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pH-Dependent Interfacial Tension and Dilatational Modulus Synergism of Oil-Soluble Fatty Acid and Water-Soluble Cationic Surfactants at the Oil/Water Interface

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Cite This: *Langmuir* 2021, 37, 11573−11581 Read Online

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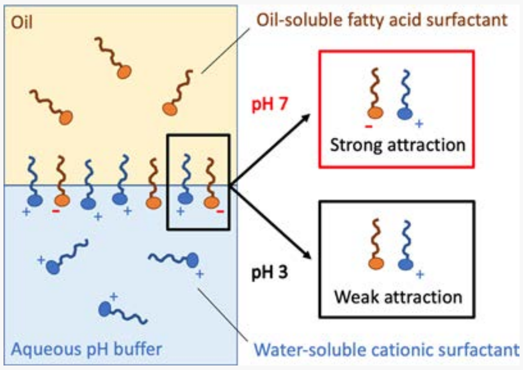


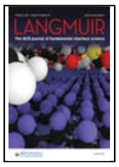
ABSTRACT: While the concept of interfacial tension synergism in surfactant mixtures is well established, little attention has been paid to the possibility of synergistic effects on the interfacial rheology of mixed surfactant systems. Furthermore, interfacial tension synergism is most often investigated for mixtures of surfactants residing in a single phase. Here, we define dilatational modulus synergism and report a study of interfacial tension isotherms and complex dilatational moduli for a binary surfactant system with the two surfactants accessing the oil/water interface from opposite sides. Using an oil-soluble fatty acid surfactant (palmitic acid, PA) that may be ionized at the oil/water interface and a quaternary ammonium water-soluble cationic surfactant (tetradecyltrimethylammonium bromide, TTAB), the binary interfacial interaction was tuned by the aqueous phase pH. Interfacial tensions and dilatational moduli were measured by the pendant drop method for the binary surfactant system as well as the corresponding single-surfactant systems to identify synergistic effects. The possible occurrence of dilatational modulus synergism was probed from two perspectives: one for a fixed total surfactant concentration and the other for a fixed interfacial tension. The aqueous pH was found to have a controlling effect on both interfacial tension synergism and the dilatational modulus synergism. The conditions for interfacial tension synergism coincided with those for the storage modulus synergism: both tension and storage modulus synergisms were observed under all conditions tested at pH 7 where PA was mostly deprotonated, for both perspectives examined, but not for any conditions tested at pH 3 where PA is mostly protonated. The loss modulus synergism exhibited more complex behaviors, such as frequency and interfacial tension dependences, but again was only observed at pH 7. The tension and modulus synergism at pH 7 were attributed to the increased attraction between ionized PA and cationic TTAB and the formation of catanionic complexes at the oil/water interface.

1. INTRODUCTION

Interfacial tension synergism describes the condition whereby a particular degree of interfacial tension reduction is achieved using a lower total concentration of a surfactant mixture than is required for either individual surfactant acting alone.[1−3] It is commonly investigated for mixtures of water-soluble surfactants at the air/water interface and much less commonly at oil/water interfaces.[2] Different approaches have been developed to model the binary surfactant interfacial tension behaviors, including but not limited to regular solution theory,[2,4] Frumkin-type adsorption models,[5,6] and some molecular-based theories.[7] In general, the synergistic effect in interfacial tension is explained by a strong attractive interaction between two surfactants at the interface. Specifically, in Hua and Rosen's model,[1] where the binary adsorbed layer is treated as a two-dimensional regular solution, the criteria of interfacial tension synergism demand a large negative interaction parameter, indicating a strong binary attraction.

There is nothing inherent in the theory of interfacial tension synergism that would preclude the application of the concept to binary surfactant systems wherein the two surfactants access the interface from different phases (so they "meet" at the interface). Such systems occur in diverse settings, such as in foods where vinegar and fatty acid-containing oils are mixed for salad dressings, in surfactant flooding enhanced oil recovery technology where the applied surfactants may interact with surface-active naphthenic acids in crude oil,[8] and in the digestive tract where bile salts emulsify oily substances laden with lipids and other surface-active compounds.[9,10] Despite its

Received: July 15, 2021
Revised: September 10, 2021
Published: September 23, 2021



https://doi.org/10.1021/acs.langmuir.1c01889
Langmuir 2021, 37, 11573−11581

relevance to natural and industrial processes, interfacial tension synergism in such systems has not been thoroughly explored.

In applications where surfactants come into contact from opposite sides of the oil/water interface, both the thermodynamic and dynamic mechanical properties of the interface play important roles, as in the process of emulsification or interfacial deformation under flow. A fundamental connection is expected between the thermodynamic phenomenon of interfacial tension synergism and interfacial dilatational rheological properties. The latter depend not only on the thermodynamic interfacial equation of state but also on the relaxation dynamics of adsorbed layers. It is of interest to establish a connection between interfacial tension synergism and the conditions that may yield synergistic increases in the magnitudes of the interfacial dilatational moduli. The literature pertaining to interfacial dilatational rheology in surfactant mixtures is limited and thus far is restricted to systems where all the surfactants were dissolved in a single fluid phase.[6,11−17]

Here, interfacial tension isotherms and dilatational moduli were investigated for an oil-soluble fatty acid surfactant, palmitic acid (PA), and a water-soluble cationic surfactant, tetradecyltrimethylammonium bromide (TTAB), at the tetradecane/water interface, both alone and in binary combinations where PA was dissolved in tetradecane and TTAB in water. The aqueous phase pH was manipulated to tune the interaction between the two surfactants, as it controls the degree of ionization of the fatty acid at the interface. It was hypothesized that the ionization of the PA carboxyl group at the interface would significantly enhance the interfacial activity of PA and strengthen its attractive interaction with the water-soluble cationic TTAB at the tetradecane/water interface.

