[CONTRIBUTION FROM THE PHYSICAL CHEMICAL LABORATORY OF MCGILL UNIVERSITY]

INVESTIGATION OF SURFACE TENSION CONSTANTS IN AN HOMOLOGOUS SERIES FROM THE POINT OF VIEW OF SURFACE ORIENTATION

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Investigations of surface energy temperature coefficients have shown that for some substances high abnormal values of the Ramsay-Shields constant are obtained. These abnormalities cannot be explained by dissociation. Ramsay and Miss Aston[1] noticed that the constant increases with the number of CH_2 groups in the molecule. Miss Homfray and Guye[2] found for amyl stearate the high value of 3.34, and similar cases multiplied in number rapidly. Walden and Swinne[3] gave an empirical relation by which they claimed that the Ramsay-Shields constant, K, could be calculated approximately, $K_e = 1.90 + 0.011\ (nA)$, where nA is the sum of the square roots of the atomic weights of the elements in the compound. Each atomic weight is multiplied by the corresponding subscript as given by the formula for the compound.

Just as Ramsay and Shields chose a molecular weight larger than the theoretical in order to account for a low value of their constant, so a high value might be explained by assuming dissociation, for in that case the proper value could be obtained by choosing a molecular weight smaller than the normal. This explanation, which was suggested by Miss Homfray and Guye, is possibly the true one for some cases, but it does not appear reasonable to apply it to a great many others in which dissociation is most unlikely. In this paper, work is described, the incentive of which was to show that high values might possibly be explained in another way. In this proposed explanation it is assumed that there are too many molecules in the molecular surface when the latter is calculated by using the normal molecular volume, but the presence of these extra molecules is ascribed to a cause other than dissociation, namely, orientation. If the axes of the surface molecules are, on the average, perpendicular to the surface, each one effectively occupies a smaller area than it would if it were not so orientated, with the result that a greater number can crowd into a given area.

An homologous series is best suited for an examination of orientation, and for this purpose the fatty acids were chosen, since their orientation in surface films has been so definitely established by the work of Langmuir[4]

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[1] Ramsay and Aston, *Z. physik. Chem.*, **15**, 101 (1894).

[2] Homfray and Guye, *J. chim. phys.*, 1, 529 (1904).

[3] Walden and Swinne, *Z. physik. Chem.*, **82**, 290 (1913).

[4] (a) Langmuir, *Met. Chem. Eng.*, **15**, 468 (1916); (b) THIS JOURNAL, **39**, 1848 (1917).

and Adam.[5] Altogether, ten acids were examined and, for comparison, a saturated hydrocarbon, dicetyl. The purification of the compounds used is described, then the method of measuring the surface tensions. The data obtained are tabulated and then discussed from the point of view of the orientation theory.

Purification of Compounds

Propionic Acid.—A specimen of Kahlbaum's acid was purified by crystallization. The procedure consisted in cooling the acid in a flask until crystallization started and then maintaining the temperature of the bath just below the freezing point.[6] The crystals grew slowly and when three-quarters of the liquid had solidified the remainder was rejected. The solid was allowed to warm up until a little melted and this liquid was shaken to wash the crystals and also rejected. The remainder was allowed to melt and was put through the same cycle. This was repeated until a constant melting point was obtained for three successive crystallizations. In all twelve crystallizations were carried out.

The criterion for the melting point was chosen as the condition where a sample two centimeters long in a sealed melting-point tube froze completely within one-tenth of a degree. Great care and patience were exercised in the melting-point determination, as the time required for equilibrium to be established between solid and liquid is long; −22.4° was found to be the melting point after each of the last three crystallizations.

The butyric acid was found to contain acetic acid as an impurity. It was therefore fractionated five times at atmospheric pressure. The fraction boiling between 160 and 163° was converted into the calcium salt by the addition of milk of lime. The solution was evaporated down and the calcium butyrate was filtered out while hot, since, unlike calcium acetate, it is less soluble in hot than in cold water. The salt was crystallized again and butyric acid was liberated by the addition of hydrochloric acid, slightly less than the theoretical quantity calculated on the basis of the calcium butyrate. The mixture was allowed to separate into two layers and the butyric acid removed with a pipet. It was then distilled in a Pyrex apparatus with joints all glass-sealed as far as the receiver. A small amount of aqueous solution came over at a little above 100°. The temperature then rose rapidly to 161.4° and nearly the whole of the acid distilled within 0.9°.

