the sulfonate group environment, the H_2O latex films were prepared in a dry box. To further investigate the effect of acid–surfactant interactions in the presence of water, H_2O latex films were prepared under ambient conditions of approximately 50% RH. For comparison, D_2O latex films were coalesced over a saturated solution of $CaCl_2$ in D_2O. The purpose of using the $CaCl_2$-saturated D_2O solutions was to maintain a controllable relative humidity of approximately 40% while avoiding undesirable H_2O

exchange.[6] Trace A of Figure 2 shows the H_2O latex film prepared under 50% RH. It is apparent that the band previously seen at 1056 cm^{-1} (trace B of Fig. 1) is now shifted to 1042 cm^{-1}. The D_2O latex (trace B) reveals a similar change.

The detected frequency shifts observed are attributed to the presence of the aromatic ring and can be considered in conjunction with the results that we have recently reported[5] for SDOSS. Sulfonate groups of SDOSS surfactant can form hydrogen bonding with the acid functionality of the copolymer, leading to a shift of the S — O symmetric stretching band to a higher frequency and with residual water left in the film after coalescence. The latter interactions result in a shift of the 1050 cm^{-1} band to 1046 cm^{-1}. Based on the data shown in Figures 1 and 2, one can hypothesize that a reversible equilibrium between acid-bonded and water-bonded SDBS surfactant exists, and depending upon the film-formation conditions, one of these interactions may predominate.

To further examine this hypothesis, let us consider the influence of hydration on the band due to the S — O symmetric stretching mode in an FTIR spectrum of the neat surfactant. Trace A of Figure 3 shows the spectrum of a concentrated solution of SDBS in H_2O that was deposited onto a KRS-5 window. While this initial spectrum exhibits the band at 1042 cm^{-1}, after drying for 48 h under a dry-air purge, the band shifts to 1046 cm^{-1} (trace B). This wavenumber corresponds to the location of the band in the spectrum of anhydrous, vacuum-desiccated surfactant (trace C). The reversibility of the sulfonate group hydration is further illustrated by examining the O — H stretching region. As illustrated in Figure 4, the hydrated surfactant (trace A) can be completely dehydrated under ambient conditions of temperature and pressure and, after 48 h (trace B), SDBS is as water-free as a vacuum-desiccated sample (trace C).

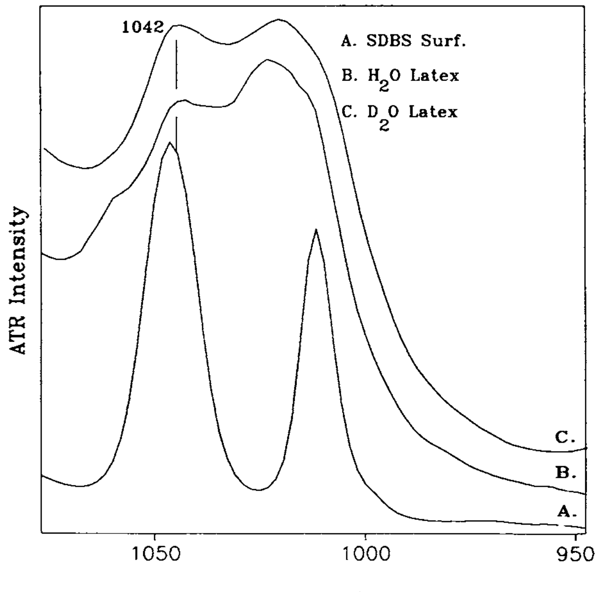

Figure 2 ATR FTIR spectra in the 1080–950 cm^{-1} region recorded at the film–substrate interfaces of the H_2O and D_2O latex films prepared with SDBS under higher humidity conditions: (A) SDBS surfactant; (B) H_2O latex (50% RH); (C) D_2O latex (40% RH D_2O).

