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Surface Tension Determinations of Some Saturated Fat Acid Methyl Esters[1,2]

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SEVERAL of the physical properties of highly purified methyl esters of the naturally occurring saturated fat acids have been studied within the past few years. These include refractive index (1, 11, 14), vapor pressure (2, 3, 10), viscosity (3), and density (3). Since surface energy phenomena have long been recognized as important properties of fats and fatty compounds, the surface tension measurements of the methyl esters of fat acids should be of value from both theoretical and practical standpoints.

Preparation and Purification of the Esters

The methyl esters were prepared by direct esterification of the appropriate fat acids with methyl alcohol. For a rough purification the esters were distilled through a Claisen-head at 2-3 mm. of mercury pressure. The resulting esters were hydrogenated in a shaker-type bomb with 10%, by weight, nickel catalyst (Universal Oil Products) at 170°C. and 1300 p.s.i. for one hour. Final purification consisted of fractional distillation through a low pressure fractionating column packed with glass curls.

The refractive indices of the methyl esters as measured by a Valentine Precision Refractometer, are recorded in Table I to an accuracy of ± 0.0001. The refractometer was calibrated with National Bureau of Standards samples of 2,2,4-trimethylpentane and of methylcyclohexane. Table I also includes the boiling temperatures of these esters at 2 and 10 mm. Hg. These values were obtained with the vapor pressure apparatus described by Liang (10).

TABLE I

Refractive Indices and Boiling Temperatures of the Methyl Esters

Methyl Esters	$n_D^{40°C.}$	Boiling Temp. °C. 2 mm. Hg.	Boiling Temp. °C. 10 mm. Hg.
Methyl caproate	1.3961	15.3	42.5
Methyl caprylate	1.4084	48.2	77.3
Methyl caprate	1.4173	77.5	108.4
Methyl laurate	1.4236	104.9	136.7
Methyl myristate	1.4288	128.6	162.1
Methyl palmitate	1.4330	147.9	184.8
Methyl stearate	1.4362	168.4	207.5

Apparatus and Methods

The more common, basic methods of determining surface tension are all difficult operations. Moreover they require time, complicated apparatus, or fairly large samples. In determining the surface tension of the fat acid methyl esters, it was of prime importance to use a rapid method requiring a minute amount of sample.

Ferguson (5, 6) has devised two related methods of determining the surface tension of 1-2 cu. mm. of liquid. They are modifications of the capillary rise method and consist of measuring the pressure that is required to force the meniscus of a liquid at the end of a capillary from a curved to a plane surface. The method used in this study employs a horizontal capillary with a plane-ground end into which is inserted a short thread of the test liquid. Pressure is then applied until the end meniscus forms a plane surface. This pressure is measured by an attached manometer and is equal to the difference in pressure across the curved surface within the capillary. Thus

$$P = h' \rho' g = 2\gamma/R$$

where P = applied pressure; h′ = manometer reading in centimeters; ρ′ = density of manometer liquid; g = acceleration due to gravity; γ = surface tension of test liquid; R = radius of curvature of the test liquid meniscus. If the contact angle between the glass and the liquid is zero, and if the bore of the capillary is small enough, the meniscus will be hemispherical. Also if the gravitational distortion of the meniscus is so slight as to be negligible, then the radius of the capillary (r) may be substituted for the radius of curvature of the meniscus (R) giving a simple working equation

$$\gamma = \tfrac{1}{2} r g \rho' h'$$

By comparing results using first a horizontal and then a vertical capillary, Ferguson (6) proved experimentally that the gravitational distortion of the meniscus was negligible if capillaries of less than 0.5 mm. radius were employed.

A diagram of the apparatus used in this work is shown in Figure 1. The procedure for making a determination is as follows: a clean, dry capillary tube is attached at (H) by means of its standard taper ground glass joint. A drop of sample is drawn into the capillary by means of capillary attraction. This thread of liquid is adjusted to between 0.50 and 0.75 cm. in length, and the excess is removed from the plane ground end of the capillary with lens tissue. The constant temperature air bath is moved into place surrounding the capillary. Next the hand lens is adjusted to catch the reflection of the lamp filament on the surface of the meniscus of the liquid in

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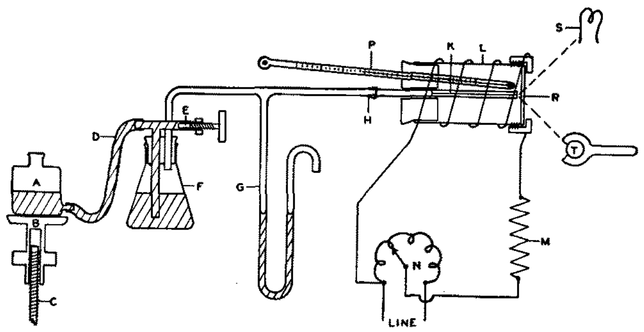

FIG. 1. Surface tension apparatus.

the capillary. While observing this reflection, pressure is applied until the curved surface of the meniscus has been forced to a plane surface. This is accomplished roughly by raising the leveling bottle (A) and finally by means of the fine adjustment set-screw at (E). The surface is considered plane when it reflects an overall, uniform sheen of light (a curved surface reflects either an image of the lamp filament or an uneven distribution of light). When the pressure has been adjusted, the temperature is read on the thermometer. Then the height of the aniline in each arm of the manometer is read by means of a cathetometer. The difference in height gives the pressure in centimeters of aniline.

