HYDROPHIL BALANCE STUDIES ON HIGH MOLECULAR WEIGHT KETONES

EVERETT J. HOFFMAN AND ANDERSON W. RALSTON
Research Laboratories, Armour and Company, Chicago, Illinois
AND
GEORGE E. ZIEGLER
Research Foundation, Armour Institute of Technology, Chicago, Illinois

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INTRODUCTION

The correlation between the film characteristics of several related ketones and the type of organic radical attached to the respective carbonyl groups has been studied by means of hydrophil balance measurements. For this purpose we chose a series of ketones containing one straight-chain aliphatic R group of seventeen members with the other R group varying throughout the series. The compounds selected as representative of such a series were as follows: methyl heptadecyl ketone, stearone, biphenyl heptadecyl ketone, and phenoxyphenyl heptadecyl ketone. Stearic acid was also included in the study for the purpose of making comparisons with published data (1).

Methyl heptadecyl ketone and stearone were selected because the former contains the smallest possible aliphatic group, whereas the latter contains a relatively long aliphatic group. On the other hand, biphenyl heptadecyl ketone and phenoxyphenyl heptadecyl ketone contain aryl groups which are similar except for the presence of an ether oxygen linkage between the two phenyl groups in the case of the latter ketone. The rôle of this ether oxygen in the molecule was thought to be of particular interest because of its possible hydrophilic nature.

Formulas, molecular weights, and observed melting points are listed in table 1.

EXPERIMENTAL PROCEDURE

Preparation of materials

Methyl heptadecyl ketone was prepared from stearonitrile and methylmagnesium iodide by means of the Grignard reaction. The product was recrystallized until the melting point was constant.

Stearone was prepared by passing stearic acid, at a rate of about 30 g.

per hour, over manganese chromite catalyst in an electric furnace heated at 410°C. ± 10°. The product was recrystallized from a mixture of ethanol and benzene until a constant melting point was obtained.

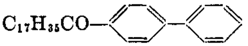
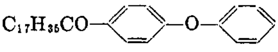
Biphenyl heptadecyl ketone was prepared by means of the Friedel–Crafts reaction from biphenyl and stearoyl chloride (5). The product was recrystallized from acetone until the melting point was constant.

Phenoxyphenyl heptadecyl ketone was prepared by means of the Friedel–Crafts reaction from phenyl ether and stearoyl chloride (5). The product was recrystallized from acetone until crystals of constant melting point were obtained.

The benzene used in preparing the solutions was Baker's thiophene-free benzene. Prior to use, it was fractionated twice through an eight-ball air-jacketed Snyder distilling column made entirely of glass. All joints were ground glass, and no stopcocks were used in the apparatus.

TABLE 1

Formulas, molecular weights, and melting points of stearic acid and the ketones

COMPOUND	FORMULA	MOLECULAR WEIGHT	MELTING POINT
			°C.
Stearic acid	$C_{17}H_{35}COOH$	284.3	70.0–0.5
Methyl heptadecyl ketone	$C_{17}H_{35}COCH_3$	282.3	55–6
Stearone	$C_{17}H_{35}COC_{17}H_{35}$	506.5	86–7
Biphenyl heptadecyl ketone		420.3	104–6
Phenoxyphenyl heptadecyl ketone		436.3	63–5

Apparatus

The hydrophil balance used in this study was of a modified Langmuir–Adam type (4). The tray used was an aluminum casting approximately 14 x 65 cm. with a phosphor bronze float attached to the sides of the tray by means of gold ribbons 4 mm. wide and 0.012 mm. thick. The force on the float was measured by means of a steel torsion wire 0.21 mm. in diameter. The sensitivity necessary for precision measurements was attained by the use of a mirror and a beam of light reflected to a screen at a distance of 100 cm. It was necessary to cover the aluminum tray with a thick layer of parowax. No hydrogen bubbles were observed with the 0.01 *N* hydrochloric acid solutions which were used throughout the investigation.

The movable barriers used were of brass, coated with a thin film of parowax. The barriers were moved continuously for all observations by means of a rack and pinion driven by a one revolution per minute synchronous motor. Four constant speeds were available: namely, 60, 20, 6.6, and

2.2 mm. per minute. This was an important item in the experimental setup as used in this investigation, because film balance force–area measurements are dependent in their absolute values upon the rate of compression of the film. In this first study on the series most of the data were obtained at the 20 mm. per minute speed. In future work the effect of changes in rate of compression will be studied.

Observations were made by setting the torsion head wire at successive steps of rotation. The barrier position was read on the scale at the moment the beam of light reflected from the torsion wire mirror reached the zero or equilibrium point on its scale. The zero point shifted with slight changes in the level of the water in the tray; hence this fact was advantageously used as a means of measurement in keeping the water level constant. No inconsistencies arose in the data obtained for the series of compounds under investigation if the water was used more than once, provided care was taken to maintain a constant water level.

