

# Local Surface Potentials and Electric Dipole Moments of Lipid Monolayers: Contributions of the Water/Lipid and the Lipid/Air Interfaces

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The water/air interface is split up into two interfaces by the formation of a lipid monolayer, i.e., the water/lipid and the lipid/air interface. The absolute contribution of the lipid/air interface to the total surface potential is determined by partial dipole compensation in a specially designed molecular assembly presented in this paper. The dipole moment per terminal CH<sub>3</sub>-group of aligned hydrocarbon chains within a close-packed monolayer is +0.35 D, directed from the monolayer (–) to the air (+).

The local and effective dipole moments of hydrated lipid head groups can now be calculated from surface potential measurements since the contribution of the lipid/air interface is known. Such data are given for various charged, zwitterionic, and unchanged lipids. © 1988 Academic Press, Inc.

# Experimental Model and Surface Potential

One component monolayer and Two component monolayer

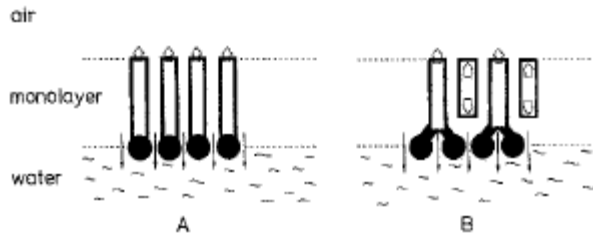


FIG. 1. Determination of the dipole moment of hydrocarbon chains in contact with air according to the partial dipole compensation approach: The density of dipoles at the monolayer/air and at the monolayer/water interfaces is the same for monolayers A and B, but, by the incorporation of symmetric molecules into the monolayer (B), every second dipole moment (large up arrow) at the monolayer/air interface is compensated by the dipole moment of the oppositely directed chain end. The dipole moments of the hydrophobic  $\text{CH}_3$ -groups are indicated with large up arrows and those of the polar head group region with thin down arrows.

The change of surface potential by formation of monolayer :  $\Delta V$

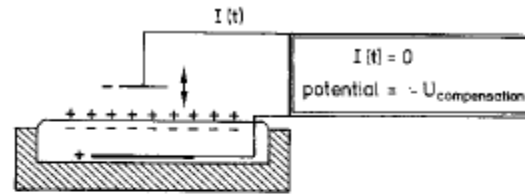


FIG. 2. The change of surface potential by the formation of a monolayer,  $\Delta V$ , is measured by the vibrating plate condenser method: One platinum electrode is put into the aqueous subphase, and the second electrode vibrates in air, at a distance of about 2 mm from the interface. The current due to the periodical capacitance changes is compensated. The air electrode is grounded.

Measure the surface potential & surface pressure!!