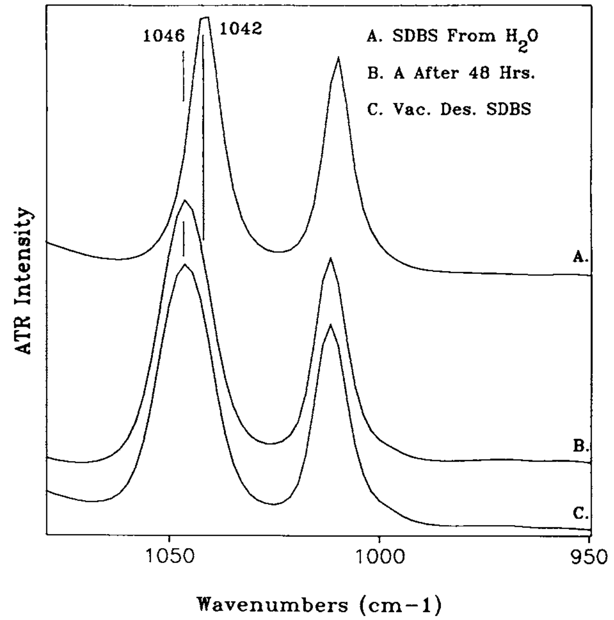

Figure 3 Transmission FTIR spectra in the 1080–950 cm^{-1} region of SDBS surfactant prepared from aqueous solution: (A) initially after deposition of solution; (B) after 48 h drying time; (C) vacuum-desiccated sample.

At this point it is appropriate to consider the vibrational energy of the band due to the S — O symmetric stretching mode of the surfactants. For that reason, let us examine the structures of the two surfactants and the structural differences in conjunction with the differences observed in the IR spectra of these species. As shown in Figure 5, the sulfonate group of SDOSS (structure A) is attached directly to an aliphatic methylene group and the band attributed to the S — O symmetric stretching mode occurs at 1050 cm^{-1}. In SDBS (structure B), however, the sulfonate group, with the S — O stretching band at 1046 cm^{-1}, is attached directly to the aromatic benzene ring. Let us consider the substituents attached to the surfactants while keeping in mind

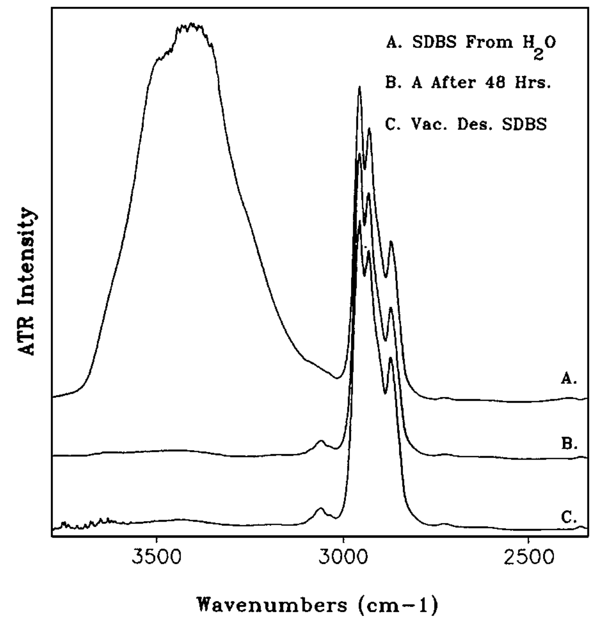

Figure 4 Transmission FTIR spectra in the 4000–2700 cm^{-1} region of SDBS surfactant prepared from aqueous solution: (A) initially after deposition of solution; (B) after 48 h drying time; (C) vacuum-desiccated sample.

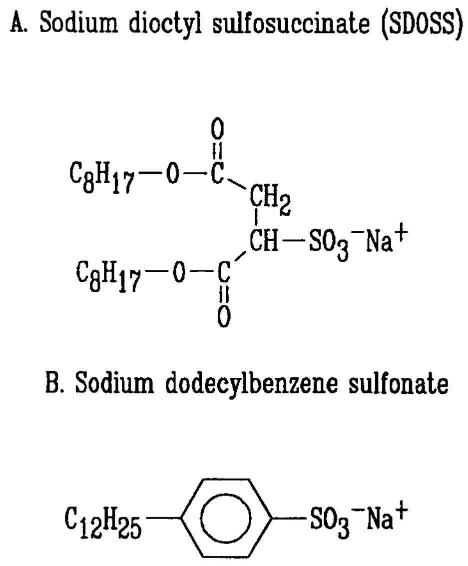

Figure 5 Structural comparison of the surfactants SDOSS and SDBS: (A) SDOSS; (B) SDBS.

that the highest-energy electrons in the hybridized molecular orbitals of the sulfonate groups are located in the antibonding orbitals. Since the central sulfur atom in the SO_3 group can be expected to be somewhat electropositive due to the electron withdrawal of the attached oxygen atoms, one would anticipate that the aromatic substituent of the SDBS surfactant may release electron density to the sulfur atom and thus increase the antibonding character of the S—O bonds. This, in comparison with SDOSS, would result in a lower-frequency S—O symmetric stretching band.

