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Mixed Composition Films of Spans and Tween 80 at the Air–Water Interface

Dongmei Lu and David G. Rhodes*

Department of Pharmaceutical Sciences School of Pharmacy, University of Connecticut,
Storrs, Connecticut 06269-2092

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Sorbitan fatty acid esters (Spans) and the corresponding polyoxyethylene (POE) adducts (Tweens) have a wide range of applications in the pharmaceutical and other industries. In some formulations, mixtures of Span surfactants and Tween surfactants are required, but some of the physical properties of these mixtures are not well defined. To assess the mixing behavior of Spans and Tweens, selected mixtures of these surfactants were studied using Langmuir compression isotherms. Our data indicate that mixtures of Tween 80 (polyoxyethylene sorbitan monooleate) with Span 80 (sorbitan monooleate), Span 83 (sorbitan sesquileate), or Span 85 (sorbitan trioleate) form expanded mixed monolayer films at the planar air–water interface. Mixing of Tween 80 with these three Spans exhibits significant repulsive nonideality except at low proportions of Tween 80 in Span 85. A model to explain the observed phase behavior is proposed.

Introduction

The nonionic surfactant sorbitan fatty acid esters (Spans) and the polyoxyethylene (POE) sorbitan fatty acid esters (Tweens) have many potential pharmaceutical applications. They are often used to improve the stability of water-in-oil-in-water (WOW) multiple emulsions, which are potentially useful vehicles for encapsulating water-soluble pharmaceutical compounds or nutrients.^{1–3} Multiple emulsion systems usually require at least two surfactants; a relatively hydrophobic surfactant to stabilize the WO emulsions and a relatively hydrophilic surfactant to stabilize the OW emulsions.^{4,5} Spans and Tweens, respectively, work well for this purpose, even though the individual surfactants alone do not produce stable multiple emulsion systems.^{6,7}

Several relationships between interfacial properties and emulsion stability have been established that provide useful insight into the development of more stable product. Surfactants stabilize emulsions by reduction of interfacial tension and formation of electrical or mechanical barriers.^{8,9} When a rigid interfacial complex forms at the primary W–O interface, emulsion stability is enhanced.^{6,7} Improved stability can also be achieved by maximizing the interfacial strength.^{10,11} In these systems it is not clear

how the interactions between Spans and Tweens in the interfaces contribute to the interface properties. In our study, we used a planar air–water interface to investigate Span–Tween interactions.

Although the surfactants are at an oil–water interface in emulsions, study of monolayer films at an air–water interface can provide useful data. At an air–water interface, the added complication of surfactant solubility in the oil phase is avoided. In addition, compared with simple surface tension measurements, this approach provides data over a much wider range of conditions. In studies with Langmuir films, the surface pressure is defined as $\pi = \gamma_0 - \gamma$, where γ_0 and γ are the surface tension of the subphase and the surfactant monolayer, respectively. The surface tension of the surfactant monolayer, γ , approaches zero when the surface pressure π is close to its maximum value γ_0 . In general, if one can attain in higher surface pressures, these conditions correspond to better surfactant interactions and more stable films.

The commercially available series of Span surfactants (Span 80, 83, and 85) and Tween 80 were used as the surfactants in the mixtures studied in this work. At room temperature, all three Spans and Tween 80 are viscous oils. Compared with Span surfactants, as shown in Figure 1, Tween 80 has a larger and more polar headgroup due to the polyoxyethylene groups. Tween 80 is water soluble up to 10% (w/w).

Experimental Materials and Methods

Materials. The surfactants Span 80 (sorbitan monooleate), Span 83 (sorbitan sesquileate), Span 85 (sorbitan trioleate), and Tween 80 (polyoxyethylene sorbitan monooleate) were obtained from Sigma-Aldrich and used without further purification. Chloroform, HPLC grade, was purchased from Fisher Scientific. Deionized water (with electrical resistance $>18 \text{ M}\Omega/\text{cm}$) was used for all experiments. Stock solutions of Span and Tween in chloroform were prepared gravimetrically. Mixtures of Span and Tween at specific mole fraction concentrations were also made by gravimetric measurements.

Monolayers. The Teflon trough of the Langmuir film balance (KSV "Mini-trough") was filled with deionized water as the subphase. The surface was then cleaned by repeated blank runs, and the surface was aspirated if any increase ($\geq 1 \text{ mN/m}$) in surface pressure was observed. Monolayers were formed by

* To whom correspondence should be addressed (telephone: 860-486-5413; fax: 860-486-1553; e-mail: d.g.rhodes@uconn.edu).

