

## Behavior of partially fluorinated carboxylic acids at the air–water interface

Hans-Joachim Lehmler<sup>a,\*</sup>, Moses O. Oyewumi<sup>b</sup>, Michael Jay<sup>b</sup>, Paul M. Bummer<sup>b</sup>

<sup>a</sup>Graduate Center for Toxicology, University of Kentucky Medical Center, 306 HSRB, Lexington KY 40536-0305, USA

<sup>b</sup>College of Pharmacy, University of Kentucky, Lexington KY 40536-0305, USA

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### Abstract

Langmuir isotherms were recorded for 1-(perfluorobutyl)undecanoic acid ( $F_3C(CF_2)_3(CH_2)_{10}CO_2H$ ), 1-(perfluorohexyl)undecanoic acid ( $F_3C(CF_2)_5(CH_2)_{10}CO_2H$ ) and 1-(perfluorooctyl)undecanoic acid ( $F_3C(CF_2)_7(CH_2)_{10}CO_2H$ ), their hydrocarbon analog, perfluorododecanoic and perfluorotetradecanoic acid after spreading onto hydrochloric acid ( $pH = 1.9–2.0$ ) at  $32^\circ C$ . All acids formed stable monolayers at the air–water interface. 1-(Perfluorobutyl)undecanoic acid shows some similarity to the compression isotherm of tetradecanoic acid while lacking the phase transition of pentadecanoic acid. The isotherm for 1-(perfluorohexyl)undecanoic acid shows a temperature-dependent phase transition similar to the liquid expanded–liquid condensed transition of pentadecanoic acid. The  $\pi$ -A isotherm of 1-(perfluorooctyl)undecanoic acid resembles the highly condensed monolayers of hepta- and nonadecanoic acid. Thus, the partially fluorinated acids seem to exhibit isotherm characteristics similar to hydrocarbon acids with shorter chain lengths. The three partially fluorinated acids have a higher limiting area compared to hydrocarbon and perfluorocarbon acids, which may be attributed to the strong dipole moment of the  $-CF_2-CH_2-$  linkage. Within this series of partially fluorinated carboxylic acids, the limiting area decreases with chain lengthening and a higher degree of fluorination. The collapse pressures of the fluorinated acids are smaller compared to their respective hydrocarbon analog. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Langmuir isotherms; DSC; Fluorinated; Perfluorinated; Carboxylic acid

### 1. Introduction

Fluorine is the most electronegative of the elements. The replacement of a hydrogen atom with fluorine in an organic molecule alters its thermal, chemical and biological characteristics significantly. The fluorine–carbon bond is very strong, but intramolecular interactions of fluorocarbons are weak. This results in an exceptional combination of properties of fluorocarbons, such as thermal, chemical and biological inertness, low solubility for water as well as polar and non-polar organic solvents, high density, fluidity, compressibility and high dielectric constants. The low surface tension and excellent spreading characteristics of perfluorinated amphiphiles has found broad technical applications in fire extinguishing media, electroplating bath, water proofing sprays, lubricants, and many other applications [1,2].

Because of the surface characteristics that result from a perfluoroalkyl chain, there is growing interest in partially

fluorinated amphiphiles for cosmetic [3], pharmaceutical and medical applications [4,5]. These amphiphiles contain a polar head group connected to a hydrocarbon spacer and a terminal perfluoroalkyl group [4]. This modular structure allows for wide combinations of different building blocks and, thus, the design of amphiphiles with novel and often surprising properties. Many of these structurally complex amphiphiles have been studied extensively in colloidal systems as well as Langmuir films and black lipid membranes [5]. There is also considerable interest in partially fluorinated materials from a theoretical point of view [6–9].

Despite the interest in partially fluorinated amphiphiles, little is known about the behavior of partially fluorinated carboxylic acids at the air–water interface. 1-(Perfluorooctyl)undecanoic acid (**3**) and analog with longer chains showed a condensed  $\pi$ -A isotherm on an aqueous subphase at  $pH = 2.2$  (Table 1) [10]. Carboxylic acids with shorter chain lengths reportedly did not form stable monolayers. Also, a comparison of terminally fluorinated octadecanoic acid ( $F_3C(CH_2)_{16}CO_2H$ ) and octadecylamine ( $F_3C(CH_2)_{17}NH_2$ ) with their hydrocarbon analogs showed that the terminally fluorinated compounds form more expanded

\* Corresponding author. Tel.: +1-859-268-5276; fax: +1-859-323-1059.  
E-mail address: hjlehml1@pop.uky.edu (H.-J. Lehmler).

