P H Y S I C A L   R E V I E W   L E T T E R S

Linactants: Surfactant Analogues in Two Dimensions

Siwar Trabelsi,[1] Shishan Zhang,[2] T. Randall Lee,[2] and Daniel K. Schwartz[1],[*]

[1]*Department of Chemical and Biological Engineering, University of Colorado, Boulder, Colorado 80309-0424, USA*
[2]*Department of Chemistry, University of Houston, Houston, Texas 77204-5003, USA*

We report a new class of molecules, linactants, that partition at phase boundaries and reduce the line tension between coexisting two-dimensional phases in molecular monolayers. The line tension between hydrocarbon-rich and fluorocarbon-rich phases was determined by monitoring the relaxation kinetics of deformed domains. Two partially fluorinated linactant molecules (with one and two tails, respectively) were synthesized and tested; the more efficient single-tail variant reduced the line tension by more than 20% at a mole fraction of only 8×10^{-4}.

Three-dimensional (3D) complex fluids, such as emulsions, foams, and colloidal or nanoparticle suspensions that tend to aggregate, coalesce, or phase separate on meso- to macroscopic length scales, require stabilization by surfactant additives. Surfactant molecules partition preferentially at phase boundaries, reducing the interfacial free energy, and thereby decreasing the thermodynamic driving force for phase separation. The ability of surfactant monolayers to support a surface tension gradient also permits the interface to resist the tangential viscous stresses associated with coalescence. In more exotic cases, the presence of surfactant leads to the spontaneous formation of nanoscale mixtures (microemulsions) and ordered mesophases (lyotropic liquid crystals). While there is significant interest in creating molecular nanostructures on surfaces (e.g., for nanoarray and molecular electronics applications), no analogous stabilization strategy has been developed in two dimensions (2D). We believe that, in analogy with surfactants in 3D systems, suitably designed line-active compounds, linactants, might be able to create and stabilize 2D molecular nanostructures.

The molecular design rules for 3D surfactants are conceptually simple: a surfactant should consist of a hydrophilic moiety (the headgroup) covalently attached to a hydrophobic moiety (the tail). Lipids are classic examples found in nature. However, neither previous observation nor the natural world offers any guidelines for the molecular design of a linactant. In the current work, our approach was to exploit the chemical dissimilarity of hydrocarbon- and fluorocarbon-based amphiphiles (fatty acids were used) to induce phase separation in an insoluble (Langmuir) monolayer at the air-water interface. We hypothesized that a third insoluble amphiphile, where the hydrophobic region was composed of distinct hydrocarbon and fluorocarbon moieties might preferentially partition to the boundary between hydrocarbon-rich and fluorocarbon-rich phases. Accordingly, two prospective linactants were designed and prepared (Fig. 1): compound 1 possessed a single hydrophobic tail consisting of a hydrocarbon block and a

fluorocarbon block; compound 2 possessed two tails, one of which was hydrocarbon, and the second was predominantly perfluorinated. Both linactants contained a phosphonic acid headgroup to anchor them at the surface.

The presence of a finite line tension between coexisting fluid monolayer phases ensures that individual droplets (or "domains") are circular at equilibrium, which minimizes the total boundary free energy. Several measurements of line tension between coexisting monolayer phases have appeared in the literature [1,2]; the most reliable and general of these involve following the relaxation dynamics
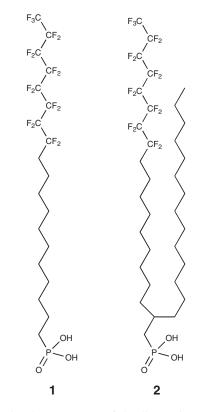

FIG. 1. Molecular structures of the line-active compounds 1 and 2.

037802-1

of deformed domains. While the deformation might be small (e.g., oval shaped) [3] or large (e.g., bola shaped) [4] and caused by surface shear [2−4] optical tweezers [1,5], or other methods [6,7], the fundamental measurement principle relies on the fact that line tension serves as the driving force for relaxation to a circular shape, and this driving force is opposed by a known viscous drag. The line tension has been measured for various systems exhibiting phase coexistence, such as fatty acids, phospholipids, and polymers. In one intriguing case, the presence of an initially unsuspected contaminant suggested that small amounts of the appropriate compound could significantly influence the line tension [8].

Mixed Langmuir monolayers were spread dropwise using a microliter syringe at the air-water interface of a custom-built Langmuir trough. After spreading, the monolayers were left 10 min to ensure solvent evaporation. The monolayer was compressed by a motorized barrier at a constant rate of 20 mm/min. Stock solutions (0.5–1 mg/ml) for monolayer experiments were prepared by dissolving pentadecanoic acid (PDA, Acros Organics), perfluoroundecanoic acid (PFUDA, Oakwood Products Inc.), and linactant 2 in choloroform (Fisher Scientific). Linactant 1 was dissolved in tetrahydrofuran (Fisher Scientific). The pH of the subphase was adjusted to 3 by adding an aqueous solution of hydrochloric acid (Mallinckrodt). LB monolayers were transferred to freshly cleaved mica substrates by vertical dipping (on the upstroke) at a surface pressure of 4 mN/m. These samples were imaged with a Nanoscope MMAFM (Digital Instruments—now Veeco). Images were obtained in contact mode using silicon nitride tips (196 μm long × 23 μm wide). All measurements were performed at room temperature, 23 ± 1 °C. The monolayer structure at the air-water interface was visualized using a custom-built Brewster angle microscope (BAM) [9,10]. The BAM was mounted on a joystick-controlled motorized XY translation stage, allowing us to track the bola-shaped domains and to follow the entire relaxation process.

