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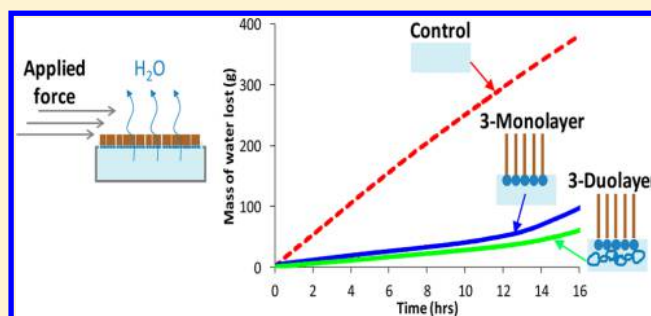
Dynamic Performance of Duolayers at the Air/Water Interface. 1. Experimental Analysis

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ABSTRACT: Understanding, and improving, the behavior of thin surface films under exposure to externally applied forces is important for applications such as mimicking biological membranes, water evaporation mitigation, and recovery of oil spills. This paper demonstrates that the incorporation of a water-soluble polymer into the surface film composition, i.e., formation of a three-duolayer system, shows improved performance under an applied dynamic stress, with an evaporation saving of 84% observed after 16 h, compared to 74% for the insoluble three-monolayer alone. Canal viscometry and spreading rate experiments, performed using the same conditions, demonstrated an increased surface viscosity and faster spreading rate for the three-duolayer system, likely contributing to the observed improvement in dynamic performance. Brewster angle microscopy and dye-tagged polymers were used to visualize the system and demonstrated that the duolayer and monolayer system both form a homogeneous film of uniform, single-molecule thickness, with the excess material compacting into small floating reservoirs on the surface. It was also observed that both components have to be applied to the water surface together in order to achieve improved performance under dynamic conditions. These findings have important implications for the use of surface films in various applications where resistance to external disturbance is required.



■ INTRODUCTION

Monolayers formed by amphiphilic molecules that can spread as single molecule thick films on the water surface have been the focus of studies in multidisciplinary areas. The unique ability possessed by certain classes of monolayer molecules has enabled them to find application in a wide range of areas including production of Langmuir–Blodgett films,^{1,2} optical devices,^{3,4} mimicking biological systems,^{5,6} and water evaporation mitigation from large water storages where traditional means are limited.^{7,8} The majority of monolayer studies are undertaken under tightly controlled, and static, conditions; however, there are numerous applications where films are exposed to dynamic conditions. For example, biological membranes are exposed to the mechanical stresses of bodily function,^{9,10} oil spills require recovery in a dynamic ocean environment,^{11,12} evaporation control products are subject to wind stress,^{8,13} and surfactant stabilized emulsions and foams are exposed to industrial processing operations.¹⁴ These applications all require an understanding of how the films behave dynamically under externally applied forces. Various methods can be employed to tailor the performance of the system to suit the required end use, including the following: altering the chemical structure of the constituent molecules,¹⁵ forming the film under different conditions, i.e., pH or temperature,¹⁶ or incorporating additional molecules into the monolayer system either directly into the subphase¹⁷ or as part

of the monolayer composition.¹⁸ Previous research on single component monolayer systems has shown that the chemical structure of the monolayer molecule can have a large effect on the subsequent performance of the film under an applied dynamic stress.¹⁵ The incorporation of an additional molecule in the monolayer composition through the addition of comb polymers such as poly(octadecyl acrylate) (PODA), poly(octadecyl methacrylate) (PODMA), and poly(vinyl stearate) (PVSt) has been found to improve the film's mechanical stability and resistance to dynamic stress;^{18,19} however, this was at the expense of evaporation control, an important requirement in the intended application of evaporation mitigation.¹⁹ A more recent development has been the discovery of the duolayer system in which a water-soluble nonionic polymer, poly(vinylpyrrolidone) (PVP) has been incorporated into the surface film composition.^{20,21} The resultant film has been shown to undergo a different formation mechanism and has a higher surface viscosity; however, its performance under exposure to dynamic stress has not previously been reported.

In this publication series, we address the issue of how the duolayer behaves under exposure to an externally applied force, with the findings extrapolated to the general behavior of surface

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films under dynamic conditions. Part 1 herein presents the experimentally observed properties of the duolayer under an applied force, while part 2 (DOI 10.1021/jp506098d) proceeds to use all-atom simulations to gain further insight into the observed behavior.²² Combined, these papers provide essential information for further refinement of surface film technology, particularly where resistance to external forces is desired, such as water evaporation mitigation applications.