Although rate of compression and water level are important factors in force–area measurements, changes in temperature are even more important because of their marked effect on film characteristics. Constant temperatures were attained by housing the film balance in a case consisting of a hair-felt-insulated, double-walled, copper box so arranged with channels between the double walls that water from a circulating thermostat could be circulated through five sides of the box. The front of the box had double glass doors, and, except for the small openings through which observations were made, the doors were covered with aluminum foil to reduce radiation. No difficulty was encountered in maintaining the temperature of the box at 25.0°C. ± 0.1°. This, however, was not true for the water in the tray itself, because of the cooling due to evaporation from the surface. This effect was especially important during the winter days of relatively low humidity. To obtain consistency in surface temperature it was necessary to install trays of water with an extensive system of wicks. This arrangement aided surface temperature control, but it was not adequate until portholes fitted with rubber sleeves were installed in the front glass so that a sample could be delivered to the surface of the water without admitting any appreciable quantity of dry air. The water in the film balance tray could also be changed without opening the case. In its final form, the case permitted the surface temperature of the tray to be held constant within 0.1°C.

Samples dissolved in carefully distilled benzene were used throughout the investigation, although check runs were made with petroleum ether whenever solubility permitted. Samples were measured by the use of an automatic microvolume pipet (3). The pipet was calibrated volumetrically, in an atmosphere saturated with benzene, for each sample. It was necessary to calibrate the pipet with each solution because with a pipet as

TABLE 2

Quantities and concentrations of solutions used

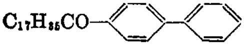
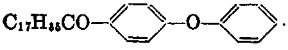
COMPOUND	VOLUME OF SAMPLE	CONCENTRATION
	cc.	*grams per cc.*
$C_{17}H_{35}COOH$	0.0428	0.00153
$C_{17}H_{35}COCH_3$	0.0427	0.00202
$C_{17}H_{35}COC_{17}H_{35}$	0.0854	0.00131
	0.0435	0.00315
	0.0426	0.00330

TABLE 3

Data obtained in force-area measurements

FORCE IN DYNES PER CENTIMETER	AREA PER MOLECULE IN Å²				
	$C_{17}H_{35}COOH$	$C_{17}H_{35}COCH_3$	$C_{17}H_{35}COC_{17}H_{35}$		
0.26	28.05	21.53	43.62	25.14	33.38
0.52	26.24	21.36	39.28	22.36	31.16
1.29	25.89	21.15	34.88	18.68	27.37
2.59	25.54	20.91	31.91	17.31	24.75
3.88				16.43	23.39
5.18	24.88	20.49	28.34	15.81	22.35
7.76	24.26	20.40	26.01	14.84	20.94
10.35	23.72	20.33	24.12	14.13	19.99
12.94	23.15	20.28	22.58	13.53	19.16
15.53	22.59	20.21	21.08	13.04	18.44
18.12	22.09	20.16	19.85	12.58	17.64
20.70	21.66	20.11	18.78	12.15	16.91
23.29	21.18	20.05	17.69	11.77	16.05
25.88	20.80	20.00	16.57	11.40	14.97
28.47		19.95	15.63	10.99	13.78
31.06		19.89	14.86	10.63	12.77
33.64		19.84	14.12	10.30	12.14
36.23	20.43	19.79	13.56	9.97	11.68
38.82		19.71	13.04	9.61	11.24
41.41		19.68	12.51	9.35	10.88
44.00		19.63	12.06	9.09	10.58
46.58	20.04		11.63	8.85	10.27
51.76			10.73	8.29	9.61
56.94			10.00	7.76	9.02
62.11			8.99		
64.70			8.46		

small as the one used, 0.043 cc., the area was large compared to the volume. This resulted in an appreciable quantity of solution remaining on the walls of the pipet. It may be of interest in the future when more data are available to work out a correlation between the film characteristics and the delivery volume. It was necessary to deliver only a very small sample of the solution to the tray to avoid dissolving parowax from the sides of the relatively narrow tray.

The quantities and concentrations of the solutions used are given in table 2.

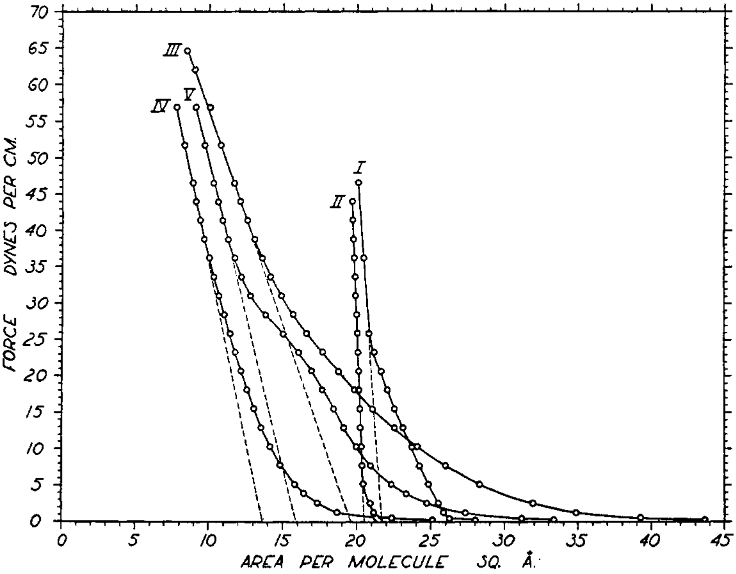


Fig. 1. Force–area measurements on films of stearic acid (I), methyl heptadecyl ketone (II), stearone (III), biphenyl heptadecyl ketone (IV), and phenoxyphenyl heptadecyl ketone (V).