According to the data presented in Figures 1 and 2, it is possible to change the nature of acid/surfactant interactions by introducing water into the latex system. Let us consider to what extent the presence of water may affect the equilibrium between acid-bonded and hydrated SDOSS. ATR FTIR spectra of films prepared under ambient conditions (approximately 50% RH) shown in Figure 6(A) reveal the 1046 and 1056 cm^{-1} bands, indicating that both the acid-bonded and hydrated species of SDOSS are present under these conditions. To investigate the influence of the water-vapor concentration on the position of this equilibrium, the SDOSS latex films were coalesced under dry-box conditions and such fully coalesced films were placed in a closed chamber saturated with water vapor. Trace B of Figure 6 shows the ATR FTIR spectrum of the films exposed to H_2O vapor in the manner outlined above for 24 h after coalescence was complete. The spectrum shows that the band at 1056 cm^{-1} is now completely absent, indicating that under

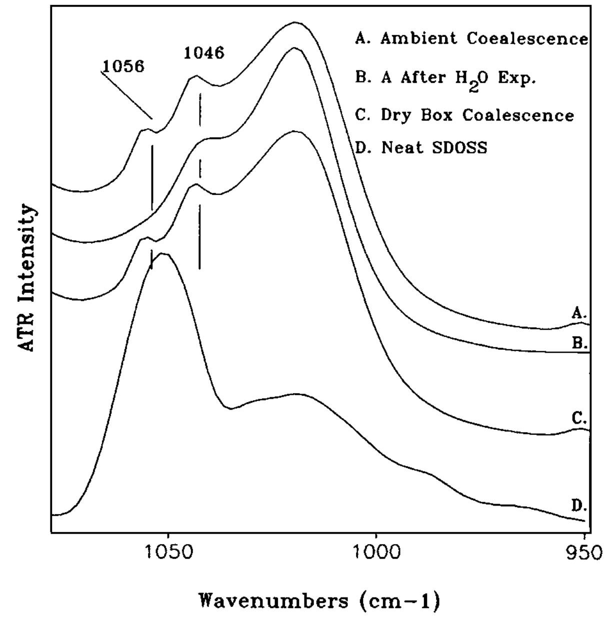

Figure 6 ATR FTIR spectra in the 1080–950 cm^{-1} region recorded at the film–substrate interfaces of SDOSS latex films prepared under various conditions: (A) coalescence at 50% RH; (B) 24 h. H_2O vapor exposure after coalescence; (C) coalescence under dry-box conditions; (D) SDOSS surfactant.

high water-vapor conditions the acid-bonded sulfonate groups will be displaced by the hydrated form of the surfactant. In contrast to SDBS, however, the spectrum of the SDOSS latex film prepared under dry-box conditions still exhibits both the 1046 and 1056 cm^{-1} bands (trace C). This indicates that SDOSS, perhaps due to its more hygroscopic nature, will not readily dehydrate under ambient conditions, even in the absence of atmospheric water vapor.

As indicated above, the S — O stretching mode in SDBS is 4 cm^{-1} lower than that observed for SDOSS. Although the higher electron density in the antibonding orbitals can account for this difference, the above model fails when we consider the influence of acid groups on the shift of the S — O symmetric stretching band. For SDOSS, this interaction results in a shift of 6 cm^{-1} to higher frequency, whereas for SDBS, the magnitude of this change is 10 cm^{-1}. According to the theory that the occupied antibonding orbitals will lower the S — O vibrational stretching energy, we would expect that the presence of acid interactions will draw electrons in the direction of the oxygen atoms. This, in turn, should make the central sulfur atom more electropositive, thereby resulting in an even greater degree of electron release from the aromatic ring to the sulfur atom. As indicated in Figure 7, this model would seem to indicate that the presence of acid-bonding interactions in the case of SDBS should result in a lower frequency shift than that observed for SDOSS. Clearly, this is not the case and other factors affect strengthening of the S — O bond reflected in the higher vibrational frequency.

