Surface and Interfacial Tensions, Viscosities, and Other Physical Properties of Some n-Aliphatic Acids and Their Methyl and Ethyl Esters[1]

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THE physical constants of the common fatty acids and their monoesters are useful in the development of processes, products, and in the design of research experiments involving these compounds. It is often desirable to know the change of a given constant among members of the homologous series as well as its exact numerical value. Despite the general availability of the common fatty acids and their monoesters and despite the relative ease and simplicity with which many of their physical properties can be measured, numerical data for surface tension, interfacial tension, viscosity, density, and refractive index are relatively scarce.

Surface tensions have been determined more frequently than some of the other physical constants. Wachs, Umstätter, and Reitstötter (21) determined surface tensions at 75° C. of the saturated *n*-fatty acids from C_{10} through C_{19} and plotted them against the number of carbon atoms in the acid chains. Surface tensions for the saturated, even-numbered *n*-fatty acids from C_4 to C_{18} over a wide range of temperatures have been given by Hunten and Maass (15). A few other determinations of surface tensions of pure fatty acids have been reported at various temperatures.

Vogel (20) measured the surface tensions of various pure monoesters of fatty acids at several temperatures. Since completion of the present experimental work an article by Nevin, Althouse, and Triebold (18) has appeared in which the surface tensions of the methyl esters of the saturated, naturally occurring fatty acids from C_6 through C_{18} are recorded. There are practically no published data for the interfacial tension of the fatty acids or their monoesters against water.

In a classical investigation of the relationship between the viscosity of liquids and their chemical nature Thorpe and Rodger (19) determined the viscosity of many compounds, including the lower members of the normal aliphatic series of acids and their methyl and ethyl esters. Later Dunstan and co-workers (8, 9) determined the viscosities of some additional fatty acids and methyl and ethyl esters of fatty acids. A number of other investigators (4, 5, 11, 13, 15) have measured the viscosity of fatty acids or their methyl or ethyl esters, but apparently the viscosities of some common methyl esters have never been reported. The viscosities of an extended series of the common fatty acids and their methyl and ethyl esters have never been compared at the same temperature.

Densities of the saturated fatty acids have been reported at many scattered temperatures, and some systematic investigations of density have been made (7, 10, 15). Densities of the methyl esters of the *n*-fatty acids from caproic to stearic were determined by Bonhorst *et al.* (5). A number of other workers have reported densities of methyl and ethyl esters of saturated acids, but the values quite often are not comparable owing to their determination at different temperatures. Also it appears that values for certain ethyl esters have never been reported.

Few systematic investigations have been made of the refractive indices of the fatty acids and their esters. The investigation by Dorinson *et al.* (7) is practically the only one of recent date concerned with fatty acids. The refractive indices of the methyl esters have been determined in three systematic investigations (10, 16, 22), but none of the three included the methyl esters of all the even-numbered *n*-fatty acids from C_2 to C_{18}. Apparently no comparable investigation has been made of the refractive indices of the ethyl esters.

In the present report values of surface tension, interfacial tension against water, viscosity, density, and refractive index, all at 75°C., will be presented for the saturated, even-numbered, *n*-fatty acids from C_2 through C_{18} and for their methyl and ethyl esters. The change in the values of the various physical properties with chain length will be shown, and the values of the physical properties for the acids, methyl esters, and ethyl esters will be compared. The effect of temperature on the various physical constants will be shown for one of the acids.

Materials

The saturated, even-numbered, *n*-fatty acids from C_4 through C_{14} used in the experimental work were obtained in pure form from a commercial source. Commercial reagent grade acetic acid was purified by fractional crystallization. Palmitic and stearic acids were prepared from commercial products of 90% purity by repeated fractional crystallization from acetone.

The fatty acids from caproic through stearic were converted to the corresponding methyl esters by refluxing one part of fatty acid with four parts of anhydrous methanol for three hours in the presence of 3% (on a fatty acid plus alcohol basis) of concentrated sulfuric acid. Most of the excess alcohol was removed from the esters by evaporation, and the mineral acid was removed by washing with distilled water. Unesterified fatty acids were removed by first washing with a dilute solution of sodium carbonate and then with distilled water.