Table 1  
Monolayer characteristics of partially fluorinated carboxylic acids (1–3) on HCl (pH = 2.0 ± 0.1)<sup>a</sup>

Surfactant	Temperature (°C)	Compression speed (mm/min)	Limiting molecular area (Å <sup>2</sup> /molecule)	Collapse pressure $\pi_c$ (mN/m)	Phase transition (mN/m)
F <sub>3</sub> C(CF <sub>2</sub> ) <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> COOH (1)	23	10	41.0 ± 0.9	29.7 ± 0.5	None
	26	10	42.0 ± 0.8	30.7 ± 0.5	None
	29.5	10	42.8 ± 0.7	31.8 ± 0.3	None
	32	10	48.0 ± 1.1	35.7 ± 0.5	None
	32	3.3	Unstable		None
F <sub>3</sub> C(CF <sub>2</sub> ) <sub>5</sub> (CH <sub>2</sub> ) <sub>10</sub> COOH (2)	32	50	39.5 ± 0.7	32.6 ± 0.7	None
	23	10	34.0 ± 1.2	35.4 ± 0.4	None
	26	10	35.2 ± 1.3	35.5 ± 0.3	2.2 ± 0.2
	29.5	10	35.0 ± 0.5	35.6 ± 0.2	4.1 ± 0.1
	32	10	37.0 ± 0.2	36.7 ± 0.4	7.0 ± 0.4
	38	10	34.9 ± 0.8	35.1 ± 0.7	11.1 ± 0.3
	44	10	36.4 ± 0.3	36.1 ± 1.1	21.2 ± 0.8
	32	1.0	34.6 ± 2.7	33.8 ± 1.5	6.7 ± 0.4
	32	3.3	33.4 ± 1.0	34.6 ± 1.4	6.7 ± 0.2
	32	50	34.4 ± 0.2	37.7 ± 0.4	6.4 ± 0.4
F <sub>3</sub> C(CF <sub>2</sub> ) <sub>7</sub> (CH <sub>2</sub> ) <sub>10</sub> COOH (3)	32	3.3	33.5 ± 0.3	38.4 ± 0.2	27.4 ± 0.2
	32	10	35.3 ± 0.3	42.8 ± 0.4	28.5 ± 0.5
	32	50	34.2 ± 0.4	45.0 ± 1.4	28.4 ± 0.9

<sup>a</sup> Dependence on temperature and compression speed.

monolayers and do not support as high surface pressures [11]. The limiting molecular areas of partially fluorinated compounds are, under some conditions, too large to be accounted for completely by the steric demand of the terminal perfluoroalkyl group [10,11]. This behavior was explained by the strong dipole which originates from the –CF<sub>2</sub>–CH<sub>2</sub>– linkage.

A more recent study gave similar results [7]. 1-(Perfluorooctyl)undecanoic acid (3) showed a condensed  $\pi$ -A isotherm on an aqueous subphase containing cadmium acetate at a concentration of  $5.0 \times 10^{-4}$  mol/l and 15°C. Increasing pH of the subphase resulted in a decrease of the molecular area (38 Å<sup>2</sup> at pH = 2–5 to 34 Å<sup>2</sup> at pH > 6) and an increase of the collapse pressure (44 mN/m at pH = 2 to 57 mN/m at pH > 6). This behavior was attributed to the formation of the cadmium salt of the carboxylate with increasing pH.

The present study describes some characteristics of three important partially fluorinated acids at the air–water interface. Comparisons are made to hydrocarbon and perfluorocarbon analogs. This information will be directly applicable to the study of other partially fluorinated amphiphiles [12–18] as well as to the design of fluorocarbon based drug delivery systems [19].

## 2. Results and discussion

Three partially fluorinated carboxylic acids with a hydrocarbon segment (11 carbon atoms) and a terminal perfluorocarbon group (4, 6 and 8 carbon atoms) were synthesized. The Langmuir isotherms of these acids (1–3) were recorded after spreading onto hydrochloric acid at

32°C. Hydrochloric acid (pH = 1.9–2.1) was employed as a subphase to form insoluble monolayers of the carboxylic acids as well as to minimize electrostatic interactions. To allow a direct comparison between perfluorinated, partially fluorinated and hydrocarbon carboxylic acids, the Langmuir isotherms of tetra- (4), penta- (5), hepta- (6) and nonadecanoic acid (7) as well as perfluorododecanoic (8) and perfluorotetradecanoic acid (9) were also recorded.

