

Mixed Monolayer of Amphiphilic Schiff Base of *ortho*-Vaniline and Stearic Acid: Isotherms and Thermodynamic Properties

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Abstract:

Surface pressure-area isotherms of pure 2-methoxy-6-[(*n*-octadecylimino)methyl]phenol (MODIMP) and its mixture with stearic acid are reported. While the monolayer of pure MODIMP is unstable, mixing it with stearic acid stabilizes and condenses it. As the proportion of stearic acid in the solution being spread increases, the monolayer gets progressively more condensed and the surface pressure-area isotherm shows a decreased compressibility. Values of excess area per molecule of the mixed monolayer compared to the individual components give an indication about the possible interactions between the molecules of the two components and their orientation at the interface. At lower surface pressures, interactions between the molecules of different components are stronger than those in the pure monolayer, while opposite is the case at higher surface pressures.

Keywords: interactions in monolayers, Langmuir films, 2-methoxy-6-[(octadecylimino)methyl]phenol, Schiff's bases

1. Introduction

Langmuir monolayers at air-water interface continue to be of interest because they serve as precursors to Langmuir-Blodgett (LB) films [1], they are used to incorporate nanoparticles into LB films [2], and they can serve as templates for two-dimensional crystal growth [3]. The study of mixed monolayers can provide insight into miscibility among the components, mutual interaction and the phase behavior [4] of the films.

Our group has been investigating interactions between components of mixed monolayers and between monolayers and the sub-phase with an objective to examine and control the reactivity in various systems such as the film of monoterpenoid alcohol, nerol, over acidic sub-phase [5], of 1-phenyl-1-hexadecanol over chromic acid [6], mixed monolayers of octadecylamine and 1-octadecanethiol [7], a long-chain thiourea and a fatty acid [8] and several others [9-14].

In continuation of these studies, an

investigation of the interaction between a Schiff base and stearic acid was considered pertinent. Schiff bases exhibiting photochromism are of interest due to their potential applications in optical switching and data storage devices [15]. Schiff bases are important compounds from a medicinal point of view [16], as they exhibit anticancer, antibacterial, antifungal, anti-leishmania, and antiviral activity. Moreover, they have extensive applications in laser dyes [17]. Thus, studies of pure and mixed monolayers of Schiff bases are of considerable interest. Here we report investigations on mixed monolayers of the Schiff base 2-[(*n*-octadecylimino)methyl]phenol (MODIMP), and stearic acid.

2. Results and Discussion

The surface pressure-area hysteresis isotherm of MODIMP at air/water interface is shown in Figure 1. MODIMP forms an expanded type monolayer. Extrapolation of the linear region of the isotherm showed that the molecular area was

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0.44 nm²/molecule. Hemakanthi and coworkers [18] have reported an area per molecule of 0.44 nm² for a Schiff base prepared from hexadecylamine and *O*-vaniline. In the hysteresis isotherms, the successive compression-expansion cycles shift to lower molecular areas, indicating a continuous loss of the monolayer material. This might be due to the rigid aromatic head groups being squeezed out from the interface as a result of the compression.

The pure SA isotherm, on the other hand, is a smoothly rising curve with a lift-off area of 0.20 nm² and a collapse pressure of about 52 mN/m [19]. The pH of the sub phase was measured to be 6.9. At this pH stearic acid monolayer is not expected to be protonated to any appreciable extent. The area/molecule of pure SA was 0.20 nm² at 25 mN/m.

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The surface pressure-area per molecule (π -A) isotherms for pure SA and for the mixed MODIMP/SA monolayers at various compositions are shown in Figure 2. The similar steepness of

the isotherm curves of the pure SA and the MODIMP/SA mixtures with the mole fraction of SA over 0.5 indicates comparable values of compressibility, though the mixed monolayer does not have a similar phase transition as shown by the pure SA monolayer.

