

On the Structure of Monolayers of Myristic Acid

N. W. H. Addink

Citation: [The Journal of Chemical Physics](#) **2**, 574 (1934); doi: 10.1063/1.1749535

View online: <http://dx.doi.org/10.1063/1.1749535>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/2/9?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Tilted phases of fatty acid monolayers](#)

J. Chem. Phys. **102**, 9412 (1995); 10.1063/1.468809

[Lattice structures and molecular tilts in Langmuir monolayers of saturated fatty acid–alcohol mixtures](#)

J. Chem. Phys. **101**, 9132 (1994); 10.1063/1.468042

[Pressure and pH dependence of the structure of a fatty acid monolayer with calcium ions in the subphase](#)

J. Chem. Phys. **96**, 1556 (1992); 10.1063/1.462139

[Homogeneous nucleation in associated vapors. III. Heptanoic, decanoic, and myristic acids](#)

J. Chem. Phys. **73**, 902 (1980); 10.1063/1.440198

[On the Structure of Monolayers of Myristic Acid. Erratum](#)

J. Chem. Phys. **2**, 822 (1934); 10.1063/1.1749398



On the Structure of Monolayers of Myristic Acid

N. W. H. ADDINK,* *Laboratory of Colloid Science, Cambridge, England*

(Received June 5, 1934)

IT IS well known that on compression of a monolayer of myristic acid on water or on dilute acid solutions there are breaks in the force-area (F, A) curve. More recently similar changes of gradient have been observed in the phase boundary potential-area ($\Delta V, A$) curve. N. K. Adam has termed that portion of the curve lying between the vaporous and liquid condensed state the liquid expanded, the nature and structure of which has been a matter of some discussion.

On compression of a vaporous film at *ca.* $860A^2$ per molecule the commencement of the new phase, the liquid expanded, is observed and on continued compression at a constant F the two phases are present together until an area of *ca.* $50A^2$ at $18^\circ C$ is reached. We would naturally expect a compression of the liquid expanded phase to commence here and at some point a transition into the liquid condensed to occur. It is found, however, that such a phenomenon is not noted but the F, A curve exhibits marked hysteresis as observed by Langmuir¹ and Adam and Jessop² and no portion of constant F is obtained.

The transition point at $20^\circ C$ into the liquid condensed was obtained at $31A^2$ and 15 dynes/cm by Adam and Jessop.² Harkins and Fischer³ obtained nearly the same value.

On the other hand, Schulman and Rideal⁴ by measurement of the phase boundary potential noted a change at $40A^2$ and 220 mv. Fosbinder and Lessig⁵ obtained $39A^2$ and 205 mv. On compression to areas less than $40A^2$ Schulman and Rideal⁴ observed that a metastable liquid expanded film could be obtained which, on standing, became converted into the more stable condensed film. Adam and Harding⁶ on repeating this work found a break in the F, A curve at $31A^2$ but their phase boundary potential measurements showed no break between 30 and $35A^2$.

Thus they obtained only what Schulman and Rideal termed the metastable expanded film; these authors attributed the transition observed by Rideal and Schulman to some collapse phenomenon and accordingly cast doubt upon the existence of a uniform condensed film.

A re-examination of both the force-area and surface potential area curve for areas less than $40A^2$ has been undertaken to discover whether a true hysteresis or a collapse phenomenon is involved so as to obtain some information as to the nature of the liquid films.

The apparatus employed consisted essentially of a Langmuir trough of the type described by Adam and Jessop (1° on the torsion head = 0.13 dyne/cm) and a phase boundary potentiometer described by Schulman and Rideal. Several purified specimens of myristic acid were employed and no differences outside the range of experimental error were observed.

In Table I are given the values of the phase

TABLE I. *Variations of surface potential due to myristic acid at $44A^2$.*

Time in minutes	Observed potentials over surface					Mean
0	189	186	187	187	186	187
8	184	183	181	181	182	182
15	178	177	178	178	180	178
35	174	173	175	175	177	175
60	175	173	175	175	177	175

boundary potential differences caused by a film of myristic acid placed on a solution of 0.01 N HCl by means of petrol ether. In general five different portions of the film were examined for uniformity.

This fall of potential with time is not due to a leak since the value obtained after some 30 minutes could be maintained for several hours. It is clear that myristic acid is appreciably soluble in 0.01 N HCl and that some confusion in the time hysteresis is due to lack of appreciation of this point, first emphasised by Fahir⁷ who,

* Ramsay Research Fellow.