$\pi$ -A isotherms of the partially fluorinated acids (1–3) are shown in Figs. 1–3. The limiting molecular areas, collapse pressures and onset of phase-transitions at different

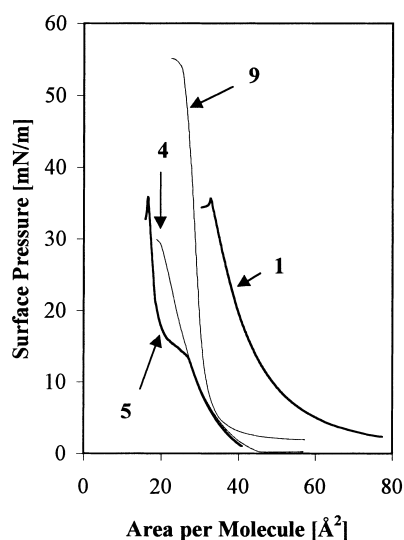


Fig. 1. Compression isotherms of 1-(perfluorobutyl)undecanoic acid (1) and pentadecanoic acid (5) at 32 ± 1°C on hydrochloric acid (pH = 1.9–2.1). The compression isotherms of tetradecanoic acid (4) and perfluorotetradecanoic acid (9) are shown for comparison.

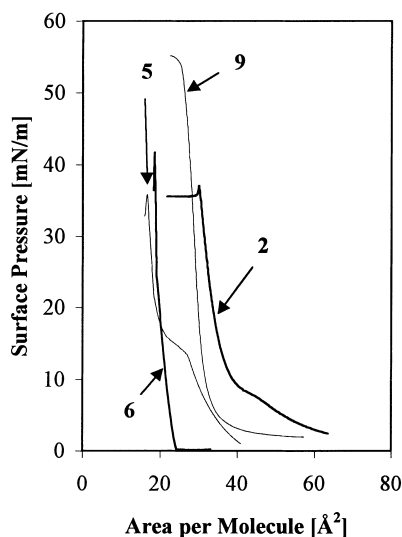


Fig. 2. Compression isotherms of 1-(perfluorohexyl)undecanoic acid (**2**) and heptadecanoic acid (**6**) at  $32 \pm 1^\circ\text{C}$  on hydrochloric acid ( $\text{pH} = 1.9\text{--}2.1$ ). The compression isotherms of pentadecanoic acid (**5**) and perfluorotetradecanoic acid (**9**) are shown for comparison.

temperatures and compression rates are summarized in Tables 1 and 2. Between 23 and  $32^\circ\text{C}$ , 1-(perfluorobutyl)undecanoic acid (**1**) lacks the phase transition of its hydrocarbon analog **5** [20], but shows some similarity to the compression isotherm of tetradecanoic acid (**4**) (Fig. 1 and Table 1). Both, acid **1** and **4** exhibit an isotherm characteristic for one single expanded phase at  $32^\circ\text{C}$ .

The isotherm for 1-(perfluorohexyl)undecanoic acid (**2**) in Fig. 2 seems to show a phase transition somewhat similar to the liquid expanded-liquid condensed transition of pentadecanoic acid. However, the onset of the phase transition of **2** occurs at a lower surface pressure and, as expected, a larger

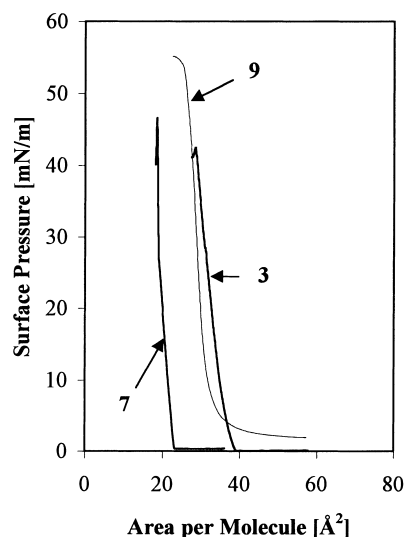


Fig. 3. Compression isotherms of 1-(perfluorooctyl)undecanoic acid (**3**) and nonadecanoic acid (**7**) at  $32 \pm 1^\circ\text{C}$  on hydrochloric acid ( $\text{pH} = 1.9\text{--}2.1$ ). The compression isotherm of perfluorotetradecanoic acid (**9**) is shown for comparison.

surface area (7.0 versus 13.5  $\text{mN/m}$  and 46.4 versus 26.6  $\text{\AA}^2$  for **2** and **5**, respectively). The onset of the phase transition is temperature dependent but appears to be independent of the compression rate. Only one condensed phase is apparent at  $23^\circ\text{C}$ , whereas a phase transition from the liquid expanded to liquid condensed state can be observed at 2.2  $\text{mN/m}$  and  $26^\circ\text{C}$ . The phase transition occurs at higher surface pressures with increasing temperatures, and has almost disappeared at  $44^\circ\text{C}$  (weak shoulder at 21  $\text{mN/m}$ , data not shown).