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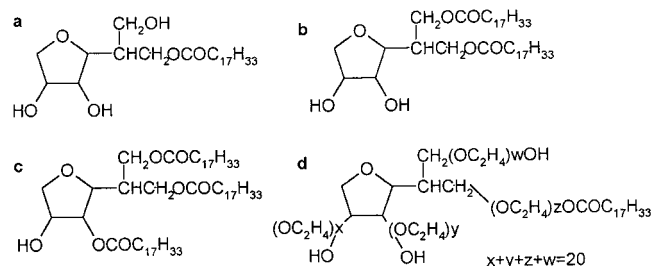


Figure 1. Structures of the Span and Tween surfactants used in this work: Span 80 (a), Span 83 (b), Span 85 (c) and Tween 80 (d).

depositing 18.67 nmol of surfactant in chloroform onto the water subphase with a Hamilton microsyringe. The starting area per molecule was 216 Å². The solvent was allowed to evaporate for 20 min prior to compression.

Isotherms. The surface pressure – molecular area ($\pi - A$) isotherms were obtained by symmetric compression with two hydrophilic Delrin barriers. The compression isotherms were performed using a constant gradient of surface pressure ($d\pi/dt = 1.0$ mN/m/min), with a maximum linear barrier speed of $dx/dt = 5$ mm/min (750 mm²/min). Surface pressure was monitored with an etched platinum Wilhelmy plate. Data were collected, archived, and presented as surface pressure as a function of mean molecular area (MMA). All isotherms were run at least three times under the same conditions with freshly prepared monolayers and subphase. All measurements were made at 20.0 ± 0.1 °C.

Excess Area Analysis. The $\pi - A$ isotherms were analyzed by evaluating the excess area per molecule of the mixture, A_E , at constant surface pressure, π , defined as

$$A_E = A_{12} - (X_1 A_1 + X_2 A_2) \quad (1)$$

where A_1 and A_2 are the areas per molecule of each of the single components at a constant surface pressure, X_1 and X_2 are their corresponding mole fractions, and A_{12} is the mean area per molecule of the mixed monolayer at the same surface pressure.¹² For a mixture of molecules that exhibits either ideal mixing or complete immiscibility, $A_E = 0$. Deviations from zero, either positive or negative, indicate miscibility and nonideal behavior.

Surface Pressure Relaxation Experiment. Relaxation studies were carried out to assess film stability by compressing the monolayer to a target surface pressure, and then following the decrease in surface pressure with time.¹³ In these experiments, films were compressed to 10 or 20 mN/m. Compression was halted and the surface pressure monitored over 20 min.

Results

Surfactant Compression Isotherms. The sorbitan headgroup of Span 80 has a single oleoyl side chain, Span 83 is a 2:1 mixture of the monooleate and dioleate, and Span 85 has three oleoyl side chains. Because all three Span surfactants have hydrophobic side chains that could easily be condensed in the air, they all yielded stable surface monolayers that could be compressed to surface pressures >30 mN/m. Based on the chemical structure (acyl chains per molecule), it would be expected that at a given surface pressure, the area per molecule of Span 83 would be larger than that of Span 80, and that of Span 85 would be the largest of the three. Figure 2 shows that this expected relationship is observed. Based on the expected area for oleate chains,¹⁴ sharp changes in compressibility of Span 83 and Span 85 isotherms (at 34 and 65 Å, respectively) probably reflected initiation of a

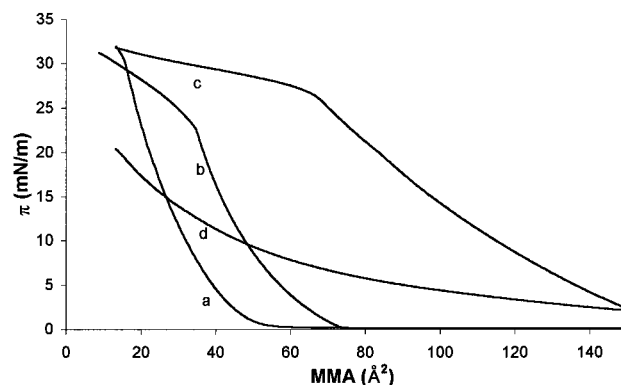


Figure 2. Compression isotherms for Span 80 (a), Span 83 (b), Span 85 (c), and Tween 80 (d).

