Phthiocerol is a higher optically active alcohol of the formula \( C_{35}H_{70}OH \) or \( C_{35}H_{69}OH \), which Stodola and Anderson (1) have isolated from the wax of the human tubercle bacillus. It is a constant and characteristic constituent of the wax of the human (2) and bovine (3) tubercle bacillus but has not been found in other acid-fast bacteria. The optical rotation \([\alpha]_D\) is \(-4.8^\circ\) and the melting point 73–74\(^{\circ}\). The hydrocarbon derived from phthiocerol melts at 58.5–59.5\(^{\circ}\) and the formula \( C_{34}H_{70} \) gives the best agreement with analysis.

The distribution of the polar groups and the structure of the hydrocarbon chain are as yet unknown and the experiments reported below were undertaken in the hope of getting some information on these points. Professor Anderson kindly put a specimen of phthiocerol at our disposal.

**EXPERIMENTAL**

The technique used has been described in Paper I (4) and Paper IV (5) of this series.

*Monolayers*¹

The results obtained with phthiocerol spread on a 0.01 N HCl substrate at different temperatures are shown in Fig. 1. It forms a typical "liquid expanded" (6) or "expanded mesomorphous" (7, 8) monolayer.

The limiting area of the fully expanded monolayer is 122 sq. Å. at 20\(^{\circ}\) and 134 sq. Å. at 34\(^{\circ}\). At 5\(^{\circ}\) the monolayer is solid condensed. The smallest area to which the monolayers can be compressed before collapse sets in is 30 to 31 sq. Å. The temperature of half expansion (Adam (6)) at 1.5 dynes pressure is about 17\(^{\circ}\). In the transition region b-c (Fig. 1) a certain amount of hysteresis is present but otherwise the mono-

¹ For the calculation of area values, the \( C_{35}H_{70}O_3 \) formula (mol. wt. 540) has been used. For the \( C_{35}H_{69}O_3 \) formula (mol. wt. 554) the area values should be multiplied by 1.026.
layers are fairly stable and reproducible. When condensed (at c), the monolayers are solid. The curves in Fig. 1 were obtained on rapid compression starting 3 minutes after spreading. The same limiting areas were found whether the compression was started 1 or 10 minutes after spreading.

The spreading of phthiocerol on 0.01 N HCl substrate at 15° was also controlled by ultramicroscopical examination with the Leitz "ультропак." The normal ring condenser, objective 11 ×, and ocular 10 × were used for the ultramicroscopical examination of monolayers. The use of this instrument for the ultramicroscopical investigation of monolayers will be described in detail by one of us (S. S.) in a forthcoming paper.

![Diagram of force-area curves for phthiocerol spread on 0.01 N HCl at different temperatures.](http://www.jbc.org/)

Fig. 1. Force-area curves for phthiocerol spread on 0.01 N HCl at different temperatures.

(total magnification 110 ×). The dark-field was completely empty, indicating proper spreading, up to a pressure of 13 dynes (about 32 sq. Å per molecule). Above this pressure there appeared, on rapid compression, a very fine "point structure" (9), which disappeared on standing or on expansion. At higher pressures the point structure became more clearly visible. A phthiocerol monolayer which had been compressed
beyond the point of collapse showed no formation of streaks parallel to the compressing barrier.

Fig. 2 shows the surface potential-area and apparent surface moment-area curves given by phthiocerol when spread on 0.01 N HCl at 20°. The surface potential is 285 millivolts at the limiting area and increases to about 510 millivolts at the point of collapse. No fluctuations greater than 6 to 10 millivolts were found in the transition region b–c. The apparent surface moment is very high, 880 millidebyes at 122 sq. Å, and falls on compression to about 450 at 31 sq. Å.

As phthiocerol contains no polar group capable of undergoing ionization, practically identical force area curves are obtained on substrates of different pH, at corresponding temperatures.
Attempts to Build Multilayers and x-Ray Experiments

By use of the Langmuir-Blodgett technique (10, 11) attempts were made to build multilayers of phthiocerol on chromium-plated slides. A large number of different substrates (distilled water, 0.01 N \( \text{HCl} \), 5 N \( \text{HCl} \), distilled water containing 40 per cent ethyl alcohol, tap water) at temperatures from 5–50° and piston pressures from 16 to 35 dynes were tried, but, as the monolayers of phthiocerol in the condensed state are very stiff under all these conditions, only poor results were obtained. With tap water as substrate and triolein as piston (spreading pressure 23 dynes) at room temperature it was found, however, that if the slide was lowered very slowly through the monolayer deposition did not occur on the down journey but occurred on the up journey of the slide (2 deposition (12)). A twenty-five layer film obtained in this way was not optically perfect, but had an optical thickness corresponding to about forty layers of standard barium stearate. The optical thickness per layer of the phthiocerol multilayer, assuming the refractive indices of both films to be equal and the optical thickness per layer of standard barium stearate to be 24.4 Å. (11), was about 39 Å.

In order to measure the long x-ray spacing, the twenty-five layer Z-deposited multilayer was subjected to x-ray analysis by the technique described previously (5, 12). In spite of very long exposures (up to 36 hours), no lines corresponding to a definite long spacing were obtained and it was evident that the phthiocerol multilayer was very poorly crystalline.