$$\Delta V = \frac{1}{\epsilon_0} n \mu$$

$$\mu = \epsilon_0 \Delta V A \quad \text{with the \# of molecules } n = 1/A$$

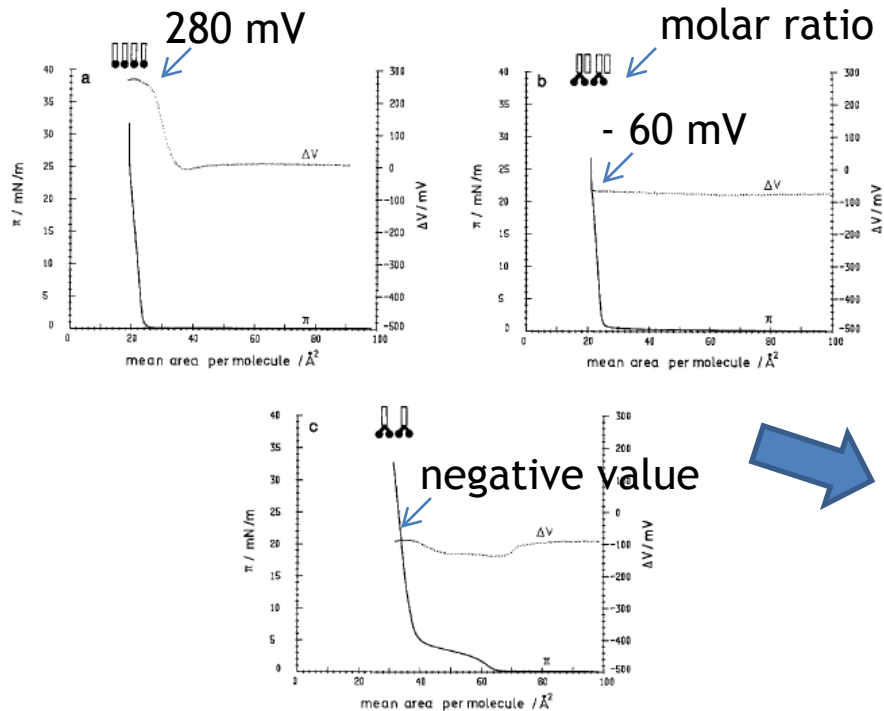
total dipole moment

$$\mu = \mu_\alpha + \mu^\omega$$

monolayer head group

terminal methyl group

# The Hydrophobic Monolayer/Air Interface



1.  $\pi$ -A isotherm show the same in a and b but a plateau region exists for the pure OMA monolayer.

The octadecane dose not contribution to the surface potential.

FIG. 3. Surface pressure ( $\pi$ ) area and surface potential ( $\Delta V$ )/area isotherms of the (a)  $C_{18}$ , (b) OMA/OD, and (c) OMA monolayers. The molecular structures are given in Table I; subphase: water, 18°C, pH 5.6, 1 Å = 100 pm.

TABLE I

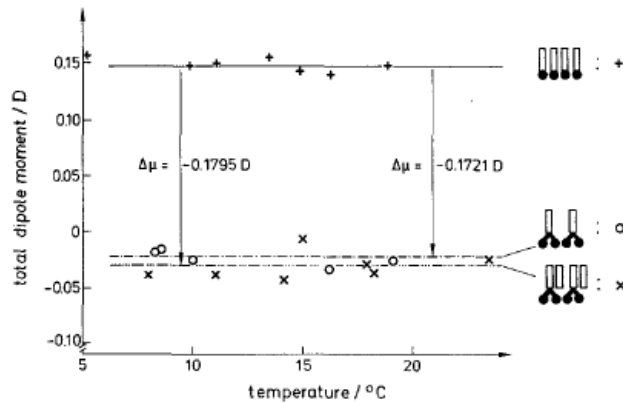
Calculation of the Dipole Moment  $\mu^{CH_3}$  per  $CH_3$ -group Embedded in a Two-Dimensional Molecular Array in Contact with Air<sup>a</sup>

Monolayer	$\begin{array}{c} CH_3 \\   \\ (CH_2)_{16} \\   \\ COOH \end{array}$	$\begin{array}{c} CH_3 \quad CH_3 \\   \quad   \\ (CH_2)_{17} / (CH_2)_{16} \\   \quad   \\ CH \quad CH_3 \\ / \quad \backslash \\ HOOC \quad COOH \end{array}$	$\begin{array}{c} CH_3 \\   \\ (CH_2)_{17} \\   \\ CH \\ / \quad \backslash \\ HOOC \quad COOH \end{array}$
	$C_{18}$	OMA/OD	OMA
Ratio of uncompensated dipole moments $\mu_{COOH}/\mu^{CH_3}$	1/1	1/2	1/2
Total dipole moment (D)	$\mu = +0.1493$	$\mu = -0.0302$	$\mu/2 = -0.0228$

<sup>a</sup> The dipole moments are calculated from surface potential data (Eq. [2]):  $\mu^{CH_3} = -2(\mu(OMA/OD) - \mu(C_{18}))$ .