collapse, rather than a transition to a solid phase. Compared with surfactants with saturated hydrophobic chains, such as sorbitan monopalmitate, these Spans produced expanded film due to the cis unsaturated bond on the oleoyl chain. The unsaturated bond not only increases the chain disorder, but is also capable of more intimate association with water molecules, thereby allowing the acyl chains of these molecules to remain closer to the water surface.^{15,16}

The nonionic hydrophilic surfactant Tween 80, is the ethoxylated derivative of Span 80. Substitution of the hydroxyl groups on the sorbitan ring with bulky polyoxyethylene groups increases the hydrophilicity of this molecule. The hydrophile–lipophile balance (HLB) value of Tween 80 is 15, and 1 mL could dissolve easily in 10 mL of water, but Tween 80 is surface active because of the oleoyl chain. On the other hand, because the polyoxyethylene side chains are bulky and soluble in the water subphase, spontaneous condensation of Tween 80 films is not expected. When Tween 80 is deposited on the water surface and compressed, one expects that as surface pressure increases, Tween 80 molecules will be forced into the subphase to a greater extent than for any of the Span surfactants. Compression of Tween 80 films (Figure 2) yielded a maximum surface pressure of $\pi \approx 20$ mN/m, which is much lower than that observed for the three Span surfactants. No collapse was observed, even when overloaded films were compressed to very small molecular areas.

Mixed Composition Isotherms. In the compression isotherm experiments with mixtures of Span 80 and Tween 80, maximum surface pressures were lower than those obtained with Span 80 alone (Figure 3a). This diminished stability suggests that acyl chains of Tween 80 disrupt the favorable acyl chain interactions of Span 80. As shown in Figure 3a, the MMA increases with increasing mole fraction of Tween 80 (X_{T80}). The compression isotherms with $X_{T80} = 0.6$ and 0.4 exhibited an instability at ~ 10 mN/m (~ 50 Å²). At this point, the surface pressure decreased significantly (0.30–1.0 mN/m), suggesting a molecular rearrangement or condensation from a metastable state. When the barrier speed was greatly decreased (1 mm/min) or increased (10 mm/min), the discontinuities were not observed. No other compositions, even $X_{T80} = 0.5$, exhibited this behavior.

The compression isotherms of mixtures of Span 83 and Tween 80 are shown in Figure 3b. At ~ 10 mN/m, the compression isotherms of $X_{T80} = 0.7$ – 0.9 exhibit shoulders,

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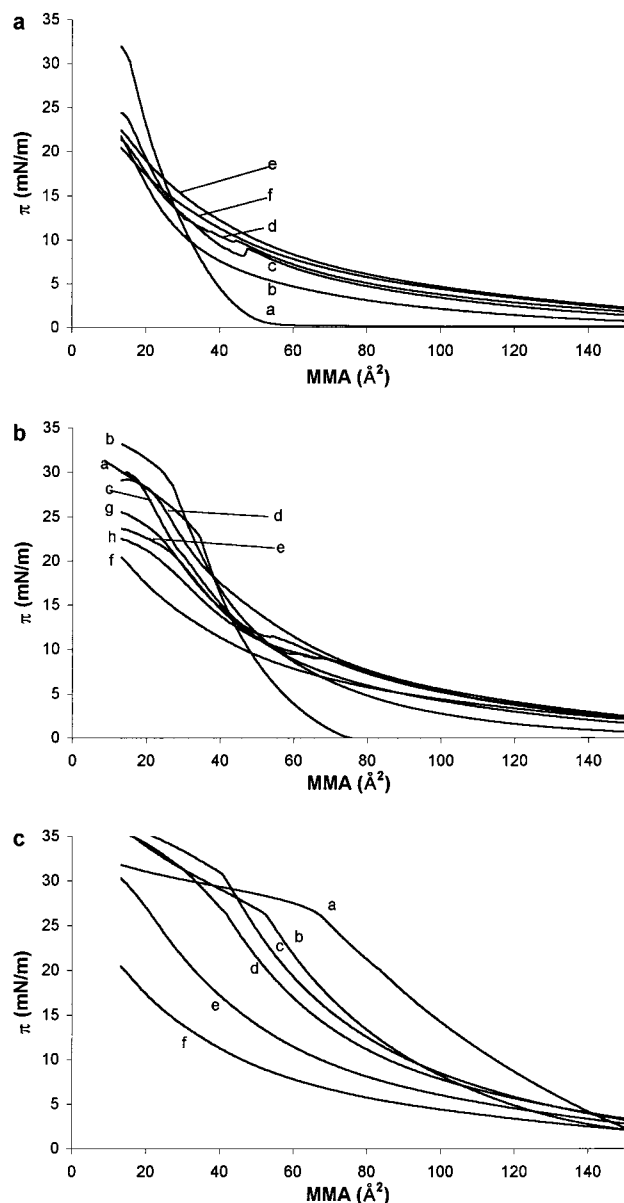