The portion of acid boiling over the 0.9° range was next distilled under reduced pressure in an apparatus which consisted of three bulbs sealed to a mercury pump. One of the bulbs was the tube in which the surface tension was to be measured. The acid, about 25 cc., was frozen in one bulb while the apparatus was evacuated as thoroughly as possible. A small amount (10 to 15 cc.) was then distilled into the third bulb, which was immediately sealed off. The second portion was distilled into the surface tension tube, which in turn was sealed off. The third fraction was used for the determination of the density.

Caproic, caprylic and capric acids were obtained from the Eastman Kodak Company. They were purified in much the same manner as was propionic acid. The whole of the purified substance chosen froze over a range of not more than 0.2 or 0.3°.

Lauric, myristic, palmitic, margaric and stearic acids were Kahlbaum's acids purified by crystallization from 95% alcohol until the melting point was constant. For instance, the stearic acid used was a specimen which was crystallized fifteen times.

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[5] N. K. Adam, *Proc. Roy. Soc., London,* **99A,** 336 (1921); **101A,** 452, 516 (1922); **103A,** 676, 687 (1923).

[6] Maass and Wright, This Journal, **43,** 1098 (1921).

The hydrocarbon dicetyl, or ditriacontane, was obtained through the kindness of Dr. R. F. Ruttan. It was crystallized from alcohol in order to get a solution which could easily be filtered from suspended impurities and then recrystallized several times from ether.

Measurement of Surface Tension.—The surface tensions were measured by the capillary rise method. The temperature bath was a 2-liter beaker of glycerin. Vigorous circulation of the glycerin was maintained by motor-driven stirrers of the propeller type. The temperature was regulated by hand, by means of a gas burner, and it was possible, by means of an auxiliary jet, to keep the temperature constant to within 0.2° over any desired length of time. All of the thermometry involved, except at temperatures below zero, was carried out by means of thermometers for which certificates of calibration of the Reichsanstalt were available. The accuracy is of the order of 0.2° absolute.

Measurements were made on each substance from the melting point up to about 150°. In the case of propionic acid the observations were continued down to the limit of supercooling, and the properties calculated were found to be continuous down to this temperature.

The tube in which the surface tensions were measured was of the type used by Richards,[7] with this modification, that millimeter scales were etched on the two arms of the tube so that the height of a column of liquid could be read directly to 0.1 mm. The capillary was kept vertical by the use of two plumb-lines. The tube was calibrated by making use of Richards' very accurate determination of the surface tension of benzene.

The readings were always taken with a falling meniscus. If necessary the tube was tilted for a moment in order that the liquid might rise, and then fall to its equilibrium position. A reading was not recorded until the top of the column had been stationary for some minutes.

In the case of margaric acid a series of readings was taken both with rising and with falling meniscus, in order to see how much difference there would be. It was found that the two readings differed by as much as 1.7 mm. near the melting point, and did not coincide until the temperature reached 170°; also that those taken with an ascending column did not lie on as smooth a curve as did the others. The descending values give correct results, as a rising column is apt to create an angle of contact due to the viscosity of the liquid. Since margaric acid gave a greater difference between the two values than did any of the others, and since it was the only one of the higher acids examined that contained an odd number of carbon atoms, it was thought of interest to measure its viscosity. The viscosity results are discussed later.

The butyric acid was distilled into the tube as described above. Of the other acids those which are liquid at ordinary temperatures were

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[7] T. W. Richards and Coombs, THIS JOURNAL, **37**, 1656 (1915); **46**, 1196 (1924).

poured in through a funnel. In the case of the solid compounds, the tube was put into a steam-jacket and the substance was melted in a specially constructed funnel. In every case the tube was supported at such an angle that the desired amount of melted acid could be introduced without any entering the capillary. The whole apparatus was allowed to cool without being disturbed until the substance had become solid, when the tube could be handled freely. The tube was sealed to a mercury pump and exhausted. It was attached to the pump in the same inclined position as before, in order that, after a preliminary exhaustion, the substance might be melted again by means of a hot water-bath, while under vacuum. After the tube was cool, it was again exhausted and then sealed off. When everything was ready for a series of readings, the substance was entirely melted and then allowed to run into the capillary. These precautions were taken in order to have a fresh surface, as any traces of impurity are likely to collect in the surface after a time and change the surface tension.