# The Hydrophobic Monolayer/Air Interface

temperature dependence



pH dependence

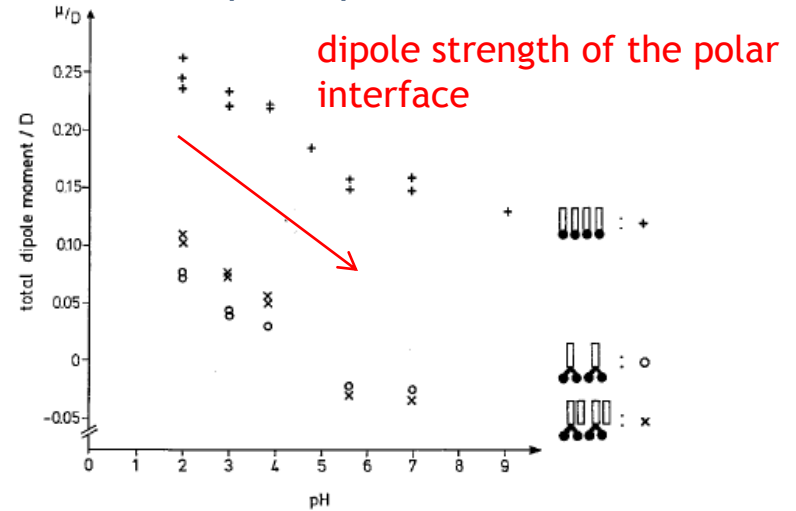
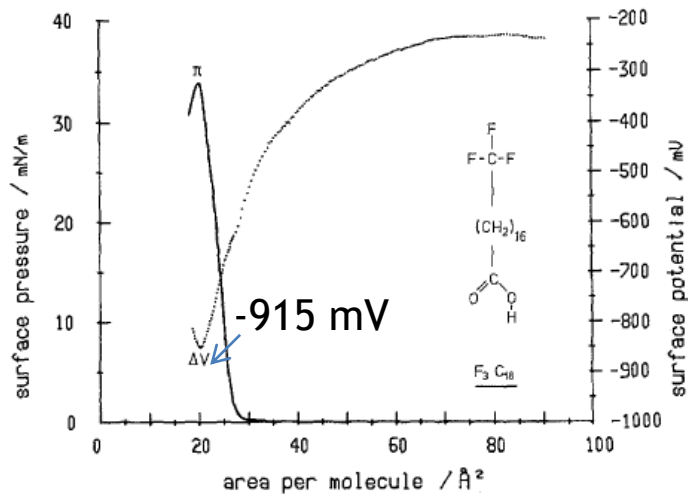


FIG. 4. Determination of the dipole moment per  $\text{CH}_3$ -group,  $\mu^{\text{CH}_3}$ , by the partial dipole compensation approach: The total dipole moment  $\mu$  calculated according to Eq. [2] is related to the same head group density for all three monolayers, i.e.,  $\mu/2$  for the OMA monolayer, and then plotted against the temperature. The shift  $\Delta\mu$  accounts for the dipole compensation of every second dipole moment at the monolayer/air interface:  $\mu^{\text{CH}_3} = -2\Delta\mu$  ( $1 \text{ D} = 3.335 \times 10^{-30} \text{ C m}^{-1}$ ).

FIG. 5. The pH dependence of the total dipole moment of the monolayers given in Fig. 4. The octadecane molecule is increasingly polarized with decreasing pH.



The effective dipole moment of methyl group is twice the difference of the total dipole moment of the  $\text{C}_{18}$  and the OMA/OD monolayer

$$\mu^{\text{CH}_3} = -2\Delta\mu \rightarrow \mu^{\text{CH}_3} = +0.35 \pm 0.01 \text{ D}$$

FIG. 6. Surface pressure ( $\pi$ )/area and surface potential ( $\Delta V$ )/area isotherm of a partially halogenated fatty acid monolayer: halogenation of the terminal  $\text{CH}_3$ -group by electronegative fluorine atoms leads to negative changes of surface potential upon monofilm compression; subphase: water,  $18^\circ\text{C}$ , pH 5.6.

# The Hydrophilic Monolayer/Water Interface

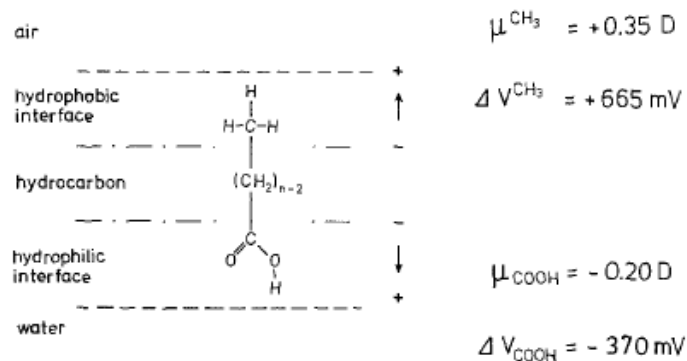


FIG. 7. The contributions of the hydrophobic and the hydrophilic monolayer interfaces to the total surface potential and dipole moment in the case of a fatty acid monolayer.

