

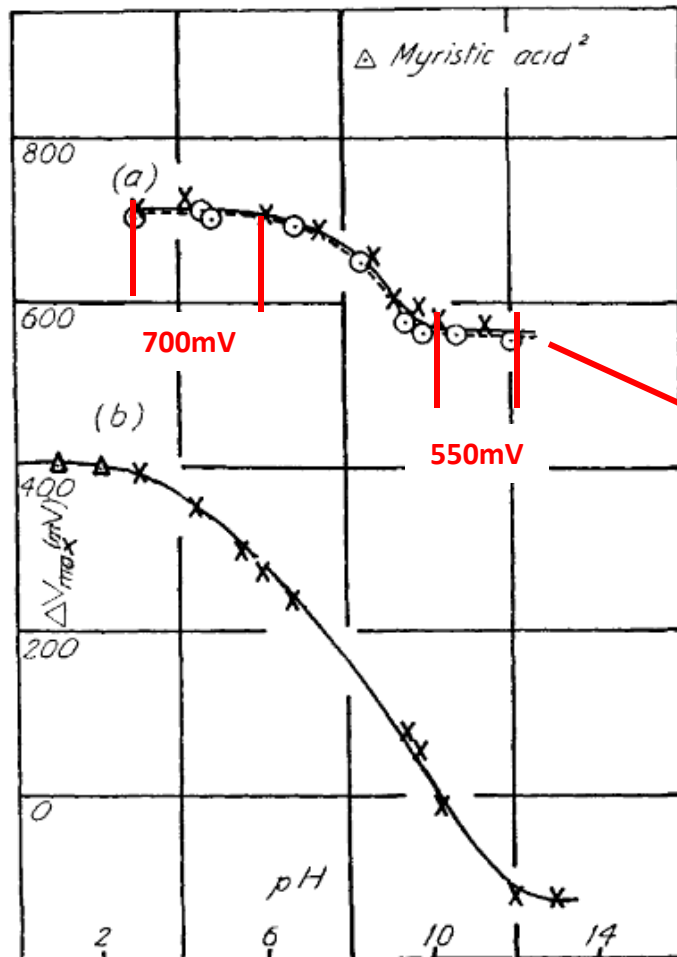
Monomolecular films of ODA at the air-water interface

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ΔV_{max} against pH curve for octadecylamine



The contribution of the non-polar side chains to the surface potential will be independent of the pH of the sub-solution whereas the $-NH_2$ groups changes with pH of the sub-solution.

Insoluble monolayer over the pH range 3.0 to 12.0 by spreading ODA on a 0.01 M NaCl substrate containing 0.005 M $NaHCO_3$ buffer.

The buffering entities (CO_2 , H_2CO_3 , HCO_3^- , CO_3^{2-}) exerted no detectable effect on the surface potential of the monolayer.

The value 550 mV corresponds to the unionized long chain amine $R-NH_2$.

- the amine head-group is completely ionized at pH 3 and the monolayer has a large overall positive charge
- during neutralization, protons are excluded from the monolayer and this expulsion will be facilitated by the repulsion between the positively charged monolayer and the proton; thus neutralization will be more easy in the surface than in the bulk

FIG. 1.— ΔV_{max} against pH curve for monolayers of (a) octadecylamine, (b) stearic acid; sub-solution 0.01 M NaCl; ○ no buffer; × 0.005 M sodium bicarbonate buffer.

Buffer solution

Definition

A buffer solution is one which resists changes in pH when small quantities of an acid or an alkali are added to it.

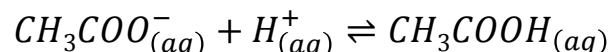
How do buffer solutions work?

A buffer solution has to contain things which will remove any hydrogen ions or hydroxide ions that you might add to it - otherwise the pH will change. Acidic and alkaline buffer solutions achieve this in different ways.

- Ethanoic acid is a weak acid, and the position of this equilibrium will be well to the left:



- The buffer solution must remove most of the new hydrogen ions otherwise the pH would drop markedly.



Isotherms of octadecylamine monolayers

ODA from 0.1 mg/mL solution in benzene on a subphase containing 0.01 M Na_2HPO_4 solution.

The pH value adjusted by adding HCl or NaOH.

The packing density of a monolayer (from the isotherm) increases as the pH value increases.

Protonated ODA molecules interact strongly by binding the divalent anion HPO_4^{2-} and the area per molecule is larger for a lower pH value.

As pH value increases until 7.5, the deprotonation of the amine molecules begins.

In a basic subphase, the area per molecule is relatively smaller.