Measurement of Density.—The densities, which are required in the calculations, were all measured over the necessary temperature ranges. A dilatometer with a bulb of about 2.5 cc. capacity was used. A millimeter scale was etched on the stem. Known weights of water were weighed with the bulb, and the volume was plotted against scale reading. The volume occupied by any substance under examination could then be read from the curve. Weighings were corrected for air displaced and allowance was made for the expansion (or contraction) of the bulb at temperatures differing from that at which the calibration was carried out. In the case of propionic acid special precautions, as described by Maass and Wright, were taken on account of the volatility of the substance.

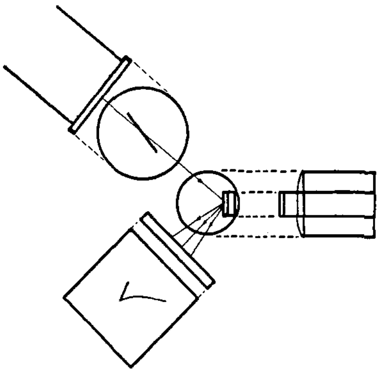

Fig. 1.

Angle of Contact.—It is commonly held that many substances make zero angle of contact with glass, but this cannot be assumed without some verification as the capillary rise method can only be used if such is the case. Specimens of the substances dealt with were examined by the optical method originated by Richards and Carver.[8]

The apparatus is illustrated diagrammatically in Fig. 1. The method consists in directing a slit-shaped beam of light rays upon the junction of solid and liquid surfaces in such a way that the reflected rays may be caught upon a screen. The diagram shows the collimator, the screen

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[8] Richards and Carver, THIS JOURNAL, 43, 827 (1921).

and the cell containing the liquid. For visual observation a ground-glass plate is used; for more minute examination and for recording, a photographic plate is substituted for the ground glass. The experiments were carried out in a dark room which itself served as a camera, and the back of an ordinary camera was held in clamps as near as possible to the cell containing the liquid. After the desired image was obtained on the ground glass, the latter was swung aside and the plate-holder was slipped in, exactly as in the regular method of manipulation of a camera. The room was then darkened, the plate was uncovered and the beam of light was turned on for the length of time required for the exposure.

The cell in which the liquid was contained was merely one-half to three-quarter of an inch of test-tube with the bottom flattened. A slip of plate glass about one and one-half inches long stood in the liquid in the cell. The latter was filled over-full, so that the junction between the liquid and the plate glass was not obscured by the wall of the cell. For the same reason it was found best to have both the collimator and the screen tilted toward the cell, so that the actual path of the rays was downward and then up again. This could not be easily shown in the diagram.

It was necessary to have the glass slip absolutely clean. Before it was used, it was cleaned with hot sulfuric acid and bichromate, if necessary, until when it was washed with distilled water and allowed to drain, interference colors would appear in the film of water upon the surface.

In the examination of the higher melting substances (60–70°) it was necessary to use a diminutive electrical heater made by rolling up asbestos paper and nichrome wire with a hollow in the middle in which the cell could be placed. The whole was not more than two inches in diameter, and could be held by a clamp in any position desired. The current was regulated by lamps. One 16-c. p. carbon lamp in series with the heater was suitable in nearly all cases. If the cell was allowed to become too hot the substance would vaporize a little and condense on the upper part of the glass slip which was, of course, comparatively cold, and spoil the photograph.

Richards and Carver placed their cell in a box, the atmosphere in which was kept saturated with the vapor of the substance in question by a dish of the warm liquid. It was not deemed necessary to take this precaution in the present work because the liquids were examined at temperatures but little above the melting point. Even in case of liquids like octane and propionic acid, which were the most volatile ones of which photographs were taken, there was no evidence of evaporation from the edge of the film at ordinary temperatures.