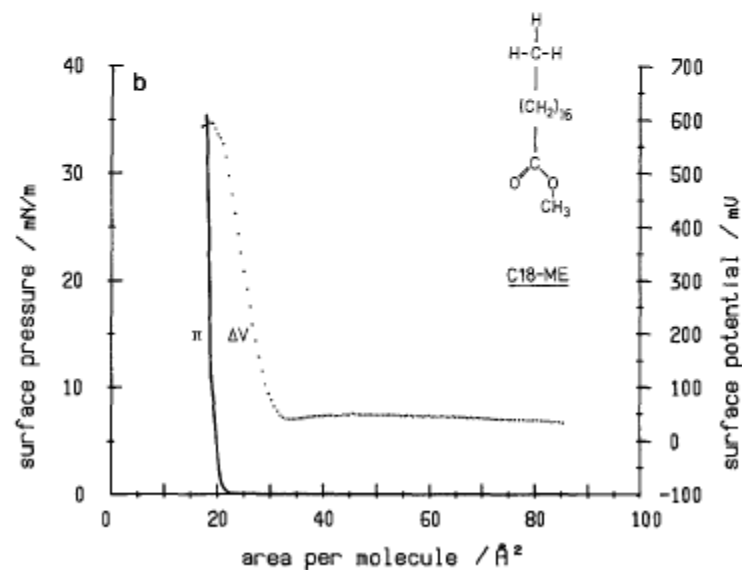
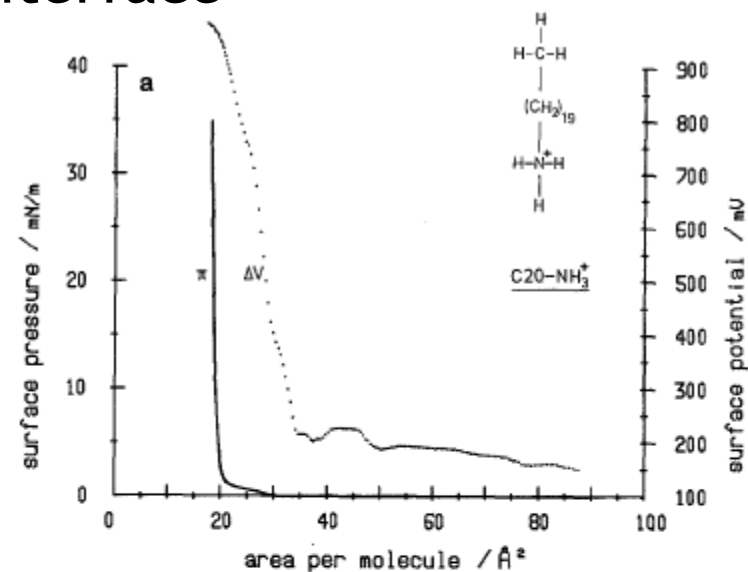


FIG. 8. Surface pressure ( $\pi$ )/area and surface potential ( $\Delta V$ )/area isotherms of the following monolayers (subphase: water, 18°C, pH 5.6, 1  $\text{\AA} = 100 \text{ pm}$ ): (a) eicosylamine ( $\text{C}_{20}\text{-NH}_3^+$ ), (b) methylstearate ( $\text{C}_{18}\text{-ME}$ ), (c) stearylalcohol ( $\text{C}_{18}\text{-OH}$ ), (d) dioctadecyl-dimethylammonium bromide (DOMA), (e) dipalmitoyl-phosphatidylcholine (DPPC), and (f) dipalmitoyl-phosphatidylethanolamine (DPPE).

