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Surface Potentials and Force–Area Relations of Monomolecular Films. II. *d*-Pimaric Acid and Tetrahydro-*d*-pimaric Acid

BY WILLIAM D. HARKINS, HERMAN E. RIES, JR., AND EVERETT F. CARMAN

I. Introduction

Through the kindness of Professor Ruzicka the writers have been able to investigate the surface potentials and force–area relations of *d*-pimaric acid, an unsaturated compound, and tetrahydro-*d*-pimaric acid, the corresponding saturated compound. These compounds contain a phenanthrene residue, and are related to certain hormones and vitamins. The carboxyl group is displaced one position from the hydroxyl group of cholesterol, and the area for the pimaric acid is slightly larger.

II. Apparatus and Procedure

The apparatus and general procedure are essentially the same as described by Harkins and Fischer.[1] The modifications that have been introduced will appear in a paper which is now being prepared for publication. A more recent improvement will be discussed here in connection with the method adopted to obtain "zero" or clean surface potentials. It has increased the accuracy of the surface potential values.

The procedure is as follows. The trough is filled with the aqueous solution (0.01 molal hydrochloric acid in these experiments) and the surface swept several times to remove initial contamination. The electrode is then lowered into a position 2 to 3 mm. above the surface and the cage closed. The system is allowed to remain in this condition for about one hour. It seems that during this time most of the additional contamination settles out from above the surface and rises from below. At the same time the surface of the silver–polonium electrode reaches equilibrium with the water vapor.

One of the features of the procedure involves the use of mechanical arms to perform the final sweepings without opening the cage or otherwise disturbing the immediate surroundings of either the surface or the electrode. It is unnecessary to raise the electrode in order to accomplish the final sweepings as thin barriers have been constructed which easily pass under the lowered silver–polonium disk. After the hour has elapsed, the surface is swept until the potential is constant to within 1 mv. for periods of ten to twenty minutes. Readings are taken immediately after the individual sweepings to ensure a clean surface during the measurement. The additional barriers for the final sweepings are taken from racks conveniently suspended above the two ends of the tray.

The importance of an accurate clean surface potential cannot be overemphasized, as it is obvious that an error here vitiates all of the film potential values. It might be added in connection with these precautions that capillary active contamination falling on the spread films has a negligible effect on the potential compared to the change introduced by the same contamination on a cleaned surface.

The films were spread from redistilled benzene solutions on 0.01 molal aqueous hydrochloric acid. Surface potential and pressure measurements were made simultaneously at minute intervals. The experiments were carried out at room temperature (28 to 30°).

III. Pressure–Area Relations and Thickness of the Films

The saturated and unsaturated compounds form monomolecular films, which give almost identical pressure–area curves until collapse begins (Figs. 1, 2 and 3). The film which is composed of the unsaturated compound withstands higher pressures than that of the saturated, and its maximum pressure is about 17 dynes on 0.01 molal hydrogen chloride. The film pressure of the unsaturated compound approaches a state of equilibrium. The maximum thickness of the mono-layer is about 12 Å. for both compounds, or slightly less than half that for a similar film of stearic acid. These compounds exhibit orientation of the perpendicular type. The films are much thicker than those in which a single chain lies flat in the surface.

The films are highly compressible, and the coefficient $[a_0 - a_1)/a_0]/(f_1 - f_0)$ has a value of 0.0068 for the saturated acid and 0.010 for the unsaturated compound.

The extrapolated molecular area at zero pressure for both the saturated and unsaturated compounds is about 53 sq. Å. but it seems possible to compress the films to an area of about 43 sq. Å. before collapse occurs. This is practically the area of two hydrocarbon chains. Our unpublished data on large rings up to thirty-four carbon atoms in the ring, and the values of Büchner, Katz and Samwel[2] on rings up to thirty carbon atoms, also give minimum areas equal to that exhibited by two single oriented hydrocarbon chains.

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

[2] Büchner, Katz and Samwel, *Z. physik. Chem.*, **B5**, 327 (1929).

The work of Harkins and Morgan[3] showed that phenanthrene spreads on water only when much salt is present. The compounds used in our work are much more saturated, which probably reduces resonance in the molecule, but has only a minor effect on the polarity. However, the presence of the dipole due to the carboxyl group, as is usual, orients the molecule with this group toward the water.