The  $\pi$ -A isotherm of 1-(perfluorooctyl)undecanoic acid (**3**) resembles the highly condensed monolayers of heptadecanoic acid (**6**) and nonadecanoic acid (**7**). Bernett and Zisman also

Table 2  
Surface data of various hydrocarbon and fluorocarbon carboxylic acids

Surfactant	Limiting molecular area ( $\text{\AA}^2/\text{molecule}$ )	Temperature ( $^\circ\text{C}$ )	Subphase (pH)	Collapse pressure $\pi_c$ ( $\text{mN/m}$ )	Literature
$\text{H}_3\text{C}(\text{CH}_2)_{13}\text{COOH}$ ( <b>5</b> )	$20.9 \pm 0.7$	32	HCl (1.9–2.1)	$35.6 \pm 0.2$	
$\text{H}_3\text{C}(\text{CH}_2)_{15}\text{COOH}$ ( <b>6</b> )	$20.6 \pm 1.2$	32	HCl (1.9–2.1)	$42.2 \pm 1.0$	
$\text{H}_3\text{C}(\text{CH}_2)_{17}\text{COOH}$ ( <b>7</b> )	$19.6 \pm 0.3$	32	HCl (1.9–2.1)	$46.5 \pm 2.0$	
	20	25	$\text{H}_2\text{O}$ (1–1.5)		[33]
$\text{F}_3\text{C}(\text{CF}_2)_7(\text{CH}_2)_4\text{COOH}$	38				[23]
$\text{F}_3\text{C}(\text{CF}_2)_9\text{CH}_2\text{COOH}$	28				[23]
$\text{F}_3\text{C}(\text{CF}_2)_3(\text{CH}_2)_{10}\text{COOH}$ ( <b>1</b> )	$48.0 \pm 1.1$	32	HCl (1.9–2.1)	$35.7 \pm 0.5$	
$\text{F}_3\text{C}(\text{CF}_2)_5(\text{CH}_2)_{10}\text{COOH}$ ( <b>2</b> )	$37.0 \pm 0.2$	32	HCl (1.9–2.1)	$36.7 \pm 0.4$	
$\text{F}_3\text{C}(\text{CF}_2)_6(\text{CH}_2)_{10}\text{COOH}$	Unstable	20	$\text{H}_2\text{SO}_4$ (2.2)	9	[10]
$\text{F}_3\text{C}(\text{CF}_2)_7(\text{CH}_2)_{10}\text{COOH}$ ( <b>3</b> )	$35.3 \pm 0.3$	32	HCl (1.9–2.1)	$42.8 \pm 0.4$	
	37.0	20	$\text{H}_2\text{SO}_4$ (2.2)	43	[10]
	$\sim 33$	15	$\text{Cd}(\text{AcO})_2^a$ , (7)	$\sim 58$	[7]
	$\sim 38$	15	$\text{Cd}(\text{AcO})_2^a$ , (2)	$\sim 44$	[7]
$\text{F}_3\text{C}(\text{CF}_2)_7(\text{CH}_2)_{10}\text{COOH}$	37.5	20	$\text{H}_2\text{SO}_4$ (2.2)	55	[10]
$\text{HF}_2\text{C}(\text{CF}_2)_{11}\text{COOH}$	29	Unknown	HCl		[26]
$\text{F}_3\text{C}(\text{CF}_2)_{10}\text{COOH}$ ( <b>8</b> )	$29.0 \pm 1.4$	37	HCl (1.9–2.1)		
$\text{F}_3\text{C}(\text{CF}_2)_{12}\text{COOH}$ ( <b>9</b> )	$31.1 \pm 0.5$	37	HCl (1.9–2.1)		
	22	25	$\text{H}_2\text{O}$ (1–1.5)		[33]

<sup>a</sup>  $5.0 \times 10^{-4}$  mol/l.

investigated 1-(perfluorooctyl)undecanoic acid **3** and several structurally related partially fluorinated carboxylic acids [10]. They report a highly condensed monolayer for acid **3**, as well as an almost identical limiting molecular area and collapse pressure (Table 2). However, the stearic acid derivative  $F_3C(CF_2)_6(CH_2)_{10}COOH$  (only one less  $CF_2$  group compared to acid **3**) shows a collapse pressure of only 9 mN/m on sulfuric acid at  $pH = 2.2$  and  $20 \pm 0.2^\circ C$  (Table 2). According to these authors, acids with even shorter chain length do not form stable monolayers at the air–water interface ( $pH = 2.2$ ) [10]. However, in contrast to Bennett and Zisman, in our study all three partially fluorinated acids (**1–3**) were found to form stable monolayers.