The dilatational modulus E is defined by the change in interfacial tension σ with respect to an isotropic change in area A, i.e., $d\sigma/d\ln A$. It is a dynamic property that is generally expressed in terms of a complex modulus (E^*). The real and imaginary parts of the complex modulus are the storage modulus (E') and the loss modulus (E''). The magnitudes and relative contributions of each are dictated by the relaxation processes that occur during interfacial area perturbations. To date, dilatational modulus models have been developed based upon various interfacial relaxation processes, including surfactant diffusion between the sub-interface and the bulk phase, as in the diffusion-limited Lucassen and van den Tempel model,[18] and other processes such as surfactant adsorption and desorption,[19] multilayer formation,[19] and micellization.[19,20] For binary surfactant systems, the only model available is the binary diffusion-limited model where the surfactant interaction effects are embedded in the binary equilibrium adsorption model.[6,21] Models do not yet exist for binary systems controlled by intrinsic interfacial dynamics such as adsorption or desorption steps or structural relaxations.

More complex scenarios may be envisioned. The binary interaction affects the dilatational properties in complicated ways as it modifies not only the equilibrium adsorption behavior and the associated interfacial equation of state but also dynamic processes that are triggered by interfacial area perturbations. For example, the presence of one surfactant at the interface may increase or decrease the intrinsic adsorption rate of the other surfactant if they attract or repel each other. Attractions or repulsions would also change the intrinsic desorption rates. When both surfactants originate from the same phase, as in binary aqueous solutions or binary oil-based solutions, surfactants will desorb into the phase whence they came when the interface is compressed. When surfactants originate from opposite phases, there is a possibility that surfactant interactions at the interface may produce complexes that allow surfactants to desorb as part of a complex into the opposite phase. Alternatively, if such complexes were poorly soluble in either phase, the barrier against desorption of either surfactant back into the phase whence it came could become prohibitively large.

Since interfacial tension is purely thermodynamic and dilatational moduli depend on both thermodynamic and dynamic properties, conditions that lead to interfacial tension synergism might, or might not, lead to dilatational modulus synergism, or vice versa. In this work, the potential for synergistic effects in the dilatational properties of the PA/TTAB model system and their pH-dependence will be explored and linked to interfacial tension synergism.

2. MATERIALS AND METHODS

2.1. Materials. The oil phase solvent, tetradecane (≥99%), was purchased from Sigma-Aldrich and purified by passage through a column of basic-activated alumina (Beantown Chemical) to remove residual surface-active impurities. Water was first de-ionized by reverse osmosis and further ultrapurified to 18 MΩcm resistivity by a Barnstead Nanopure Diamond system. The oil-soluble fatty acid surfactant, PA (≥99%), and the water-soluble cationic surfactant, TTAB (≥99%), were purchased from Sigma-Aldrich and used as received. Phosphoric acid (≥99.999%), monosodium phosphate monohydrate (≥98%), and disodium phosphate heptahydrate (≥98%) were purchased from Sigma-Aldrich and used as received to prepare pH 3 and pH 7 buffer solutions. A corresponding conjugate base to acid weight ratio of 12.55 was used for pH 3 buffer and 2.66 for pH 7 buffer. The ionic strength of both the pH 3 and pH 7 buffers was fixed at 20 mM. The aqueous phase solutions were prepared by dissolving TTAB in the appropriate buffer. The oil phase solutions were prepared by dissolving PA in the purified tetradecane. The two surfactants are known to be practically insoluble in the other phases. This was supported by the lack of conductivity change in either phase after equilibrating tetradecane against an aqueous TTAB solution, equilibrating a pH 7 aqueous buffer against a tetradecane solution of PA, or equilibrating PA and TTAB solutions against each other (see the Supporting Information for details). The highest concentration of PA in tetradecane used in this work was 18 mM, slightly below the solubility limit of PA in tetradecane reported at 23.5 ± 1.5 °C.[22,23] Here, all samples were prepared and experiments were performed at a room temperature of 21.4 ± 0.3 °C. All prepared solutions were transparent with no visible indication of aggregation.

2.2. Interfacial Tension Measurements. The interfacial tension at the tetradecane/water interface was measured by pendant drop tensiometry (Biolin Scientific Optical Tensiometer) at various concentrations of PA in tetradecane and TTAB in water for two different aqueous pH conditions. A drop of aqueous phase solution was generated at the tip of a needle immersed in the oil phase solution and imaged as a function of time as surfactants adsorbed from solution to the tetradecane/water interface. With the One Attension software (Biolin Scientific Optical Tensiometer), the drop shape was digitized and used to calculate the interfacial tension by fitting to the Young-Laplace equation.[24] Drop shapes were verified not to deviate significantly from the Young-Laplace shapes by a method described in detail elsewhere.[25] The dynamic interfacial tension was monitored until the interfacial tension reached a steady state, which we practically defined as when the interfacial tension decreased by less than 0.2 mNm^{-1} min^{-1}.