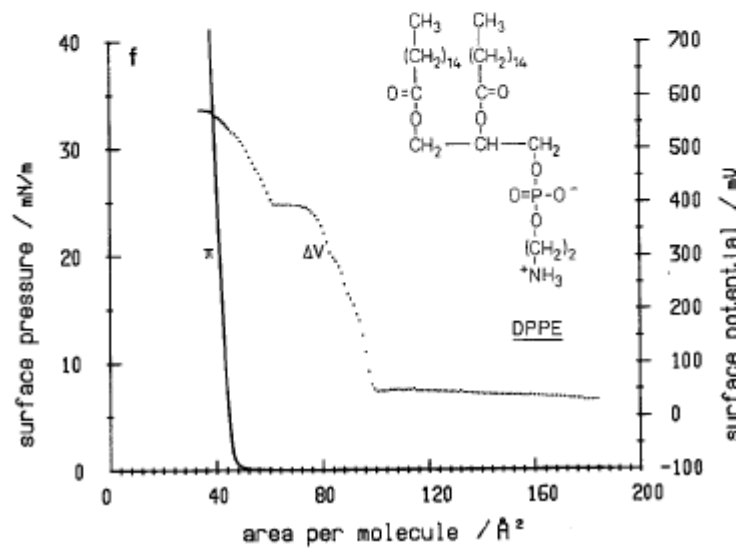
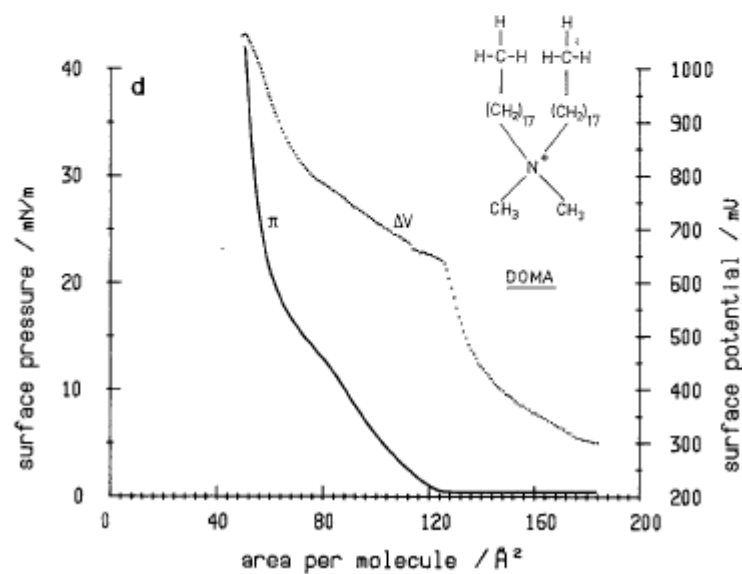
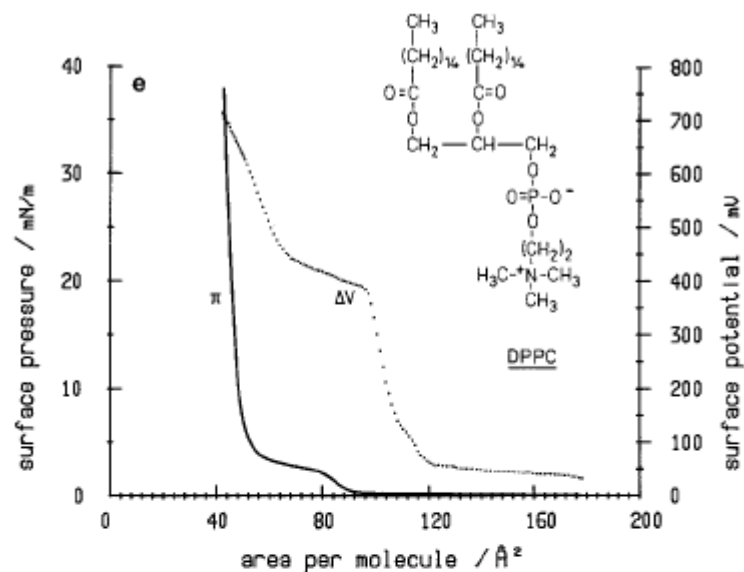
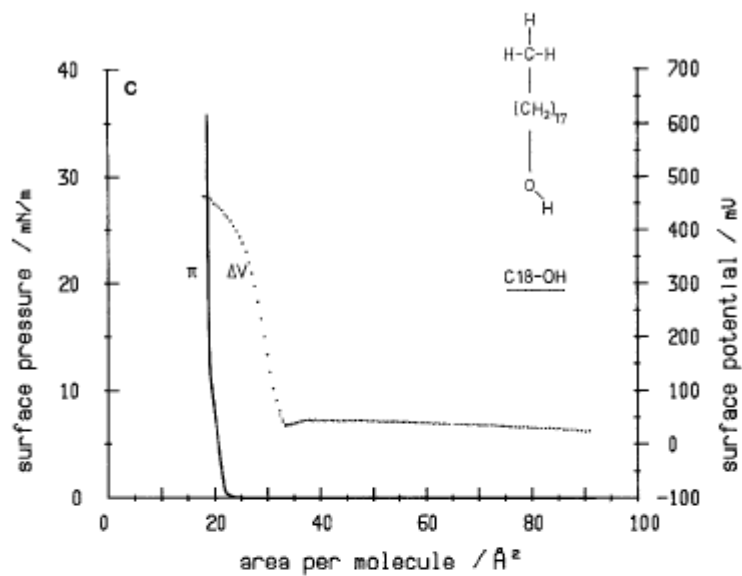