The reason why we were able to observe stable monolayers for partially-fluorinated carboxylic acids of less than 18 carbons, whereas Bennett and Zisman [10] were unable to form stable structures is unknown. The data listed in Table 2 show that the characteristics of the compression isotherms of acids **2** and **3** exhibit no strong dependence upon the compression rates employed in the range studied. On the other hand, compression rate appeared to strongly influence the results observed for acid **1**. We were able to reproduce an unstable monolayer for **1** when a compression rate of 3.3 mm/min was employed, whereas kinetically-stable monolayers were obtained at higher compression rates. These results suggest that differences in techniques between our study and that of Bennett and Zisman [10] may be responsible for the differing observations.

A comparison of the  $\pi$ -A isotherms of the partially fluorinated (**1–3**) as well as the hydrocarbon acids (**4–7**) shows a tendency toward condensed monolayer formation with increasing chain length (Figs. 1–3). It is well known that molecular areas of amphiphiles at the air–water interface decrease with chain lengthening for a homologous series of amphiphiles as a result of increased attractive chain–chain interactions. For example, such a trend was observed with partially fluorinated phosphatidylcholines [15] and amphiphilic derivatives of mannitol [21]. However, the  $\pi$ -A isotherms of the partially fluorinated acids **1–3** differ significantly from the  $\pi$ -A isotherms of the corresponding hydrocarbon acids **4–7**. It appears that the isotherm of a partially fluorinated acid has more in common with that of a hydrocarbon acid with a shorter chain length.

As shown in Table 2, the limiting area of the hydrocarbon acids **5–7** is  $20 \text{ \AA}^2/\text{molecule}$ , which is in good agreement with literature values [22]. Perfluorinated amphiphiles generally occupy molecular areas between 28 to  $30 \text{ \AA}^2/\text{molecule}$  [23–26], although, a limiting molecular area of  $22 \text{ \AA}^2/\text{molecule}$  has been reported recently for perfluorotetradecanoic, which is probably due to the different experimental conditions employed (temperature, compression rate, spreading solvent) [33]. Our results with perfluorododecanoic acid ( $29 \text{ \AA}^2/\text{molecule}$ ) and perfluorotetradecanoic acid ( $31 \text{ \AA}^2/\text{molecule}$ ) are in agreement with these data (Table 2).

The partially fluorinated acids **1–3** have a higher limiting area compared to hydrocarbon and perfluorocarbon compounds. Within the series of partially fluorinated carboxylic acids **1–3**, the limiting area decreases with chain lengthening and a higher degree of fluorination: the shortest fluorinated acid **1** occupies an area of  $39\text{--}48 \text{ \AA}^2/\text{molecule}$ , whereas the long-chain derivatives occupy only an area of  $33\text{--}37 \text{ \AA}^2/\text{molecule}$  (Table 1). The limiting molecular areas of acids **2** and **3** appear to be largely independent of the compression rate as well as the temperature.

In earlier work, partially fluorinated, long-chain (18–31 C-atoms) carboxylic acids of the general formula  $F_3C(CF_2)_n(CH_2)_mCOOH$  exhibited a molecular area of  $33\text{--}38 \text{ \AA}^2/\text{molecule}$  after spreading on a aqueous subphase [10]. Kato and co-workers report a slightly larger molecular area of  $38 \text{ \AA}^2$  at  $pH = 2$  on 0.5 mM/l  $Cd(AcO)_2$  [7]. The limiting area of acid **3** ( $35 \text{ \AA}^2/\text{molecule}$ ) found in this study is similar to the values reported by Kato and co-workers, despite the fact that our study was performed at a higher temperature (32 versus  $15^\circ C$ ).

