



# Equilibrium spreading pressure and Langmuir–Blodgett film formation of omega-substituted palmitic acids



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## ABSTRACT

Langmuir–Blodgett isotherms and equilibrium spreading pressures were measured for compounds of the series  $X-(CH_2)_{15}COOH$ ,  $X = CH_3, SH, OH, F, Cl, Br$ . Only the  $CH_3$  and  $F$  terminated compounds formed monolayers with sufficient stability for accurate isotherm measurement, film transfer and X-ray photoelectron spectroscopic analysis. The presence of the terminal heteroatom substituents significantly diminished the stability of the L–B film and depressed the equilibrium spreading pressures (20 °C) from 15.4 mN/m for the  $CH_3$  terminated compound to a range of 0.95 to 0.08 mN/m for the other members of the series. These characteristics are attributed to the monolayer film being in a metastable state and the dipole moment of the heteroatom terminal group increasing the monolayer film kinetic instability by facilitating the formation of three-dimensional structures.

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## 1. Introduction

Omega-substituted palmitic acids ( $X-(CH_2)_{15}COOH$ ,  $X = CH_3, SH, OH, F, Cl, Br$ ; compounds **1–6** respectively) are a homologous series of compounds with streamlined amphiphilic structures and very similar molecular shapes and molecular volumes. The methyl-terminated member and its longer and shorter chain fatty acid homologues ( $CH_3(CH_2)_nCOOH$ ,  $n = 11$  to 34) are well known to form monomolecular films as two-dimensional close-packed assemblages of commonly oriented molecules [1]. When formed at an air–water interface by the Langmuir–Blodgett (L–B) technique, transferrable films with a relatively well-defined structure and high collapse pressure are obtained. Several excellent texts and reviews describe many details of preparation, characterization and application for L–B films [1–5]. Modification of the structure of the fatty acid can significantly influence the L–B film formation behavior. Other strong hydrogen bonding functional groups (e.g.  $-CH_2OH, CONH_2$ , etc.) may be substituted for the acid head group, and one still obtains L–B films with high collapse pressures ( $>50$  mN/m), while weak hydrogen bonding groups ( $-CH_2OCH_3, -SH$ , etc.) in the head position result in unstable films with low collapse pressures, and very weak hydrogen bonding groups ( $-CH_2Br, -CH_2Cl$ , etc.) in this position result in no monolayer films being obtained [1,3]. As such, the positioning of very small and weakly hydrogen bonding substituents at the  $\omega$ -position of a long chain fatty acid could be conjectured to have a nominal perturbing effect on L–B film formation and to serve, as well, as a spectroscopic probe for analytical purposes.

The impetus for undertaking this work was the need for an experimental standard for an X-ray photoelectron spectroscopy (XPS) measurement of molecular packing density in self-assembled monolayers (SAMs). The molecular area and surface packing density obtained from a well-defined L–B pressure–area isotherm were envisioned as forming the basis for such a standard presuming that the L–B film could be quantitatively transferred to a substrate for XPS analysis. The alkanethiol-on-gold system was initially thought to be suited for this purpose but, unfortunately as indicated above and found experimentally [6], long-chain alkanethiol compounds do not form stable transferrable monolayer L–B films. Our intended application for such a standard was in the evaluation of  $-COOH$  terminally functionalized alkanethiol SAMs as monolayer adsorbents for amine vapors. The terminal  $-COOH$  group disrupts molecular order and packing in SAMs prepared from  $HS(CH_2)_nCOOH$ ,  $n = 5, 10$ , and 15, onto a gold surface [7], and it was conjectured that the  $HS(CH_2)_{15}COOH$  molecule might form a stable and transferrable L–B film that could serve as an index for XPS determination of the surface density of  $-COOH$  groups in the SAM even though the orientation of this molecule would presumably be reversed in the L–B film. The L–B isotherm for this molecule displayed an unusually high collapse pressure but with a molecular area that is one half ( $11 \text{ \AA}^2$ ) of that expected ( $22 \text{ \AA}^2$ ). Thinking this behavior might be attributable to chemical interactions involving the  $-SH$  group, it was then hypothesized that substitution of a halogen in place of the  $HS-$  group at the tail of the  $HS(CH_2)_{15}COOH$  molecule would be more likely to promote L–B film formation with good stability for transfer and a rational molecular area. Such a film would position the halogen at the outer surface of the L–B film and alleviate the need of an XPS attenuation correction. The work that follows is an L–B film formation study of the  $\omega$ -substituted palmitic acid

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compound series described above and the use of the equilibrium spreading pressure (ESP) to analyze the unexpected behavior observed.

## 2. Experimental section

### 2.1. General methods and materials

$^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 300 NMR system operating at 300, 75.5, and 282 MHz, respectively. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Magna 750 FTIR spectrometer from thin film samples on a NaCl window. Compound melting points and purity assessments were determined by differential scanning calorimetry (DSC) on a TA Instruments DSC Q100. L–B pressure–area isotherms and equilibrium spreading pressures were measured using a Nima Technologies L–B Trough 611 MC.