The methyl esters were dried by heating under vacuum and stripping with hydrogen. The methyl esters from caproate through myristate were distilled through a fractionating column under a constant pressure of 10 mm. of mercury. The column, which was 18 mm. in inside diameter, 56 cm. long, and packed with 3/16-in. single-turn, glass helices, was surrounded

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with hot circulating Arochlor[3] in a double-walled Thiele-tube insulating jacket (17) to maintain the distillation as adiabatic as possible. The methyl ester fractions, boiling at the temperatures established by Althouse and Triebold (2), were used in making the physical measurements.

The methyl palmitate and methyl stearate were purified by repeated fractional crystallization from acetone. Methyl butyrate and all of the ethyl esters were obtained in the pure form from a commercial supplier.

Purities of the acids and esters were estimated to be 99% or higher. These estimations were based in part on comparisons of the neutralization values of the acids and the saponification values of the esters (3) with their respective theoretical values. The melting points of those acids and esters which were solid above 0°C. were determined and were found to check closely with the accepted literature values. Also the values for surface tension, refractive index, etc., determined for the acids and esters agreed with the accepted literature values where such were available.

Measurements

Surface and interfacial tensions were measured with a Cenco-du Noüy Interfacial Tensiometer[3] using a platinum-iridium ring of 6.010 cm. mean circumference. The ratio of the radius of the ring to that of the wire of the ring (R/r) was 52.0. Measurements were made in 250-ml. beakers having an inside diameter of approximately 7 cm. For the surface tension measurements a relatively small amount of acid or ester was placed in the beaker and, in order to submerge the ring below the surface of the acid or ester, the shaft connecting the ring to the tensiometer was lengthened with a short piece of stainless steel tubing.

The beakers in which the surface and interfacial tension measurements were made were immersed in a constant temperature bath and each measurement was made within ± 0.5°C. of the desired temperature. All experimental values obtained were corrected by applying the correction factors determined by Harkins and Jordan (14).

Coefficients of viscosity were determined in capillary viscosimeters of the Ostwald-Cannon-Fenske type (6). The viscosimeters, of 5-ml. capacity, were calibrated with carbonate-free water, which has a viscosity of 0.3806 centipoise at 75°C. During the measurements the viscosimeters and their contents were maintained at the desired temperature in a thermostatically controlled water bath. An average value of six to eight determinations on each compound was used in the calculations. Corrections for the kinetic energies of efflux were considered negligible.

Density determinations were made using Weld-type specific gravity bottles of approximately 10-ml. capacity. The filled bottles were suspended in a thermostatically controlled water bath, the temperature of which was maintained at 75 ± 0.1°C. All determinations were repeated once or twice as a check on the values obtained.

Indices of refraction were determined at 75°C. with a Valentine Precision Refractometer[3] using a sodium vapor lamp as the source of light. The prism temperature was controlled to ± 0.1°C. by circulating water from a constant temperature bath around the prism. The refractometer was calibrated with the aid of a test plate of known refractive index attached to the upper prism by a film of monobromonaphthalene. Values were read to ± 0.0001 index unit.

The temperature of 75°C. was chosen for most of the measurements because it was just above the melting point of stearic acid, which was the highest-melting compound under investigation. At this temperature only methyl acetate (B.P., 57.1°C.) was too volatile for measurements to be made.

Results and Discussion

Surface Tension. With the information presently available the surface tension of a liquid can be related to its molecular structure in only a very general manner. It is influenced by factors which include temperature; the size, shape, and degree of association of the molecules of the liquid; their degree of mutual attraction; and their degree of orientation in the surface of the liquid. The surface of a saturated fatty acid, which is quite polar in nature, would be predicted to be more highly oriented than that of its methyl or ethyl ester; consequently the surface tension of the fatty acid would be greater than that of its esters. This prediction is borne out by the data plotted in Figure 1. The surface tension values for the fatty acids are consistently about 2.0 dynes/cm. higher than the values for the corresponding ethyl esters. The difference between the fatty acids and methyl esters is approximately 1.8 dynes/cm. The surface tensions for the methyl esters are from 0.2 to 0.4 dyne/cm. higher than those for the corresponding ethyl esters.