The collapse pressure,  $\pi_C$ , of 1-(perfluorohexyl)undecanoic acid (**2**) and 1-(perfluorooctyl)undecanoic acid (**3**) is lower than the hydrocarbon analogs **6** and **7**. On the other hand, F-pentadecanoic acid (**1**) and its hydrocarbon analog **5** have a similar collapse pressure of  $\sim 35 \text{ mN/m}$ . The collapse pressure of the partially fluorinated acids (**1–3**) does increase with increasing chain length, but compared to the hydrocarbon series, the dependence of the collapse pressure on the chain length is less (Table 2). Within the series of partially fluorinated compounds (**1–3**) there appears to be a slight increase in the collapse pressure with increasing compression rate (Table 1). Both perfluorinated acids have a collapse pressure  $>50 \text{ mN/m}$ , which is significantly higher than both hydrocarbon and partially fluorinated carboxylic acids.

Earlier studies report that monolayers of perfluorinated [25] or partially fluorinated amphiphiles [15,21] are more stable compared to their hydrocarbon analogs, as evidenced by a higher collapse pressure,  $\pi_C$ , of the partially fluorinated amphiphiles. In contrast to these findings, the collapse pressure  $\pi_C$  of 1-(perfluorohexyl)undecanoic acid **2** and 1-(perfluorooctyl)undecanoic acid **3** is slightly smaller compared to their hydrocarbon analogs **6** and **7**, whereas the pentadecanoic acid derivatives **1** and **5** have a similar collapse pressure of  $\sim 35.6 \text{ mN/m}$ . The collapse pressure of the partially fluorinated acids (**1–3**) increases with increasing chain length, but compared to the hydrocarbon series the increase of the collapse pressure seems to be related to the increasing degree of fluorination (Table 2). A similar general trend was reported for partially fluorinated phosphatidylcholines [15] and amphiphilic derivatives of mannitol [21].

Both perfluorinated acids have a collapse pressure  $>50 \text{ mN/m}$  and, thus, form monolayers more stable to high surface pressure compared to the other carboxylic acids (**1–7**) studied. Based on the melting point behavior of

Table 3  
Melting points of hydrocarbon and fluorocarbon carboxylic acids

Carboxylic acid	mp <sup>a</sup> (found) (°C)	mp (literature) (°C)
F <sub>3</sub> C(CF <sub>2</sub> ) <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> COOH ( <b>1</b> )	48.8 ± 0.2	54–55 [32]
F <sub>3</sub> C(CF <sub>2</sub> ) <sub>5</sub> (CH <sub>2</sub> ) <sub>10</sub> COOH ( <b>2</b> )	62.5 ± 0.4	67–69 [32]
F <sub>3</sub> C(CF <sub>2</sub> ) <sub>7</sub> (CH <sub>2</sub> ) <sub>10</sub> COOH ( <b>3</b> )	85.7 ± 0.1	87–90 [32]
Tetradecanoic acid ( <b>4</b> )	51.8 ± 0.5	55.1 <sup>b</sup>
Pentadecanoic acid ( <b>5</b> )	48.5 ± 0.0	51–53 <sup>b</sup>
Heptadecanoic acid ( <b>6</b> )	58.3 ± 0.2	59–61 <sup>b</sup>
Nonadecanoic acid ( <b>7</b> )	64.8 ± 0.3	68–70 <sup>b</sup>
Perfluorododecanoic acid ( <b>8</b> )	108.7 ± 0.0	107–109 <sup>b</sup>
Perfluorotetradecanoic acid ( <b>9</b> )	130.4 ± 0.4 <sup>c</sup>	112 <sup>b</sup>

<sup>a</sup> Melting points are given as onset of the phase transition.

<sup>b</sup> Melting points as given by the supplier (Aldrich, Sigma and Oakwood as listed under Section 3).

<sup>c</sup> Maximum of main transition; the onset of this transition was ~123.59°C.

perfluoroalkyl compounds (Table 3), the high stability of monolayers of perfluoroalkyl carboxylic acids might be the result of a more dense packing of the perfluorinated hydrophobic chains, compared to the hydrocarbon analog, in the monolayer. Several factors may influence the shape of the Langmuir isotherms of the partially fluorinated acids **1–3** and contribute to a less condensed character of the monolayer. First of all, the chain–chain interactions of fluorinated compounds are weaker [27], which may explain the observed trend of partially fluorinated compounds to form more expanded monolayers. In addition, the terminal perfluoroalkyl segment could also weaken the lateral chain–chain interactions between individual acid molecules because of its larger space demand [10]. Finally, the dipole moments associated with the –CF<sub>2</sub>–CH<sub>2</sub>– linkage are oriented in the same direction at the air–water interface, thus, resulting in a repulsive interaction and a larger limiting molecular area of partially fluorinated acids **1–3** [11,28,29]. Thus, the perfluoroalkyl groups appear to prevent the optimal packing of the hydrophobic chain which would result in overall weaker interactions and, hence, a more expanded character of the monolayer as well as a reduced stability (collapse pressure) compared to the monolayer of the hydrocarbon analog. However, our data seem to indicate that an increasing length of the perfluoroalkyl portion in part counteracts the effects which weaken the monolayer, probably by allowing a more optimal alignment of the hydrophobic tails (i.e. the perfluoroalkyl part of the tail).