2.3. Dilatational Modulus Measurements. After the adsorption steady state was achieved, the drop volume was subjected to small-amplitude oscillatory perturbations, resulting in sinusoidally oscillating drop area with an area strain amplitude of ∼1%. Oscillation frequencies (f) were varied from 0.05 to 1 Hz. Changes in interfacial

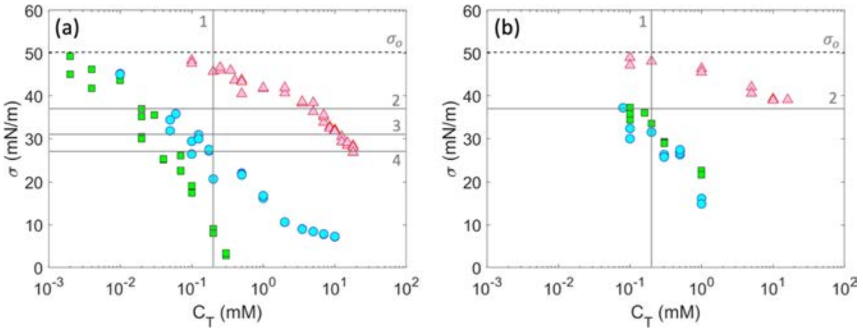


Figure 1. Interfacial tension isotherms for single PA (red triangles), single TTAB (blue circles), and 1:1 PA/TTAB (green squares) systems with the aqueous phase at (a) pH 7 and (b) pH 3. Dashed lines denote the interfacial tension of the clean interface (σ_o= 50.2 ± 0.1 mN/m). Solid lines, marked 1−4, denote the basis for comparison of dilatational moduli in Section 3.2.

tension were monitored during area perturbations and the complex dilatational moduli were calculated as

$$E^*(f) = \frac{F_f\{\Delta\sigma\}}{F_f\{\Delta \ln A\}} = E'(f) + iE''(f) \tag{1}$$

where F_f is the Fourier transform evaluated at the driving frequency of the imposed perturbation (f), $\Delta\sigma$ is the change in interfacial tension, and $\Delta \ln A$ is the areal strain.

3. RESULTS AND DISCUSSION

3.1. Interfacial Tension Synergism.

The measured interfacial tension of the clean tetradecane interface with purified, unbuffered water was constant at 50.2 ± 0.1 mN/m. Switching the water to either the pH 3 or pH 7 buffer solution did not change the interfacial tension beyond the uncertainty of the measurement. The lack of any detectable time dependence for the interfacial tension with purified water or the two buffers indicates that none of these liquids contained significant amounts of surface-active species. In addition, dissolving TTAB in either aqueous buffer had no effect on the pH level.

Figure 1 reports the interfacial tension isotherms for the following interfacial conditions: PA in tetradecane vs aqueous buffer, tetradecane vs TTAB in aqueous buffer, and PA in tetradecane vs TTAB in aqueous buffer. For the binary surfactant condition, the ratio of the molar PA concentration in tetradecane to the TTAB concentration in the aqueous phase was fixed at 1:1, while the total concentration was varied. These conditions were investigated at pH 3 and at pH 7. The concentration reported in the isotherms, C_T, is either the total concentration reported for the 1:1 binary system as the sum of the PA and TTAB concentrations in their corresponding phases or simply the concentration of PA in tetradecane or TTAB in water for the two single-component systems. Note that the plots below should be called interfacial tension vs initial concentration relations, as the surfactant in the drop phase (TTAB) may be partially depleted at the lowest concentrations as adsorption equilibrates.[5,26] For convenience, the term "interfacial tension isotherms" will still be used to describe those relations. Note that dilatational moduli were measured using experimental conditions that match these interfacial tension isotherm measurements.

The aqueous pH had a controlling effect on the systems involving PA, both in the presence and absence of TTAB, but it barely affected the interfacial tension isotherm of single-component TTAB, which, being a quaternary ammonium salt, does not have a pH-dependent charge. At pH 7 (Figure 1a), PA exhibited greater interfacial tension reduction against the TTAB-free aqueous buffer than it did at pH 3 (Figure 1b), and the 1:1 PA/TTAB binary system showed a clear interfacial tension synergism for interfacial tensions sampled below ~37 mN/m at pH 7 (for example, see the cut lines 2−4 in Figure 1a). In contrast, at pH 3, the PA/TTAB system showed no interfacial tension synergism under any condition considered. As noted above, interfacial tension synergism is defined as occurring when the total concentration of a surfactant mixture required to produce a particular degree of interfacial tension reduction is less than that required by either of the surfactants acting in the absence of the other. This is readily identified in the interfacial tension isotherms (Figure 1) if the binary surfactant isotherm is on the left (toward lower concentration) of the other two. An alternative way to define the tension synergism is by comparing the interfacial tensions at a fixed total concentration. In this sense, a binary system would exhibit interfacial tension synergism if it achieved a lower interfacial tension than either of the single-component systems at the same total concentration (for example, see the cut line 1 in Figure 1a).