EXPERIMENTAL SECTION

Materials. Ethylene glycol mono-octadecyl ether (C18E1) was synthesized according to the general method²³ and was characterized by ¹H NMR using a Varian Unity 400 (400 MHz) spectrometer (>95% pure). Details have already been reported elsewhere.¹⁵ Poly(vinylpyrrolidone) (PVP) (MW = 1.3 mill) was obtained from Sigma-Aldrich and used as received. Carmoisine was purchased from Bronson and Jacobs. Chloroform (AR grade) and ethanol (AR grade) were used as received. Poly(vinylpyrrolidone₉₀-co-brown155₁₀) (poly(VP-co-brown155)) was synthesized with the following chemicals: 1-vinyl-2-pyrrolidone (99%), acryloyl chloride (98%), and azobis(2-methylpropion-amidine) dihydrochloride (AMPA, 97%) were purchased from Sigma-Aldrich, whereas Brown 155 was obtained from All Color Supplies Pty Ltd. Deuterated dimethyl sulfoxide (DMSO-*d*₆, 99.8%) was purchased from Cambridge Isotope Laboratories, Inc. Triethylamine (99%, Scharlau), tetrahydrofuran (THF, AR grade), acetone (AR grade), and methanol (AR grade) were used as received.

Apparatus. A Teflon Langmuir trough (76 cm × 10 cm, Nima Technology Ltd.) model 711D with a single Delrin barrier (11.2 cm × 1.6 cm) was used to characterize the properties of the surface film. Before each experiment, the trough and barrier were thoroughly cleaned with chloroform (AR grade, Chem-Supply) and a Wilhelmy plate (2.35 cm × 1 cm, Whatman CHR1 filter paper) was attached to the pressure sensor. The trough was then filled with Milli-Q water (18.2 MΩ·cm Millipore) and allowed to equilibrate with the air at a temperature of 25 ± 1 °C. The water surface was swept clean until the surface pressure reading was zero. The appropriate surface film composition was applied to the water surface and left for 30 min to allow the solvent to evaporate.²⁴

Synthesis of Poly(vinylpyrrolidone-co-brown155). Brown 155 (1.30 g, 2.0 mmol), acryloyl chloride (0.2 mL, 2.0 mmol), and triethylamine (0.65 mL, 5 mmol) were added to 40 mL of tetrahydrofuran (THF), and the reaction was stirred at 0 °C for 12 h. The solvent was removed by rotary evaporation, leaving the desired product: modified brown 155. ¹H NMR (400 MHz, DMSO-*d*₆, δ_H ppm): 9.01–8.78 (m, 2H, 2ArH), 8.21–7.82 (m, 6H, 6ArH), 7.81–7.22 (m, 4H, 4ArH), 6.47–6.41 (d, 1H, CHH=CH—), 6.19–6.10 (m, 1H, CH₂=CH—), 5.85–5.79 (d, 1H, CHH=CH—), 5.17–5.12 (m, 2H, —CH₂OC(=O)—). Modified brown 155 (0.60 g, 0.9 mmol), 1-vinyl-2-pyrrolidone (1.0 g, 9 mmol), and AMPA (0.012 g, 0.05 mmol) were added to 10 mL of methanol. This solution was subjected to three freeze–pump–thaw cycles to prevent possible side reactions. The reaction was heated to 60 °C and stirred for 24 h. The resultant polymer was isolated by precipitation in cold acetone and recovered by filtration. [VP]₀/[brown 155]₀/[I]₀ = 90/9/1; *M*_n theo = 99.1 kDa, *M*_n GPC = 107.1 kDa, *M*_w/*M*_n = 1.42; ¹H NMR (400 MHz, DMSO-*d*₆, δ_H ppm): 9.01–8.78 (m, 2H, 2ArH), 8.21–7.82 (m, 6H, 6ArH), 7.81–7.22 (m, 4H, 4ArH), 5.17–5.12 (m, 2H, —CH₂OC(=O)—), 3.95–3.80 (m, 1H, —CH₂C(N)H—), 3.42–3.05 (m,

2H, —(N)CH₂—), 2.33–2.27 (m, 2H, —CH₂—), 2.21–2.10 (m, 1H, —CH₂CH—), 2.07–2.00 (m, 2H, —CH₂—), 1.98–1.69 (m, 2H, —CH₂CH—).

Characterization of Poly(vinylpyrrolidone-co-brown155). Gel permeation chromatography multiangle laser light scattering (GPC-MALLS) was performed using a Shimadzu liquid chromatography system fitted with a Wyatt DAWN EOS MALLS detector (λ = 690 nm) and a Wyatt OPTILAB DSP interferometric refractometer (λ = 690 nm), using three phenogel columns (500, 10⁴ and 10⁶ Å porosity, 5 nm bead size) operating at 30 °C and distilled H₂O with 0.05 M NaNO₃ (1 mL/min) as the mobile phase. Aliquots (0.5 mL) from each reaction mixture were diluted with an appropriate amount of eluent and passed through a 0.45 μm filter and injected into the GPC for analysis. Astra software (Wyatt Technology Corp.) was used to determine the molecular weight characteristics using known dn/dc values. For proton magnetic resonance spectroscopy (¹H NMR), a Varian Unity (400 MHz) spectrometer was utilized, where the samples were dissolved in DMSO-*d*₆.

Preparation of Solutions. Solutions were prepared by dissolving the water-insoluble monolayer forming component and the water-soluble polymer separately, typically in chloroform, at a known concentration of 1 mg/mL. To make the combined solutions, typically at a 1:1 molar ratio of monolayer component to polymer monomeric unit, the appropriate ratios of the two solutions were mixed. For example, with 1 mg/mL solutions of C18E1 and PVP, 0.35 mL of PVP was added to 1 mL of C18E1.

