

LETTERS

Can Hydrophobic Oils Spread on Water as Condensed Langmuir Monolayers?

Yuka Tabe,* Takahiro Yamamoto, Isa Nishiyama, Keiko M. Aoki, Makoto Yoneya, and Hiroshi Yokoyama

Yokoyama Nano-structured Liquid Crystal Project, Japan Science and Technology Corporation, and Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan

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In contrast to the long-held belief that only amphiphilic molecules can form stable Langmuir monolayers, we show here that even nonvolatile hydrophobic oils can be reversibly spread into liquid-condensed Langmuir films, if the material is in or close to liquid-crystal phase in the bulk. The stability origin of the hydrophobic Langmuir monolayers is entropic, rather than energetic as in the stabilization of common amphiphilic monolayers, primarily driven by the interaction between the polar head and water. This extraordinary spreading mechanism may have impact on the nature of colloidal and biomembrane stabilities.

Stability of molecular films at solid–liquid and liquid–liquid interfaces is a significant factor that seriously affects a wide variety of industrial processes, such as wetting, friction, lubrication, and emulsification, and is also of essential relevance to the structure and function of biological membranes. A Langmuir monolayer is a monomolecular-thick film of organic molecules formed at the air–water interface, which has been intensively studied for over a century and widely exploited as a model of biological membranes.¹ Ever since the pioneering studies of Langmuir,² Harkins,³ and Adam,⁴ there exists a firmly established belief that the monolayer-forming molecules should have sufficiently strong amphiphilic character like that of fatty acids, fatty alcohols, and phospholipids.^{1–4} The polar or charged hydrophilic head of an amphiphilic molecule interacts attractively with water, while the hydrophobic aliphatic chains prevent the molecules from being dissolved into the water, thereby efficiently reducing the interfacial free energy. This is clearly consistent with the Gibbs adsorption equation, which states that substantial surface adsorption of molecules (to such an extent to form a condensed monolayer) can occur, if and

only if the molecule is highly surface active or equivalently is strongly capable of reducing the interfacial tension on adsorption.

Hydrophobic liquids and solids such as long chain *n*-alkanes, on the other hand, do not spontaneously spread from their bulk phase on water surface; it is indeed our daily experience that oil drops put on a water surface remain indefinitely as a thick lens. This is generally because the cohesive energy of such hydrophobic substances, mainly due to dispersion forces, is larger than that of water, which accounts only for ~ 20 mJ/m² of its surface tension over 70 mJ/m². In other words, the water behaves as if it were a low surface tension liquid for those hydrophobic substances that solely interact via dispersion forces.⁵

This general picture, however, is known to break down for short chain *n*-alkanes up to octane.^{6,7} These materials have a relatively high vapor pressure and chemical potential at room temperature and hence can promote substantial adsorption on water surface even though the nature of the interaction remains the same as that for the longer chain homologues. Furthermore, it has recently been shown by several groups^{8,9} that even highly hydrophobic long-chain fluorocarbons and *n*-alkanes (chain length $n > 30$) can form a two-dimensional (2D) crystalline

* To whom correspondence should be addressed. E-mail: tabe-yuka@aist.go.jp.

TABLE 1: Dialkylated Nonpolar LC Compounds and Their Phase Behaviors

$1 \quad \text{C}_n\text{H}_{2n+1}-\text{C}_6\text{H}_4-\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{C}_n\text{H}_{2n+1}$									
$2 \quad \text{C}_n\text{H}_{2n+1}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}_n\text{H}_{2n+1}$									
1					2				
<i>n</i>	Cr	Sm	N	I	<i>n</i>	Cr	Sm	N	I
7	• 39	—	—	• 47	•	5	• 25	• 52	•
8	• 48	—	—	(• 41)	•	6	• 34	• 53	•
9	• 37	• 52	—	—	•	7	• 19	• 61	•
10	• 42	• 53	—	—	•				