Not only fatty acids but also a few related compounds and a few quite unrelated ones were examined. The degree of difficulty experienced in obtaining the continuous surface may be roughly given as follows: lower fatty acids, water, lower saturated hydrocarbons, higher fatty acids, higher saturated hydrocarbons except paraffin wax, hexadecylene (the only unsaturated hydrocarbon examined), concentrated sulfuric acid, glycerol, paraffin wax.

The end desired was achieved, namely, to show that the surface tension measurements made on the fatty acids were not vitiated by the existence of a finite angle of contact.

Viscosity.—As was mentioned above, it was deemed advisable to measure the viscosity of margaric acid in relation to that of its neighbors in the series. Accordingly the viscosities of palmitic, margaric and stearic acids were measured over a range of temperature.

The viscosities were measured in the same tube as was used for surface tension, which had a 2-cc. bulb just above the capillary. To provide a means of drawing the liquid into the upper bulb, a small tube bearing a cork was plugged into the main tube of the viscosimeter just below the side arm. The narrow tube passed up through a T-tube and was continued to a safe distance away from the vapors of the bath. The T-tube was connected to the top of the viscosimeter by a short length of wide rubber tubing and the top of the T was made air tight by a rubber sleeve through which the small tube could be moved up or down. By applying suction to the side arm of the T, the liquid could be pulled up. Before it passed the upper mark on the way down, the small tube bearing the plug was pulled above the side arm of the viscosimeter in order to allow the air pressure to be the same on both sides. The tube was calibrated at 30.3° with water according to the method described by Maass and Boomer.[9]

The values obtained for the absolute viscosities are given in the following table.

TABLE I

RESULTS OF VISCOSITY DETERMINATIONS

Palmitic acid		Margaric acid		Stearic acid	
Temp., °C.	Viscosity, millipoises	Temp., °C.	Viscosity, millipoises	Temp., °C.	Viscosity, millipoises
74.0	71.7	67.6	92.6	100.7	45.6
91.3	48.0	76.0	74.7	115.9	34.3
111.4	32.8			130.3	26.7
127.5	24.9	107.1	40.3		
144.0	19.4				

When plotted on graph paper it was seen that the viscosity of margaric acid was almost identical with that of stearic acid, both of them being about 10% higher than the viscosity of palmitic acid at 90°.

The results of the determinations of surface tensions and densities are given in Table II, which also contains the surface energies calculated from them.

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[9] Maass and Boomer, THIS JOURNAL, **44**, 1709 (1922).

TABLE II

RESULTS OF SURFACE TENSION AND DENSITY DETERMINATIONS

Temp., °C.	Surface tension, dynes	Molecular surface energy, ergs	Density, vac.
	Propionic Acid		
−36.0			1.05623
−35.1	32.8	558	
−32.6			1.05253
−30.4	32.4	553	
−29.6			1.04918
−25.4	32.0	547	
−21.0			1.03977
−20.4	30.95	535	
−15.4	30.4	527	
−10.8			1.02862
− 8.5	29.7	513	
− 2.9	29.1	506.5	
+ 0.1			1.01713
2.5	28.55	498	
5.0			1.01194
14.9			1.00085
20.9	26.4	432	
23.1			0.99211
29.1			.98560
30.9	25.4	453	
39.4			.97462
40.8	24.5	439.5	
50.5			.96275
53.8	23.2	421	
64.9	22.2	405	
70.8			.94060
80.5			.92988
90.5			.91973
95.4	19.2	359	
98.1			.91157
110.5	17.6	334	
111.4			.89726
118.5			.88948
125.7	15.9	304	
140.3	14.9	289	
	Butyric Acid		
8.6	28.0	565	0.9707
9.7	27.8	562	.9695
18.4	27.1	550	.9615
26.5	26.2	535	.9527
38.9	25.1	517	.9408
50.3	23.8	494	.9292
60.7	22.9	479	.9187
73.2	21.7	459	.9066
77.2	21.4	453	0.9030
68.1	22.3	470	.9119
44.8	24.4	505	.9349
0.1	29.2	590	.9792
1.6	28.7	579	.9773
19.5	26.9	547	.9597
37.5	25.2	520	.9421
91.7	20.1	430	.8838
107.2	18.5	405	
120.7	17.5	382	
131.3	16.4	364	
	Caproic Acid		
−20.1			0.9651
−20.0	31.2	760	
−11.2			.9574
−10.1	30.7	751.5	
− 0.5			.9477
+ 1.6	29.6	730	
6.0	28.9	716	
9.9			.9386
19.9			.9301
25.0			.9254
25.7	27.0	677	.9254
35.6	26.2	660	.9168
49.6	25.1	638	.9045
70.3	23.4	603	.8859
90.7	21.6	565	.8678
100.8	20.7	545	.8591
	Caprylic Acid		
16.1	28.5	830.5	0.9157
19.9	28.3	826	.9125
25.3	27.9	818	.9083
29.9	27.7	813	.9044
34.6	27.3	804	.9004
40.1	26.6	785	.8962
45.1	25.9	770	.8921
49.2	25.7	765	
62.4	24.5	734	.8779
79.7	22.8	691	.8639
91.6	22.0	671	.8543
100.2	21.6	662	.8475
115.0	20.3	631	.8354
123.9			.8281
129.1	19.3	603	
142.8	18.3	576	