The pH effect on tension synergism could be attributed to the difference in the degree of ionization of adsorbed PA at the two pH values, leading to a significantly different binary attractive interaction between PA and TTAB at the interface. The two pH values in this work were ~2 pH units above or below the typical p*K*a of a carboxylic group in water (~5),[27] so a significantly more ionized PA adsorbed layer at pH 7 and a sparsely ionized one at pH 3 are to be expected. Ionization increases the amphiphilicity of PA and thus favors adsorption from tetradecane to the tetradecane/water interface, as indicated by the greater interfacial tension reduction caused by PA at pH 7 than at pH 3 (compare Figure 1a and Figure 1b). Furthermore, its negative charge would favor a stronger attractive interaction with the cationic TTAB at the interface. Since interfacial tension synergism occurred at pH 7, but not pH 3, PA ionization was evidently the primary driver of interfacial tension synergism in this system.

3.2. Synergistic Effect in the Interfacial Dilatation Properties.

Section 3.1 showed that equilibrium interfacial tension synergism could be turned on or off by controlling the pH of the bulk aqueous phase. In this section, with the same system, another pH-dependent synergistic effect, now concerning the dynamic complex dilatational modulus (E^*), will be addressed. To motivate the results to be presented in this section, we note that the binary surfactant interaction is expected to affect the dynamic dilatational modulus in a more

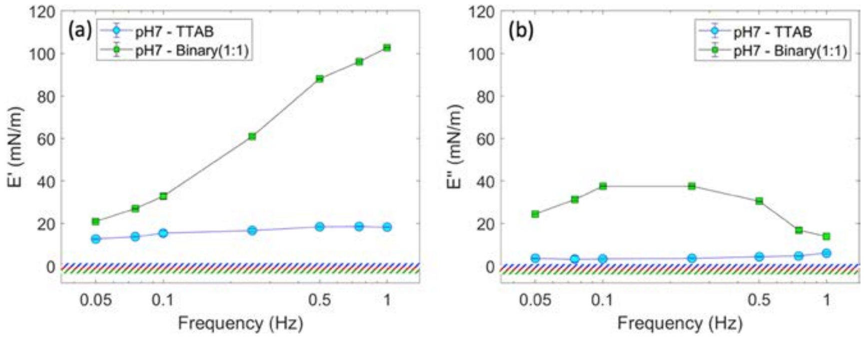


Figure 2. Frequency dependence of (a) storage and (b) loss moduli for systems at a total surfactant concentration of 0.2 mM: single TTAB at pH 7 (blue circles) and 1:1 PA/TTAB at pH 7 (green squares). The striped bands represent data for single-component PA at pH 7 and data for all systems at pH 3, which are indistinguishable from the noise. Corresponding interfacial tensions for 0.2 mM total concentration: 45.7, 20.7, and 8.0 mN/m for PA, TTAB, and binary systems at pH 7, respectively; 48.1, 31.5, and 33.6 mN/m for the same systems at pH 3. Uncertainties estimated from the difference between two replicate experiments were smaller than or comparable to the symbol size.

complicated fashion than the equilibrium interfacial tension. It will affect not only the underlying thermodynamic effects but also dynamic interfacial relaxation processes that contribute to the dilatational modulus.

First, the equilibrium interfacial tension will depend on the surface excess concentrations (Γ_i) of both surfactants (i = 1,2) according to their binary interfacial equation of state $\sigma(\Gamma_1, \Gamma_2)$. The dilatational modulus approaches the thermodynamic Gibbs elasticity, $E_G = -\sum \left(\frac{\partial\sigma}{\partial \ln \Gamma_i}\right)_{\Gamma_{j\neq i}}$, in the high frequency limit.[21] Thus, the details of the binary interfacial equation of state dictate that the limiting behavior of the binary system must differ from that of either of the single-component systems.

Second, in addition to the binary surfactant diffusion relaxation demonstrated in the literature,[21] other interfacial relaxation processes including adsorption and desorption from the interface and structural relaxations within the layer for the binary surfactant system will all differ from the single-component surfactant system. For the sake of illustration, consider that the adsorption or desorption dynamics may be altered by the effects of binary surfactant interactions on their energy barriers. Strong intermolecular association could produce surfactant complexes that have large energy barriers against desorption or that display stronger elastic resistance to deformation. Currently, no existing dilatational rheology models account for these complexities or for the effects of surfactant interactions on the intrinsic adsorption or desorption kinetics in binary surfactant systems.

Before proceeding to the dilatational modulus data, we consider how to define dilatational modulus synergism. Since surfactant formulation design often focuses on concentrations or achieving a certain value of interfacial tension, we choose to define modulus synergism according to two perspectives. The first perspective for reporting dilatational modulus synergism is to make the comparison at a fixed total surfactant concentration (following the vertical cut lines in Figure 1). The second perspective compares dilatational moduli for a fixed interfacial tension (following the horizontal cut lines in Figure 1). In both cases, we report the storage modulus (E') and the loss modulus (E'') separately for each single surfactant system and for the binary system and then identify the conditions under which the binary system shows larger storage and/or loss moduli than both of the single-component systems. Since dilatational modulus synergism is not uniquely defined as either at fixed concentration or at fixed tension, we examine both. This contrasts with publications in which one may identify modulus synergism in binary surfactant systems. In those studies, dilatational moduli synergism could only be identified for either a fixed total concentration[12,15−17] or a fixed tension[13] condition, but not both. Modulus synergism may be observed in either the storage modulus, the loss modulus, or perhaps both moduli. In the following, modulus synergism will be discussed based upon the two perspectives and then comparisons will be made between this work and the literature where binary surfactant layers adsorbed from one single phase also show modulus synergism.