Compounds **1**, **2**, **3** and **6** were purchased from commercial sources. Compounds **4** and **5** were synthesized as described below. All six of these compounds were subjected to a rigorous purification procedure and analysis as described below. The water used on the L–B trough was triple distilled from a three-stage quartz still.

### 2.2. Synthesis of 16-fluoro-1-hexadecanoic acid, **4**

There are four reported syntheses of **4** by two different routes, both starting with 16-hydroxyhexadecanoic acid (**3**) and converting it to the methyl ester,  $\text{HO}(\text{CH}_2)_{15}\text{CO}_2\text{CH}_3$ . The first route converts the hydroxyl group to the tosylate (TsO),  $\text{TsO}(\text{CH}_2)_{15}\text{CO}_2\text{CH}_3$ , then by reaction with tetrabutylammonium fluoride (TBAF) displaces the tosylate with fluoride,  $\text{F}(\text{CH}_2)_{15}\text{CO}_2\text{CH}_3$ , followed by hydrolysis of the ester to yield **4** [8,9]. The second route converts the hydroxyl group directly to the fluoride by reaction with diethylaminosulfur trifluoride (DAST) followed by hydrolysis of the ester to also yield **4** [10–12]. After two attempts by the first route, it was found that displacement of the tosylate group on the alkane chain with fluoride from the TBAF reagent did not proceed to a yield greater than 15–20%, and losses in the subsequent purification made this synthesis route unviable. The alternate route involved modification of that reported by Kraft and Moore [12]. This modified procedure is described in the following paragraphs.

$\text{HO}(\text{CH}_2)_{15}\text{CO}_2\text{CH}_3$ . This methyl ester was prepared by reflux of  $\text{HO}(\text{CH}_2)_{15}\text{CO}_2\text{H}$  (1.302 g, 4.78 mmol) in 32 ml  $\text{CH}_3\text{OH}$  and 8 drops conc.  $\text{H}_2\text{SO}_4$  and isolated by ether extraction to yield 1.107 g (81%) with MP (55 °C) and spectroscopic features matching those reported for this compound [12].

$\text{F}(\text{CH}_2)_{15}\text{CO}_2\text{CH}_3$ . The initial preparation attempt of this compound utilizing the 1:1 DAST: $\text{HO}(\text{CH}_2)_{15}\text{CO}_2\text{CH}_3$  reagent mole ratio [12] in our hands produced 54% conversion and a  $\text{F}(\text{CH}_2)_{15}\text{CO}_2\text{CH}_3$ – $\text{HO}(\text{CH}_2)_{15}\text{CO}_2\text{CH}_3$  mixture that was difficult to separate. Increasing the reagent mole ratio to 2:1 resulted in 88% isolated yield. Our procedure is as follows. In thoroughly dried glassware and inert atmosphere vacuum dried  $\text{HO}(\text{CH}_2)_{15}\text{CO}_2\text{CH}_3$  (0.556 g, 1.94 mmol) was dissolved in 2 ml of distilled alumina-dried  $\text{CH}_2\text{Cl}_2$  and added dropwise to a solution of DAST (0.625 g, 3.88 mmol) in 2 ml of distilled alumina-dried  $\text{CH}_2\text{Cl}_2$  at –78 °C. The product was isolated by diluting with  $\text{CH}_2\text{Cl}_2$ , extracting with water, drying, and chromatographing on alumina (activity 1) to yield 433 mg (77%) product with MP (38 °C) and spectroscopic features identical to those reported for this compound [12].

$\text{F}(\text{CH}_2)_{15}\text{CO}_2\text{H}$ , **4**. Our initial attempts to obtain this compound from the saponification of  $\text{F}(\text{CH}_2)_{15}\text{CO}_2\text{CH}_3$  utilizing the conditions described in Ref. [12] ( $\text{NaOH}/\text{H}_2\text{O}/\text{dioxane}$ ) gave very low conversions (10–20%). An alternate saponification procedure utilizing  $\text{KOH}/\text{CH}_3\text{OH}$  was found to produce a much higher conversion and was adapted to this synthesis as follows. The  $\text{F}(\text{CH}_2)_{15}\text{CO}_2\text{CH}_3$  (307 mg/10 ml) was refluxed in a solution of  $\text{KOH}/\text{CH}_3\text{OH}$  (307 mg/10 ml) for 4 h, concentrated to dryness, neutralized in 25 ml  $\text{H}_2\text{O}$  with conc HCl, extracted into  $\text{CH}_2\text{Cl}_2$  dried