Figure 3. Compression isotherms for mixtures of Span 80 and Tween 80 (a), Span 83 and Tween 80 (b), and Span 85 and Tween 80 (c). Traces are for $X_{T80} = 0.0$ (a), 0.2 (b), 0.4 (c), 0.6 (d), 0.8 (e), and 1.0 (f). Additional traces in (b) are for $X_{T80} = 0.7$ (g) and 0.9 (h).

which suggested a phase coexistence region or relaxation from a metastable state as seen with the Span 80 data. At higher pressure, some of the mixed films had sharp transitions to higher compressibility, similar to that observed with films of pure Span 83.

Span 85 yielded highest surface pressure for pure surfactant, and high surface pressures were also attainable for mixtures with $X_{T80} = 0.1$ –0.6 (Figure 3c). There are no apparent low-pressure phase transitions in the compression isotherms for the mixtures of Span 85 and Tween 80.

Excess Area Analysis. In an ideal or immiscible mixed composition film, the mean molecular area will vary linearly with the mole fraction composition. Deviations from ideal mixing will be reflected by positive deviations from ideality if one component excludes the other, or negative deviations if one component induces condensation.¹² Data from all mixtures of Tween 80 and Span 80 or Span 83, and $X_{T80} = 0.4$ –0.9 mixtures for Tween 80 and

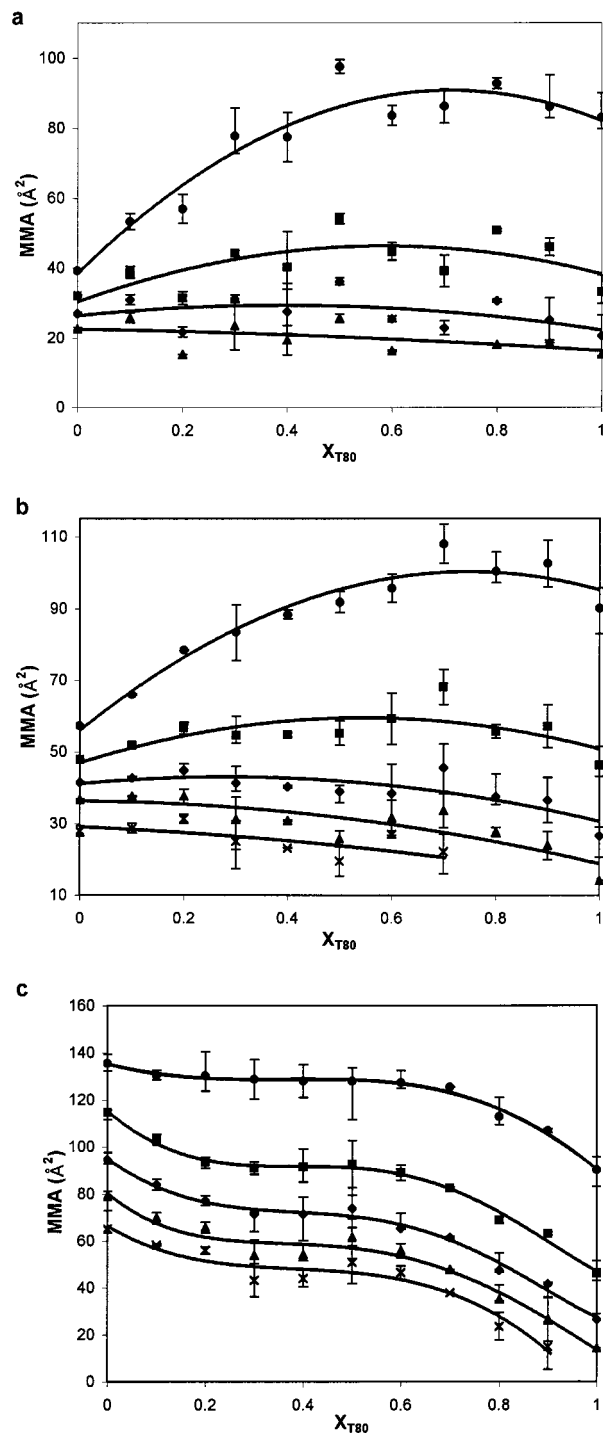


Figure 4. Mixing behavior for mixtures of Span 80 and Tween 80 (a), Span 83 and Tween 80 (b), and Span 85 and Tween 80 (c). Traces correspond to $\pi = 5$ mN/m (●), 10 mN/m (■), 15 mN/m (◆), 20 mN/m (▲), and 25 mN/m (X).