The film balance equipment was constructed so that in the future films might be studied through a range of temperatures and at different rates of compression. Studies at different hydrogen-ion concentrations may also be made. The use of a wider tray of a material other than aluminum is contemplated for these additional measurements.

RESULTS

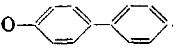
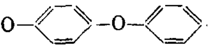
Force–area measurements were made on each of the films under exactly similar experimental conditions. The data obtained were averaged and are presented in table 3 and figure 1. It was found that individual readings did not differ from the average value by more than 4 per cent.

The extrapolated values of the molecular areas were read from figure 1, where they are indicated for the upper portion of the curves by the broken lines. The broken lines for the lower portion of the curves are omitted to avoid confusion on the graph. These values are listed in table 4. Since methyl heptadecyl ketone, stearone, and biphenyl heptadecyl ketone do not have any lower slopes, no extrapolated values are listed.

The nature of the films was also studied by means of lycopodium powder and a stream of air. It was found that methyl heptadecyl ketone was free moving at all compressions. Stearone had about the same rigidity as stearic acid. Biphenyl heptadecyl ketone and phenoxyphenyl heptadecyl ketone are very much more rigid than stearic acid.

TABLE 4

Extrapolated values of the molecular areas

COMPOUND	AREA PER MOLECULE IN Å^2	
	Upper portion	Lower portion
$C_{17}H_{35}COOH$	21.7	26.1
$C_{17}H_{35}COCH_3$	20.5	
$C_{17}H_{35}COC_{17}H_{35}$	19.7	
$C_{17}H_{35}CO$— 	13.7	
$C_{17}H_{35}CO$— 	15.9	22.9

CONCLUSIONS

From the force-area curves of figure 1 it is evident that the film of stearone is more compressible than that of methyl heptadecyl ketone. This fact, together with our observation that methyl heptadecyl ketone is a free moving film even at the highest compression, leads us to believe that there is a high repulsion between the molecules of methyl heptadecyl ketone. We interpret this as due to the non-symmetrical nature of methyl heptadecyl ketone as compared to stearone.

From the curves in figure 1 it is evident that at low pressures (expanded film) the area of the phenoxyphenyl heptadecyl ketone molecule is considerably greater than that of the biphenyl heptadecyl ketone molecule, while at high pressures the two curves approach each other quite closely. This observation can be explained by attributing hydrophilic properties to the ether oxygen in the phenoxyphenyl heptadecyl ketone molecule. As the force on the film is increased the ether oxygen is removed from contact with the water (as the force increases from 21 to 36 dynes per centimeter), and the two areas become approximately the same. The ether oxygen should exhibit hydrophilic character because of its four unshared electrons, but this effect should be considerably less than that of the carbonyl oxygen because of the steric effect of the adjacent phenyl groups. Experimental results appear to conform to this prediction.

Comparisons between various hydrophil balance studies are unreliable because of the influence of numerous factors involved in the experimental technique: *viz.*, rate of compression of the film, time elapsing between the application of the film and the start of the run, the amount of contamination, the age and the pH of the aqueous solution in the tray, and the temperature. From our own observations we conclude that the relative humidity of the surrounding atmosphere plays an important rôle in temperature control.

Since biphenyl heptadecyl ketone and phenoxyphenyl heptadecyl ketone are relatively new compounds, no film balance data are available for comparison. Our force-area curve for methyl heptadecyl ketone is in excellent agreement with that obtained by Adam, Danielli, and Harding (2). These same authors state that in an attempt to spread stearone a scarcely perceptible surface pressure was observed. This result does not agree with our observations.

Various values for the molecular area of stearic acid have been reported. Harkins and Anderson (3) report a value of 23.8 $Å.^2$ for the expanded film and 20.4 $Å.^2$ for the condensed film at zero pressure. Adam (1) reports a value of 24.9 $Å.^2$ for the expanded film and 21.0 $Å.^2$ for the condensed film. These are at some variance with our values of 26.1 and 21.7 $Å.^2$ for the expanded and condensed films, respectively.

Further work, in which the effect of temperature, pH, and the rate of compression of the films of these and related compounds will be studied, is contemplated. It is hoped that these further data will permit more extensive conclusions regarding the behavior of these compounds.

SUMMARY

1. Hydrophil balance studies have been made on a series of several related ketones: *viz.*, methyl heptadecyl ketone, stearone, biphenyl heptadecyl ketone, and phenoxyphenyl heptadecyl ketone.
2. Important refinements in the usual apparatus for film studies permitting careful temperature and humidity control have been outlined.
3. An explanation has been offered for the behavior of these films under compression.

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