¹ Langmuir, J. Am. Chem. Soc. **39**, 848 (1917).

² Adam and Jessop, Proc. Roy. Soc. **A112**, 362 (1926).

³ Harkins and Fischer, J. Chem. Phys. **1**, 852 (1933).

⁴ Schulman and Rideal, Proc. Roy. Soc. **A130**, 259 (1930).

⁵ Fosbinder and Lessig, J. Frank. Inst. **25**, 425 (1933).

⁶ Adam and Harding, Proc. Roy. Soc. **A138**, 411 (1932).

⁷ Cf. Marcelin, Ann. de physique **104**, 459 (1925).

however, attributed all changes in force-area to solubility and neglected the change in phase. After carefully sweeping the film off the surface the potential of the cleaned surface is found to fall 14 mv gradually in the course of two hours, indicating a return of dissolved acid to the clean surface; blank experiments revealed no such change. This effect due to bulk solubility can be partly eliminated by spreading a succession of films on the surface or by saturating the bulk phase with crystals of myristic acid. Small changes, however, do occur under these conditions since the solubility of myristic acid in the form of crystals is different from that as a film and this indeed varies with the state and compression of the film. The solubility of myristic acid in the form of crystals exceeds that of a film in the expanded state and will cause the surface potential to rise in three hours from 174 mv to 206 mv.

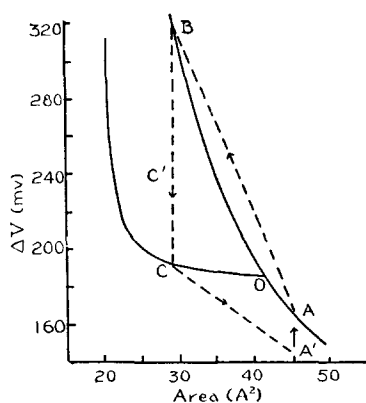


FIG. 1. Surface potential curve of myristic acid. Temp. 20°C. Transition point, 41Å², 205 mv.

In Fig. 1 is shown the plot of a ΔV -area curve for myristic acid on 0.01 N HCl saturated with myristic acid in equilibrium with a film in the liquid expanded state at 45Å².

The film is put on at $A = 45\text{Å}^2$, $\Delta V = 187 \pm 1$ mv in the liquid expanded state and it is found that the film can be compressed to 42Å² ($\Delta V = 200 \pm 1$ mv) or expanded to 48Å² ($\Delta V = 175 \pm 1$ mv) and can be reversibly restored to 45Å² without any change in phase boundary potential. If we now compress to areas less than 41Å² (O), e.g., to B at 28Å² we obtain a high value for the phase boundary potential of 340 mv which falls in the course of four hours to a value C of 210 ± 1 mv

for a homogeneous film. Similar results are obtained over the whole region of area 23Å² to 33Å². There is thus a stable homogeneous film over this region. On expansion to 45Å² from C, however, the potential does not return to A but to a point A' some 20 mv below A; the potential shows a tendency to rise till it remains constant at 15 mv below A. Clearly for the metastable expanded film at B the solubility of myristic acid is greater than for the liquid condensed or stable expanded film, and during compression to B and the four hours waiting until C is attained some myristic acid goes into solution. This effect can be diminished by employing 0.1 N HCl in lieu of 0.01 N HCl. After compression to 28Å² the same value, viz., 340 mv, was obtained; the potential, however, did not fall to 210 mv but only to C' at 260 mv even after prolonged waiting (six hours) and after expansion to 45Å² the value of the potential was only 3 to 4 mv less than the original value of A (175 mv) instead of the 15 mv on 0.01 N HCl.

If the solution were previously saturated with crystals of myristic acid a film on compression to B only falls to 270 mv and on expansion to 45Å² instead of the potential being 3-4 mv less than A it is some 11 mv higher because molecules of myristic acid have entered the film from the solution, which is supersaturated in respect to a film although saturated in respect to the crystals.

It is clear that over the region 23Å² to 33Å² two states of film can exist; a metastable liquid expanded film OB and a stable homogeneous film. It is almost impossible to obtain an accurate value for the ΔV -area curve for the stable homogeneous film because on account of the difference in bulk solubilities of the films in various states and stages of compression the exact number of molecules in the film is unknown. It is clear, however, that the stable film must possess a surface potential area curve lying between OC' and OC.