3.2.1. Modulus Synergism at a Fixed Total Concentration.

The first perspective considers the modulus synergism at a fixed total concentration. As a control, the dilatational storage and loss moduli of the clean tetradecane/aqueous buffer interfaces were found to be undetectably small for the frequency range probed. Figure 2 shows the storage and loss moduli as a function of oscillation frequency for interfacial layers formed by spontaneous adsorption from bulk phases of the same total surfactant concentration of 0.2 mM (the cut line 1 in Figure 1). Each system produced a different equilibrium interfacial tension at this total concentration. These are reported in the caption of Figure 2.

At this concentration, the binary system yielded significant storage and loss moduli at pH 7. The only single-component system to yield a significant modulus was TTAB at pH 7, which yielded storage and loss moduli that were significant but smaller than those of the binary system. All other conditions yielded undetectably small moduli (the striped bands around zero modulus in Figure 2), where the interfacial tension responses to area perturbation were indistinguishable from noise across the examined frequency range.

The undetectably small storage and loss moduli at 0.2 mM total concentration for the single-component PA system at pH 7 and for all systems at pH 3 have two possible origins. Either (1) the interface is so dilute that the Gibbs elasticity is undetectably small under these conditions or (2) all modes of interfacial relaxation in these systems relax on shorter timescales than that of the largest imposed dilatational frequency (1 Hz). In the latter case, neither surfactant adsorption nor desorption, bulk diffusion, nor any important internal adsorbed layer stress relaxations would have occurred at sufficiently slow rates to produce a detectable modulus. To experimentally differentiate between these possibilities, direct

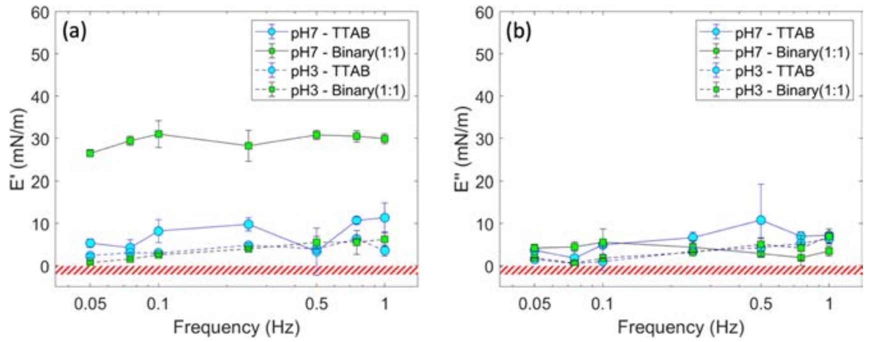


Figure 3. Frequency dependence of (a) storage and (b) loss moduli for systems at a fixed equilibrium interfacial tension of 37 ± 2 mN/m: single TTAB (blue circles) and 1:1 PA/TTAB (green squares) at pH 7 (solid lines) and pH 3 (dashed lines). The striped bands represent data for PA at pH 7 and pH 3, which are indistinguishable from the noise. Corresponding total concentrations: 5, 0.06, and 0.015 mM for PA, TTAB, and binary systems at pH 7, respectively; 16, 0.08, and 0.16 mM for the same systems at pH 3. Uncertainties were estimated from the difference between two replicate experiments.

measurements of the Gibbs elasticity with high-frequency rheological methods[28] may be needed. As an alternative, the Gibbs elasticities could be estimated for the single-component systems by applying the Langmuir adsorption model to their tension isotherms. This method is only suitable when the surface coverage is low. This requirement is met for PA at 0.2 mM, and this analysis indicated that the Gibbs elasticities of single-component PA systems for both pH values at 0.2 mM were less than 5 mN/m. This would favor the first possibility. When the surface coverage is high, this analysis method is prone to overestimation.[29] Therefore, we would not attempt to estimate the Gibbs elasticity when the modulus measurements were conducted for conditions in the large slope region of the tension isotherm (Figure 1).

At pH 7, TTAB produced a storage-dominant dilatational response with a nearly frequency-independent storage modulus, which indicates that some interfacial dynamic modes did not fully relax within the frequency range tested. Both the storage and loss moduli for the binary system at pH 7 were significantly larger than those of the single-component TTAB system. The binary system transitioned from having nearly equal storage and loss moduli at 0.05 Hz to a storage-dominant behavior as the frequency increased to 1 Hz. The storage modulus increased monotonically, while the loss modulus passed through a maximum.

Having significantly larger storage and loss moduli compared to the single-surfactant PA and TTAB systems at pH 7, the binary system exhibited synergism for both moduli. All the moduli at pH 3 were undetectably small so any synergy that may have existed at pH 3 was too weak to detect. The enhanced modulus for the binary system at pH 7 may be attributed to the formation of catanionic surfactant complexes at the interface. These complexes will likely have altered desorption kinetics and denser packing at the interface, similar to catanionic surfactant complexes adsorbed at the interface from aqueous phases.[15−17,30,31] At pH 3, where PA was not significantly ionized, there was little driving force to form catanionic complexes, and no significant modulus developed in the binary system.