TABLE 2: Dialkylated LC Compounds with Centered Dipole and Their Phase Behaviors

$3 \quad \text{C}_n\text{H}_{2n+1}-\text{C}_6\text{H}_4-\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{OC}_m\text{H}_{2m+1}$									
$4 \quad \text{C}_n\text{H}_{2n+1}\text{O}-\text{C}_6\text{H}_4-\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{OC}_m\text{H}_{2m+1}$									
$5 \quad \text{C}_n\text{H}_{2n+1}\text{O}_x-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{O}_y\text{C}_m\text{H}_{2m+1}$									
3					4				
(<i>n,m</i>)	Cr	Sm	N	I	(<i>n,m</i>)	Cr	Sm	N	I
(8,6)	• 40	• 45	• 78	•	(6,8)	• 27	• 58	• 66	•
(8,7)	• 53	• 60	• 77	•	(6,9)	• 24	• 70	• 71	•
(10,9)	• 42	• 81	• 82	•	(10,10)	• 36	• 77	—	•
5									
(<i>n,m,x,y</i>)	Cr	Sm	N	I	(<i>n,m,x,y</i>)	Cr	Sm	N	I
(6,5,1,0)	• 19	• 23	• 61	•	(6,6,0,1)	• 44	—	—	• 53
(8,5,1,0)	• 37	• 56	• 65	•	(8,5,1,1)	• 58	• 63	• 81	•
(8,7,1,0)	• 26	• 62	• 67	•	(8,8,1,1)	• 62	• 72	• 88	•
(6,5,0,1)	• 41	—	—	• 44	(12,6,1,1)	• 61	• 85	—	•

monolayer on water by solution spreading owing to their strong internal cohesion and structural anisotropy. This 2D crystal is only metastable and readily yields to the formation of 3D crystals in short time, however. These observations suggest that the inability of hydrophobic oils¹⁰ to spread on water may be marginal or that they are so close to the spreading regime that there may well be a mechanism to drive them to spread as thermodynamically stable “liquid-condensed” Langmuir monolayers. The purpose of this paper is to demonstrate that this is in fact the case.

We examined more than 20 dialkyl-terminated hydrophobic materials as listed in Tables 1 and 2. Azobenzene derivatives were synthesized according to the standard procedures and purified by column chromatography. Structural analyses were performed by elemental analysis, ¹H NMR, and mass spectroscopy. Phenylpyrimidine derivatives were purchased from Midori Kagaku Co. Ltd., and the rest of the compounds were gifts from A. Yoshizawa, Hirosaki University.

All of the compounds are achiral and possess a simple rodlike shape composed of a mesogenic core, both ends of which are

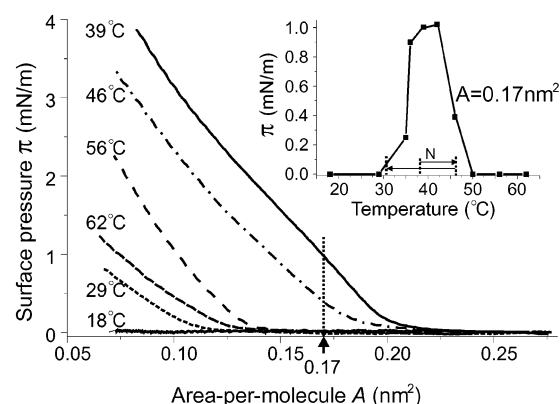


Figure 1. Surface pressure/molecular area isotherms of 7AB7 at 18, 29, 39, 46, 56, and 62 °C. 7AB7 has the bulk phase sequence as crystal|39 °C|nematic|47 °C|liquid for heating and crystal|31 °C|nematic|47 °C|liquid for cooling. The arrow gives $A = 0.17 \text{ nm}^2$ point at which the multidrops appear on compression. The inset shows the temperature dependence of π at $A = 0.17 \text{ nm}^2$.