If the film is compressed within the region 41Å² to 38Å² a similar metastable film is obtained which falls back to stable potentials along the curve OC but the film is not uniform in this region; thus, at 38Å² the fluctuations amount to ± 6 mv even after prolonged periods of time. In this case also A' is found to be slightly lower than A except on myristic acid saturated solutions.

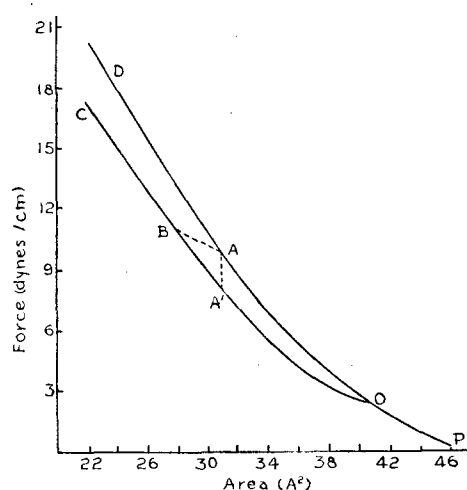


FIG. 2. Force-area curve of myristic acid. Temp. 20°C. Dotted line corresponds with Adam's curves.

In Fig. 2 are shown the force-area curves for myristic acid on 0.01 N HCl.

It will be seen that both the metastable expanded curve *OAD* and the stable curve *POBC* are obtained with the commencement of the curve *OBC* at *O* at 41\AA^2 . The curve *POABC* is one of the type actually obtained by Adam and Jessop⁸ since at higher compressions the change from the metastable to the stable film occurs fortuitously (in this case at 31\AA^2) and the portion *OB* is not noted so readily. The forces obtained, however, are not as high as obtained by these investigators.³

If we compare the times necessary to obtain stable films as determined by the changes in force or change in phase boundary potential we observe the very interesting fact that no further change takes place in the force after *ca.* 25–30 minutes whilst a slow change takes place in the phase boundary potential for several hours.

This difference can be observed in Table II where the results of compressing a film to 22\AA^2 are given.

The greater solubility of the film both in the metastable expanded and in the condensed states than in the stable expanded state can be demonstrated by measuring the force as well as the phase boundary potential. On carrying out the cycle *POAA'OP* a lowering of *F* by 0.3 to 0.4 dynes per cm is obtained which, after waiting for

half an hour at *P*, rises to almost the original value.

These observations lead us to confirm the reality of the metastable liquid expanded film commencing at 41\AA^2 and to conclude that this metastable film, on standing, is converted into a stable film which is homogeneous over the area 23\AA^2 to 33\AA^2 but inhomogeneous from 41\AA^2 to 38\AA^2 . The conversion from the metastable to the stable form takes time; the process of conversion is partly reflected in a change in *F* ($\frac{1}{2}$ hour) but a slower process (4 hours) is only revealed by changes in the phase boundary potential. The view that in the liquid expanded state the tops of the chains cling together and the polar heads are freely moving in the water has been advanced on the basis of several considerations.⁹ Cary and Rideal considered that the change from the liquid expanded to the liquid condensed state was due to a decreased hydration of the heads. Langmuir views the change from the liquid expanded to the liquid condensed state as due to the formation of orientated micellar aggregates presumably swimming in a liquid expanded film which grows smaller as compression continues.

These views suggest that one of the important factors in the transition is the squeezing out of water from the lower portions of the chains. It seemed possible to obtain some confirmation of this hypothesis by the adsorption of some dehydrating agent underneath the film. Bungenberg de Jong¹⁰ employed 0.2 percent tannic acid as dehydrating agent for effecting a transition from emulsoids to suspensoids. After a few experiments it was found possible to spread a film of myristic acid on a solution containing 5 g tannic acid (Kahlbaum zur Analyse) in 1000 cc 0.01 N HCl.

TABLE II.

Time in minutes	Phase boundary potential difference in mv	Force in dynes/cm
0	335 ± 10	20.2
5	332 ± 13	19.6
10	332 ± 9	17.5
25	291 ± 3	17.2
180	251 ± 2	17.2

⁹ Langmuir, ref. 1 and J. Chem. Phys. **1**, 756 (1933); Schofield and Rideal, Proc. Roy. Soc. **A110**, 167 (1926); Cary and Rideal, Proc. Roy. Soc. **A109**, 301 (1925); Schulman and Rideal, ref. 4.