TABLE II (*Continued*)

Temp., °C.	Surface tension, dynes	Molecular surface energy, ergs	Density, vac.
	Capric Acid		
31.9	27.7	923	0.8931
33.6			.8920
41.7	27.2	910	
50.5	26.9	904	.8789
57.9	26.5	896	.8730
71.2	25.1	857	.8627
90.5	23.4	808	.8480
107.7	22.0	768	.8349
121.4	21.1	742	.8242
140.1	19.7	702	.8096
151.2	19.2	688	
	Lauric Acid		
41.8			0.8740
45.0	28.5	1070	
55.0	27.8	1047	
58.0			.8624
66.0			.8565
67.0	26.8	1018	
76.5			.8485
78.3	26.0	992	
88.5	25.0	961	
91.5			.8370
103.3	23.9	927	
115.5	22.9	893	
122.0			.8152
129.0	21.9	861	
135.5			.8051
141.0	20.8	826	
	Myristic Acid		
76.2	27.0	1120	0.850
66.2	27.6	1135	.856
56.8	28.6	1170	.862
60.3	28.4	1165	.860
74.2	27.3	1125	.851
89.2	25.7	1070	.841
109.2	24.2	1020	.828
129.2	22.7	965	.815
149.3	21.3	915	.801
138.3	22.0	940	.808
119.2	23.6	1005	.822
	Palmitic Acid		
64.3			0.854
65.2	28.6	1280	
69.2	28.2	1270	
74.2			.849
79.2	27.5	1240	
85.2			0.842
89.2	26.7	1210	.839
98.2			.834
99.2	26.0	1180	
109.2	25.3	1160	.827
118.2			.821
119.2	24.5	1130	
129.2	23.8	1100	.813
134.2			.810
139.2	22.9	1060	.807
149.3	22.1	1030	.800
	Margaric Acid		
66.9	27.9	1297	
90.6			0.8355
90.8	26.0	1225	
100.7			.8282
110.9			.8213
112.0	24.4	1164	
126.1	23.8	1128	
129.0			.8092
135.7			.8039
141.0	22.5	1076	
146.5			.7961
	Stearic Acid		
70.0	28.9	1395	0.8480
78.3			.8430
78.5	28.4	1375	
87.5	27.7	1348	
88.0			.8355
95.0	27.1	1326	
98.5			.8292
102.0	26.6	1304	
109.0	26.0	1280	
110.5			.8210
115.5	25.5	1262	
119.0			.8153
121.0	25.1	1245	
130.5	24.4	1217	
131.5			.8066
136.5	23.9	1196	
141.5			.7995
145.0			.7975
150.0	22.9	1157	
	Dicetyl		
73.2	27.2	1890	0.7791
83.7	26.4	1840	.7735

TABLE II (*Concluded*)

Temp., °C.	Surface tension, dynes	Molecular surface energy, ergs	Density, vac.	Temp. °C.	Surface tension, dynes	Molecular surface energy, ergs	Density, vac.
92.2	25.8	1810	0.7680	149.3	21.7	1570	0.7311
101.2	25.1	1760	.7622	123.7	23.4	1670	.7479
110.2	24.4	1721	.7565	86.2	26.0	1820	.7717
129.2	23.0	1640	.7440	119.2	23.7	1680	.7508
139.3	22.4	1610	.7375	139.3	22.3	1600	.7378

The precision which may be claimed in the measurements tabulated above is one part in two hundred for the surface tensions and one part in two thousand for the densities. All values were plotted on large scale graph paper and the temperature coefficients of the surface tensions and the Ramsay-Shields constants were determined from these graphs.