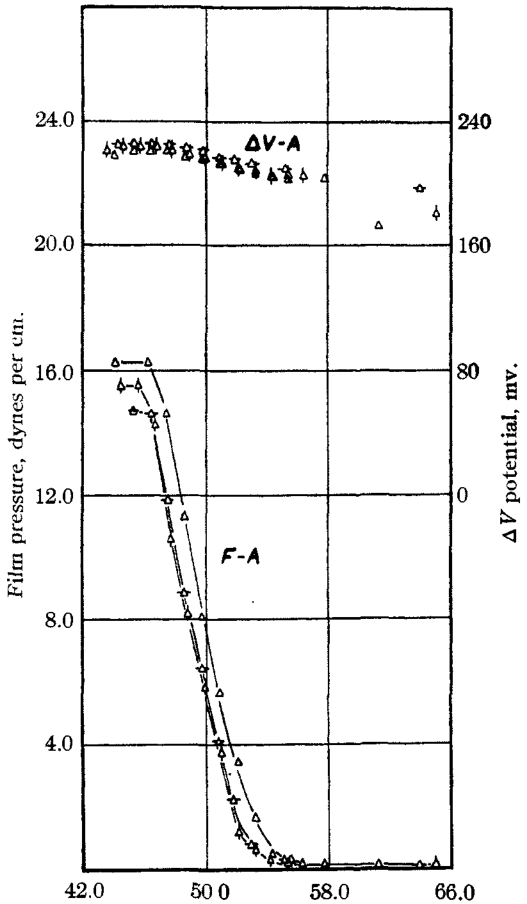

Fig. 1.—Tetrahydro-*d*-pimaric acid on 0.01 molal hydrochloric acid.

	Expt.	Temp. °C.
△	199	28.0
⊥△⊤	200	28.0
-△-	206	29.5

IV. Structure and Orientation of the Pimaric Acids

It is of interest to compare the structures and orientations in films of the pimaric acids with those of cholesterol. If the side chains, which, due to interpenetration of the molecules probably contribute very slightly to the cross-sectional area, are neglected the similarity between the pimaric acid nucleus (phenanthrene residue) and the A, B, C ring structure of cholesterol (Fig. 4) is obvious. The significant point of difference is the location of the polar, water-attracting group.

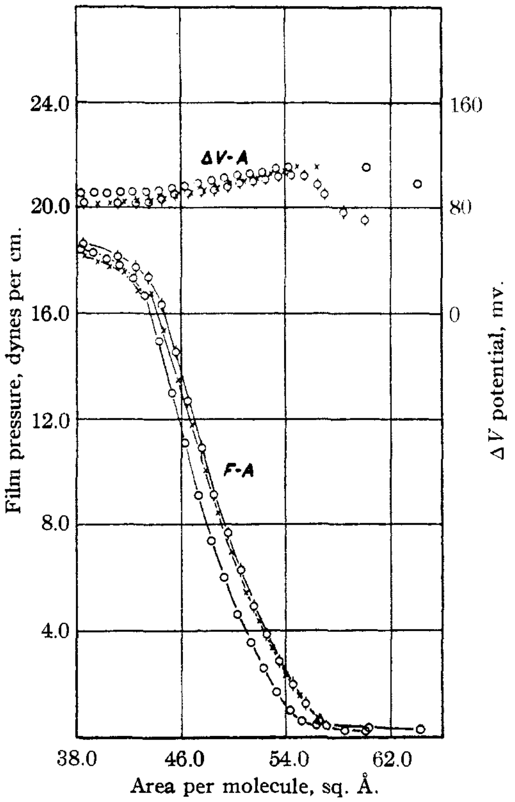

Fig. 2.—*d*-Pimaric acid on 0.01 molal hydrochloric acid.

	Expt.	Temp. °C.
X	197	30.0
⊥○⊤	198	28.0
O	205	28.0

In pimaric acid the carboxyl group is on carbon atom number 4, whereas in the cholesterol compound the hydroxyl group occupies position number 3. It is evident that if the molecule is oriented so that the polar group is located at the lowest point, one would expect the pimaric acids should be tilted in such a way as to occupy more area in the surface than the vertically oriented cholesterol. The cross-sectional area of a molecule obtained from film balance measurements is of course dependent on the orientation.