The area/molecule values of the monolayers are shown in Table 1. The values are comparable to one another. The area/molecule values of the mixed monolayers are lower than those for the pure MODIMP, indicating that there is an interaction between MODIMP and SA. This could be due to formation of hydrogen bonds between the carboxyl group of the stearic acid and the OH of the adjacently located molecules (Scheme 1) [18]. The same kind of hydrogen bond formation of Schiff bases with barbituric acid has been reported by Jiao and coworkers [20]. The large decrease in the area/molecule values of the mixed film compared to that of the pure MODIMP is possibly due to a change in the orientation plane of the molecules at the air/water interface [21]. This might be caused by the formation of a ring structure as shown in Scheme 2. Such a scenario was reported for the Cu²⁺ complexes of MODIMP [22] and for a number of Schiff bases [23].

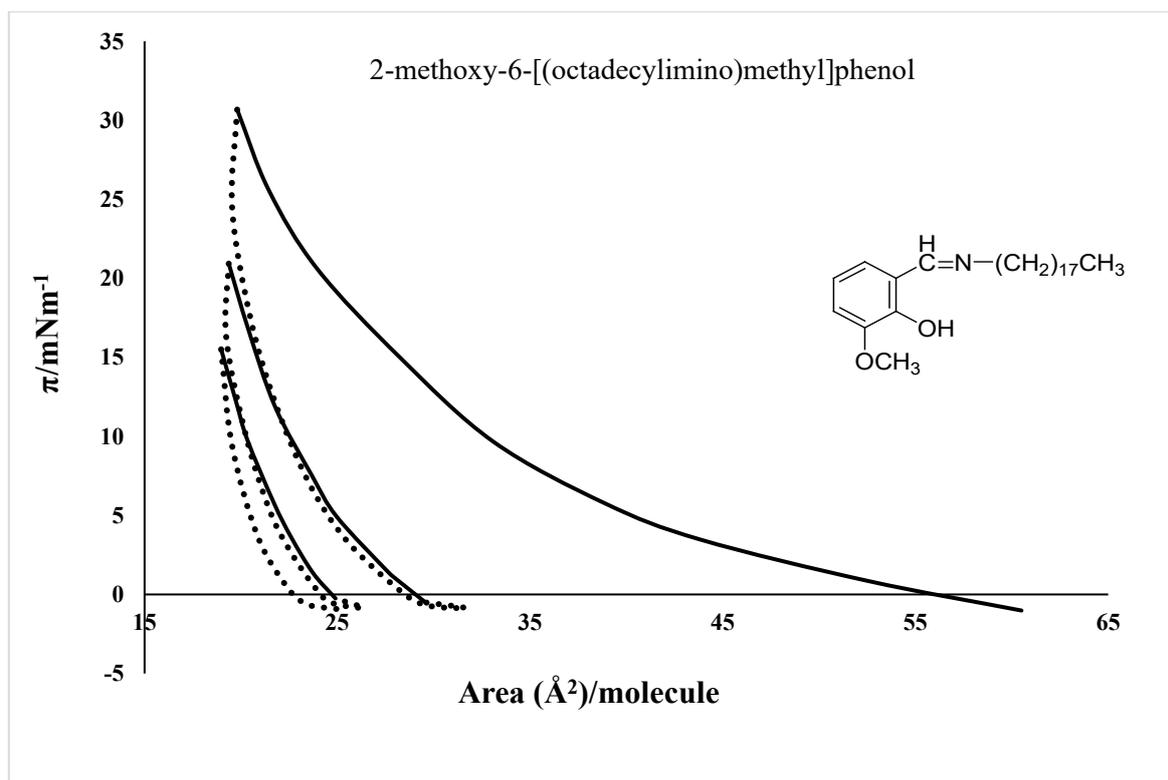


Figure 1. Surface pressure-area hysteresis isotherm of MODIMP spread over air/water interface at 25 °C. Solid curve represents compression, and the dotted curve is for expansion.