### 3. Experimental details

#### 3.1. Materials

1-(perfluorobutyl)undecanoic acid (F<sub>3</sub>C(CF<sub>2</sub>)<sub>3</sub>(CH<sub>2</sub>)<sub>10</sub>COOH, (**1**)), 1-(perfluorohexyl)undecanoic acid (F<sub>3</sub>C(CF<sub>2</sub>)<sub>5</sub>(CH<sub>2</sub>)<sub>10</sub>COOH, (**2**)) and 1-(perfluorooctyl)un-

decanoic acid (F<sub>3</sub>C(CF<sub>2</sub>)<sub>7</sub>(CH<sub>2</sub>)<sub>10</sub>COOH, (**3**)) were synthesized as described earlier [30–32]. In contrast to the literature, we were unable to recrystallize the free acids from dichloromethane or methanol. All three acids are highly soluble in both solvents. During an attempt to find a suitable solvent for the recrystallization, the pure starting material and not the free acid was obtained after recrystallization from methanol at low temperatures (–40°C). Instead, the pure acids were obtained as white and flaky crystals after two recrystallizations from *n*-hexanes. The spectroscopic data (<sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F-NMR and FT-IR) are in agreement with the proposed structure [30–32], and the melting points as determined by differential scanning calorimetry (see Section 3.3) are identical with literature values (Table 3). Their purity as determined by gas chromatography was >99% (based on relative peak area). Tetra- (**4**), penta- (**5**), hepta- (**6**) and nonadecanoic acid (**7**) were obtained from Sigma in >99% purity and used without further purification. Perfluorododecanoic acid (**8**) was purchased from Oakwood and recrystallized from toluene. Perfluorotetradecanoic acid (**9**) with a purity of >97% was obtained from Aldrich and used without further purification. The perfluorinated acids **8** and **9** used in the differential scanning calorimetry (DSC) experiments were purchased from Oakwood and used without further purification. 2-Propanol and *n*-hexanes were HPLC grade and were purchased from Fisher Scientific. Concentrated hydrochloric acid was also obtained from Fisher Scientific. Deionized water was distilled first from basic potassium permanganate, followed by sulfuric acid.

#### 3.2. Monolayer experiments

All monolayer experiments were carried out in a rectangular Teflon trough (306 × 150 mm) held at 32 ± 1°C (KSV-3000, Finland). The surface pressure was measured by the Wilhelmy plate method. Paper plates (15 mm × 58 mm) were used because of wetting difficulties with a platinum plate. Every surface area–surface pressure isotherm was determined on a freshly poured subphase (hydrochloric acid, pH = 1.9–2.1 after compression). The subphase was allowed to equilibrate for 10 min. Surface active impurities were removed from the air–water interface with a slight vacuum after compression of the barrier. Surfactant solutions at a concentration of 1–2 mg/ml were freshly prepared daily in *n*-hexanes:2-propanol (9:1) [10]. A known quantity (30–80 μl) of solutions was spread on the surface, and exactly 10 min were allowed to elapse for solvent evaporation before the start of the compression. A constant compression speed of 10 mm/min (1500 mm<sup>2</sup>/min) was used, unless otherwise noted. All experiments were repeated at least three times. All acids showed some hysteresis in a compression–expansion cycle. The limiting molecular area was determined by linear regression of the steep, linear part of the Langmuir isotherm.

### 3.3. Differential scanning calorimetry

A Thermal Analysis 2920 Differential Scanning Instrument was used for the DSC studies. The carboxylic acids (2–5 mg) were weighed into DSC aluminum pans and an excess of distilled water (approximately 30% of the sample weight) was added. Both the sample pans and the reference pans containing no sample were sealed and placed in the calorimeter. The DSC cell was purged with 60 ml/min and the refrigerated cooling system (RCS) with 140 ml/min dry nitrogen, respectively. A modulated program was used at a heating rate of 3°C/min and an amplitude of  $\pm 0.5^\circ\text{C}$  with a period of 40 s. Isothermal measurements were carried out for 5 min. All samples were subjected to two subsequent heating cycles. A third cycle was run after 24 h. All experiments were carried out in triplicate. From the transition curves, the onset temperatures of the main transitions were determined.