The capillaries were prepared from 0.25-0.75 mm. I.D. thick-walled, Pyrex glass tubing. The working ends were ground to a plane, perpendicular surface using progressive abrasives, including a final polishing with jewelers' rouge. Diameter of each capillary was measured at the plane-perpendicularly ground end by means of a traveling microscope equipped with a vernier reading to 0.001 mm. By rotating the capillary through 45°, readings were taken at eight different diameters. All measurements agreed within ± 0.001 mm. The radius of the capillary was then taken as being one-half of the measured diameter. The capillaries were cleaned in hot sulfuric-dichromate cleaning solution and rinsed for two to three hours by running distilled water through them before each surface tension measurement. The capillaries were dried in an oven at 100°C. Just before use, filtered, dried air was drawn through them for four to five minutes.

The aniline used as the manometer liquid was redistilled over zinc dust through a Vigreaux column. Its density was determined and calculated to be 1.021 gm./ml. at 20°C.

The manometer readings were made with a cathetometer provided with a vernier permitting measurements to ± 0.01 cm. This cathetometer was calibrated by direct comparison with a more precise cathetometer which had a variance of less than ± 0.001 cm./cm. as determined by a standard meter bar. No corrections were applied to any of the manometer measurements made in this work because the limit of error of the cathetometer used was found to be ± 0.005 cm./cm.

The acceleration of gravity has been accurately determined at the Meteorological Laboratory and Observatory in State College, Pennsylvania, and is recorded as 980.134 cm./sec.^{2}

Surface Tension Measurements of Water and Benzene

In surface tension determinations water and benzene are accepted as "standards." The following values, taken as absolute, are those recorded in the International Critical Tables (9):

> Water at 20°C. in air—72.75 ±0.05 dynes/cm. This value was obtained from the capillary height determinations of Richards and Coombs (13), Harkins and Brown (8), Richards and Carver (12), and Young and Gross (15).
>
> Benzene at 20°C. in air—28.88 ± 0.03 dynes/cm. Similarly, this was the value obtained by Richards and Coombs (13), Richards and Carver (12), and Harkins and Brown (8).

The water used in this work was triple distilled conductivity water. The sample was stored in a Pyrex glass-stoppered bottle which had been leached in boiling distilled water 25 times previous to its use. The benzene used was Merck's, thiophene free, reagent grade which was redistilled through a glass packed fractionating column.

Surface Tension Determinations of the Methyl Esters

Surface tension measurements were made on the purified methyl esters at three different temperatures: 40° C., 60° C., and 80° C. ± 0.5° C. A minimum of 12 separate determinations was made on each ester at each temperature. The centimeters of aniline measured could be checked to ± 0.01 cm. from the mean. This gives an accuracy for the calculated surface tension of ± 0.15 dynes/cm. Since all other measurements used in the determinations are to a higher degree of accuracy than the cathetometer readings, the surface tensions of the methyl esters are reported in Table II with a limit of error of ± 0.15 dynes/cm.

TABLE II

Surface Tensions of the Methyl Esters at Various Temperatures

Methyl Esters	Surface Tension[a] Dynes/cm. at Atmos. Pressure			
	40°C.	60°C.	80°C.	$-\frac{\Delta\gamma}{\Delta t}$
Methyl caproate	24.2	22.5	20.7	.0875
Methyl caprylate	25.2	23.6	21.8	.0850
Methyl caprate	26.1	24.6	22.8	.0825
Methyl laurate	27.0	25.4	23.8	.0800
Methyl myristate	27.8	26.0	24.6	.0800
Methyl palmitate	28.4	26.8	25.3	.0775
Methyl stearate	29.1	27.5	26.0	.0775

[a] Limit of error ± 0.15 dynes/cm.

With the limited data obtained it is seen that the surface tensions of the methyl esters of the fat acids decrease with increasing temperature, apparently in a linear manner (Figure 2). This is in accordance with the same relationship in other homologous series. As the molecular weight of the methyl ester series increases, the surface tension increases, but at a slowly decreasing rate, which appears to be the same at the three temperatures studied (Figure 3). This relationship between molecular weight and surface tension is in very close agreement with what would be expected by calculations from the parachor formula.