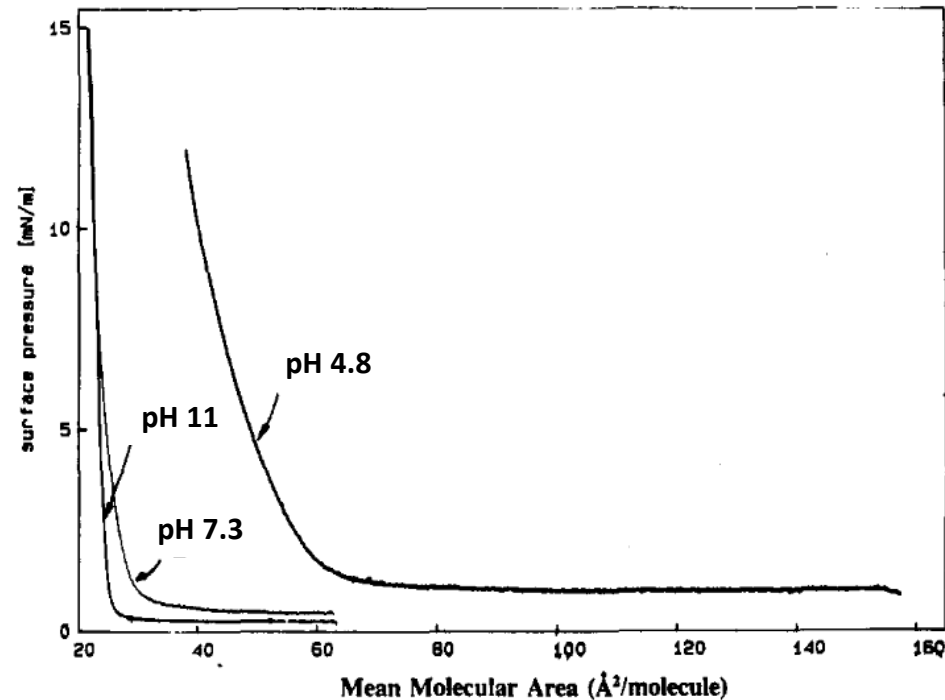


Figure 3. Force area isotherms of ODA monolayers.

Isotherms of octadecylamine monolayers

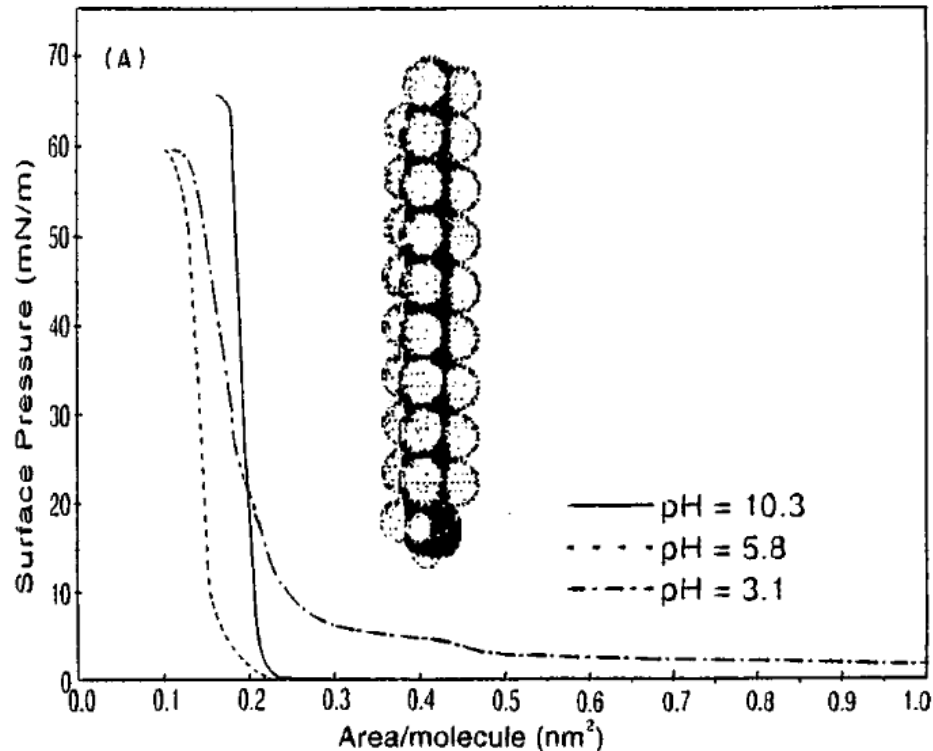


Figure 1. (A) Surface pressure-area isotherms (20 °C) of octadecylamine monolayers on distilled water subphase at pH 3.1 (with HCl_{aq}), 5.8, and 10.3 (with NaOH_{aq}).