The data of interest are condensed in Table III. The last columns refer to "parachors," the apt name invented by Sugden[10] for the volume temperature relationship suggested by McLeod.[11] The experimental values of the parachor are the average obtained over eighty-degree tem-

TABLE III

CONDENSED DATA

Substance	Total surface energy, ergs	Ramsay-Shields constant	Parachor			Observers[a]
			Obs.	Calcd.	$\left(\frac{\text{Calcd.-obs.}}{\text{Obs.}}\right)100$	
Formic acid	68.3	0.90	93.3	102.2	+9.5	(1)
Acetic acid	58.0	1.35	130.8	141.2	+7.4	(2)
Propionic acid	56.8	1.53	168.7	180.2	+6.8	(3)
Butyric acid	54.6	1.65	209.1	219.2	+4.8	(3)
Caproic acid	53.4	2.04	287.2	297.2	+3.5	(3)
Caprylic acid	53.9	2.12	265.6	375.2	+2.6	(3)
Capric acid	55.2	2.36	447.7	453.2	+1.2	(3)
Lauric acid	54.4	2.56	532.8	531.2	−0.3	(3)
Myristic acid	54.9	2.80	605.8	609.2	+0.4	(3)
Palmitic acid	54.4	2.92	693.2	687.2	−0.9	(3)
Margaric acid	52.7	3.00	733.2	726.2	−1.0	(3)
Stearic acid	54.6	3.04	778.0	765.2	−1.7	(3)
Ethane	45.7	1.98	110.5	112.2	+1.6	(4)
Propane	50.0	2.15	150.8	151.2	+0.3	(4)
Hexane	45.5	2.11	270.4	268.2	−0.4	(5)
Octane	46.7	2.24	347.2	346.2	−0.3	(6)
Hexacosane	51.0	3.90	1082.0	1048.2	−3.0	(7)
Dodriacontane	52.0	4.20	1322.0	1282.2	−3.1	(3)
Hexacontane	47.0	5.50	248.0	2374.2	−5.1	(7)

[a] (1) Morgan and Neidle, THIS JOURNAL, **35**, 1856 (1913); (2) Morgan and McAfee, *ibid.*, **33**, 1275 (1911); (3) Authors; (4) Maass and Wright, ref. 6; (5) Harkins and Cheng, THIS JOURNAL, **43**, 35 (1921); (6) Ramsay and Shields, *Z. physik. Chem.*, **12**, 433 (1893); (7) Schenck and Kintzinger, *Rec. trav. chim.*, **42**, 759 (1923).

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[10] Sugden, *J. Chem. Soc.*, **125**, 1177 (1924).

[11] McLeod, *Trans. Faraday Soc.*, **19**, 38 (1923).

perature ranges. For all substances tabulated the parachor varied less than 1% over the eighty-degree range. Sugden discovered the additive character for the parachor and his values for carbon, hydrogen, oxygen and the double bond were used in the calculated values. Data required for the discussion based on experimental determinations not described in this paper are also included in Table III, together with the source from which they were obtained.

The first column in Table III is of particular interest from the point of view of the theory of orientation of Harkins[12] and Langmuir.[4b] Briefly this may be stated as signifying that the surface molecules are orientated with the most strongly attracting groups toward the bulk of the liquid and that the total surface energy is determined by the outer groups. According to this, then, the total surface energy in an homologous series should reach a constant value, and in the case of straight chain compounds the same value for all homologous series should be reached, namely, that of the saturated hydrocarbons. The first of these predictions seems to be proved by the values of the total surface energy of the fatty acids. There is a marked decrease in total surface energy from formic to acetic to propionic acid, but by the time the 4-carbon acid is reached a value is obtained which differs only slightly from the values of the subsequent acids up to the 18-carbon acid.