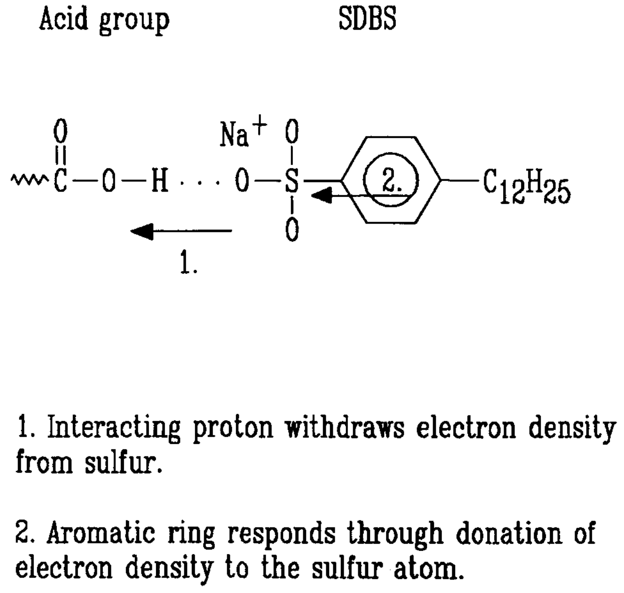

Figure 7 Schematic depiction of changes in electron distribution induced by the presence of acid-bonding interactions.

In an effort to identify the origin of the vibrational energy differences between SDOSS and SDBS, let us focus on the structural differences between the two surfactants. As mentioned previously, the primary difference between the two is the presence of the aromatic ring in SDBS, which leads to the possibility of both inductive and resonance effects that may influence the S — O bond characteristics. As we indicated above, the changes in electron distribution that are brought on by the presence of the aromatic ring can readily be employed to explain the differences in the S — O stretching modes of the neat surfactants. Despite the utility of the model in making these predictions, the changes invoked by the antibonding molecular orbital principles fail to account for the effects observed in the presence of acid–surfactant interactions.

As indicated in Figure 8, the presence of the aromatic ring adjacent to the sulfonate group may, through inductive or resonance effects, release electron density to the sulfonate group and serve to destabilize the system, thus shifting the S — O stretching mode to lower frequencies relative to SDOSS. If we now consider the presence of a carboxylic acid group near the $SO_3^-Na^+$ ion pair (structure B), hydrogen bonding will occur between the acidic hydrogen atom and the oxygen functionality of the surfactant. This interaction will result in a change in the overall distribution of electron density within the system, and it is likely that due to resonance on the aromatic ring the local electron distribution will change the system such that an overall greater degree of stabilization of the sulfonate group relative to SDOSS will result. The $SO_3^-Na^+$ · · · HOOC — pair can also be considered as the acid–base interactions in a Lewis sense[7-9] or the hard-soft-acid-base theory,[10-12] where the sulfonate group next to the aromatic ring behaves as a stronger Lewis base or as a stronger electron pair donor. Similarly to the SDOSS, the S — O bonds in SDBS not involved in the interactions with the acid groups exhibit greater Π character, whereas those that are involved have lesser degree of the double-bond characteristics.

Unlike the behavior observed for acid-bonding interactions, the magnitude of the hydration appears to be independent of the substituent attached to the sulfonate group. Let us consider the situation in which there is a relatively high concentration of water within the latex film matrix. This may occur, for example, when the latex film is exposed to water