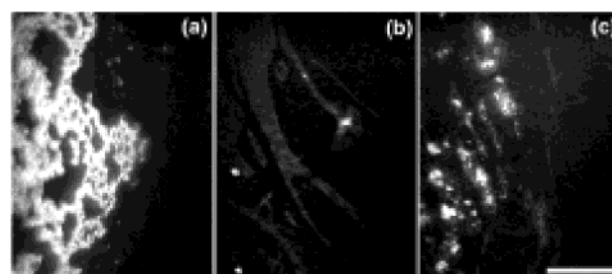


Figure 2. BAM images of 7AB7 on water at $A = 0.2 \text{ nm}^2$: (a) 18 °C (solid in bulk); (b) 25 °C (solid in bulk); (c) 50 °C (isotropic liquid in bulk). The white bar in panel c represents 500 μm .

terminated by *n*-alkyl or *n*-alkoxy groups with the chain length ≥ 5 . The molecules in Table 1 are structurally symmetrical and are thus nonpolar, while those in Table 2 have a small dipole moment inside or near the mesogenic core and could show a slight amphiphilicity. All of the compounds have one or more thermotropic liquid crystal (LC) phases near room temperature as indicated in the tables.

The compound was first dissolved in chloroform to make a 10^{-3} mol/L solution and was then spread on the surface of distilled and deionized water in our homemade Teflon trough equipped with a double movable barrier placed inside a thermostated enclosure. After allowing the solvent to evaporate for a few minutes, we obtained the Langmuir film. The surface pressure was measured with a Wilhelmy-type film balance; in all of the experiments reported below, the pressure (π) vs area-per-molecule (A) isotherms were measured at a constant relative compression rate of $d \log A/dt = 10^{-4} \text{ s}^{-1}$. Optical textures of the spread films were observed in-situ with a homemade depolarized reflected-light microscope (DRLM)¹¹ and Brewster angle microscope (BAM).¹²

For each of the seven nonpolar compounds in Table 1, the π – A isotherm measurements and microscopic observations have been simultaneously performed at several different temperatures between 15 and 70 °C. All of the compounds displayed essentially similar temperature-dependent behaviors, showing anomalously stable monolayer formation at intermediate temperatures corresponding to the bulk mesophases; typical results for 4,4′-diheptylazobenzene (hereafter referred to as 7AB7) are shown in Figures 1–3. At the temperatures at which the material is well inside either the crystal or the isotropic liquid phase in bulk, the spread film on water surface instantaneously phase-separates into tiny bulk crystallites or liquid drops floating in

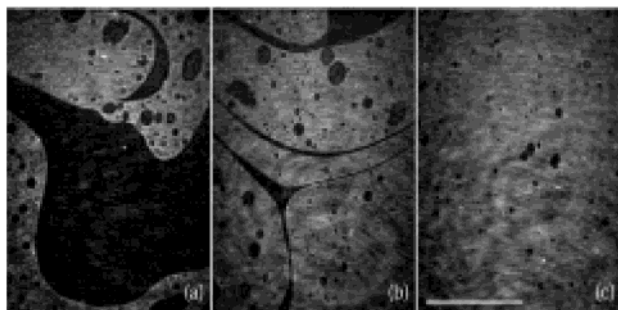


Figure 3. BAM images of 7AB7 monolayer at 43 °C (bulk LC temperature): (a) at $A = 0.5 \text{ nm}^2$; (b) at $A = 0.3 \text{ nm}^2$; (c) at $A = 0.2 \text{ nm}^2$. The bar in panel c represents $500 \mu\text{m}$. The bright areas indicate the high molecular density domains, and the dark areas correspond to the 2D gaseous phase.

coexisting gaseous or metastable condensed monolayers with almost zero surface pressure (see Figure 2). This inhomogeneous state persists all the way to the highly compressed region with the apparent molecular area A well below the cross sectional area of the rodlike molecule. The bulk domains, that is, crystallites and drops, are hard to coalesce with each other, and their number density increases on compression. The surface pressure tends to show a slight increase at molecular areas much less than the close pack molecular area of $A = 0.17 \text{ nm}^2$. The π - A isotherm at this small molecular area becomes hysteretic showing a gradual drop of pressure to $\sim 0 \text{ mN/m}$ when the compression is stopped. The coexistence of bulk phase, the absence of uniform liquid-condensed monolayer, and the π - A isotherm hysteresis are common signatures of hydrophobic compounds and have been understood to be the unmistakable attributes of nonspreading materials. Interestingly, however, the degree of phase separation becomes less conspicuous as the temperature approaches the bulk liquid-crystal region, finally leading to the formation of uniformly condensed monolayer with a substantial surface pressure despite their apparent hydrophobicity.