The variation in total surface energy between butyric and stearic acids is given by 54 ± 1 ergs. The question arises whether even this variation really exists. Undoubtedly the experimental determinations of the surface tensions were made with greater accuracy than necessary to detect this variation. However, in spite of the precautions taken in the purification of the compounds some of the rarer acids may have contained sufficient impurity to account for the variations found, and taking into account those acids for which large quantities were available and which could therefore be purified to a greater extent, the variation is given by 54.6 ± 0.3. On the whole, therefore, it may be concluded that the total surface energy reaches a constant value in this homologous series after the first few members of the series. However, as far as can be judged from the total surface energies of the saturated hydrocarbons, the series value for the acids is definitely higher. It is true that dicetyl and hexacosane have values approaching that of the fatty acids and that the low value for hexacontane may easily be due to an impurity in the latter. Nevertheless, taking all the evidence so far established, the value is decidedly less.

It does not seem probable that there is complete orientation in the surfaces of pure liquids such as exists in a monomolecular film spread over the surface of water. That there is a certain amount of orientation

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[12] Harkins, *This Journal*, **39**, 541 (1917).

may explain the rapidity with which the total surface energy reaches a constant value in the fatty acid series. These compounds have a polar group and a tendency for orientation in the surface exists. But this tendency is counteracted by thermal agitation with the result that the surface orientation is partial. By partial orientation is meant that, taken over a time interval, the average position of the axes of the surface molecules is perpendicular to the surface with the polar group nearest the main body of the liquid. The surface orientation differs from regional orientation (which may exist in the bulk of the liquid) both in its greater magnitude and in the fact that it is always in the same direction in the surface, whereas the direction of momentary orientation inside a liquid region changes from instant to instant.

The extent of the orientation in a surface will be increased by a strong polar group and by increased molecular size. In the paraffins, where there is no polar group, it seems probable that there is less chance for orientation and consequently the series constant will be reached far more slowly, which is in agreement with the facts.

The series constants of the fatty acids and the paraffins approach one another. This is, however, no proof of complete orientation since it seems likely that in any case the effect of X on the total surface energy in differentiating $C_nH_{2n+1}X$ from $C_nH_{2n+1}H$ must become nil when n is large enough.

It is desirable to bring more conclusive evidence in support of these views by further experimental determinations of the constants for the saturated hydrocarbon series and work along this line is under way.

The Ramsay–Shields constant K_e increases in a continuous way with length of carbon chain and this might be accounted for by orientation if $K_e = 2.12$ for all equimolecular surfaces. If all the fatty acids are completely orientated, the area occupied by any acid molecule is the same as the area occupied by a formic acid molecule. Hence, the volume which should be considered in the case of the higher fatty acids to obtain equimolecular surfaces is not that given by their molecular volume but by the portion which is proportional to the volume of formic acid. This reasoning gives $K_e = 0.94(M/46)^{2/3}$, where 0.94 is arbitrarily taken as the constant for formic acid (molecular weight 46) and K_e the constant for a higher acid of molecular weight M. The values for K_e calculated in this way are given in Table IV and are seen to be in reasonable agreement with the experimental values.

The above calculation is anything but rigorous and besides assumes that all the acids are associated to the same extent and have the same density. The agreement between calculated and experimental values may be purely accidental. Another relationship, based on still more dubious reasoning, gave $K_e = N^{1/2}(2.12/3.95)$, where N stands for the