Canal Viscometry. The Langmuir trough was prepared as described previously. A specially designed Delrin barrier containing a central 2 mm wide canal (6 mm high) was attached to the standard Delrin barrier. The two barriers were closed to create an area of 100 cm² close to the pressure sensor. Three times the amount of the appropriate composition needed to cover this area with one theoretical monolayer (three monolayers) was applied to the water surface. After the films were left for various holding times between 15 min and 16 h, the standard barrier was then opened at a rate of 50 cm²/min while leaving the canal barrier in place. Surface film flows through the canal, reducing the surface pressure measured by the pressure sensor. This decrease in surface pressure with time was recorded. Each measurement was repeated three times to ensure reproducibility.

Spreading Rate. The Langmuir trough was prepared as described previously. An amount of surface film composition containing 3 times the amount of monolayer forming material required to cover the entire surface of the trough was applied at the opposite end of the trough to the pressure sensor. The measurement was recorded first for 10 s before the monolayer was applied to the water surface within the accumulated 30 s time frame. The change in surface pressure was then monitored as the film spread down the length of the trough.

Evaporation Resistance. A gravimetric method was used to measure evaporation reduction under both static and dynamic wind conditions. For the dynamic method, the wind was generated by a centrifugal fan (RS Components Pty Ltd.) connected to a wind tunnel made in-house. The wind tunnel ensured that the air flow out of the tunnel was laminar, and the wind speed was set at 25 km/h (7.0 m/s, measured by a hot wire anemometer (Control Company) placed at the mouth of the wind tunnel). The mouth of the wind tunnel was positioned at the end of a digital balance (Mettler-Toledo

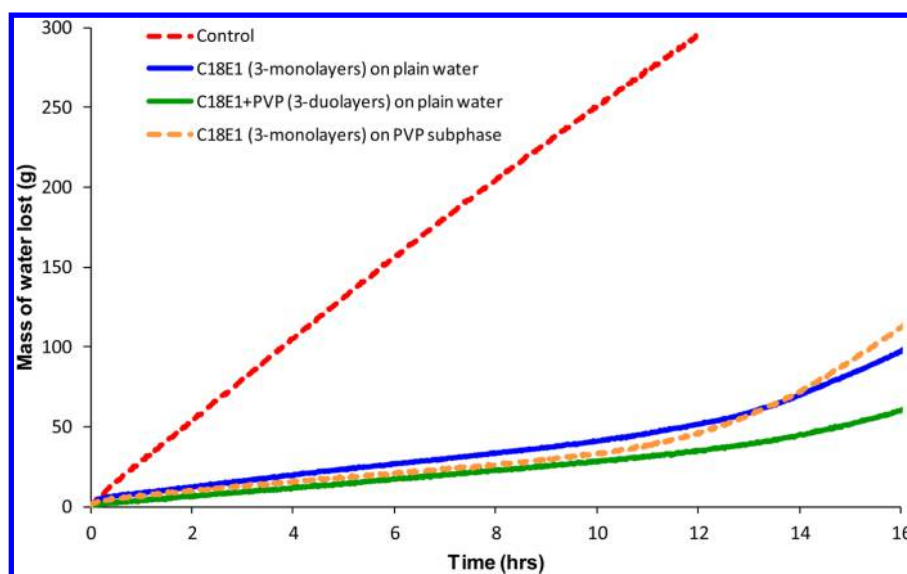


Figure 1. Mass of water lost over time for C18E1 (three monolayers) and C18E1+PVP (three duolayers) applied to a plain water surface and C18E1 (three monolayers) applied to water containing PVP (4×10^{-7} M), compared to a control with no monolayer, under exposure to an external force (wind at 25 km/h).

Limited) where a rectangular container (10.5 cm \times 16.3 cm) filled with 800 mL of Milli-Q water was placed on top. The digital balance was connected to a computer installed with the BalanceLink program, which was set to record the mass of the container and water every minute. Three times the amount of insoluble monolayer material required to form one monolayer was applied to the water surface and left for 30 min before turning on the fan. The change in weight of the container and water was monitored for 16 h. Static evaporation resistance was measured using the same experimental setup except the fan was not switched on. Control experiments were carried out using a container of water with no film, and also a container with the equivalent amount of PVP added into the subphase prior to application of C18E1 onto the water surface. An average of three measurements was taken for each sample.

Brewster Angle Microscopy (BAM). Images of both the monolayer and duolayer film at the air–water interface were obtained using a Brewster angle microscope (BAM, KSV NIMA), mounted on a Langmuir trough (KN 2003, KSV NIMA). The BAM was equipped with a 50 mW laser emitting p-polarized light with a wavelength of 658 nm which was reflected off the air–water interface at the Brewster angle (ca. 53°). The lateral resolution of the microscope was 2 μ m. Images were processed using the accompanying software. Three times the amount of the appropriate composition needed to cover this area with one theoretical monolayer was applied to the water surface on the trough. The films were left undisturbed for 2 h to allow them to equilibrate before images were obtained.