During a dilatational rheology measurement, the interface is driven away from its equilibrium state by perturbing the interfacial area. The rates of surfactant adsorption and desorption, and diffusion to or from the perturbed interface, will depend on the degree to which the entire system—consisting of two bulk phases and the interface—is driven away from equilibrium. As a result, the measured dilatational response may depend on whether or not solute partitioning between the two bulk phases has reached equilibrium prior to the start of the dilatational measurement. Thus, to verify that the results presented here correspond to a fully equilibrated system, additional measurements were made wherein a solution of PA in tetradecane was pre-equilibrated for three days with a pH 7 aqueous solution of TTAB, with a total concentration of 0.2 mM that corresponds to the measurements described in this section. Three days is far longer than the time required for the interfacial tension to reach its steady state and ensures that the bulk partitioning is fully equilibrated. An oil/water interface was then created from these pre-equilibrated solutions, allowed to reach the interfacial tension steady state, and subjected to dilatational rheology measurements, with results reported in Supporting Information Figure S1. The interfacial tension matched that reported here, as did the plots of the frequency dependence of storage and loss moduli. Thus, the results reported here are consistent with a fully equilibrated system.

3.2.2. Modulus Synergism at a Fixed Interfacial Tension.

The second perspective considers modulus synergism at a fixed interfacial tension. In this case, modulus synergism will be specified as the condition when binary surfactant systems produce larger storage and/or loss moduli compared to both single-component surfactant systems having the same interfacial tension. As an example, Figure 3 reports the frequency dependence of the storage and loss moduli for adsorbed layers with an equilibrium interfacial tension of 37 ± 2 mN/m (refer to cut line 2 in Figure 1). Each system required a different surfactant concentration to produce this equilibrium interfacial tension. Those concentrations are reported in the caption of Figure 3.

At this interfacial tension, the moduli of PA at both pH values were undetectably small across the frequency range tested (the striped bands in Figure 3). All other systems have detectable but small moduli except for the binary system at pH 7, which had a significantly larger storage modulus than the others. The undetectably small moduli of PA at pH 3 and 7 have the same possible origins as in the previous section. The binary system at pH 7 showed a storage-dominant dilatational response with a nearly constant storage modulus, indicating no significant relaxation of stress-determining modes even at the lowest frequency examined (0.05 Hz), similar to the case of the single-component TTAB system at pH 7 in Figure 2a. At pH 7,

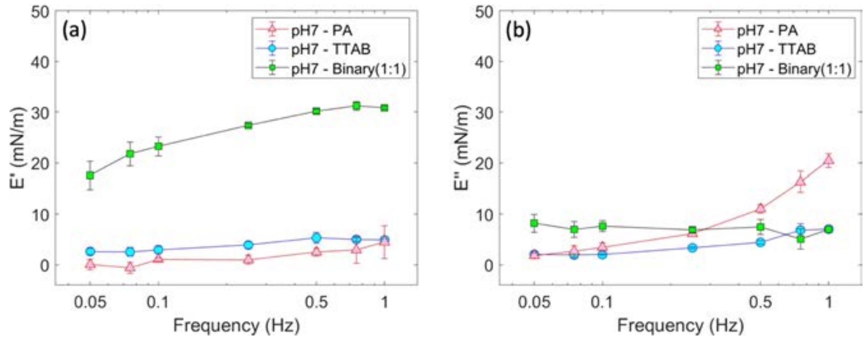


Figure 4. Frequency dependence of (a) storage and (b) loss moduli for systems at an equilibrium interfacial tension of 31 ± 2 mN/m and at pH 7: single PA (red triangles), single TTAB (blue circles), and 1:1 PA/TTAB (green squares). Corresponding total concentrations: 10, 0.125, and 0.02 mM for PA, TTAB, and binary systems, respectively. Uncertainties based on three replicate experiments.

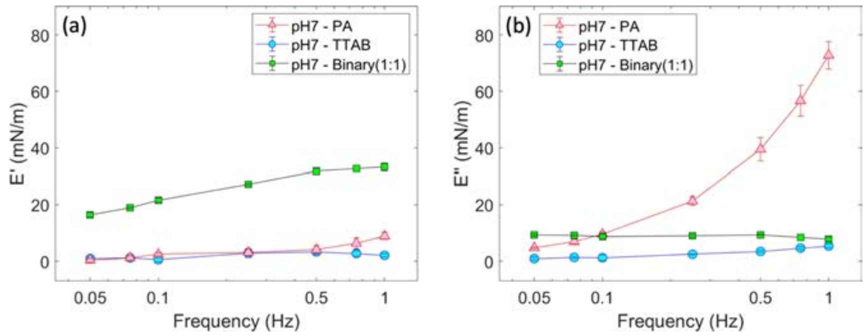


Figure 5. Frequency dependence of (a) storage and (b) loss moduli for systems at an equilibrium interfacial tension of 27 ± 2 mN/m and at pH 7: single PA (red triangles), single TTAB (blue circles), and 1:1 PA/TTAB (green squares). Corresponding total concentrations: 18, 0.175, and 0.04 mM for PA, TTAB, and binary systems, respectively. Uncertainties based on three replicate experiments.

a synergistic effect was clearly observed for the storage modulus. At pH 3, the storage and loss moduli for the binary system were indistinguishable from those of the single-component TTAB system. Any synergistic effect that may have been present at pH 3 was too weak to be observed given the experimental uncertainties. This strong pH dependence shows again the importance of the role of PA ionization in favoring synergistic effects. For the loss modulus, any synergistic effect of the binary system under these conditions was below the detection limit.