As the BAM images show in Figure 3, at temperatures inside or close to the bulk LC phase region, all seven materials could be reproducibly spread over the water surface to form a liquid-condensed monolayer. Given their molecular structure with no hydrophilic or polar groups in it, this behavior is quite surprising, showing sharp contrast to the common sense of Langmuir monolayers. At molecular areas much larger than the cross sectional area of the rodlike molecule, $\sim 0.17 \text{ nm}^2$, there occurs a coexistence of the liquid-condensed monolayer (bright region) and the 2D gas (dark region), as shown in Figure 3a. The smooth boundary and the near circular shape of the trapped 2D gas domains unambiguously indicate the fluid nature of the liquid-condensed monolayer. Furthermore, no contrast was observed under the DRLM in the liquid-condensed monolayer, providing evidence that the monolayer should be optically isotropic in the plane with the molecules oriented perpendicular to the surface on average. Under 2D compression, the liquid-condensed domains become dominant (Figure 3b) and finally cover the entire surface at a point where A is slightly larger than $\sim 0.2 \text{ nm}^2$ (Figure 3c). Hereafter, the surface pressure starts to rise. When the molecular area reaches $A \approx 0.17 \text{ nm}^2$, the monolayer begins to collapse into small multilayer domains, and the collapse continues on further compression, making the surface pressure reach a value as large as $\pi \approx 4.0 \text{ mN/m}$ or even higher. In contrast to the collapse behaviors in the bulk crystal or isotropic liquid region, the π - A isotherm is completely reversible up to the highest surface pressure, so the surface pressure

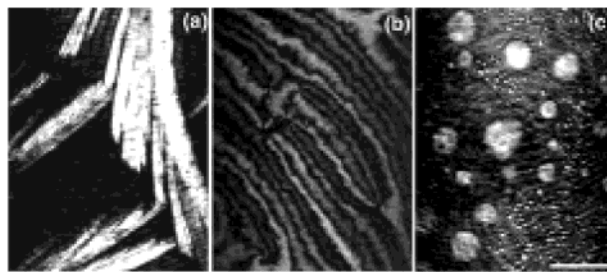


Figure 4. DRLM images of 4'-hexyloxyphenyl-4-hexylbenzoate (bulk phase sequence, crystal|44 °C|nematic|53 °C|liquid) on water at $A = 0.3 \text{ nm}^2$: (a) 20 °C (solid in bulk); (b) 45 °C (LC in bulk); (c) 60 °C (isotropic liquid in bulk). In panel b, the striped schlieren texture with vigorous flicker is the typical structure for 2D soft liquid crystals.^{15,16} The white bar in panel c represents $50 \mu\text{m}$.

faithfully follows the same curve on expansion with the swift disappearance of multilayer domains.

The same line of behaviors as above was also found to apply to the compounds in Table 2, except for the region of large area-per-molecule where a slight amphiphilicity associated with the weak polar group as $-\text{COO}-$ or pyrimidine can emerge by allowing the molecule to lie flat on the surface.^{13,14} Figure 4 shows the temperature dependence of the monolayer stability at $A \approx 0.17 \text{ nm}^2$. The separation of bulk crystallites (Figure 4a) and liquid drops (Figure 4c) is even more conspicuous, while a stable condensed monolayer forms at the bulk LC temperature (Figure 4b). A particularly notable side-effect of the introduction of polar group is the slight tilting of the molecule away from the surface normal ($\sim 10^\circ$) that makes the liquid-condensed monolayer to be 2D liquid crystalline^{15,16} (Figure 4b). Thanks to the in-plane optical anisotropy, we could observe the change of the molecular tilt¹⁶ as a function of density, showing intriguing phenomena as a compression-induced isotropic-anisotropic orientational transition; the details of which will be reported elsewhere.