Fourier Transform Infrared (FTIR) Spectroscopy. The substrates used for FTIR measurements were prepared using the Langmuir–Schaefer (LS) deposition method. The Langmuir trough was prepared as described previously. A custom-size prism (silicon wafer) was manually lowered in a horizontal position until it touched the water surface. The prism was then lifted and allowed to dry at room temperature (25 $^\circ$ C) prior to measurements. A Nicolet 5700 Fourier Transform Infra Red spectrometer from Thermo Electron Corporation was used to collect the IR spectrum of the coated

prisms. The instrument was equipped with a potassium bromide (KBr) beamsplitter and a variable angle ATR accessory from CIC Photonic (Albuquerque, MN, USA). 256 scans with a resolution of 4 cm^{-1} were done using a DTGS KBr detector. The mirror velocity and the gain setting were set at 0.6329 cm/s and 8, respectively.

Visualization of Surface Film with Dye and Tagged PVP. Individual solutions of carmoisine, tagged PVP:poly(VP-co-brown155), and C18E1 were prepared in ethanol at 1 mg/mL. Mixtures containing 1:1 molar of C18E1 and carmoisine and C18E1 and poly(VP-co-brown155) were made by mixing appropriate amounts of each solution. A plastic rectangular container (10.5 cm \times 16.3 cm) was filled with 700 mL of Milli-Q water. Six times the amount of insoluble monolayer material (C18E1) required to form one monolayer was applied to the water surface. For controls, the equivalent amount of dye or tagged PVP alone was applied to the water surface in separate containers. To some of these containers, C18E1 was then added to the water surface. All containers were left for 30 min for solvent to evaporate before images were taken.

RESULTS AND DISCUSSION

Our previous work^{20,25} has identified the duolayer system comprising ethylene glycol mono-octadecyl ether (C18E1) and poly(vinylpyrrolidone) (PVP) as having unique and improved properties over the monolayer film of C18E1 alone, under static conditions. To investigate this duolayer system under dynamic conditions, the dynamic gravimetric evaporation resistance test method was utilized.¹⁵ There is an increase in surface area when wind-induced waves are present and it has previously been found that 3 times the theoretical amount of C18E1 needed to form a single monolayer film on the water surface (three monolayers) is the minimum amount of material necessary to form a robust surface film capable of resisting an external force.¹⁵ Therefore, the evaporation resistance of the duolayer under exposure to an externally applied force was carried out using a three-monolayer C18E1 film and a three-duolayer C18E1+PVP film, along with a control sample containing no film. The results are shown in Figure 1.

Table 1. Evaporation Rate (k) and Effectiveness ($1 - \phi$) for the Monolayer and Duolayer throughout the 12 h Comparable Experiment, under Static and Dynamic Conditions

	static		dynamic	
	evaporation rate k (mol s ⁻¹ cm ⁻²)	effectiveness ($1 - \phi$)	evaporation rate k (mol s ⁻¹ cm ⁻²)	effectiveness ($1 - \phi$)
control	2.6×10^{-7}		22.2×10^{-7}	
C18E1 (three monolayers)	0.9×10^{-7}	0.65	4.0×10^{-7}	0.82
C18E1+PVP (three duolayers)	0.8×10^{-7}	0.67	2.6×10^{-7}	0.89

An improvement in the dynamic evaporation resistance of the duolayer film is observed in the first 13 h when compared to the monolayer alone, indicating that the presence of the water-soluble polymer has a positive effect on evaporation control of the film under wind stress (Figure 1). After 13 h, the rate of water loss for the C18E1 monolayer system increased sharply, to a rate similar to that of the control experiment, suggesting that some of the monolayer material was lost from the water surface and the residual monolayer molecules were insufficient to maintain the solid packing of the monolayer required to suppress evaporation. On the other hand, the rate of water loss from the C18E1+PVP duolayer system also increased after 13 h, but the rise was milder than that for the monolayer system. To demonstrate that this effect is observed only when both components are mixed and applied to the water surface together, a control experiment using an alternative modification technique was carried out, with the equivalent amount of PVP added to the subphase (concentration of 4×10^{-7} M), prior to application of C18E1 onto the water surface. Wind test results demonstrated a similar performance to C18E1 alone on clean water, indicating both components have to be premixed and applied to the water surface together in order to observe the improvement in performance.

To quantify these results, the evaporation rate per unit area (k , mol s⁻¹ cm⁻²) up until 12 h was calculated from the slope of the curves in Figure 1.²⁶ This data can be used to determine the performance of a surface film, which is often reported as the ratio (ϕ) of the evaporation rate with a monolayer to the rate for water alone ($\phi = k_m/k_w$), with the effectiveness of the monolayer then defined as $1 - \phi$.²⁷ These results are shown in Table 1 for the dynamic system. There is a distinct improvement in the water evaporation rate with the presence of the duolayer when compared to monolayer alone, with an effectiveness of 0.89 observed compared to 0.82.

As a comparison for evaluating the influence the externally applied force has on the surface film properties, the same experiment was carried out; however, in this case, the centrifugal fan was not switched on, providing directly comparable results in a static environment. The water evaporation rates and effectiveness over 12 h were calculated and are shown in Table 1 as the static system.