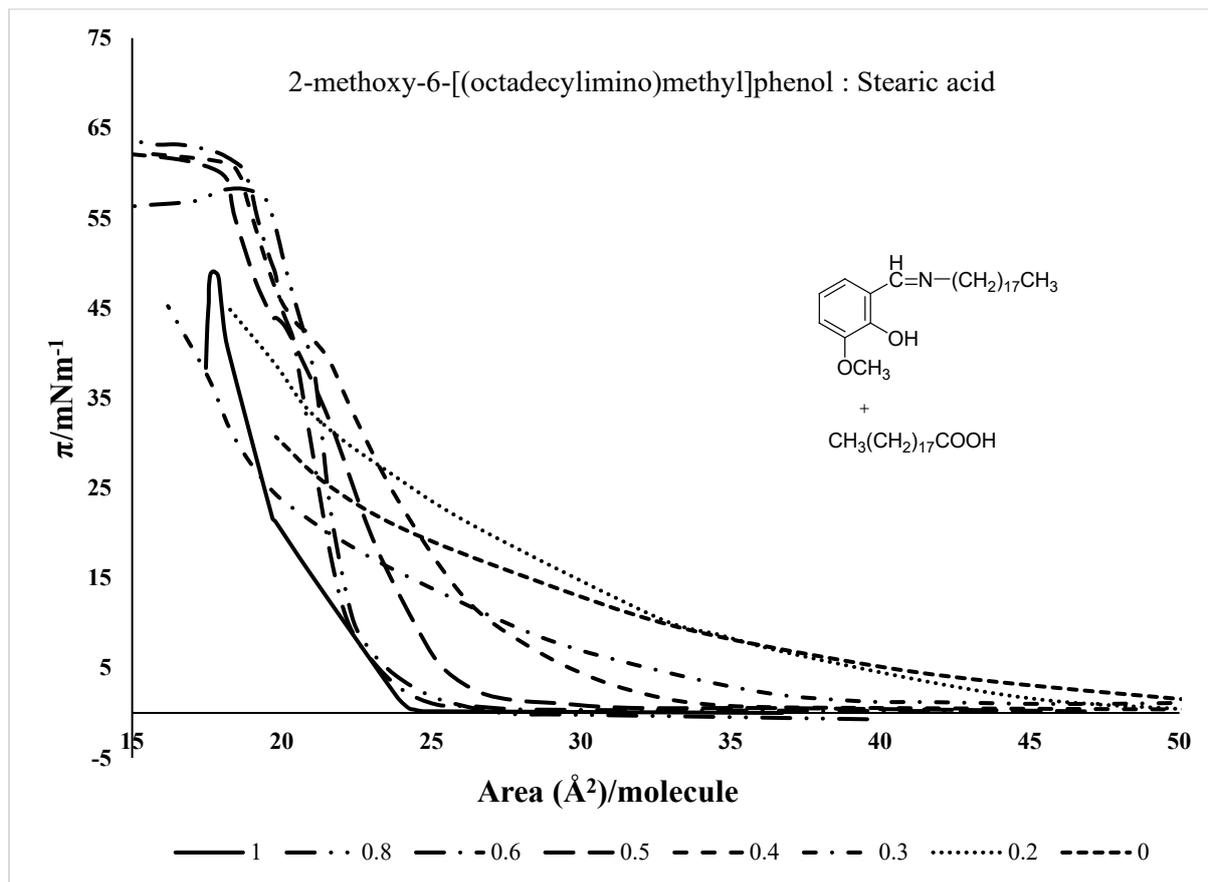
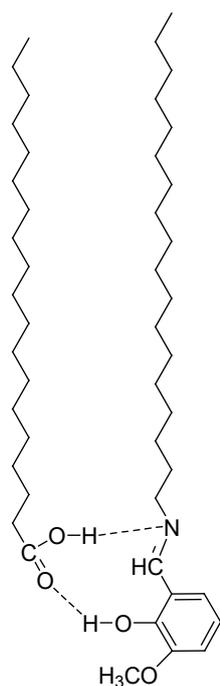


Figure 2. Surface pressure-area per molecule isotherms of mixed MODIMP/SA monolayers over water at 25 °C, prepared by premixing the two solutions prior to spreading. The solid line is for pure stearic acid.



