The constants for this equation listed in Table I reproduce the data within the experimental accuracy from λ 0.7065 to λ 0.4047.

<div align="center">

TABLE I

THE CONSTANTS OF EQUATION (2)

Temp., °C.	a^2	k	m	l^2
0.5	2.0083	0.00432	0.01175	0.01832
10.0	2.0041	.01828	.00873	.03954
20.0	1.9778	.00610	.01082	.02256

</div>

The Lorenz–Lorentz molecular refractivities for the sodium D line are $R_{0.5} = 19.24$, $R_{10} = 19.26$, $R_{20} = 19.31$. Using the atomic refractivities[10] of carbon, hydrogen, chlorine and bromine, one finds the atomic refractivity of fluorine at λ 0.5893 and 20° to be 0.956.

Attempted Resolution.—Three types of procedure for accomplishing the resolution of fluorochlorobromomethane suggest themselves: (a) formation of solid addition compounds with optically active substances; (b) utilization of vapor pressure differences in asymmetric solvents; and (c) selective adsorption on optically active adsorbents. Limitations of time have not permitted an extensive investigation of these proce-

(10) "Organic Chemistry, An Advanced Treatise," edited by H. Gilman, John Wiley and Sons, Inc., New York, N. Y., 1938, p. 1739.

dures, though indications of positive results were obtained with the first method.

It was found that digitonin[11,12] forms an insoluble digitonide with fluorochlorobromomethane. This digitonide cannot be dried and characterized since it very readily loses its volatile component. The halide was added to an aqueous alcoholic solution of digitonin at 0°; after vigorous shaking the mixture was centrifuged, and the precipitate was then warmed to 55° under a slow stream of air to sweep the vaporized halide into a dry-ice-cooled receiver. The distillates thus obtained had rotations varying from zero to +0.15° (1-decimeter tube). The irreproductibility of the results, and the poor recovery of the very expensive digitonin make further experiments along this line seem unpromising.

Summary

Fluorochlorobromomethane was prepared in pure form, and its boiling point, melting point, density and refractive dispersion determined. Inconclusive results were obtained in attempts to resolve the substance through its insoluble digitonide.

(11) Windaus and Weinhold, Z. physiol. Chem., **126**, 299 (1923).
(12) Windaus, Klänhardt and Weinhold, ibid., **126**, 308 (1923).

NEW HAVEN, CONNECTICUT   RECEIVED FEBRUARY 5, 1942

The Pressure–Area–Temperature and Energy Relations of Monolayers of Octadecanenitrile

BY L. E. COPELAND AND WILLIAM D. HARKINS

1. Introduction

Until recently only three liquid phases have been known to exist in monolayers. These are (1) the liquid expanded or L_1 phase, (2) the intermediate or I phase, and (3) the liquid condensed or L_2 phase. Any one of these may exist at low pressures, and therefore may be designated as a low pressure liquid phase. Recently a new liquid $LS^{1,2}$ phase has been discovered, but is found to exist only at high film pressures, since it is formed by a transition from the liquid condensed (L_2) phase when the pressure is raised to a sufficiently high value. Except at the lowest temperatures at which this new phase is formed, the transition

(1) W. D. Harkins and L. E. Copeland, J. Chem. Physics, **10**, 272 (1942).
(2) L. E. Copeland, W. D. Harkins and G. E. Boyd, ibid., **10**, June (1942).

is of the second order, so at the transition point the molecular area is the same in the high pressure LS phase as in the low pressure L_2 phase. However, by increase of pressure the area for the LS phase may be reduced below any possible area, for the given temperature, at which the L_2 phase may exist. This new high pressure phase has been found to form in monolayers of the normal long chain paraffin alcohols, but its lower limiting molecular area is 19.98 sq. Å., since below this it transforms into the "solid" or S phase.

At the highest pressure at which a low pressure liquid alcohol monolayer is stable, its molecular area may be below that possible for the stable existence of the high pressure liquid phase. Thus at 2.85° and 14 dyne cm.⁻¹ the molecular area for octadecanol is 19.8 sq. Å., the lowest area

thus found for any liquid phase. The area at 0° as obtained by extrapolation would be about 19.7 sq. Å.