A significantly higher evaporation rate (8.5× higher) is observed in the dynamic system compared to the static system. This is due to a combination of factors including an increased surface area due to wave formation under wind flow and wind-enhanced movement of humid air away from the water surface, increasing the driving force for evaporation.²⁸

Comparison of the three-monolayer system with the three-duolayer system under static conditions shows that the inclusion of the polymer in the surface film composition does not have a significant effect on the effectiveness (0.65 cf. 0.67). However, under dynamic conditions, an appreciable improvement is observed with the inclusion of polymer with an

increased effectiveness of 8.5% observed in this system. This result indicates that the presence of PVP has a positive effect on increasing the dynamic performance of the duolayer system.

Surprisingly, the application of an externally applied force results in a significant improvement in the effectiveness of the surface films with regard to evaporation control, with a 26–33% improvement observed. Such a direct comparison has never been observed in the past. While part 2 (DOI 10.1021/jp506098d) of this publication series utilizes theoretical all-atom simulations to gain further insight into this observed improvement, the following experiments will investigate the performance differences of the multimonomolayer and duolayer systems under various experimental conditions.

Canal Viscometry. Canal viscometry was used to gain performance data on the multimonomolayer and duolayer systems. This method was previously used to demonstrate that the one-duolayer C18E1+PVP system, when compressed to a surface pressure of 25 mN/m, showed increased viscosity when compared to one monolayer alone; however, this effect only lasted for a short period of time.²⁰ In this case, the experiment was carried out using the same conditions as the dynamic evaporation test in order to gain mechanistic insights which could be applied to other systems exposed to dynamic conditions. Therefore, the Langmuir trough barriers were used to enclose a small area of the trough. To this area, three monolayers of material were applied and allowed to come to equilibrium, producing a film equivalent to that used in the dynamic test. This film was then held for various waiting times before the solid barrier was opened and the film allowed to flow through the canal. The resulting surface pressure decrease for C18E1 alone and the C18E1+PVP three-duolayer system are shown in Figure 2a. The rate of surface pressure decrease (mN/m·s) was calculated from the gradient of the curves over the first 100 s of the experiment, and was taken as a measure of the surface viscosity of the film.²⁹ This length of time was chosen, as it is the initial flow through the canal, when the film transitions from a solid to a liquid state, where the presence of polymer is observed to impact film performance. The calculated rates of surface pressure decrease are shown as a function of film holding time in Figure 2b.

Under these conditions, the three-duolayer shows increased viscosity when compared to C18E1 alone, taking twice as long to flow through the canal to zero surface pressure, after a 1 h holding time (500 s cf. 250 s). This can also be seen in Figure 2b where the rate of surface pressure decrease over the initial 100 s is approximately 3 times faster for the three-monolayer film. This demonstrates that the presence of polymer has a significant effect on the initial surface viscosity, with the effect reducing as the surface pressure decreases (as evidenced by the increased gradient observed in the second half of the three-duolayer curves in Figure 2a).

The rate of surface pressure decrease of the three-duolayer film is shown to be slower than the three-monolayer film over the entire holding time range investigated. This indicates that

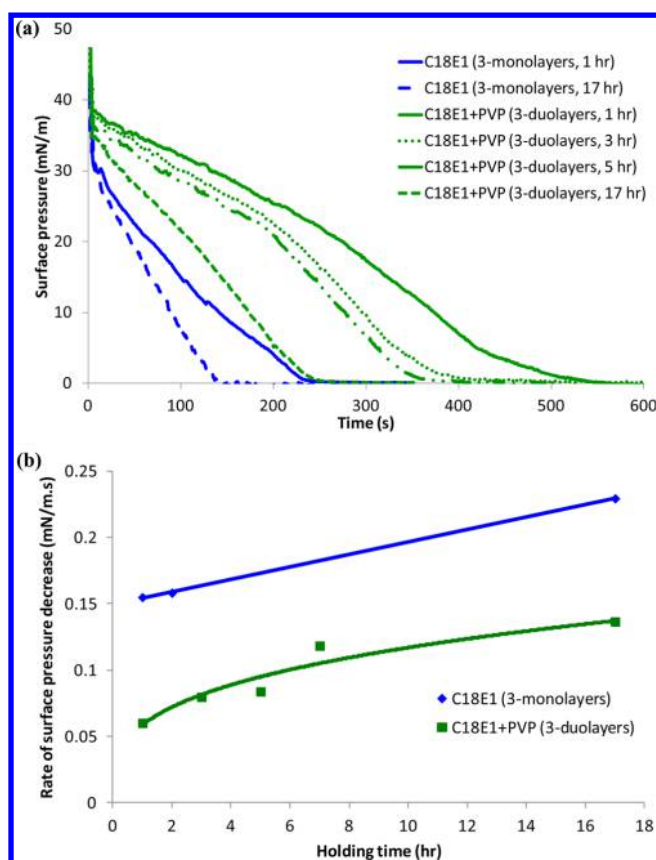


Figure 2. Canal viscometry results for films of three layers of C18E1 alone and C18E1+PVP held for different holding times before flowing through the canal: (a) the change in surface pressure over time as the films flow through the canal; (b) the rate of surface pressure decrease over the first 100 s for the curves shown in part a.

the inclusion of polymer in this film continues to provide improvements to the surface viscosity over a substantial length of time. It is proposed that the increased longevity of the three-duolayer film when compared to the one-duolayer film is due to the extra material that is applied to the surface (in order to account for the increased surface area under wind stress) acting as a reservoir to replace the PVP as it slowly diffuses away from the interface, thereby lengthening the duolayer effect.