Scheme 1. Schematic illustration of structure of MODIMP/SA complex.

Table 1. Area/molecule of MODIMP/SA mixed film.

Composition of MODIMP:SA	Area/molecule (nm ² /molecule)
0.202: 0.798	0.23
0.403: 0.597	0.24
0.503: 0.497	0.25
0.594: 0.406	0.26
0.692: 0.308	0.23
0.797: 0.203	0.19

There is a decrease in surface pressure as the MODIMP content in the monolayer increases, indicating a decreased stability of the mixed monolayer. The observed trend suggests that the interaction between the MODIMP and SA is more favorable when the mole fractions of MODIMP are lower.

Miscibility of the components in the monolayer

A monolayer in which the two components are mutually miscible would be homogeneous and its collapse pressure would not necessarily correspond to the collapse pressures of the pure monolayers. On the other hand, a film in which the components are not mutually miscible would retain the characteristics of both the pure monolayers and would show two collapse pressures corresponding to each of the components [24]. By this criterion it can be concluded that MODIMP and SA are miscible at the air/water interface.

In an ideally mixed film, or in one in which the components are totally immiscible, the area per molecule is simply equal to the sum of the areas per molecule of the two components. Thus $A_{id} = (X_1A_1 + X_2A_2)$; where A_{id} is the area per molecule in the ideally mixed monolayer and A_1 and A_2 are the corresponding values for the individual

components, whose respective mole fractions are X_1 and X_2 . In a non-ideally mixed monolayer, the measured area is different from the area calculated from the values for the pure monolayers. This difference, or excess area, A_{ex} , can be expressed as: $A_{ex} = A_{12} - A_{id} = A_{12} - (X_1A_1 + X_2A_2)$ [25];

It follows that for an immiscible monolayer (or an ideal mixed one), the excess area will be zero and A_{12} will be linear in X_1 , as shown below.

If $A_{ex} = 0$, $A_{12} = (X_1A_1 + X_2A_2)$; Since $X_2 = 1 - X_1$,
 $A_{12} = X_1A_1 + (1 - X_1)A_2$;

$$A_{12} = X_1A_1 + (1 - X_1)A_2.$$

$$A_{12} = X_1(A_1 - A_2) + A_2$$

Since A_1 and A_2 are constants, A_{12} will vary linearly with X_1 for an immiscible system. The non-linearity shown by the mixed MODIMP/SA system is depicted in Fig. 4.

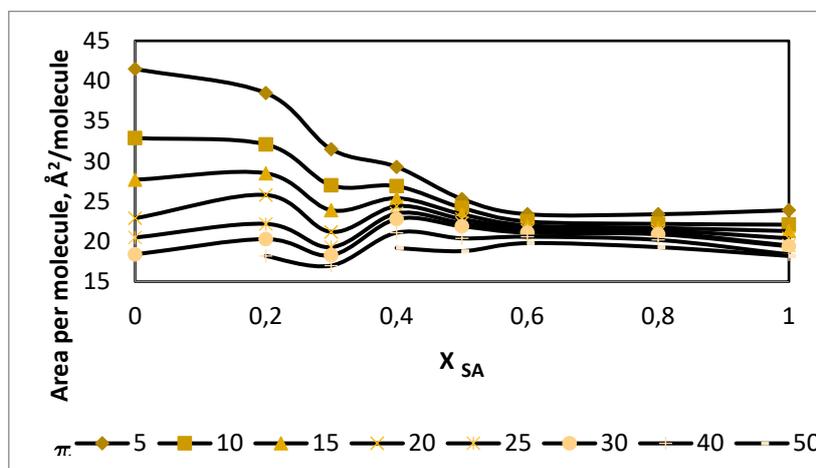


Figure 4. The mean area per molecule (A_{12}) as a function of composition for mixed MODIMP/SA monolayers at various surface pressures.