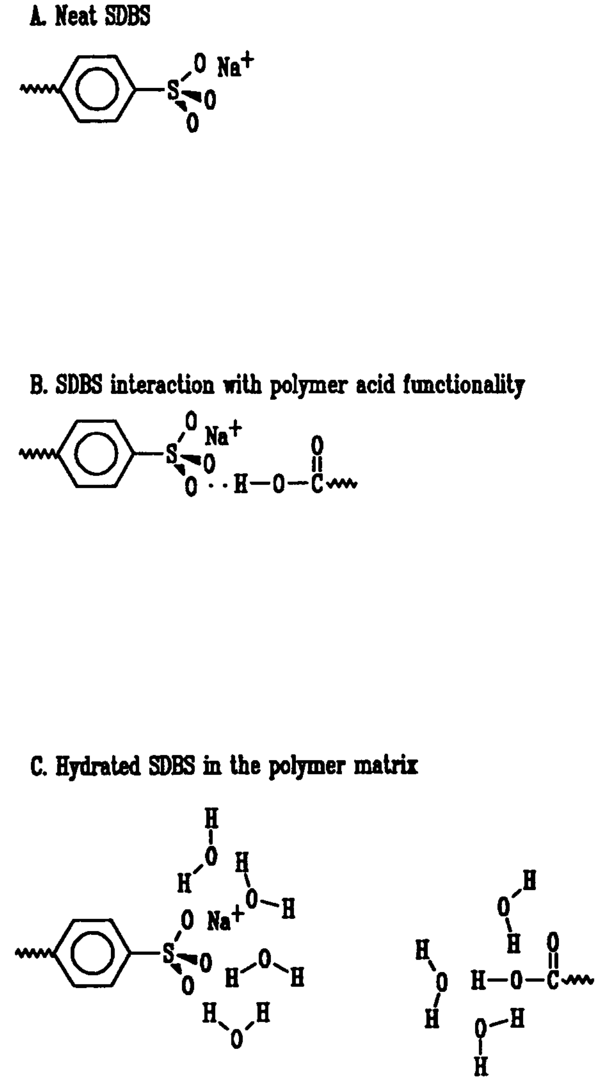

Figure 8 Schematic depiction of possible surfactant–latex system interactions: (A) neat surfactant; (B) acid-bonded surfactant; (C) hydrated surfactant; acid interactions are precluded.

vapor after coalescence. Under these conditions, the surfactant is in the hydrated form and no significant interactions with acid polymer groups would be expected. At this point, water plays the dominant role in the interactions between the carboxylic acid and the sulfonate group. The increased water concentration results in the SO_3^- groups being completely surrounded by water molecules, leading to a barrier that prevents the acid–sulfonate interactions. Additionally, carboxylic acid groups can be strongly hydrated by water and this is likely to further impede the interaction of the acid functionality with the surfactant. This is summarized in structure C of Figure 8.

Based on the magnitude of the observed frequency shift for SDBS that results upon hydration, this interaction appears to be insensitive to the presence of the adjacent aromatic ring. Although one could provide numerous explanations, two potential sources of interaction appear to dominate the observed effects. First, there is the possibility of hydrogen-bonding interactions between the oxygen atoms of the sulfonate groups and the hydrogen atoms of the water molecules. However, there is also the possibility of hydration of the sodium cation, and it is likely that this interaction, by changing the relative local position of the cation with respect to the sulfonate group, will also exert an influence on the sulfonate group. Based on the magnitude of the frequency shift observed for SDBS, it is apparent that these interactions do not exert nearly as significant an effect as the acid–sulfonate interactions and it seems likely this relatively weak perturbation does not induce a significant response from the group adjacent to the sulfonate group.

The authors are thankful to the Hitachi Chemical Company for a financial support of these studies.

REFERENCES

1. M. W. Urban and K. W. Evanson, *Polym. Commun.*, **31,** 279–282 (1990).
2. K. W. Evanson and M. W. Urban, *Surface and Interfacial Phenomena and Fine Particles in Water-Based Coatings and Printing Technology,* M. K. Sharma and F. J. Micale, Eds., Plenum Press, New York, 1991, pp. 197–213 and references therein.
3. K. W. Evanson, T. A. Thorstenson, and M. W. Urban, *J. Appl. Polym. Sci.,* **42,** 2297–2307 (1991).
4. K. W. Evanson and M. W. Urban, *J. Appl. Polym. Sci.,* **42,** 2309–2320 (1991).
5. K. W. Evanson and M. W. Urban, *J. Appl. Polym. Sci.,* **42,** 2287–2296 (1991).
6. R. C. Weast, Ed., *Handbook of Chemistry and Physics,* 69th ed., CRC Press, Boca Raton, FL, 1988.
7. G. N. Lewis, *J. Franklin Inst.,* **226,** 293–313 (1938).
8. R. S. Mulliken, *J. Chem. Phys.,* **19,** 514–515 (1951).
9. R. S. Mulliken and W. B. Person, *Molecular Complexes: A Lecture and Reprint Volume,* Wiley-Interscience, New York, 1969.
10. R. G. Pearson, *J. Am. Chem. Soc.,* **85,** 3533–3539 (1963).
11. R. S. Drago and B. Wayland, *J. Am. Chem. Soc.,* **87,** 3571–3577 (1965).
12. W. B. Jenson, *J. Adhesion Sci. Technol.,* **5**(1), 1–21 (1991).

Received February 12, 1992
Accepted April 2, 1992