Spreading Rate. A possible contributing factor for the observed improved performance shown by the three-duolayer system under dynamic stress conditions is the rate at which the compositions form a closely packed surface film. This rate contributes to the ability of the film to recover during, and after, exposure to an external force. Therefore, the effect of including a water-soluble polymer in the surface film composition on the spreading rate of the resultant duolayer was investigated, using the same conditions as the dynamic evaporation test, with the results shown in Figure 3.

The inclusion of PVP into the surface film composition doubles the spreading rate of the resultant film. While a film formed from C18E1 alone took 25 s to reach the end of the Langmuir trough and register a rise in surface pressure (material was applied at time = 10 s), the film formed from the composition containing PVP took only 5 s. Not only that, but the surface pressure of the duolayer film also increases considerably faster compared to the film prepared from C18E1 alone, indicating that PVP assists in rapidly forming a solid-phase surface film. The ability of the surface film to spread

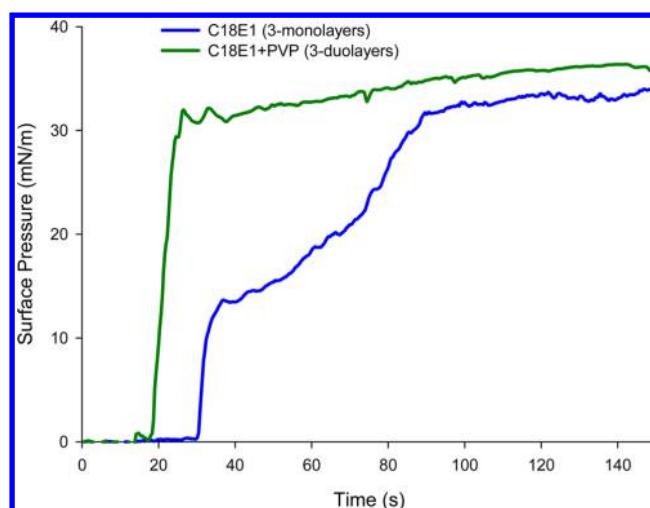


Figure 3. Spreading rates of films prepared from compositions containing monolayer alone and one containing PVP. The film was applied at a time of 10 s.

rapidly across the water surface and form a close-packed film is of critical importance in a dynamic environment. This ability allows the film to rapidly reform following any disturbances, and therefore better maintain desired properties such as evaporation resistance.

BAM Imaging. Brewster angle microscopy (BAM) is an established technique to characterize the morphology of ultrathin surface films at the air–water interface. Monolayer film or other surface moieties present at the air–water interface can be visualized from the reflection of a p-polarized incident light at the Brewster angle, which would otherwise be perfectly transmitted through a pure water surface. Therefore, the morphology of the monolayer film can be shown from the varying intensity of the reflected light. In this paper, BAM was used to image the films comprising C18E1 alone and the duolayer system containing C18E1 and PVP, at the application dosage of three layers, in order to investigate whether initial film formation may contribute to the different performances observed. These images are shown in Figure 4.

There is no distinct difference between the films formed from three monolayers alone and those formed from three duolayers. In their respective natural equilibrium state, before application of dynamic stress, both the monolayer and duolayer systems form a smooth and homogeneous film (gray color in the image) with floating islands of white excess material of varying sizes scattered on the film surface. On the basis of the evaluation from the BAM software, the films created by the monolayer and duolayer systems were both found to be almost identical with a film thickness of around 2.3 nm, with fluctuations in both cases from the islands of excess material. Although the theoretical length of the C18E1 molecule is about 2.6 nm, molecular modeling in our previous study¹⁵ and in part 2 (DOI 10.1021/jp506098d) of this study has shown that the monolayer molecules are likely to be packed on the water surface with a slight tilt rather than standing upright on the water surface, thus reducing the actual thickness of the monolayer film.

These results revealed that the excess monolayer material applied on the water surface (three layers) did not assemble into a homogeneous layer-by-layer multilayer structure spreading on the water surface. Instead, when a sufficient amount of