and recrystallized from hexane to yield 298 mg (92%) of platelet crystals, MP 70–73 °C (lit. 60–61 °C [9]; 74–76 °C [12]). This compound was further subjected to three successive recrystallizations described below which narrowed the DSC melting endotherm but did not significantly raise the melting point. IR (neat):  $\nu_{\text{max}}/\text{cm}^{-1}$  3450 (br,w), 2916, 2848, 1706, 1463, and 721.  $^1\text{H}$  NMR (4 mg/650 mg  $\text{CDCl}_3$ ):  $\delta$  4.415 (dt, 47.4 Hz, 6.3 Hz, 2H), 2.327 (t, 7.8 Hz, 2H), 1.65 (m, 4H), and 1.24 (m, 22H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  179.01, 85.35, 33.87, 30.53, 30.27, 29.61, 29.57, 29.53, 29.50, 29.41, 29.23, 29.05, 25.17, 25.09, and 24.68.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  –218.45 (tt, 46.5 Hz, 24.0 Hz).

### 2.3. Synthesis of 16-chloro-1-hexadecanoic acid, **5**

This compound was prepared from  $\text{HO}(\text{CH}_2)_{15}\text{CO}_2\text{H}$  (**3**) by reaction with thionyl chloride/pyridine followed by hydroxide treatment using a procedure adopted from Fox and Price [13]. In thoroughly dried glassware and inert atmosphere  $\text{SOCl}_2$  (437 mg, 3.67 mmol) dissolved in 1 ml distilled  $\text{CHCl}_3$  was added dropwise to a solution of compound **3** (400 mg, 1.47 mmol) and pyridine (290 mg, 3.67 mmol) dissolved in 5 g distilled  $\text{CHCl}_3$  at 0 °C followed by 1 h at 0 °C, 12 h at 20 °C and 12 h reflux (65 °C). After cooling and additions of 5 ml  $\text{CHCl}_3$  and 5 wt.%  $\text{NaOH}/\text{H}_2\text{O}$ , a precipitate was vigorously stirred for 3 h with addition of more  $\text{CHCl}_3$  as needed to maintain stirring. The mixture was then neutralized with conc HCl, and the  $\text{CHCl}_3$  phase was separated. The aqueous phase was extracted 4× with 15 ml  $\text{CHCl}_3$ . The combined  $\text{CHCl}_3$  phases were concentrated to dryness and recrystallized from hexane to yield 264 mg (62%) product as platelet crystals MP 59–61 °C (lit. 61–61.5 °C [13]). IR (neat):  $\nu_{\text{max}}/\text{cm}^{-1}$  3500 (br,w), 2918, 2848, 1722, 1465, and 718.  $^1\text{H}$  NMR (7 mg/641 mg  $\text{CDCl}_3$ ):  $\delta$  3.61 (t, 6.3 Hz, 2H), 2.40 (t, 8.1 Hz, 2H), 1.53 (m, 4H), and 1.23 (m, 22H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  178.82, 45.05, 35.88, 33.66, 30.87, 30.58, 29.67, 29.56, 29.51, 29.49, 29.40, 29.10, 25.22, 25.13, and 24.71.

### 2.4. Recrystallization of $X-(\text{CH}_2)_{15}\text{COOH}$ , XCH<sub>3</sub>, F, Cl, Br, OH, SH

The level of compound purity has been found to be particularly important for obtaining reproducible L–B isotherm and equilibrium spreading pressure measurements [14]. A recommended procedure for obtaining such purity is a slow overnight recrystallization from an inert volatile solvent [15]. The following procedure for final recrystallization of the  $\omega$ -substituted palmitic acids prior to L–B isotherm and equilibrium spreading measurements was adopted from this reference.

Saturated solutions of the six compounds were prepared at 60 °C by stirring an excess of each compound in 10 ml distilled hexane for compounds **1** and **4**, or 10 ml distilled cyclohexane for compounds **2**, **3**, **5** and **6**. These solutions were then gravity-filtered through a 60 °C preheated coarse glass frit into a recrystallization vial, tightly capped and placed in a 60 °C twenty one-liter water bath. After the bath slowly cooled over 16 h and a seed crystal added if needed, the liquor was carefully decanted. The bath and recrystallization vials were reheated to 60 °C, and aliquots of solvent added until dissolution was observed. This recrystallization–decantation was repeated two more times followed by 48 h vacuum drying. The effectiveness of this purification procedure was assessed by obtaining DSC thermograms of the melting process for each compound. Impurities lower and broaden the melting point and are assessed by the maximum temperature of the DSC melt endotherm peak and its width at half maximum. These values are summarized in Table 1 along with melting points and optical microscope observations of the 3× recrystallized crystallite form and dimensional range. It is interesting to note that any terminal substituent has an elevating and broadening effect on the melting point.

### 2.5. L–B isotherm measurement and film transfer

Surface pressure–area isotherms were measured on a commercial L–B trough (Nima Technologies 611 MC) with surface pressure

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