Figure 5 shows how the ratio A_{ex}/A_{id} varies with composition of the mixed monolayer at various surface pressures. At low surface pressures, A_{ex} tends to be negative, indicating that under these conditions, the unlike molecules have a stronger mutual interaction compared to the like ones. At higher surface pressures ($\pi > 15$) on the other hand, the opposite is true, as A_{ex} is generally positive. These results can be interpreted in terms of the condensing effect of stearic acid on MODIMP through the formation of hydrogen

bonds between the head groups of MODIMP and stearic acid as shown in Scheme 2. At higher values of π , repulsion between the head groups would likely offset the effect of the hydrogen bonding. Such an effect has been reported earlier. Thus, mixed monolayer systems, 1,2-dipalmitoyl-sn-glycerophosphocholine (DPPC)/cholesterol [26] and octadecyl amine/stearic acid [4] showed repulsive interaction at higher surface pressures.

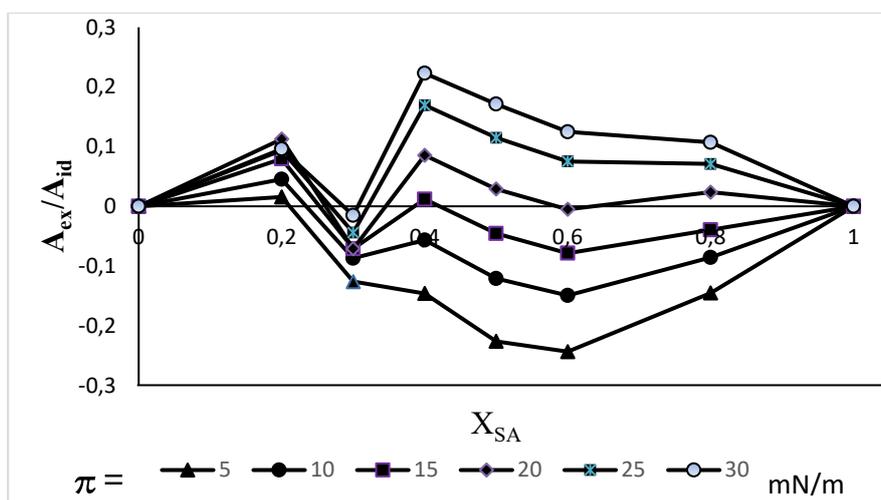


Figure 5. A_{ex}/A_{id} as a function of composition for mixed MODIMP/SA monolayers at various surface pressures.

An evaluation of the Gibbs free energy of mixing can give quantitative information about the interaction between the components in a mixed monolayer, and the relative thermodynamic stabilities of the mixed and the pure monolayers can thus be investigated. At constant surface pressure and temperature, ΔG_{mix} is given by

$$\Delta G_{mix} = \Delta G_{ex} + \Delta G_{id}$$

$$\Delta G_{ex} = \int_0^\pi [A_{12} - (X_1 A_1 + X_2 A_2)] d\pi$$

Thus, ΔG_{ex} can be evaluated from the π - A isotherms [27].

$$\Delta G_{id} = RT (X_1 \ln X_1 + X_2 \ln X_2)$$

This enabled the various ΔG_{mix} values to be calculated (Figure 6). All the values are negative, implying thermodynamic stability of the mixed film.