DISCUSSION

For the expanded part of a liquid expanded film (a–b in Fig. 1) Langmuir (14) has given the following equation of state

\[
(F - F_0) (a - a_0) = kT
\]

where

- \( F \) = surface pressure observed in dynes per cm.
- \( a \) = area observed in sq. Å.
- \( F_0 \) and \( a_0 \) = empirical constants
- \( k \) = gas constant in two dimensions
- \( T \) = temperature in °K.

Normal chain compounds, such as myristic acid, obey the above equation very well. The constants \( F_0 \) and \( a_0 \) depend on the structure of the molecules.

\[^3\]A more detailed x-ray investigation of phthiocerol is in progress. In a note published after this paper had been written, Spiegel-Adolf and Henny (13) state that phthiocerol gives a complicated diffraction pattern but report no long (001) spacing.
For phthiocerol the equation

\[(F + 6.0) (a - 65) = kT \quad (F_0 = -6.0; a_0 = 65)\]

agrees with the part a-b in Fig. 1 of the force-area curve at 34°. It appears, however, that \(F_0\) and \(a_0\) are not independent of temperature, as the agreement at 20° is not so good.

The interpretation of the surface experiments in terms of molecular structure is in the case of phthiocerol difficult owing to the lack of material for comparison. The fact that it forms a typical liquid expanded monolayer with a smallest stable area of 30 to 31 sq. \(\mu\) suggests that phthiocerol is essentially a very long molecule with one or more of the polar groups in a position at or very near one end; and, if side chains other than the methoxyl group are present, that these are short, probably methyl. Apart from this, very little can be said with any degree of certainty. No information is given by the surface potential measurements, as nothing is known about the way the three different polar groups contribute to the surface potential. The hydrocarbon (C\(_{34}\)H\(_{70}\)) derived from phthiocerol melts at 58.5–59.5°, while \(n\)-tetra-triacontane melts at 72.6–72.8° (15). As mixtures of normal chain higher hydrocarbons have melting points intermediate between those of the components (15), the low melting point of the hydrocarbon cannot be explained on the assumption that it is a mixture of normal chain homologues, and it is therefore probable that it has a branched chain. An x-ray investigation might give some useful information.

\(\alpha\) - and \(\beta\)-octadecyl glyceryl ethers, which contain the same polar groups as phthiocerol (two hydroxyls and one ether oxygen) and have a straight chain with 18 carbon atoms, form liquid expanded films with temperatures of half expansion of 31° and 11.5° respectively. As phthiocerol contains 14 or 15 carbon atoms more and the temperature of half expansion in long chain compounds generally increases several degrees for each added carbon atom, the structure of phthiocerol must contain features which counteract the condensing effect of the large number of carbon atoms. Factors that cause expansion (for a given polar group or set of polar groups and a given number of carbon atoms) are (a) branching of the hydrocarbon chain. Apart from possible alkyl side chains, in phthiocerol the methoxyl group very probably plays the rôle of a side chain. (b) The molecule contains a hydrocarbon part that on compression is forced down into the water below the polar groups. This factor is well known from the behavior of long chain esters (17). (c) The polar groups are situated a large distance apart. Long chain dibasic acids and esters give vapor or vapor expanded films (18). In phthiocerol all three of these

---

4 Measurements by N. K. Adam in a paper by Davies et al. (16).
factors may contribute to the fact that, in spite of the large number of carbon atoms in the molecule, it forms a liquid expanded monolayer with a temperature of half expansion below room temperature.

We are greatly indebted to Professor R. J. Anderson for the specimen of phthiocerol used, and for his interest in the work. The x-ray experiments on multilayers were carried out in 1939 in the x-ray Crystallography Laboratory, Cambridge, England. We are indebted to Dr. A. J. Bradley for his courtesy. Grants from the Rockefeller Foundation and the Swedish Association against Tuberculosis are gratefully acknowledged.

**SUMMARY**

Phthiocerol forms on different substrates a typical liquid expanded monolayer. At pH 2, the temperature of half expansion is 17° and the smallest area per molecule to which the monolayers can be compressed before collapse is 30 to 31 sq. Å. In the condensed state the monolayers are solid. The apparent surface moment is 880 millidebyes at the limiting area and falls to 450 at the point of collapse.

It was not found possible to build perfect multilayers of phthiocerol and x-ray experiments on an imperfect Z-deposited film showed that the multilayer was poorly crystalline.

The surface behavior of phthiocerol suggests that it is a very long molecule with only short side chains, and with one or more of the polar groups near one end.

**BIBLIOGRAPHY**

MONOLAYERS OF COMPOUNDS WITH BRANCHED HYDROCARBON CHAINS: V. PHTHIOCEROL
Stina Ställberg and Einar Stenhagen


Access the most updated version of this article at http://www.jbc.org/content/143/1/171.citation

Alerts:
- When this article is cited
- When a correction for this article is posted

Click here to choose from all of JBC's e-mail alerts

This article cites 0 references, 0 of which can be accessed free at http://www.jbc.org/content/143/1/171.citation.full.html#ref-list-1