Span 85 showed positive deviations from ideality at all pressures for which this parameter was evaluated (Figure 4), indicating a repulsive interaction between the two surfactants. This deviation is most pronounced at lower pressures. Mixtures of Span 85 and Tween 80 exhibited nearly ideal behavior at low X_{T80} (Figure 4c). At higher surface pressures, there is little expansion. It is likely that at elevated pressures, Tween 80 is being squeezed from the monolayer into the subphase. The observed nonideality can also be expressed by excess area analysis.

The excess areas for mixtures of Span 80 and Tween 80 are shown in Figure 5a. For $X_{T80} = 0.9$, A_E was essentially

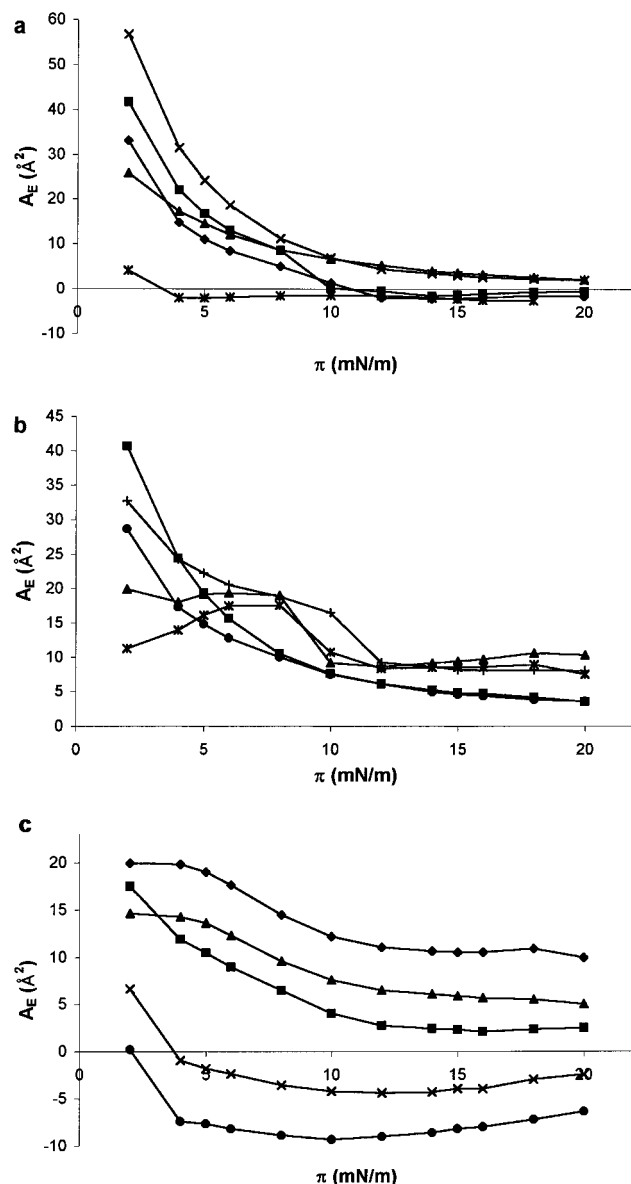


Figure 5. Excess area (A_E) analysis for mixtures of Span 80 and Tween 80 (a), Span 83 and Tween 80 (b), and Span 85 and Tween 80 (c). Traces in each graph are for $X_{T80} = 0.2$ (●), 0.3 (x), 0.4 (■), 0.6 (◆), 0.7 (+), 0.8 (▲), and 0.9 (*). Traces for $X_{T80} = 0.3$, 0.7, and 0.9 are omitted for clarity in some figures. Data were obtained for $X_{T80} = 0.1$ and 0.5, but not all are included in the plot.

zero at $\pi > 4$ mN/m. Other compositions showed positive deviation under all conditions except $\pi > 12$ mN/m for $X_{T80} = 0.4$ or 0.6. A discontinuity at $\pi \approx 10$ mN/m was observed for $X_{T80} = 0.4$.

Positive molecular excess area was obtained for all Span 83–Tween 80 mixtures under all conditions tested (Figure 5b). For $X_{T80} \leq 0.6$, A_E decreased with π . For $X_{T80} \geq 0.7$, A_E remained high or increased for $5 \text{ mN/m} < \pi < 10 \text{ mN/m}$. This region of data is the same as that which showed a discontinuity or phase transition in the compression isotherms.