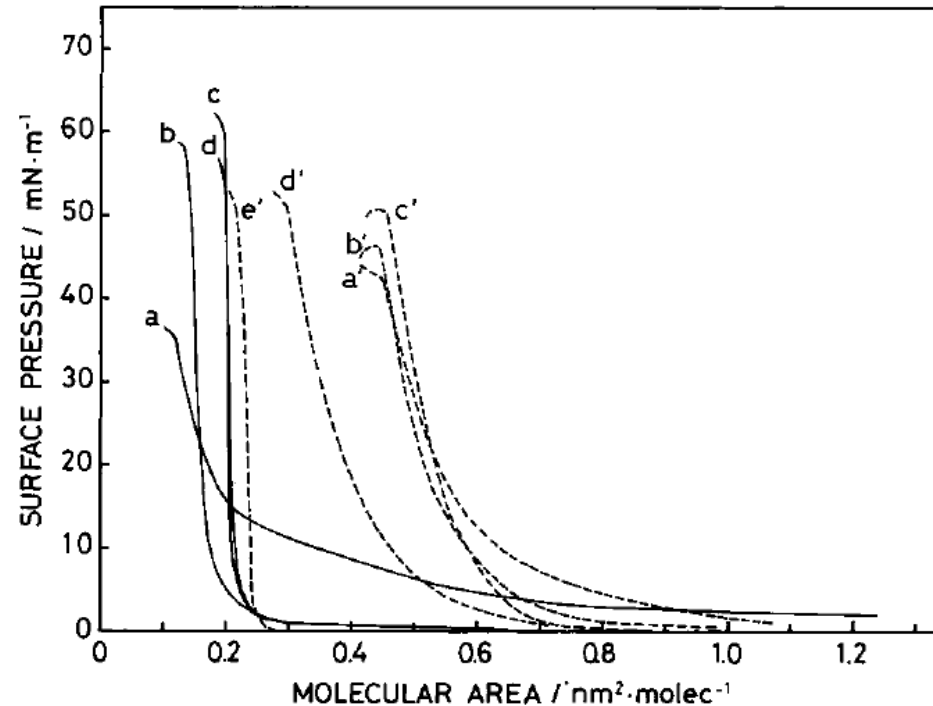


Figure 1. π -A isotherms of the ODA monolayers on a distilled water (solid line) and an aqueous NO solution (dotted line) at 20 °C. pH: a, 3.0; b, 5.7; c, 10.1; d, 11.7; a', 2.2; b', 5.4; c', 9.3; d', 10.5; e', 11.5.

At basic pH the protonation of the amino group in the ODA molecule is practically forbidden.

π -A isotherms of ODA with different subphase pH values



- When the pH decreased, i.e. $[\text{H}^+]$ increased, the equilibrium moved towards the left, and the polar group existed mainly as RNH_3^+ and the isotherm showed that the monolayer was a gas-like one because of the repulsion between charged groups.
- When the pH increased, i.e. $[\text{H}^+]$ decreased, the polar group existed mainly as RNH_2 and the repulsion between groups decreased and the isotherms became a solid-like monolayer.

The molecule area of octadecylamine with different subphase pH

pH	3.3	4.3	5.2	6.3	7.4	8.3
Area ($\text{\AA}^2/\text{molecule}$)	26.5	27.0	24.3	21.8	20.3	18.6