No interfacial tension less than 37 mN/m was produced by the single-component PA system at pH 3 before reaching its solubility limit in tetradecane (Figure 1), so no attempt could be made to investigate the dilatational modulus synergism for lower interfacial tensions at pH 3. The comparison is possible at pH 7. When comparing moduli for the binary system with the single-component systems at lower interfacial tensions at pH 7 (the cut lines 3 and 4 in Figure 1a), modulus synergism was observed in both storage and loss moduli, depending on frequency. Figures 4 and 5 show the frequency dependence of storage and loss moduli at pH 7 for systems with equilibrium interfacial tensions of 31 ± 2 mN/m (Figure 4) or 27 ± 2 mN/m (Figure 5), respectively. The corresponding surfactant concentrations for each case are reported in the captions.

At these two interfacial tensions, the single-component TTAB systems had detectable but small moduli. Whereas the PA system exhibited no detectable moduli for an equilibrium interfacial tension of 37 ± 2 mN/m (Figure 3), it exhibited a loss-dominant behavior with both storage and loss moduli increasing with frequency at 27 ± 2 mN/m (Figure 5) and 31 ± 2 mN/m (Figure 4) interfacial tensions. While the storage modulus weakly increased with frequency, the increase in the loss modulus with frequency was striking, and the increase was more significant at 27 ± 2 mN/m than at 31 ± 2 mN/m. This loss-dominant behavior is a direct indicator of the single-component PA system violating the single-component diffusion-limited model,[18,19] where the loss modulus never exceeds the storage modulus. Possible controlling mechanisms may be a significant energy barrier for the PA desorbing back to the oil phase, for palmitate ion desorbing into the aqueous phase, or for multiple species (both PA and palmitate ion) diffusing to and from the interface.

The binary systems had almost identical dilatational responses across the frequency range for these two interfacial tensions: plots of modulus vs frequency were similar at both interfacial tensions, for the storage (Figures 4a and 5a) as well as the loss (Figures 4b and 5b) moduli. The binary system response was storage-dominant at both 31 ± 2 and 27 ± 2 mN/m. The storage modulus increased with frequency, while the loss modulus weakly decreased with frequency. For the storage modulus (Figures 4a and 5a), a synergistic effect was observed at both interfacial tensions across the frequency range probed, just as occurred in the previous cases (for a fixed total concentration in Figure 2a and for a higher fixed interfacial tension at pH 7 in Figure 3a). There was synergism in the loss modulus (Figures 4b and 5b) at low frequency, but there was a threshold frequency above which synergism no longer occurred and the PA system exhibited the largest loss modulus.

3.3. Overall Comparisons of Tension and Modulus Synergism.

It is worth mentioning that due to the different natures of the interfacial tension (a thermodynamic property) and the dilatational modulus (a dynamic property), the conditions leading to interfacial tension synergism may not necessarily coincide with those leading to dilatational modulus synergism and the existence of one synergism might not ensure the existence of the other. In the system under investigation here, the conditions for interfacial tension synergism do coincide with the conditions for storage modulus synergism. Both synergistic effects were observed only at pH 7, where deprotonated PA and TTAB strongly attract one another. More varied behaviors were observed for loss modulus synergism, including cases where the loss modulus synergism was undetectable (fixed concentration of 0.2 mM and fixed tension of 37 ± 2 mN/m) and cases where loss modulus synergism was detected below a threshold frequency (fixed tensions of 31 ± 2 and 27 ± 2 mN/m). Despite the more varied loss modulus synergism behaviors, all cases where loss modulus synergism was observed were at pH 7. Loss modulus synergism was not observed at pH 3, reinforcing the importance of PA ionization at the interface as a necessary condition for synergistic effects on either interfacial tension or dilatational moduli.

Although the phenomenon of dilatational modulus synergism has not been referred to as such in the literature, data showing both interfacial tension synergism and modulus synergism (either for storage, loss, both storage and loss, or the magnitude of the complex modulus) can be found for binary surfactant systems containing surfactant pairs of opposite charges in the same liquid.[15−17] The biggest difference between this work and the literature is the formation mechanism of the catanionic complex at the interface. In the current system with an interface between tetradecane solutions of PA and aqueous TTAB solutions, the catanionic species must form at the interface as surfactants adsorb from opposite sides, rather than forming by adsorption from the same side with possible dimerization in the bulk prior to adsorption. Regardless of this difference, the overall dilatation properties of the binary PA/TTAB system at pH 7 are qualitatively (showing similar frequency dependence) and quantitatively (having similar magnitudes of both moduli) comparable to those of water-soluble sodium dodecyl sulfate (SDS)/dodecyl trimethylammonium bromide (DTAB) systems at the kerosene/water interface reported previously.[16] The binary 2:1 SDS/DTAB mixture at the kerosene/water interface exhibits storage-dominant moduli and a concentration-dependent synergism in both storage and loss moduli. In addition, binary systems exhibiting modulus synergism without tension synergism can also be found, such as SDS with nonionic ethoxylated ether C_nEO_m surfactants[12,32] and some binary mixtures of water-soluble short-chain phospholipids.[13]