Results of excess area calculations for mixtures of Span 85 and Tween 80 are different from the analogous results for Span 80 or Span 83 data. For compositions of $X_{T80} = 0.4$ –0.9, positive deviation was observed, indicating repulsive molecular interaction. In contrast, negative molecular excess area was obtained for $X_{T80} = 0.1$ –0.3, indicating condensation of the films (Figure 4c). This result

Table 1. Relaxation Experiments

molar fraction of Tween 80 X_{T80}	$\Delta\pi$ (mN/m) ^a	
	$\pi = 10$	$\pi = 20$
0	0.95	0.74
0.2	0.59	0.48
0.4	1.02	2.76
0.8	3.23	3.34

^a $\Delta\pi$ is the surface pressure change at $t = 20$ min when the film compression is halted at $\pi = 10$ or 20 mN/m.

suggests that relatively condensed monolayers were formed in these monolayers.

Relaxation Experiments. The idea that Tween 80 is stabilizing Span 85 films is supported by relaxation experiments (Table 1). Films with high X_{T80} exhibited rapid decreases in surface pressure at 10 or 20 mN/m. At $X_{T80} = 0.4$, relaxation was rapid for $\pi = 20$ mN/m but relatively slow at 10 mN/m. Films of pure Span 85 also relaxed slowly, but the slowest relaxation was observed for Span 85 films with small amounts ($X_{T80} = 0.2$) of Tween 80.

Discussion

Addition of a second surfactant to a film at the air–water interface could increase, decrease, or have no effect on the molecular area. Similarly, the second surfactant could stabilize the film, have no effect, or destabilize the film. Increased stability can be reflected in increased collapse pressure or, prior to collapse, condensation of the film due to favorable intermolecular interactions between the two surfactants and/or increased ability to maintain surface pressure if compression is halted. If two surfactants have compatible structures, the film of one surfactant can be a better “solvent” for the second surfactant on the mixed film, thus these two can form a phase that resists collapse. If the two surfactants do not mix well, due to steric incompatibility, for example, the free volume per molecule is increased and the film expanded.

Data from this study show that the Tween films are significantly less stable than any of the Span films, but even the Span films have low collapse pressures. Because all of these surfactants have oleate chains, they are not expected to have a solidlike phase at 20 °C. Although films of saturated C18 surfactants normally self-condense at this temperature, most oleate-based surfactants require much lower temperature to exhibit monolayer phase transitions. This fact, taken with the fact that the nonionic headgroups of surfactants such as Spans and Twens are relatively weak (compared with charged headgroups such as carboxylates or sulfates) helps to explain why the collapse pressure is so low. Tween-containing films have the additional complication that the surfactant has substantial water solubility and may be forced into the subphase as monomers or micelles at high pressures. This assumption was confirmed by compressions at higher and lower speed hysteresis experiments and kinetic experiments (data not shown). If the Tween films are compressed slowly (150 mm^2/min), the surface pressure is quite close to that obtained under conditions used for most measurements (750 mm^2/min) until the surface pressure reaches 5–10 mN/m. From this point on, the slower compression yields lower pressure. Similarly, rapid compression (1500 mm^2/min) resulted in surface pressure higher than that obtained in routine measurements. Further, in hysteresis experiments with Tween-containing films, the surface pressure during expansion was always significantly lower than during the preceding compression phase. For Tween-containing films that were compressed and then halted at a molecular area, the surface pressure exhibited relaxation to lower pressure due to loss of Tween.

For Span 80 and Span 83, some unusual features were observed in the compression isotherms at ~ 10 mN/m. In isotherms obtained with mixtures of Span 80 and Tween 80 at $X_{T80} = 0.4$ and 0.6 , it appeared that the film entered a metastable phase and then relaxed to a lower energy phase. In isotherms obtained with mixtures of Span 83 and Tween 80 ($X_{T80} = 0.7-0.9$), a similar instability appeared more like a coexistence region indicative of a phase transition, but fluctuations in the isotherms suggested that even this may be an unstable phase. In each case, it appeared that the pressure had exceeded a limit beyond which the film had to adapt through some change of structure or composition. One explanation that has been offered to explain similar data asserts that at low surface pressure, unsaturated oleoyl chains can remain in contact with the water surface. The discontinuity suggests a conformational change as the chains are forced to leave the water surface.¹⁷

It is also possible that the discontinuities observed in Tween 80 mixtures with Span 80 or Span 83 at $\pi \sim 10$ mN/m occur when the surface pressure reaches that required to force Tween into the subphase. The metastable mixture may result from partial stabilization of Tween 80 in the Span films. Such a mixed phase appears to have very specific surface pressure and composition limits. Whether these conditions are found in nonplanar oil-water interfaces remains to be demonstrated. In addition, the mole fraction of Tween 80 in equilibrium, uncompressed mixed films has not been measured, but such measurements will be difficult because of the nonideality demonstrated here.