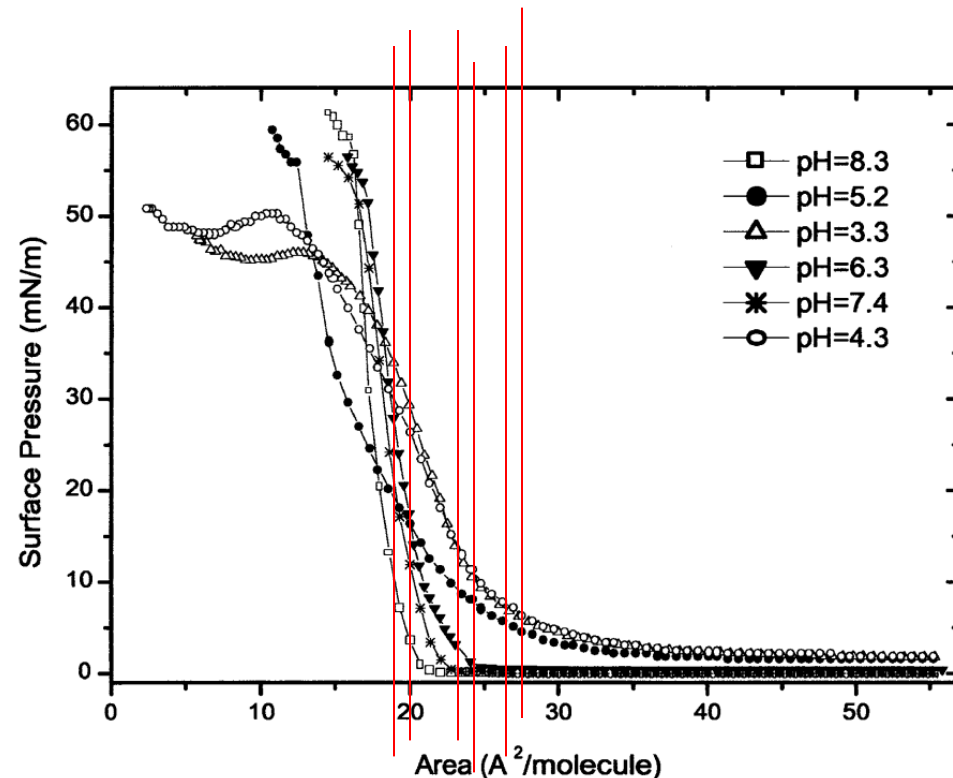


Fig. 3. Surface pressure-area (π -A) isotherms of octadecylamine with different subphase pH values. The subphase pH was adjusted by ion exchange resin.

A series of isotherms of ODA at 24.5 °C with varying pH

- When the pH drops the ODA headgroups become ionized and this leads to a higher solubility.
- At high pH the headgroup of the ODA molecules is not charged, while at low pH it will be protonated. Therefore the films tend to expand with decreasing pH.
- It is difficult to decide where the pK of ODA is, but it is likely less than pH 5.5, which means that in monolayers of ODA the pK is much less than in bulk. (pKa=10.6 of ODA)

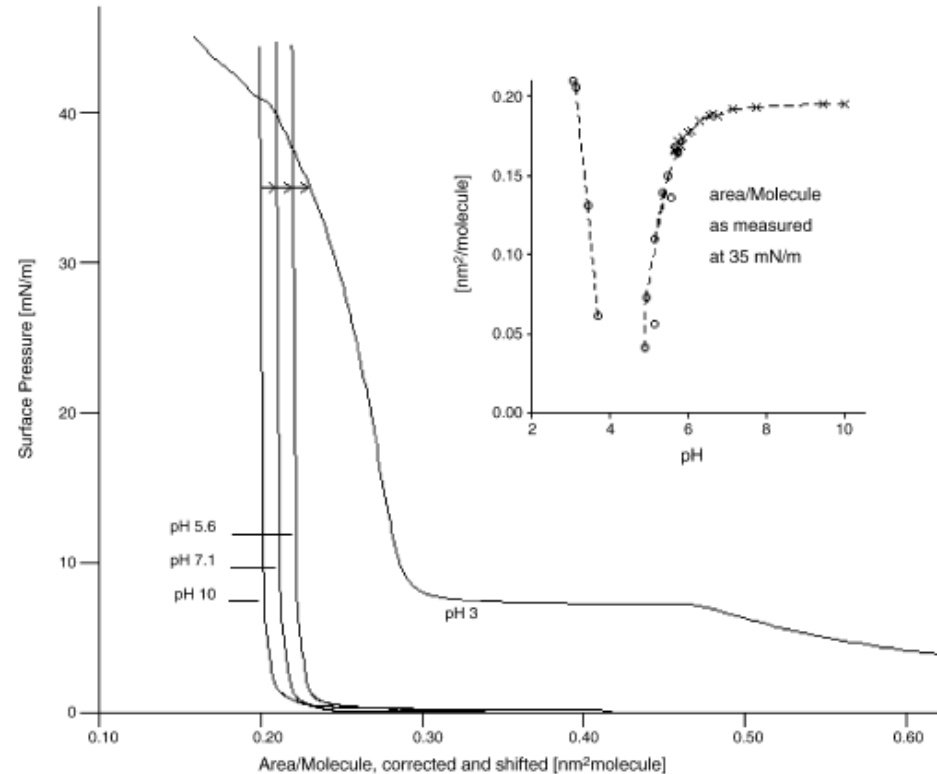


Fig. 3. A series of isotherms of ODA at 24.5 °C with varying pH. Areas are corrected for losses of material due to solubility. The inset shows the measured area at 35 mN/m as a indicator for the solubility of the monolayer.

Summary

1. In acidic subphase the molecule area of ODA expand and in basic subphase it decrease.
2. At high pH the headgroup of the ODA molecules is not charged, while at low pH it will be protonated.
3. At pH around 3.0 all authors has different results, in our case we found no monolayer at pH 3.5.

Long chain amines group

Amine	Formula	Molecular weight
Hexadecylamine	$CH_3(CH_2)_{14}CH_2NH_2$	241.46
Octadecylamine	$CH_3(CH_2)_{16}CH_2NH_2$	269.51
Eicosylamine	$CH_3(CH_2)_{18}CH_2NH_2$	297.56
Docosylamine	$CH_3(CH_2)_{20}CH_2NH_2$	325.61