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### References

- [1] K. Johns, G. Stead, *J. Fluorine Chem.* 104 (2000) 5.
- [2] E. Kissa, *Fluorinated Surfactants*, Vol. 50, Marcel Dekker, New York, 1994.
- [3] M.P. Krafft, *Cosmet. Sci. Technol. Ser.* 19 (1998) 195.
- [4] J.G. Riess, *J. Drug Targ.* 2 (1994) 455.
- [5] J.G. Riess, M.P. Krafft, *MRS Bull.*, 1999, 42.
- [6] H. Ichinose, T. Kato, M. Tafeku, Y. Suezaki, *Langmuir* 15 (1999) 4705.
- [7] T. Kato, M. Kameyama, M. Ehara, K.-I. Iimura, *Langmuir* 14 (1998) 1786.
- [8] H. Schönherr, G.J. Vancso, *Langmuir* 13 (1997) 3769.
- [9] P. Hendlinger, A. Laschewsky, P. Bertrand, A. Delcorte, R. Legras, B. Nysten, D. Möbius, *Langmuir* 13 (1997) 310.
- [10] M.K. Bennett, W.A. Zisman, *J. Phys. Chem.* 67 (1963) 1534.
- [11] H.W. Fox, *J. Phys. Chem.* 61 (1957) 1058.
- [12] L. Clary, C. Santaella, P. Vierling, *Tetrahedron* 51 (1995) 13073.
- [13] T.J. McIntosh, S.A. Simon, P. Vierling, C. Santaella, V. Ravily, *Biophys. J.* 71 (1996) 1853.
- [14] J.B. Nivet, M. Le Blanc, J.G. Riess, *Eur. J. Med. Chem.* 26 (1991) 953.
- [15] J.-P. Rolland, C. Santaella, P. Vierling, *Chem. Phys. Lipids* 79 (1996) 71.
- [16] C. Santaella, P. Vierling, J.G. Riess, *New J. Chem.* 15 (1991) 685.
- [17] C. Santaella, F. Frezard, P. Vierling, J.G. Riess, *FEBS Lett.* 336 (1993) 481.
- [18] C. Santaella, P. Vierling, J.G. Riess, T. Gulik-Krzywicki, A. Gulik, B. Monasse, *Biochim. Biophys. Acta* 1190 (1994) 25.
- [19] H.-J. Lehmler, P.M. Bummer, M. Jay, *Chemtech* 29 (1999) 7.
- [20] K.S. Birdi, *Lipid and Biopolymer Monolayers at Liquid Interfaces*, Plenum Press, New York, 1989.
- [21] E. Rogalska, R. Bilewicz, T. Brigaud, C. El Moujahid, G. Foulard, C. Portella, M.-J. Stebe, *Chem. Phys. Lipids* 105 (2000) 71.
- [22] G.L. Gaines, *Insoluble Monolayers at Liquid-Gas Interfaces*, Interscience Publishers, New York, 1966.
- [23] S.W. Barton, A. Goudot, O. Bouloussa, F. Rondelez, B. Lin, F. Novak, A. Acero, S.A. Rice, *J. Chem. Phys.* 96 (1992) 1343.
- [24] D. Jacquemain, S.G. Wolf, F. Leveiller, M. Lahav, L. Leiserowitz, M. Deutsch, K. Kjaer, J. Als-Nielsen, *J. Am. Chem. Soc.* 112 (1990) 7724.
- [25] R. Elbert, T. Folda, H. Ringsdorf, *J. Am. Chem. Soc.* 106 (1984) 7687.
- [26] C.H. Arrington Jr., G.D. Patterson, *J. Chem. Soc.*, 1953, 247.
- [27] P. Mukerjee, T. Handa, *J. Phys. Chem.* 85 (1981) 2298.
- [28] G.L. Gaines, *Langmuir* 7 (1991) 3054.
- [29] E.G. Shafrin, W.A. Zisman, *J. Phys. Chem.* 61 (1957) 1046.
- [30] N.O. Brace, *J. Org. Chem.* 37 (1972) 2429.
- [31] N.O. Brace, *J. Fluorine Chem.* 20 (1982) 313.
- [32] N.O. Brace, *J. Chem. Soc.*, 1962, 4491.
- [33] T. Imae, T. Takeshita, M. Kato, *Langmuir* 16 (2000) 612.