The mixed films all showed nonideal behavior, indicating that the surfactants were at least partially miscible. However, data for Span 80 and Span 83 indicated a strong repulsive interaction, suggesting that these Spans are not easily miscible with Tween 80. Mixtures of these Spans and Tween 80 tend to form expanded films in mixed monolayers. Some mixtures of Tween 80 with Span 83 ($X_{T80} = 0.1-0.3$) exhibited little nonideality above $\pi = 10$ mN/m, but this apparent $\pi-A$ relationship may simply reflect Tween being lost to the subphase.

Could Tween lost to the subphase explain the apparent nonideality (Figure 4)? If the Tween 80 had not been forced into the subphase, the area at a given pressure would be even higher, so the apparent nonideality is a minimum estimate.

It has been suggested elsewhere that Span and Tween molecules at air-water interfaces are likely to be located at different depth of the headgroup in the aqueous phase because of their different solubilities in water.^{18,19} At low pressure, assuming miscible surfactants, the association of Tween 80 molecules with the film was facilitated by the Span surfactants. At low pressure and/or low X_{T80} , Tween-Tween interactions were negligible (Figure 6A). At higher pressure or higher X_{T80} , the POE chains on the headgroup experience steric interaction and are either forced from the monolayer (Figure 6B) or impose a larger molecular area (Figure 6C). If the Span molecules have more acyl chains, the hydrophobic area per molecule would be larger and the film would be better able to accommodate a single-chain surfactant like Tween (Figure 6D).

When surfactants mix together in a film, several factors determine the response of the system to high pressure when the film approaches steric and energy limits: the

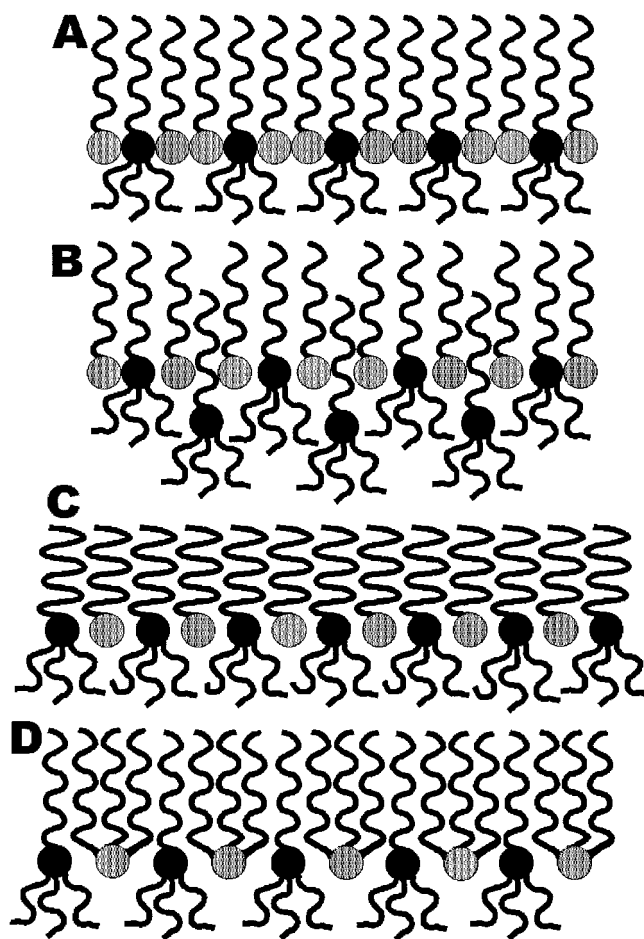


Figure 6. Mixed monolayer of Span (stippled) and Tween (solid). At low X_{T80} (A), a film can be compressed without forcing Tween 80 POE chains to interact. At higher X_{T80} , interaction occurs more easily. At the same molecular area illustrated in (A), Tween 80 molecules are forced into the subphase (B). At lower π , POE interaction can be minimized but acyl chains will be more disordered (C) and occupy a larger area. If the hydrophobic surfactant has more acyl chains, the hydrophobic area can be filled and chain order increases (D).

overall shape compatibility of the surfactants, the extent of favorable interactions of hydrophobic tails, and potential repulsive interactions between headgroups. For the Span surfactants used in this work, the energetic contribution due to hydrophobic interaction is the strongest for Span 85 and weakest for Span 80. The repulsive interaction between Tween 80 molecules is probably due to steric interaction. The aqueous solubility of Tween 80 allows for the number of Tween 80 molecules at the interface to decrease as a response to stress. In different mixtures, this response occurs at conditions that reflect various hydrophobic interactions and shape compatibility.