Measurements of molecular models indicate that for oriented sterol ring systems with the polar group in position 3, the cross-sectional area should be about 37 sq. Å. and for the same system with the polar group in position 4 about 42

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[3] Harkins and Morgan, *Proc. Nat. Acad. Sci.*, **11**, 637 (1925).

sq. Å. Measurements on models and the effects of the positions of polar groups in similar compounds have been discussed in a paper by Danielli and Adam.[4] The calculations agree quite well with the film areas per molecule at the collapse pressure. The area obtained for the unsaturated acid at the collapse pressure is about 43 sq. Å. The extrapolated area, 53 sq. Å., is considerably greater because of the expanded nature of the film.

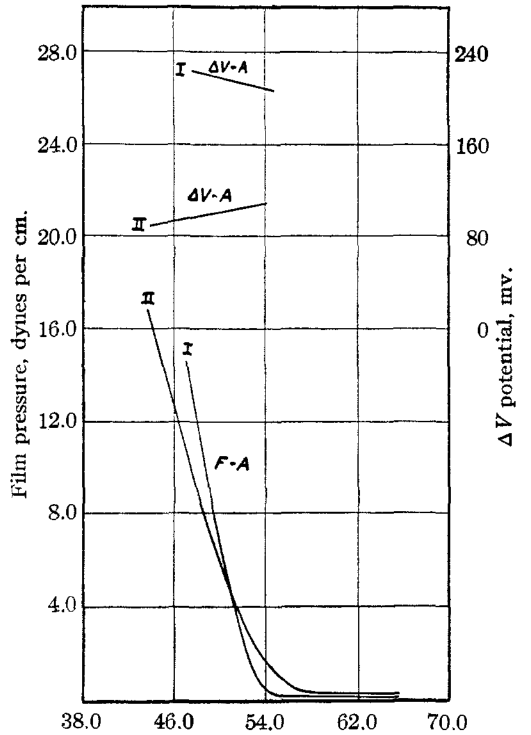

Fig. 3.—Average curves: I, tetrahydro-*d*-pimaric acid; II, *d*-pimaric acid.

It may be noted here that the curve of the more condensed film of tetrahydro-*d*-pimaric acid crosses the curve for the unsaturated acid. Consequently, the reduced compound has a larger area at the collapse point and a smaller extrapolated area at zero pressure than does the unsaturated acid. The increased polarity of the unsaturated compound is probably the cause of the expanded nature of the film. This will also account for the greater adhesion to the water surface and the resultant higher pressure.

V. Surface Potentials

The surface potential (Δ*V*), defined as the difference in the contact potential when the film is present and when it is absent, exhibits some anomalies not previously found. The surface potentials of the condensed films are low, with a value of about 100 mv. for the unsaturated and about 200 mv. for the saturated compound. The film of *d*-pimaric acid exhibits a behavior heretofore unobserved in that the surface potential of the condensed film *decreases* as the film is compressed.

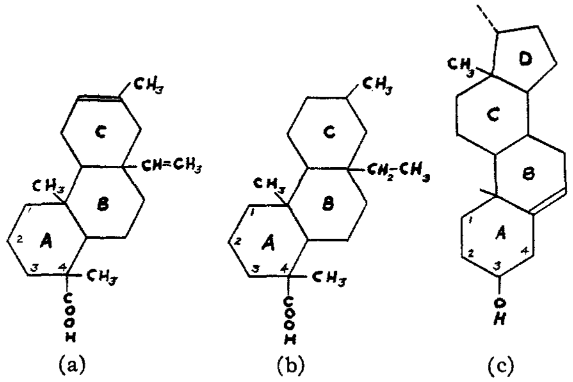

Fig. 4.—Vertical orientation of molecules at air–water interface: (a) *d*-pimaric acid; (b) tetrahydro-*d*-pimaric acid; (c) cholesterol (chain omitted).

In connection with the surface potential of tetrahydro-*d*-pimaric acid, it should be noted that the measurements for this compound gave about 200 mv., which is approximately half of the value obtained for a straight chain acid of the type of stearic acid. This is largely because the area per molecule or area per polar group for this reduced pimaric acid is roughly twice that of the stearic acid type, so its polar group surface density is approximately half that of condensed stearic acid films. However, there are a number of complicating factors which include effects due to orientation of adjacent dipoles, water dipoles, and shifts of electrolyte ions.