In our experiments, shear is created within a monolayer simply by dragging a syringe needle through the interface. Figure 2 shows BAM images of a mixed monolayer consisting of 96.5% PDA and 3.5% PFUDA following the cessation of shear. The monolayer displays bright domains rich in PDA, surrounded by dark regions rich in PFUDA. PFUDA is dark in BAM images due to the fact that the refractive index of fluorocarbons is similar to that of water. Most of the domains shown in Fig. 2(a) have already relaxed to their circular equilibrium shape. However, one domain, which presumably experienced a large shear strain, remains in a bola shape, consisting of two circular disks, with radius R, connected by a thin string. The entire domain has length L. The connecting string is never observed to rupture, even when it is several times longer than the radius of the bola. These bola domains gradually relax
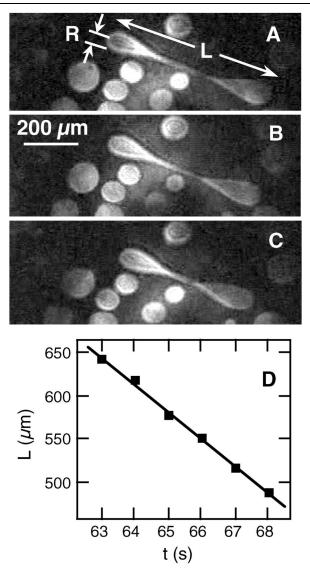

FIG. 2.   (a)–(c) BAM images of a mixed Langmuir monolayer of PDA (96.5%) and PFUDA (3.5%) at $\prod$ = 6 mN/m showing bola relaxation. (d) Plot of the length of the bola-shaped domain, L, as a function of time.

to their equilibrium shape by a simple shortening of the connecting string with a small change in the size of the two disks [Figs. 2(a)–2(c)]. In this regime of large deformation, the relaxation dynamics are linear, such that $L = L_0 - 2Vt$, where V is the velocity of a single bola. Figure 2(d) shows the explicit time dependence of L for the domain shown in Figs. 2(a)–2(c).

As described by Benvegnu and McConnell [4], the line tension force bringing the two disks together is opposed by the viscous drag of the subphase. Equating these two forces (in the low Reynolds number limit), one can express relaxation velocity as

$$V = \frac{3\lambda}{8\eta R},\tag{1}$$

where λ is the line tension, and η is the viscosity of the aqueous subphase. Thus, the line tension can be extracted from this relationship; in particular, it is proportional to the slope of the graph of V versus $1/R$ [see Fig. 3(a)]. For a two-component PDA/PFUDA monolayer, the measurement of the relaxation velocity as a function of domain size yielded a line tension of $\lambda = 1.57 \pm 0.07$ pN. This value is the "bare" line tension of the two-phase two-component system that we hypothesized might be reduced by the addition of an appropriate linactant.

Domain relaxation measurements were also performed for sheared monolayers in which a small amount of 1 or 2 was added to the same PDA/PFUDA mixture. We found that the relaxation kinetics were slowed significantly compared to the two-component system [see Fig. 3(a)], suggesting a reduction in the line tension. A quantitative analysis of the relaxation velocity versus domain size found that the line tension decreased systematically as a function of the concentration of either 1 or 2 [Fig. 3(b)]. Notably, the single-tail linactant 1 was dramatically more efficient than 2. Whereas the addition of 1 mol% of 2 reduced the line tension to ~80% of its bare value, the presence of only 0.08 mol% of 1 led to an even greater reduction.

Experimental limitations prevented the extension of these measurements to higher linactant concentrations. For higher concentrations of 2, the circular domains became so small that the surface shear was incapable of producing bola deformation. Since the equilibrium domain size is a consequence of the competition between line tension and electrostatic repulsion [11], small domains are consistent with a reduction of line tension. In the case of 1, higher concentrations led to a domain-shape instability, and peanut-shaped domains were typically observed (see Fig. 4). Such shape instabilities are predicted theoretically when the radius of a 2D domain significantly exceeds the equilibrium radius [11], which can also be caused by small values of the line tension.