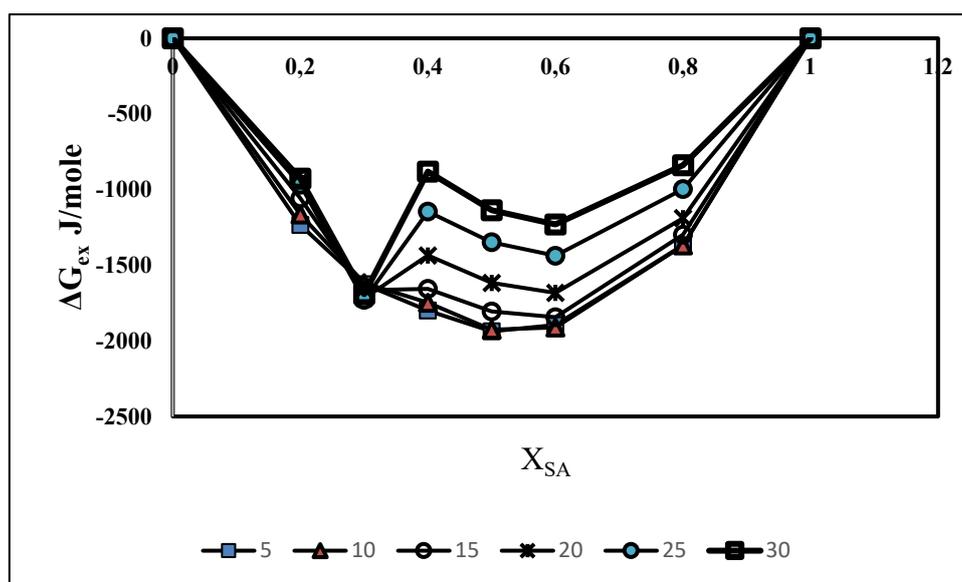


Figure 1. The free energy of mixing (ΔG_{mix}) as a function of composition for mixed MODIMP/SA monolayers at various surface pressures.

3. Material and Methods

The water used as the sub-phase was

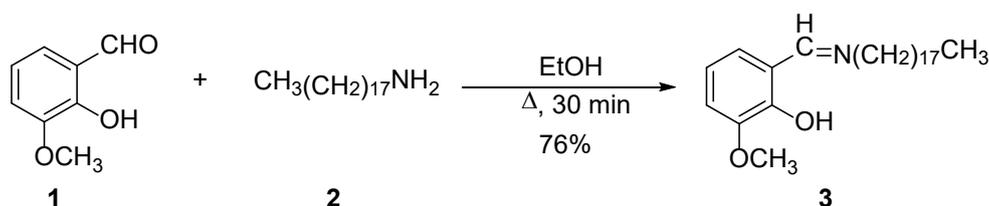
prepared by taking distilled water and redistilling it in an all quartz two-stage distillation apparatus.

Commercial stearic acid (SA) (90%, UnivAR,

South Africa) was recrystallized from *n*-hexane. The *ortho*-vaniline and *n*-octadecylamine were procured from Aldrich. The ^1H NMR and ^{13}C NMR spectra were recorded in a CDCl_3 solution at 300 MHz and 75.4 MHz, respectively, on a BrukerTM 300 MHz spectrometer.

2-Methoxy-6-[(*n*-octadecylimino) methyl]phenol (MODIMP) (**3**) was synthesized by the condensation of *ortho*-vaniline and *n*-octadecylamine in distilled ethanol in equimolar

ratio (Scheme 2) [28]. A solution of 0.7858 g (~5 mmol) of *ortho*-vaniline (**1**) and 1.3907 g (~5 mmol) of *n*-ODA (**2**) in distilled ethanol was refluxed in a 100 mL round bottomed flask for 30 min. The solution was allowed to attain room temperature. The yellow solid product was filtered under suction and recrystallized from ethanol to yield MODIMP in 76% yield (m. p. 71-73 °C). The structure of the compound was confirmed by spectral data (IR, ^1H NMR and ^{13}C NMR) as described below.



Scheme 2. Synthesis of 2-methoxy-6-[(*n*-octadecylimino)methyl]phenol.