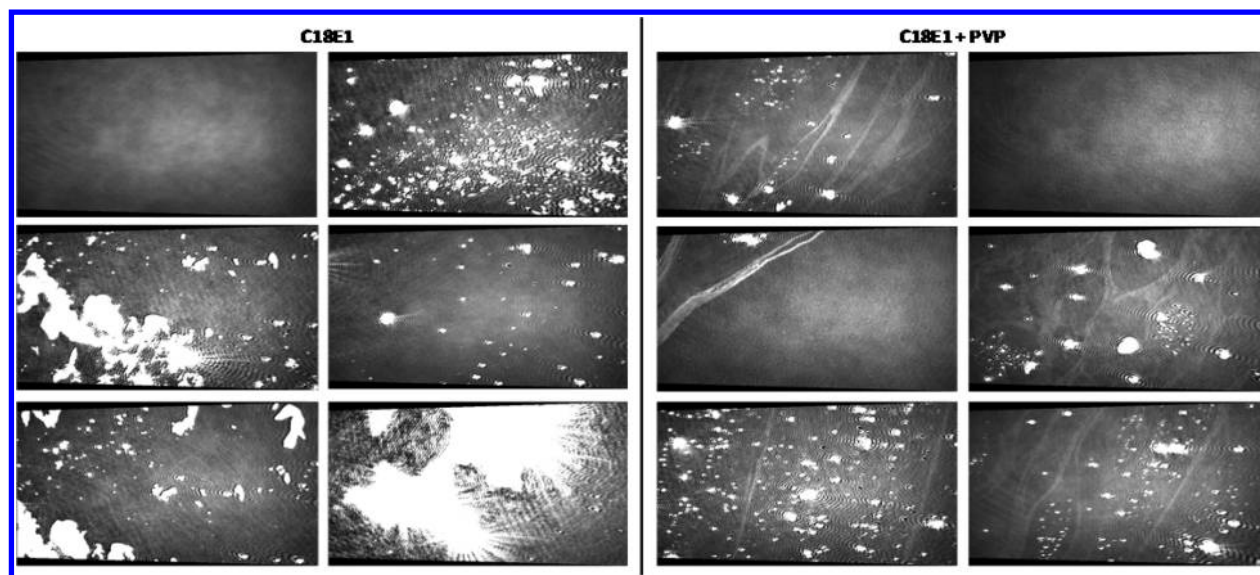
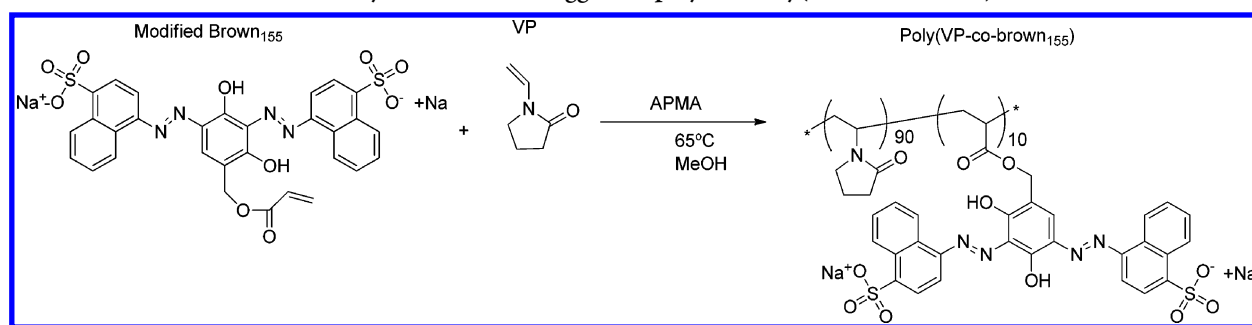


Figure 4. BAM image of the films formed from C18E1 alone (left-hand side) and the C18E1+PVP duolayer system (right-hand side) when applied at three-layer dosage. The field of view is $720\ \mu\text{m} \times 400\ \mu\text{m}$.

Scheme 1. Reaction Scheme for the Synthesis of the Tagged Copolymer Poly(VP-co-brown155)



the insoluble monolayer molecules have spread over the water surface to form the homogeneous monolayer film, the residual excess materials are compressed into globular shaped islands and just float on, or in between, the assembled monolayer film. As shown in the dynamic evaporation resistance, the excess material does not impede the packing of the monolayer but in fact aids the monolayer to overcome the disturbance caused by the externally applied force for up to 13 h. Our results also suggest that the white floating islands for the C18E1+PVP duolayer system contain PVP as well as excess C18E1, as evidenced by the fact that the improved viscosity effect was shown to last much longer (over 17 h) when applied at three duolayers, compared with the 1 h limit when just one duolayer is applied, as shown in our previous studies.²⁰ This suggests that some of the excess PVP has been retained on the surface and released slowly over time, replenishing the polymer that was gradually diffusing away from the interface and into the bulk water body.

Detection of Duolayer. The presence of polymer at the interface was examined by using Fourier transform infrared (FTIR) spectroscopy to analyze films obtained on a silicon wafer using the Langmuir–Schaefer horizontal lifting method. Films were prepared from C18E1 alone and C18E1 and PVP. No polymer was detectable in the films prepared from C18E1 and PVP. It is possible that the polymer was not transferred to the film from the interface, or the level of polymer at the interface is below the level detectable by the FTIR method. It is

known from previous work that only a small amount of polymer is sufficient to affect the behavior of the monolayer on the water surface, and similar systems have also demonstrated the levels of polymer are undetectable by standard techniques.³⁰

Due to the difficulty in obtaining direct evidence of the presence of polymer at the air/water interface, a visualization method was employed. A tagged copolymer was designed to maintain the same interactions with C18E1 through the vinylpyrrolidone units, while providing color through the brown 155 dye units (10% of the total polymer). The reaction scheme for the synthesis of this copolymer is shown in Scheme 1. A small water-soluble dye, carmoisine, was also used for comparison. Specifically, the water-soluble polymer, PVP, was replaced in the composition with either the water-soluble dye or the tagged copolymer of PVP: poly(vinylpyrrolidone-co-brown155).