FIG. 8—Continued.

FIG. 8—Continued.

TABLE II

Surface Potentials and Effective Dipole Moments of Lipid Monolayers and Their Head Group Regions  
(see Fig. 8) at the Water/Air Interface<sup>a</sup>

Monolayer	Surface pressure (mN/m <sup>2</sup> )	Area <i>A</i> (Å <sup>2</sup> )	Potential		Dipole moment	
			$\Delta V_{\text{total}}$ (mV)	$\Delta V_s$ (mV)	$\mu_{\text{total}}$ (D)	$\mu_s$ (D)
DOMA	20.0	62.0	+930	+502	+1.52	+0.82
C <sub>20</sub> -NH <sub>3</sub> <sup>+</sup>	21.6	18.7	+965	+270	+0.48	+0.14
DPPC	19.3	46.1	+669	+99	+0.82	+0.12
C <sub>18</sub> -ME	19.4	19.0	+592	-100	+0.30	-0.05
DPPE	20.5	41.4	+555	-83	+0.61	-0.09
C <sub>18</sub> -OH	19.7	19.3	+458	-230	+0.23	-0.12
C <sub>18</sub>	20.7	20.6	+275	-367	+0.15	-0.20

<sup>a</sup> The surface pressure  $\pi$ , the mean area per molecule *A*, and the surface potential  $\Delta V_{\text{total}}$  are experimental values, whereas the effective dipole moment  $\mu_{\text{total}}$  (Eq. [2]), the dipole moment of the hydrated head group  $\mu_s$  (Eq. [3]), and the surface potential at the monolayer/water interface  $\Delta V_s$  (Eq. [2]) are calculated based on the dipole value of the terminal CH<sub>3</sub>-groups of  $\mu^{\text{CH}_3} = +0.35$  D (Table I); subphase: water, pH 5.6, 18–19°C, accuracy  $\pm 10$  mV (1 D =  $3.335 \times 10^{-30}$  C m<sup>-1</sup>).

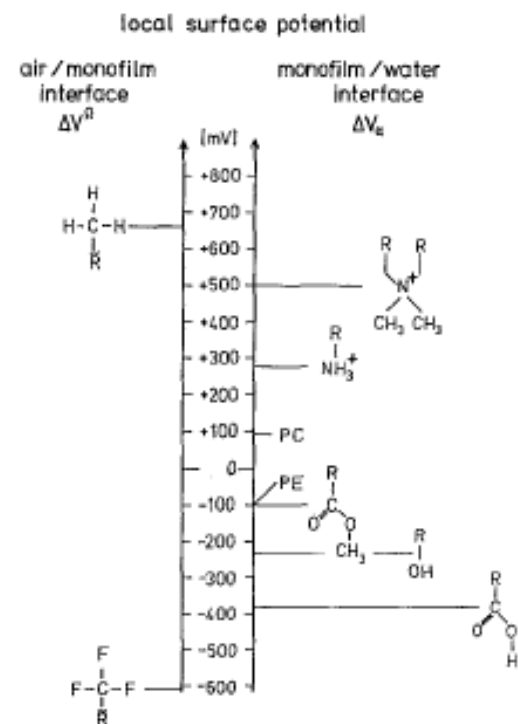


FIG. 9. Local surface potential of close-packed monolayers at the monolayer/air interface (left) and the monolayer/water interface (right) calculated from the data given in Fig. 8 and Table II.  $\pi = 20$  mN m<sup>-1</sup>, subphase: water, pH 5.6, 18°C.  $\bar{R}$  refers to the long chain with the hydrophilic group of the amphiphile (left) and R to the hydrophobic chain (right).