To explore the role of the linactants at a microscopic scale, atomic force microscope (AFM) images were obtained of monolayers transferred (by the Langmuir-Blodgett method) to cleaved mica substrates. Images of two-component PDA/PFUDA monolayers were consistent with BAM images, showing roughly circular domains surrounded by a lower phase [see Fig. 5(a)]. The slightly irregular boundaries and porous interiors shown in Fig. 5(a) might be due to structural changes that occurred during LB transfer. In the AFM images of the two-component monolayer [Fig. 5(a)], the boundary between high and low areas was always sharply defined, and the boundaries themselves were relatively smooth. In monolayers where linactant 1 was added [Fig. 5(b)], the boundaries between high and low areas were rough, with fingers extending into the surrounding phase. In monolayers where linactant 2 was added [Fig. 5(c)], the boundaries were surrounded by distinctive circular bubblelike features. These features were roughly 1 μm in size with a narrow size distribution. Thus, the domain boundaries of samples containing linactant had characteristic appearances that were qualitatively different from each other, and from domain boundaries in the two-component system. These structural observations, combined with the reduction in the line tension by the linactant, are consistent with the partitioning of linactant molecules at the two-phase boundary.
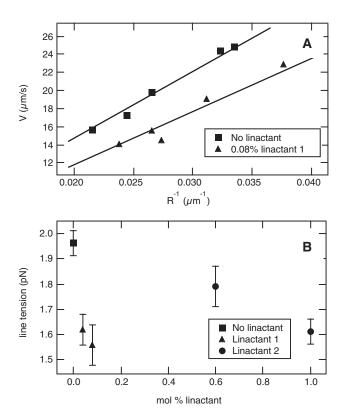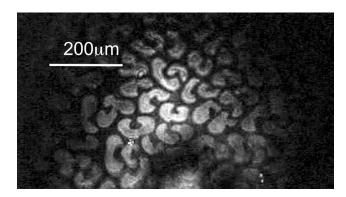

FIG. 3.   (a) The bola relaxation velocity as a function of bola disk radius for the bare two-component mixture (96.5% PDA and 3.5% PFUDA), and for the mixture with 0.08% linactant 1 added. (b) Calculated line tension as a function of linactant concentration for a monolayer composed of PDA (96.5%) and PFUDA (3.5%) at $\prod = 6$ mN/m.

FIG. 4.   A BAM image of a Langmuir monolayer composed of PDA (96.5%), PFUDA (3.5%), and linactant 1 ($> 0.08\%$) showing peanut-shaped domains.
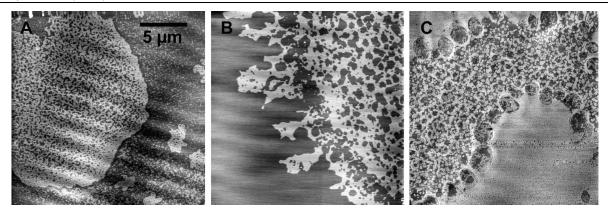
FIG. 5.   AFM images of LB films composed of PDA (96.5%) and PFUDA (3.5%) with (a) no linactant, (b) linactant 1 added at 0.08 mol%, and (c) linactant 2 added at 1 mol%. The monolayers were transferred onto mica at 4 mN/m.

These results confirm that small amounts of the appropriate molecular compound can significantly reduce the line tension (boundary free energy) between coexisting 2D phases in molecular monolayers. It appears that a linactant should consist of three distinct chemical moieties: an anchoring "headgroup" that determines the molecular orientation, and two other chemical groups, each of which is chemically compatible with one of the coexisting phases (fluorocarbon and hydrocarbon in this case). Two different stabilization mechanisms were observed. In the case of compound 1, individual molecules appear to have adsorbed at the phase boundaries; no mesoscale structural features were observed. However, the presence of compound 2 led to the formation of mesoscopic aggregates that adsorbed to phase boundaries as distinct particles. This second mechanism required more than an order of magnitude more linactant for the same reduction of line tension. The observations reported here suggest that there is an underlying mechanistic correlation between molecular architecture and linactant efficiency, the details of which are not immediately obvious. We expect that additional testing of other linactant molecules will provide further insight into the structural basis of linactancy.

*To whom all correspondence should be addressed.
Daniel.Schwartz@colorado.edu

[1] P. Steffen, S. Wurlitzer, and T. M. Fischer, J. Phys. Chem. A **105**, 8281 (2001).
[2] J. Lauger *et al.*, Langmuir **12**, 5630 (1996).
[3] E. K. Mann *et al.*, Phys. Rev. E **51**, 5708 (1995).
[4] D. J. Benvegnu and H. M. McConnell, J. Phys. Chem. **96**, 6820 (1992).
[5] S. Wurlitzer, P. Steffen, and T. M. Fischer, J. Chem. Phys. **112**, 5915 (2000).
[6] S. Riviere, S. Henon, and J. Meunier, Phys. Rev. Lett. **75**, 2506 (1995).
[7] M. J. Roberts, E. J. Teer, and R. S. Duran, J. Phys. Chem. B **101**, 699 (1997).
[8] D. J. Benvegnu and H. M. McConnell, J. Phys. Chem. **97**, 6686 (1993).
[9] S. Henon and J. Meunier, Rev. Sci. Instrum. **62**, 936 (1991).
[10] D. Honig and D. Mobius, J. Phys. Chem. **95**, 4590 (1991).
[11] H. M. McConnell and V. T. Moy, J. Phys. Chem. **92**, 4520 (1988).