Surface adsorption of molecules is driven by the free energy gain, $\gamma_w - \gamma = \pi_e$, associated with the reversible transfer of molecules from the bulk onto the water surface; here, γ_w and γ are the surface tensions of the bare and the film-covered water surfaces, respectively, and π_e is the equilibrium spreading pressure¹. This free energy gain can be decomposed into energetic and entropic contributions as $\pi_e = -(\Delta u - T\Delta\sigma)$. They are thermodynamically connected with the temperature variation of π_e by $\Delta\sigma = \partial\pi_e/\partial T$ and $\Delta u = -\pi_e + T(\partial\pi_e/\partial T)$. For a substantial degree of surface adsorption to occur, that is, $\pi_e \gg 0$, we must have $\Delta u \ll 0$ or $T\Delta\sigma \gg 0$ or both. By use of the Gibbs adsorption equation,¹ we further obtain

$$\frac{\partial\pi_e}{\partial T} = \Gamma(s_s - s_b) \quad (1)$$

where Γ is the number of adsorbed molecules per unit area, and s_s and s_b are the surface excess entropy per adsorbed molecule relative to the bare water surface and the molecular entropy in the bulk phase, respectively. It follows from eq 1 that π_e should be continuous as a function of temperature, and at discontinuous bulk phase transitions occurs a sudden change in the slope.⁴

Langmuir monolayers with $\pi > \pi_e$ are thermodynamically metastable. Hence, once the monolayer collapses into bulk phase by excessive 2D compression, the surface pressure irreversibly drops to π_e and there appears a hysteresis in the π - A isotherm. The temperature-dependent compression behaviors as described above for the bulk LC hydrophobic materials reveal that $\pi_e \approx$

0 in both bulk crystal and isotropic liquid regimes, while π_e increases beyond 1 mN/m in the bulk LC regime (see, the inset of Figure 1). Given the fact that the transition from nonspreading to spreading states takes place over a few degrees near the bulk-phase boundary, the rate of increase of π_e from the bulk crystal to LC phase is larger than 0.2 mN/(m K), which in combination with a modest value of $\Gamma \approx 5 \times 10^{18} \text{ m}^{-2}$ yields $s_s - s_b \approx 4 \times 10^{-23} \text{ J/K}$. For the free energy gain on adsorption, we then obtain $T\Delta\sigma \approx 60 \text{ mJ/m}^2 > 0$ and $\Delta u \approx 60 \text{ mJ/m}^2 > 0$. This shows that the spreading of the hydrophobic LC oils is driven by the entropy increase on adsorption against the energetic barrier.

The estimated lower bound for the entropy increase per molecule on adsorption is $\sim 3k_B$ with k_B being the Boltzmann constant, which is comparable with the transition entropy of the bulk melting. Therefore, if we can assume that the melting in the monolayer state on water preempts the bulk melting by a few degrees, the occurrence of such an adsorption-induced entropy increase seems plausible. Surface-induced phase transitions of long-chain *n*-alkanes have indeed been observed^{17,18} and attributed to the positive excess entropy at their surfaces.^{19–21} The origin of the entropy increase is envisaged to be the conformational entropy of alkyl chains²¹ or the translation entropy associated with thermal roughening of the surface.^{19,20} Whichever the reality is, for both mechanisms to work, the molecule should be rod-shaped and neither too short nor too long, limiting the chain length in the range of $14 < n < 50$, which is necessary to prevent the molecular cohesion from becoming too large, while allowing for sufficient complexity on the molecule to have high enough degrees of freedom. These conditions are perfectly in line with the well-known requisites for the formation of LC phases and appear nicely compatible with the present observation that the anomalous spreading of hydrophobic oils can occur only around their bulk LC phases.

In summary, we demonstrated that dialkyl-terminated hydrophobic oils can spontaneously spread on water surface to form liquid-condensed Langmuir monolayers, if they are in the liquid-crystal phase in 3D. On thermodynamic grounds, we argued

that the spreading is primarily driven by the entropy gain on adsorption, which overcomes the cost of energy increase at the oil–water interface. This is in sharp contrast with conventional spreading of amphiphiles. This finding will not only dramatically widen our choice of molecules to form soft Langmuir monolayers but also opens up a new path of molecular architecture for molecular engineering.

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