Some insight into the origin of the storage-dominant dilatational modulus synergism in the PA/TTAB system at pH 7 may be inferred from observations reported by Sumino and co-workers[22,23,33] of a dynamic interfacial "blebbing" deformation process that occurred when a drop of PA-in-tetradecane solution made contact with an aqueous solution of stearyltrimethylammonium chloride (STAC). This is similar to the binary system investigated here. Although this blebbing process was not detected in the drop shape imaging under the conditions reported in Figure 1, the 1:1 PA/TTAB binary system at pH 7 did show blebbing motion when a total concentration exceeding ~0.35 mM was tested. For example (see still photographs in Figure 6 and the corresponding video in the Supporting Information), when contacting a PA-in-tetradecane solution with an equimolar TTAB solution in pH 7 buffer in a vial, the system with a total concentration of 1 mM showed an interfacial blebbing motion. This spontaneous motion lasted about 5 min and was accompanied by formation of interfacial aggregates that penetrated into the aqueous phase, suggesting the possibility of cross-interface PA transport. Blebbing was not detected for 0.05 or 0.2 mM total concentrations.

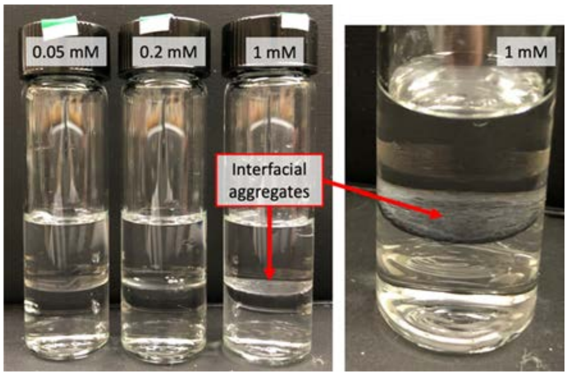


Figure 6. Samples of the 1:1 PA/TTAB system at pH 7 at different total concentrations (left) and a zoomed-in picture of the 1 mM vial (right), which showed spontaneous interfacial blebbing motion and interfacial aggregates. Upper phase: PA solution in tetradecane. Lower phase: TTAB solution in pH 7 aqueous buffer.

In this 1 mM case, the interfacial tension was too small to be measured by drop shape tensiometry, so dilatational measurements were not conducted. In their small-angle X-ray scattering (SAXS) study,[33] Sumino and co-workers suggest that the elastic stress generated by a lamellar−lamellar transition of STAC/PA gel-like aggregates is responsible for the blebbing motion. This may indicate a potential origin for storage-dominant, dilatational modulus synergism in this type of oil-soluble fatty acid and water-soluble alkyl quaternary ammonium catanionic system investigated here. Another investigation[34] of this STAC/PA system provides additional insight into the possible role of PA transport from the oil phase into the aqueous phase. When a PA-in-tetradecane solution drop was placed onto an aqueous STAC solution subphase, the air/water surface tension decreased. This can be explained by PA transport across the interface into the aqueous STAC solution and subsequent adsorption to the air/water interface, by PA passing through the three-phase contact line directly onto the aqueous surface, or a combination of the two effects.

4. CONCLUSIONS

Oil/water interfacial tension and dilatational rheology were investigated for a binary surfactant system consisting of an oil-soluble fatty acid with a pH-dependent degree of protonation when at the interface and a water-soluble cationic alkyltrimethylammonium quaternary amine surfactant with a pH-independent positive charge. The aqueous pH was manipulated to change the strength of the binary surfactant interaction at the interface. The contact between the oil-soluble PA and water-soluble TTAB ensured that surfactant interactions were initiated at the oil/water interface. At pH 7 where adsorbed PA was more deprotonated and thereby was more strongly attracted to the tetradecyltrimethylammonium cations at the interface, interfacial tension synergism was observed. In contrast, at pH 3 where PA would be mostly protonated and only weakly interacting with TTAB at the interface, there was no tension synergism. To our knowledge, this work is the first to report interfacial tension synergism at the oil/water interface considering two surfactants accessing the interface from different sides and meeting at the interface.

In addition to this thermodynamic effect, the dynamic dilatational measurements showed that pH also had a strong effect on interfacial dilatational moduli and controlled whether or not modulus synergism would occur. Two perspectives were offered to characterize a synergistic effect in the storage and loss moduli: at a fixed total concentration or a fixed interfacial tension. For both perspectives, storage modulus synergism coincided closely with pH conditions that produced interfacial tension synergism, while the loss modulus synergism had more varied behaviors. Loss modulus synergism occurred at the lowest interfacial tensions examined but not at the higher interfacial tension. Nevertheless, the aqueous pH still controlled whether loss modulus synergism occurred. No synergism of interfacial tension or dilatational modulus was observed with PA in its weakly charged interfacial state at pH 3. Thus, fatty acid deprotonation at the oil/water interface as controlled by aqueous phase pH determined whether synergism occurred for both interfacial tension synergism and dilatational modulus synergism.

By establishing controlling parameters to manipulate dilatational rheological properties, this work may facilitate more efficient fluid interfacial processing and fluid formulation strategies, especially in multiphase systems with surfactant-laden natural oils. Because many different dynamic processes are possible in such binary systems with surfactants accessing the interface from opposite sides, more direct probes of time-dependent adsorbed layer composition and degrees of interfacial ionization would help elucidate the origin of the interfacial relaxation mechanisms responsible for the rheological response.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.1c01889.

Conductivity procedure and results for equilibration tests (PDF)

Video of the interfacial blebbing process (MP4)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This material is based on work supported by the National Science Foundation under grant CBET-1705432.

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