As indicated above the surface potential of the unsaturated *d*-pimaric acid is about 100 mv., or one-half that of the saturated compound, although the two substances have practically the same molecular surface density. One would therefore be led to believe that the dipoles associated with the double bond in the ring or in the side chain or possibly in both are oriented in such a way as to oppose the dipole of the carboxyl group, even at the initial stages of the compression. Then, on compression, further internal opposition or compensation of the dipoles may be said to result in the decreasing surface potential observed. As shown by Harkins, Ries and Carman[5] the surface

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[4] Danielli and Adam, *Biochem. J.*, **28**, 1583 (1934).

[5] Harkins, Ries and Carman, This Journal, **57**, 776 (1935).

potential (ΔV) may rise considerably less rapidly than the surface density of the film (13% less rapidly in the case of certain polymers of ω-hydroxydecanoic acid). This is usually attributed to the mutual effect of the surrounding dipoles. However, it is quite probable that in the case of the *d*-pimaric acid, the conspicuous *decrease* in the surface potential with increased surface density is due to a changing orientation of the individual molecules in such manner as to further the opposition or compensation of the intramolecular dipoles.

Additional studies relating potential variations to temperature changes are now in progress.

VI. Summary

1. Surface potential and force–area relations for monomolecular films of a saturated and unsaturated pimaric acid were studied. The corresponding curves are shown.
2. An improved procedure for obtaining more accurate clean-surface potentials is described.
3. The maximum thickness of the mono-layer is about 12 Å. for both compounds. The coefficients of compressibility are calculated.
4. The structures of the pimaric acids are compared with that of cholesterol, and their orientations in surface films are related to the different positions in which the polar groups are located. The experimental data compare favorably with the results to be expected from model measurements.
5. The surface potential of the tetrahydro-*d*-pimaric acid is about 200 mv., whereas that of the unsaturated compound is about 100 mv. An unprecedented decrease in the surface potential on compression was observed in the case of the unsaturated acid films. It is considered probable that these facts may be related to an increasing intramolecular dipole compensation on compression.

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[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Heterogeneous Reaction Kinetics. The Effect of Light Exposure on the Kinetics of Thermal Decomposition of Silver Oxalate

BY ARTHUR F. BENTON AND GEORGE L. CUNNINGHAM

In reactions of the type A(s) = B(s) + C(g), which are normally autocatalytic in nature, existing evidence shows that the rate depends on two separate factors, formation of nuclei of product and subsequent growth of these reaction centers. However, a satisfactory quantitative treatment of the kinetics has not yet been attained. With this objective in view we have studied, both experimentally and theoretically, the rate of decomposition of a light-sensitive solid on which nuclei have previously been produced by controlled irradiation.

Silver oxalate was chosen as a suitable material, since it decomposes at convenient temperatures and apparently yields only silver and carbon dioxide, uncomplicated by side reactions. MacDonald and Hinshelwood[1] found the reaction to be autocatalytic, and the rate sensitive to adsorbed ions and to oxygen. Sheppard and Vanselow[2] showed that sulfur compounds greatly accelerate the reaction. Arens and Eggert[3] found that silver oxalate–gelatine plates were made developable by exposure, and resembled silver chloride emulsions both in sensitivity and spectral range.

Experimental Methods

Approximately 1-g. samples of silver oxalate were decomposed in the dark in Pyrex bulbs heated by suitable vapor baths provided with electric heating and regulated pressure. The evolved gas was continuously removed by means of a Sprengel pump and fed into the lower end of a water-jacketed, mercury-filled buret, where its volume was measured at regular intervals. Absence of leaks in the all-glass apparatus was assured by overnight test before each experiment.

In the later experiments (Oxalate II), samples were illuminated when desired with light from a 1000-watt tungsten-filament lamp provided with a reflector. The light, after traversing in order a lens system, 6 cm. of running water, a suitable color filter and a shutter, was reflected downward to the bulb by a metallic mirror. The filter was Corning G586AW, which transmits from about 320 to 400 $m\mu$, with a maximum at 370 $m\mu$. All exposures were made with the oxalate at room temperature. The

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(1) MacDonald and Hinshelwood, *J. Chem. Soc.*, **127**, 2764 (1925); see also Hoitsema, *Z. physik. Chem.*, **21**, 137 (1896).

(2) Sheppard and Vanselow, THIS JOURNAL, **52**, 3468 (1930).

(3) Arens and Eggert, *Phot. Korr.*, **67**, Congress No., 17 (1931).