Reliable measurements of the molecular areas of the normal long paraffin chain acids have not been made at such low temperatures but even at 25° the L_2 film of nonadecanoic acid has a minimum value of 20.2 sq. Å., while the minimum for octadecanol is 20.53 sq. Å. Thus the data seem to indicate that at 25° the minimum area for the acid is lower than that for the alcohol. The molecular areas obtained at 25° by extrapolation to zero pressure are 22.41 sq. Å. for the alcohol and 24.41 for the acid when the molecule of each contains 18 carbon atoms. The larger area for the acid at low pressure and the nearly equal areas at high pressure are explained by the higher mean compressibility of the monolayer of the acid as compared with that of the alcohol.

The fact that the minimum molecular area for the acid is lower than that of the alcohol may be misleading if the pressure of the transformation of liquid (L_2) into the high pressure phase is not taken into account, since the transition pressure is much higher (24 dyne cm.$^{-1}$) than for the alcohol (14 dyne cm.$^{-1}$). At this latter pressure the areas are 20.53 sq. Å. for the alcohol, but 21.7 for nonadecanoic, and 21.9 for stearic, acid, so at equal pressures the acid has the higher area.

2. The Liquid Condensed Monolayer of Octadecanenitrile

Since in monolayers of the long chain alcohols and acids the polar groups are oriented toward the water, they are also brought close together, if the film is condensed. With either of these substances there is a possibility that there may be hydrogen bonding either in (1) the film itself, or (2) between polar groups in the film and molecules of water.

It is, therefore, of interest to learn the effect, upon the molecular area, which is produced by the elimination of the first possibility, that is, of hydrogen bonding in the film. This may be eliminated by the use of a long chain nitrile.

The pressure–area–temperature relations obtained with monolayers of octadecanenitrile are exhibited in Fig. 1. From this figure it is evident that the —C≡N group gives a much higher area (with a minimum of 25.82 sq. Å. at 15.1°) in the monolayer than either —CO·OH or —OH. Adam[3] explains the relations on the basis of the assump-

(3) N. K. Adam, "The Physics and Chemistry of Surfaces," Oxford, Clarendon Press, 1938, p. 53.

tion that the nitrile group is the largest, and the hydroxyl group the smallest of the three. However, it does not seem possible that the nitrile group, with its two atoms and a carbon–nitrogen distance of only 1.15 Å., can be larger than the carbonyl group with its content of four atoms, even though one (H) of the latter is small. Therefore it seems necessary to reject Adam's hypothesis, and to seek another cause for the high area in the nitrile monolayers. Obviously if there is intra-monolayer hydrogen bonding in the case of the acids and alcohols, its absence in the nitrile films would give a sufficient explanation of their higher areas. Unfortunately the existence of this type of bonding in the film itself has not been demonstrated, even in the case of the alcohols and acids.

Some investigators assume, without solving the statistical mechanics of the problem, that the dipoles in monolayers of this type always repel each other. If this were assumed the higher dipole moment of the nitriles (3.56×10^{-18}) as compared with those of the acids (1.4×10^{-18}) and the alcohols (1.7×10^{-18}) would give a sufficient cause for the higher areas exhibited by the nitriles. This problem will be considered in a later paper which considers other relations of the nitrile mono-layers.

3. The Intermediate Phase

The interesting feature revealed by Fig. 1, as related to the intermediate phase of octadecanenitrile, is that the pressure (π)–area (σ) curves are very much steeper than those exhibited by the normal long chain paraffin acids. Thus the compressibilities of the nitriles, in this phase, are very much smaller. In contrast the esters give much larger compressibilities than the acids.

At 25.8° the intermediate phase of the nitrile has a compressibility of 0.06 at areas close to that at which this phase is formed by a transition, on increase of pressure, from the liquid expanded state. As the area is reduced the compressibility falls to about 0.015. Adam and Harding[4] have obtained a maximum compressibility of the order of 0.45 for the intermediate phase of margaric nitrile, but their value is very much higher than any obtained by us at any temperature with the 18 carbon atom nitrile.