As neither of these dyes is soluble in chloroform, ethanol was used as the solvent system for these experiments. Although the use of ethanol might result in the loss of some film material into the subphase,³¹ this loss is not relevant for the purpose of this visualization study. The tagged-PVP copolymer was first tested under the dynamic evaporation conditions, showing the same performance as the original PVP three-duolayer system, indicating the tagged polymer performs the same as unaltered PVP (results not shown).

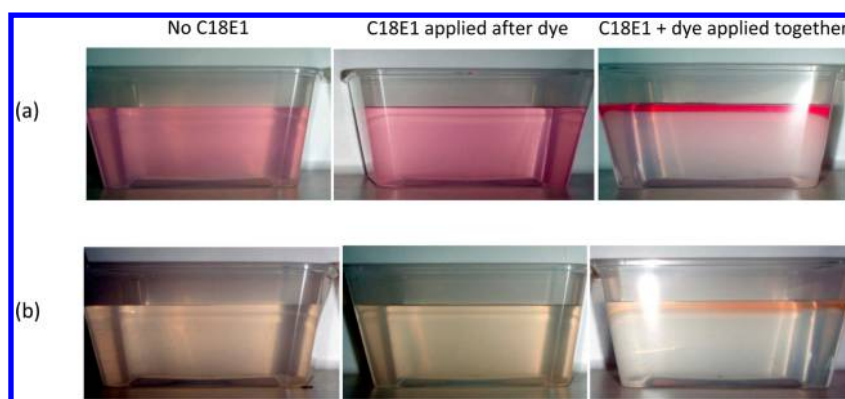


Figure 5. Visualization of duolayer film with dyes: (a) Small molecule dye: carmoisine, applied to the water surface alone, or mixed with C18E1. (b) Tagged polymer: poly(VP-co-brown155) applied to the water surface alone, or mixed with C18E1.

To visualize the multiduolayer, C18E1 monolayer mixed with either carmoisine (six duolayers) or tagged PVP at a 1:1 molar ratio (six duolayers) was applied to the water surface in one container, while in another container the equivalent amount of dye alone was applied to the water surface. Figure 5 clearly shows that both the small molecule dye and tagged polymer are concentrated at the air/water interface when applied in combination with C18E1. In contrast, when the dye or tagged polymer is applied alone to the water surface, it immediately disperses into the bulk phase and is not concentrated at the interface. Also, if the dye is applied to the water surface first, and then C18E1, representing another possible method of modifying the surface film properties,³⁰ the concentrated layer at the air/water interface is not observed. This provides further evidence that in order to observe improved performance under dynamic conditions both components have to be applied together.

These dye experiments demonstrated that there is an interaction between the insoluble monolayer material and water-soluble component when they are applied to the water surface together. This interaction results in an increased concentration of the water-soluble component at the air/water interface, essentially forming a duolayer system.

In part 2 (DOI 10.1021/jp506098d) of this work, all-atom simulations on the dynamic performance of duolayers at the air/water interface will provide the mechanistic insights and theoretical understanding of the experimental observations reported here and provide further elucidation into the effect of externally applied forces on thin surface films.

CONCLUSIONS

Under dynamic wind conditions, the three-duolayer system has been shown to have superior performance when compared to the single three-monolayer system. Both systems also showed superior evaporation reduction effectiveness under dynamic conditions than static conditions. Further insights into the reasons behind the observed performance improvements were gained through the use of canal viscometry and spreading rate experiments. The three-duolayer film was shown to spread faster than the monolayer, allowing it to form and reform a closely packed film more rapidly after external disturbances. Furthermore, canal viscometry showed an increased surface viscosity effect with the three-duolayer system, with this improvement shown to reduce over time, the likely reason being the PVP gradually diffusing away from the interface. Brewster angle microscopy was able to visually demonstrate

that, even when applied in the excess amounts (three-monolayer or three-duolayer) necessary to account for surface waves under dynamic conditions, the majority of the surface still consisted of a homogeneous film of single molecule thickness. The excess material was shown to be compacted into small floating reservoirs integrating into the monolayer on the water surface. The multiduolayer formed by the use of the dye tagged copolymer provided direct observation of the initial interaction between the insoluble monolayer and the water-soluble component when they are applied to the water surface together. This provides further evidence that the observed improvements of the duolayer system under wind stress are due to interactions between the monolayer and polymeric component. The insights gained from the experimental works in this paper increase the understanding of the performance of surface film systems exposed to externally applied forces, and contribute vital knowledge to the future development of thin surface films, in particular in the field of evaporation suppression.

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Notes

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ABBREVIATIONS

x -monolayer(s) = x times the amount of C18E1 sufficient to cover the surface with one theoretical monolayer (e.g., three monolayers = 3 times the amount for forming one theoretical monolayer of C18E1); x -duolayer(s) = x times the amount of C18E1+PVP sufficient to cover the surface with one theoretical

duolayer (e.g., three duolayers = 3 times the amount for forming a single theoretical duolayer of C18E1 and PVP)

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