As illustrated in Figure 7, single-chain surfactants, such as Span 80, might be better suited to a positive curvature surface such as a bubble or an oil-water interface in which the free volume between acyl chains could be occupied by molecules of the oil phase. Addition of Tween 80 to a Span 80 film at the air-water interface does nothing to facilitate hydrophobic interaction between surfactant molecules. Thus, the film does not strongly support or retain Tween 80 under pressure or high X_{T80} . The situation is only slightly improved with Span 83, in which the film is a mixture of single- and double-chain surfactants.

Because Span 85 has three acyl chains, capable of stable van der Waals interactions, films of this surfactant at an air-water interface can be compressed to higher surface

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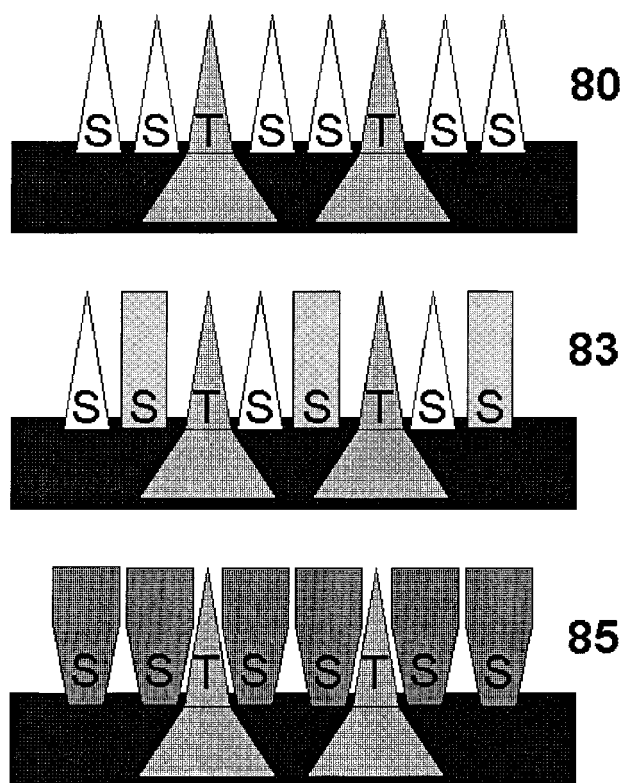


Figure 7. Interaction model of surfactants Span 80 and Tween 80 (a), Span 83 and Tween 80 (b), and Span 85 and Tween 80 (c).

pressure than those of Span 80, Span 83, or Tween 80. Span 85 has a large hydrophobic cross-sectional area relative to that of its headgroup,²⁰ so molecules with small

hydrophobic cross-sectional areas and large headgroups might complement molecules in a Span 85 film. Thus, at low X_{T80} and/or low surface pressure, Tween 80 can fit easily into a Span 85 film and can actually condense a film of Span 85. As the pressure increases and/or X_{T80} increases, steric interactions between the POE chains of Tween 80 eventually overcome favorable hydrophobic interactions, and the Tween 80 is forced into the subphase. Figure 4c supports this model. At low X_{T80} , Span 85 at the air–water interface can accommodate and stabilize Tween 80 molecules, so the mixing behavior appears nearly ideal. However, as Tween 80 becomes the dominant surfactant, the steric repulsion begins to dominate and the mixture becomes nonideal.

Relaxation data (Table 1) also support the conclusion that moderate amounts of Tween 80 can stabilize Span 85 films. The relaxation results not only indicate that small amounts of Tween 80 can be accommodated by a Span 85 film, but also that mixed films at low X_{T80} are even more stable than films of Span 85.

Conclusions

Stable Span 80, Span 83, or Span 85 films can be formed at the air–water interface. The presence of Tween 80 destabilizes Span 80 or Span 83 films but some stabilization is observed for Span 85 at low X_{T80} . Tween 80 is miscible with all three Span surfactants in monolayers at the air–water interface, but the mixture is generally nonideal.

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