4. The Liquid Expanded Phase

The compressibilities exhibited by the liquid expanded phase of the nitriles are of the same order

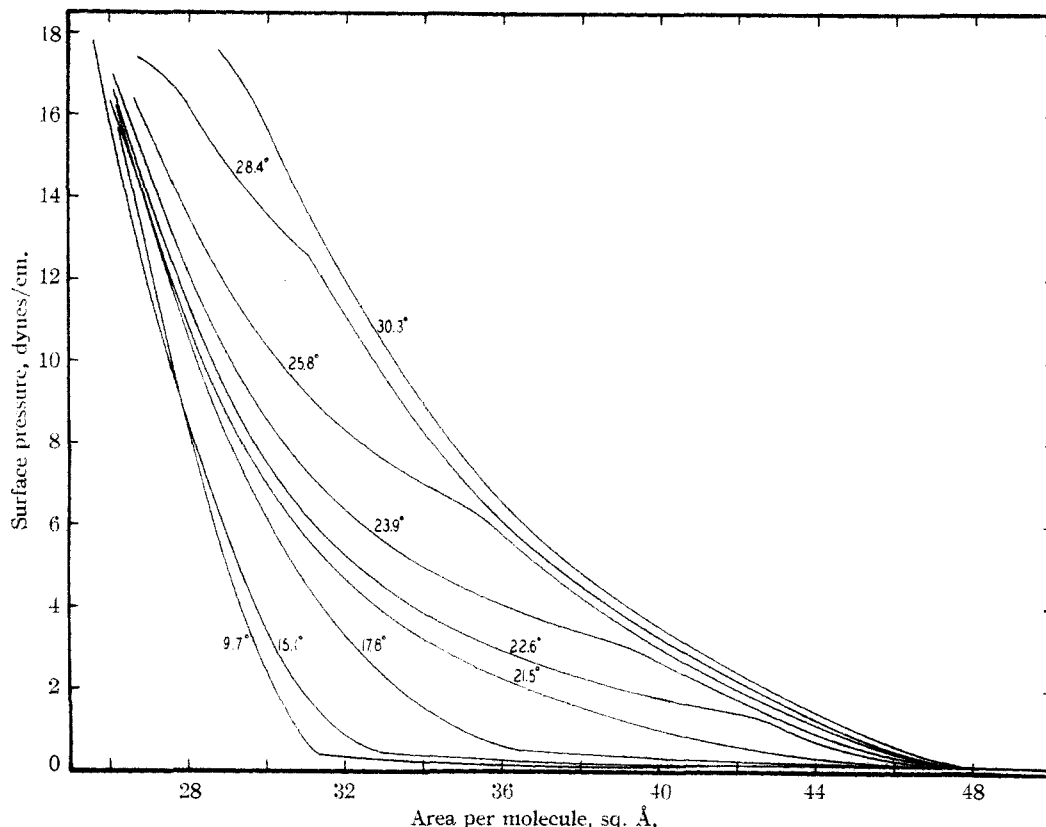(4) N. K. Adam and J. B. Harding, Proc. Roy. Soc. (London), A143, 104 (1934).

Fig. 1.—Pressure–area–temperature relations of monolayers of octadecane nitrile on water.

of magnitude as those of the acids. That the phase is of the liquid rather than of the vapor type is indicated by the areas at which the film pressures become small, and which are of the order of those to be expected when a liquid expanded film begins to vaporize. At 22.6° and 30.3° the areas are 46 and 48 sq. Å., while with pentadecylic acid, known to be in the liquid expanded state, the areas are 44 and 49 sq. Å. at 17.9 and 35.2°. In the case of myristic acid the transition occurs at 42 and 46 sq. Å. at 4° and 25°.

5. Energy of Spreading and Extension

The values of the energies of extension of the surface of clean water, which are the same as the energies of surface formation, are given in the first row of Table I. The energies of extension of the water covered by the nitrile monolayer are all higher (than those of water), except for the free energies which are lower. Any energy of spreading may be obtained from the corresponding energy of extension by subtracting the value for water. As usual there is a decrease of free energy but an increase of total energy, and of entropy, and of absorption of heat when the monolayer spreads.