Spectroscopic data: (IR, neat, cm^{-1}): 3315 (O-H), 2915, 2848, 1658 (C=N), 1587, 1512. ^1H NMR (CDCl_3 , δ ppm): 0.93 (t, 3H, CH_3); 1.30 (s, 30H, fifteen methylene protons); 1.73 (m, 2H, CH_2); 3.61 (t, 2H, N- CH_2); 3.93 (s, 3H, OCH_3); 4.42 (br, 1H, OH) 6.94 (d, 1H, arom.), 7.10 (dd, 1H, arom.), 7.13 (d, 1H, arom.), 7.47 (d, 1H, arom.); 8.19 (s, 1H, $\text{CH}=\text{N}$). ^{13}C NMR (CDCl_3 , δ ppm): 14.1 (CH_3); 22.7, 27.4, 29.4, 29.5, 29.7, 30.0, 32.0 (CH_2); 56.0 (O- CH_3); 61.5 (N- CH_2); 108.4 114.2, 123.9, 128.9, 147.3, 148.5 (six aromatic carbons); 160.7 ($\text{CH}=\text{N}$).

Preparation of monolayer films

The procedure and the equipment used for the experiments have been described previously [13]. The film balance used for the measurements was manufactured by Nima Technology, Coventry, England. It consisted of a trough of dimensions 30 cm x 20 cm x 0.5 cm milled from a single slab of PTFE and divided into two compartments of equal areas. The experiments described here were performed using one of the compartments, which had a surface barrier made of PTFE. The barrier could be moved to change the area available to the monolayer thus compressing or expanding it. One end of the trough had a microbalance from which a Wilhelmy plate, cut from a filter paper, was suspended. The plate dipped into the aqueous phase and the force on

it, as measured by the microbalance, was displayed on a computer screen. Prior to each measurement, the inside of the trough was cleaned with soapy water, and then rinsed with distilled water. It was then wiped clean using a tissue paper soaked in *n*-hexane. Finally, it was rinsed thoroughly with triply distilled water. For the measurements, the trough was filled with triply distilled water that had been brought to 25 °C in a thermostatted water bath. Before carrying out measurements on the monolayers, blank runs were made with pure water and water with the pure solvent spread over it. An absence of surface pressure on compression indicated that the surface was free of any surface-active impurity. For the actual measurement, 3.881×10^{-3} M SA and 2.180×10^{-3} M MODIMP were prepared in chloroform. To prepare a pure monolayer, 25 μL solution was spread on triply distilled water (the sub-phase) using a micro syringe. Mixed monolayers were prepared by first mixing the suitable volumes of both solutions and spreading 25 μL of the mixture on the sub-phase.

The solvent was allowed to evaporate for about 10 minutes. The monolayer was then compressed by moving the barrier to decrease the area available to the monolayer at a rate of 10 cm^2/min . The instrument displayed a graph between the area available to the monolayer and the surface pressure.

To investigate the hysteresis behavior MODIMP, the monolayer was compressed to a point just before its collapse, at which point it was allowed to expand by reversing the motion of the barrier. After the monolayer expanded fully to its initial area, the direction of the barrier was reversed again to start compression. Three compression-expansion cycles were recorded.

4. Conclusions

2-Methoxy-6-[(*n*-octadecylimino) methyl] phenol, spread on air-water interface, does not form a stable Langmuir monolayer. However, when it is mixed with stearic acid prior to spreading, a stable mixed monolayer result. As the proportion of stearic acid in the solution that is being spread increases, the monolayer gets progressively more condensed and the surface pressure-area isotherm shows decreased compressibility as judged from the steepness of the curves. The limiting areas per molecule of the mixed films remain largely unchanged except where the mole fraction of stearic acid is around 0.3. The values of the Gibbs' free energy of mixing indicate that the mixed monolayers are thermodynamically stable.

Supporting Information

[¹H, ¹³C, DEPT NMR, and IR spectra of MODIMP.](#)

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