TABLE IV

CALCULATED VALUES FOR THE RAMSAY-SHIELDS CONSTANT, K_e

No. of carbon atoms in acid	K_e, experimental	K_e calcd. by $K_e = 0.94\text{-}(M/46)^{2/3}$	K_e calcd. by $K_e = M^{4/9}\text{-}(2.12/3.95)$	No. of carbon atoms in acid	K_e, experimental	K_e calcd. by $K_e = 0.94\text{-}(M/46)^{2/3}$	K_e calcd. by $K_e = N^{4/9}\text{-}(2.12/3.95)$
1	0.90	0.94	0.85	10	2.36	2.26	2.36
2	1.35	1.22	1.16	12	2.56	2.50	2.56
3	1.53	1.29	1.38	14	2.80	2.73	2.80
4	1.65	1.45	1.57	16	2.92	2.95	2.92
6	2.04	1.74	1.88	17	3.00	3.06	2.99
8	2.12	2.01	2.14	18	3.04	3.16	3.04

number of carbon atoms in the acid. In Table IV the values of K_e calculated in this way are shown to be in close agreement with all the experimental values and in absolute agreement as far as the last seven acids are concerned. This relationship may, therefore, be used as an empirical one but possessing sufficient accuracy for extrapolating the values of K_e for higher fatty acids.

If the high values of the Ramsay and Shields constant are to be explained by the complete orientation in the surfaces of the fatty acids, then the high values of this constant in the case of the higher paraffins show that these are orientated to the same extent. The fatty acid with 32 carbon atoms would have a value 4.0, which is approximately that found for dicetyl. This might not be so bad were it not for the values of the Ramsay and Shields constant which have been obtained for tristearin and tripalmitin.[13] These are 5.4 and 5.5, respectively, whereas the extrapolated values for straight chain fatty acids of 57 and 51 carbon atoms are 4.9 and 5.1, respectively. In other words, the tristearin molecule has the same effect on the Ramsay-Shields constant as a fatty acid of the same number of carbon atoms, although the latter is three times as long. It seems unlikely, therefore, that the high values for the Ramsay-Shields constant can be accurately interpreted in terms of complete orientation. It is far more striking that hexacontane, tristearin and a fatty acid of similar carbon atom content have practically the same abnormally high value for the Ramsay-Shields constant.

It is of considerable interest to compare simultaneously the Ramsay-Shields constant and the percentage difference of calculated and observed values of Sugden's parachor. The parallelism is perhaps to be expected due to the manner in which the two are related. The figures in Table III show that in both series the Ramsay-Shields constant is first too low and then too high and that the observed parachor is at first too low and then too high. That the latter are too high in the case of the compounds of high molecular weight is established beyond the limit of experimental error.

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[13] Walden, *Z. physik. Chem.*, **75**, 55 (1910).

It has been suggested that where the observed value of the parachor is too low this is due to association, just as the low value of the Ramsay-Shields constant is ascribed to the same cause. If this is so it appears reasonable to suppose that the cause for the abnormally large values of parachor and Ramsay-Shields constant are due to the same cause, whatever it may be. From the nature of the constants the Ramsay-Shields constant is more sensitive to the surface tension factor, while the parachor is more sensitive to the density factor. The former shows a more marked change from the normal than the latter with increase in molecular weight, so that something must be taking place which affects the surface in an abnormal way. That this something is a partial orientation of the surface molecules is a plausible hypothesis. The suggestion that the variation from the normal in the case of the Ramsay-Shields constant is due to the form of the molecule or spiral formation is not sufficient unless orientation in the surface is supposed to take place also.

Summary

The surface tensions and densities of ten fatty acids and one long chain paraffin have been measured over a hundred degree range of temperature and their angles of contact with glass were shown to be zero.

The viscosities of palmitic, margaric and stearic acids were measured.

It was shown that the total surface energies of the fatty acids quickly reach a series constant, whereas the series constant for the paraffins is reached more slowly. As far as can be judged from the known experimental data the two series constants approach each other but do not reach the same value rapidly.

The Ramsay-Shields constant was shown to increase rapidly in the case of the fatty acids and could be represented by the relationship $K_e = N^{4/9}(2.12/3.95)$. The constant was found to have abnormally high values in the case of the higher paraffins.

The parallel variation from the normal of the Ramsay-Shields constant and Sugden's parachor was pointed out and ascribed to the same cause, whatever it might be.

It was shown in the discussion on the total surface energy and the abnormally high values of the Ramsay-Shields constant that the former do not indicate complete orientation at the surface and the latter cannot be calculated quantitatively in terms of complete orientation. Nevertheless, it is suggested that a partial orientation takes place in the surface of a pure liquid and that the regularities in the former and the abnormal values of the latter are due to this partial orientation.

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