TABLE I

THE ENERGIES OF THE MONOLAYER OF OCTADECANE-NITRILE IN THE VARIOUS STATES AT 20°

Energy in erg cm.$^{-2}$ and entropy in erg cm.$^{-2}$ deg.$^{-1}$

Phase	Area	Process	f	h	q	s
Clean water			72.75	116	43.2	0.148
L_1	40.0	extension	72.25	155	82.2	.282
		spreading	−0.49	38.8	39.3	.134
I	32.0	extension	69.00	170	201	.685
		spreading	−3.75	154	158	.537
L_2	28.0	extension	66.38	124	57.5	.197
		spreading	−6.37	7.9	14.3	.049

The effect of pressure and temperature upon the energy values for the monolayers, as obtained at various constant areas, are given in Table II. The values are not extremely high, as in the case of the alcohols,[1,2] but are of somewhat the same order of magnitude as those for pentadecylic acid. As is usual they are very much higher for the intermediate phase than for the expanded and condensed liquid phases.

Summary

TABLE II

THE EFFECT OF PRESSURE ON A MONOLAYER OF OCTA-
DECANENITRILE AT VARIOUS AREAS

Phase	t, °C.	s_a	q_a	h_a
	28 sq. Å./molecule			
L_2	6.3	19.60	0.00	00	0
	6.5	21.05	.203	60	54
I	7.0	22.64	.442	131	124
	8.0	24.60	.600	179	171
	9.0	25.85	1.12	322	313
	10.0	26.80	0.917	275	265
L_1	11.0	28.30	.00	0	0
	32 sq. Å./molecule			
I	3.0	18.40	0.337	98	95
	4.0	20.46	.564	166	162
	5.0	22.00	.770	217	212
	6.0	23.31	.770	230	224
	7.0	24.51	.902	268	261
	8.0	25.60	.972	290	282
L_1	9.0	27.35	.104	31	22
	40 sq. Å./molecule			
·I	1.0	18.85	0.203	59	58
	2.0	20.96	.815	240	238
	3.0	22.05	.797	235	232
	4.0	23.52	.541	160	156

by its grant any of the statements made or views expressed therein.

Summary

1. The lowest area thus far found, in accurate work, for any n-long chain paraffin derivative in its monolayer on water is 19.57 sq. Å. This was obtained with n-octadecanol in the S-phase at 2.85°. At lower temperatures somewhat lower areas could be obtained. In solid three dimensional crystals the area of the hydrocarbon chain is 18.5 sq. Å. Nonadecanoic acid in its monolayer at 25° has been compressed to 20.2 sq. Å. At 25° the extrapolated area at zero pressure is, for the liquid condensed phase, 22.41 sq. Å. for octadecanol and 24.41 sq. Å. for stearic acid.

2. In monolayers of the alcohols and acids there is the possibility of hydrogen bonding between the polar groups in the film itself as well as with water. In monolayers of n-octadecane nitrile hydrogen bonding in the film itself is no longer possible, and it was found that the minimum area obtained at any temperature and pressure employed was 25.8 sq. Å. at 15.1° and 18 dyne cm.$^{-1}$, while the lowest area found by extrapolation at zero pressure was 30 sq. Å. Thus the —C≡N end group gives much less condensed films than either the —COOH or the —OH groups. Unfortunately the dipole moment of the nitrile is much higher (3.56×10^{-18}) than that of the alcohol or the acid, so there is a possibility that this produces a repulsion which accounts for the greater area. The decision as to which factor is responsible for the high area, is left to later work.

3. The hypothesis that the larger area of the nitrile is due to a large size of the —C≡N group, with its interatomic distance of only 1.15 Å., as compared with the —COOH group, is rejected.

4. The pressure–area curves for the intermediate phase are much steeper than those for the long chain acids. Thus in this phase the nitriles exhibit a much smaller compressibility.

5. The pressure–area curves for the expanded phase fall to low pressures at just those areas characteristic of the liquid expanded state, so these films are not gaseous. Thus at 22.6° and 30.3° these areas are 46 and 48 sq. Å., while with pentadecylic acid at 17.9° and 35.2° the corresponding areas are 44 and 49 sq. Å.