¹⁰ Bungenberg de Jong, Rev. trav. chim. **42**, 437 (1923).

⁸ Adam and Jessop, Proc. Roy. Soc. **A112**, 362 (1926).

It was found that provided the film were not unduly expanded, thus permitting tannic acid to come up to the surface, the surface potentials did not differ from those on aqueous solutions containing no tannic acid. In Table III the

TABLE III. Behavior of a film of myristic acid on a solution containing 0.5 percent tannic acid in 1 L 0.01 N HCl in water. Temperature = 20°C. Zero potential = 193 mv.

Area A ² (min.)	Time	Observed ΔV values (mv)							Mean	Conditions of film
43½		190	190	193	192	192	192	192	homogeneous	
28	0	301	283	304	309	305	300	300	heterogeneous	
28	10	296	276	291	294	290	289	289	heterogeneous	
28	20	293	274	285	289	281	284	284	heterogeneous	
28	34	286	261	285	285	282	280	280	heterogeneous	
28	65	259	252	222	243	259	247	247	heterogeneous	
28	80	251	243	218	237	245	239	239	heterogeneous	
28	90	230	227	222	227	228	227	227	heterogeneous	
28	120	226	223	222	224	225	224	224	homogeneous	
28	130	217	214	213	215	216	215	215	homogeneous	
28	160	216	215	215	216	214	215	215	homogeneous	
43½	0	148	147	146	154	155	150	150		
43½	5	160	160	157	157	164	160	160		
43½	10	161	154	161	159	166	160	160		
43½	20	168	165	169	168	168	168	168		

changes in surface potential with time are given.

It will be noted that the equilibrium is attained in some two hours when tannic acid is present, instead of four to six hours in its absence.

As Langmuir has pointed out the change from the liquid expanded to the liquid condensed state may be regarded as, in effect, a change from molecules attached to one another by their chains with water separating their carboxyl heads to micellar aggregates in which the molecules are parallel to one another, these micelles floating about in a film of the liquid expanded state. If this be the case the stable film over an area of 41A² to 22A² should be inhomogeneous containing both micelles and residual expanded film. In point of fact the stable film has been found to be inhomogeneous from 41A² to 37A² but between 33A² and 25A² it appears to be homogeneous presumably because the micellar distribution is now so great that the travelling electrode cannot pick out the inhomogeneities. The changes observed in both ΔV and F with time are clearly associated with the formation of the micelle and, as we note, this operation takes place in two stages; one a fairly rapid one which affects both F and ΔV and a second one which

scarcely affects F but is indicated by a slow change in ΔV .

If we regard the molecules in the liquid expanded state as being hydrated both in respect to their heads and at least the lower portion of the chains, the first operation on compression consists in squeezing out the excess water from between the chains. If we regard the two-dimensional pressure as due to the factors, the kinetic agitation of the solvated heads of the portions of the chains which are hydrated and the cohesion of the ends of the chains, then

$$F = \sigma_{\text{COOH}} - \sigma_{\text{chain}}$$

$$F = \sigma_{\text{COOH}} + \sigma_{(\text{chain}) \text{ interface}} - \sigma_{\text{chain (oil)}}.$$

During the process of squeezing out the water, the contribution due to σ interface becomes smaller and that due to σ chain rises and consequently F falls. The much slower process which is revealed by the gradual change in the phase boundary potential is in all probability due to two operations which proceed relatively slowly. The compressed film from which the interchain water has been squeezed out consists initially of a two-dimensional liquid, i.e., the chains are more or less in random distribution although the polar groups of all the chains are in the substrate; during the process of conversion into the micelle and eventually the liquid condensed film, the originally irregularly orientated molecules orientate themselves parallel to one another, a process akin to the formation of a liquid crystal from a true liquid. The evidence that the molecules are orientated parallel in the liquid condensed state rests chiefly on the observations that in those films which form two-dimensional solids the conversion from the liquid condensed state to the solid is sharp; both the optical as well as the physical properties of the solid films suggest that they are two-dimensionally crystalline.

This process of molecular orientation in the film proceeds slowly; possibly in addition more water is exuded from between the head groups which affects the dielectric constant and the phase boundary potential of the film.

I wish to thank Professor E. K. Rideal for suggesting this investigation and to express my indebtedness to the Ramsay Memorial Fellowship Trust for financial assistance.