Gibling (7) has produced what appears to be one of the best systems of parachor calculations. He assigns parachor values to groups of atoms, based

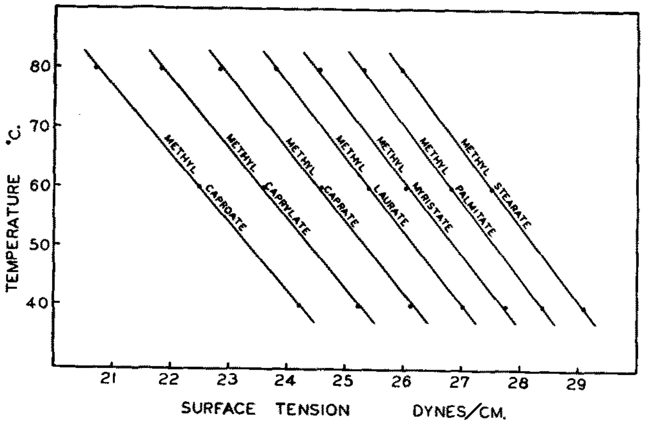

FIG. 2. Relation of surface tension to temperature of the methyl esters of some saturated fat acids.

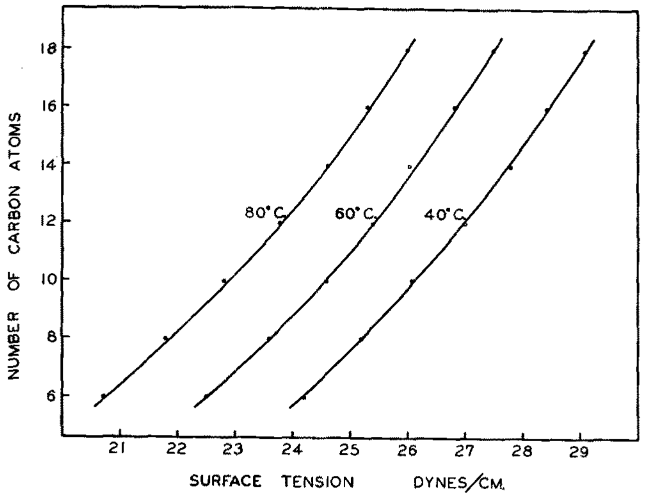

FIG. 3. Relation of surface tension to number of carbon atoms of the methyl esters of some saturated fat acids at various temperatures.

upon composition and linkage. Furthermore he proposes that the ΔCH_2 difference is not constant in any homologous series but increases progressively from member to member.

The calculated parachors used in our work are based upon Gibling's system of values. In Table IV they are compared with the experimental parachors determined at three different temperatures. In determining the experimental parachors the liquid densities of the methyl esters were calculated to the third decimal place from values reported by Bonhorst (3) (Table III). The densities of the saturated vapor of the methyl esters were neglected. This was done only after estimating the vapor densities of the two lower members of the series by the following correlations (4).

$$\log (D_v/D_b) = 5\,[T/T_b - 1]$$

$$D_b = 0.0122\,M/T_b$$

Where D_v equals the density of the vapor in gm./cc., D_b the density of the liquid at its normal boiling point, T the absolute temperature in °K., T_b the absolute normal boiling point in °K., and M the molecular weight. These two vapor densities were considerably less than the precision to which the liquid densities are taken.

TABLE III

Densities of the Methyl Esters at Various Temperatures

Methyl Esters	Densities in gm./ml.		
	40°C.	60°C.	80°C.
Methyl caproate	0.865	0.846	0.827
Methyl caprylate	0.860	0.842	0.824
Methyl caprate	0.856	0.840	0.823
Methyl laurate	0.854	0.838	0.822
Methyl myristate	0.852	0.836	0.821
Methyl palmitate	0.850	0.835	0.820
Methyl stearate	0.851	0.836	0.821

TABLE IV

Parachors of the Methyl Esters at Various Temperatures

Methyl Esters	Calculated Parachor	Experimental Parachor		
		40°C.	60°C.	80°C.
Methyl caproate	333	334	335	335
Methyl caprylate	413	412	413	415
Methyl caprate	493	491	492	493
Methyl laurate	574	572	573	573
Methyl myristate	654	654	654	656
Methyl palmitate	735	734	735	738
Methyl stearate	816	815	818	823

Table IV shows good correlation between the calculated and experimental parachors considering the experimental error of the surface tension measurements.

Summary

Methyl esters of saturated naturally occurring fat acids from C_6 through C_{18} were prepared and purified by fractional distillation. Refractive indices were used as a measure of their purity. A micro surface tension apparatus was constructed to comply with a modified capillary rise method devised by Ferguson. The surface tensions of water and of benzene were determined at several temperatures. The results obtained compared quite favorably with the values listed in the International Critical Tables. The surface tensions of the methyl esters were determined at 40°C., 60°C., and 80°C. with an accuracy of ± 0.15 dynes/cm. Similar to other homologous series the surface tensions of the fat acid methyl esters decrease with increasing temperature, apparently in a linear manner. As the molecular weight of the methyl ester series increases, the surface tension also increases. Close correlation is shown for the methyl esters between the calculated parachors based upon Gibling's system of values and the experimental parachors.

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