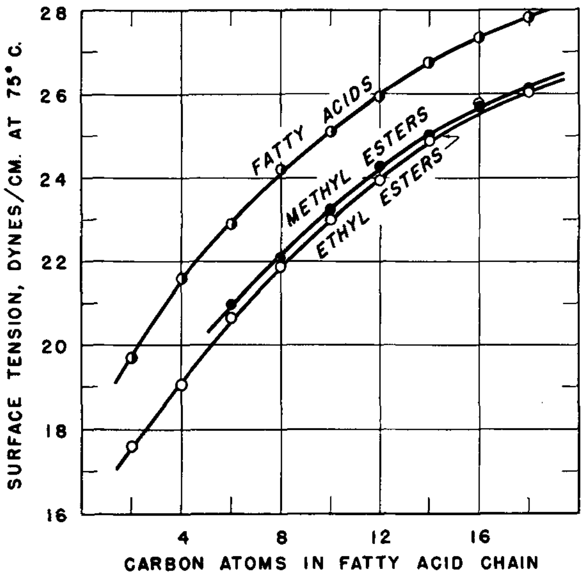

FIG. 1. Surface tensions at 75°C. of the *n*-fatty acids and esters as a function of the number of carbon atoms in the fatty acid chains.

The surface tension values for the homologous series of saturated even-numbered, *n*-fatty acids increase from 19.65 dynes/cm. for acetic acid to 27.74 dynes/cm. for stearic acid, but this increase is not linear with the increase in the number of carbon atoms in the acid chain. This behavior is also in accord with generally accepted theory. The carbon chains of the fatty acids tend to orient themselves so that the hydrocarbon ends of the molecules are

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[3] The mention of trade products does not imply that they are endorsed by the Department of Agriculture over similar products not mentioned.

TABLE I

Physical Constants of Saturated, Even-Numbered *n*-Fatty Acids and Their Methyl and Ethyl Esters at 75°C.

Carbon atoms in fatty acid chain	Surface tension, dynes/cm.			Interfacial tension against water, dynes/cm.			Viscosity, centipoises			Density, g./cc.			Refractive index, n_D		
	Fatty acid	Methyl ester	Ethyl ester	Fatty acid	Methyl ester	Ethyl ester	Fatty acid	Methyl ester	Ethyl ester	Fatty acid	Methyl ester	Ethyl ester	Fatty acid	Methyl ester	Ethyl ester
2	19.6	......	17.8	......	......	......	0.622	......	0.269	0.8978	......	0.8320	1.3505	......	1.3442
4	21.6	......	19.0	......	......	......	0.728	0.328	0.363	0.9043	0.8359	0.8205	1.3758	1.3608	1.3658
6	23.0	21.0	20.8	2.1	13.9	14.6	1.279	0.407	0.537	0.8796	0.8313	0.8198	1.3944	1.3803	1.3849
8	24.2	22.1	21.9	5.8	17.2	18.2	1.855	......	0.716	0.8662	0.8287	0.8191	1.4069	1.3937	1.3946
10	25.1	23.3	23.1	8.0	20.0	21.2	2.563	0.985	0.999	0.8583	0.8271	0.8196	1.4149	1.4033	1.4041
12	25.9	24.3	23.9	8.7	22.0	22.9	3.836	1.131	1.230	0.8516	0.8259	0.8195	1.4208	1.4099	1.4107
14	26.8	25.0	24.9	9.2	23.5	24.3	5.060	1.528	1.643	0.8481	0.8252	0.8197	1.4251	1.4148	1.4148
16	27.3	25.7	25.7	9.2	25.5	25.5	7.082	......	2.003	0.8446	0.8247	0.8198	1.4288	1.4196	1.4190
18	27.7	26.1	26.1	9.5	26.2	25.2	9.040	2.360	2.590	0.8431	0.8244	0.8218	1.4318	1.4231	1.4225

toward the surface and the chains are perpendicular to the surface. As the length of the chain increases, the disruptive effect of thermal agitation becomes less pronounced and the surface tension increases. It would be expected that the effect of increasing chain length on surface tension would be more marked for the shorter-chain acids.

Reasoning somewhat analogous to that used regarding the fatty acids can also be applied to the homologous series of methyl and ethyl esters. The exact numerical values of the surface tensions and other physical constants of the saturated even-numbered *n*-fatty acids and their methyl and ethyl esters are recorded in Table I.

The surface tension of a liquid generally decreases with increasing temperature and, in many cases, this decrease is approximately linear over long temperature ranges. The fatty acids and their methyl and ethyl esters follow these general rules. The change in surface tension per degree change in temperature reported by Nevin *et al.* (18) for the methyl esters from caproate through stearate was approximately 0.08 dyne/cm. for the temperature interval 40° to 80°C. In the present investigation the surface tension of myristic acid at different temperatures is recorded in Table II. In the temperature range shown the surface tension of myristic acid decreases about 0.09 dyne/cm. for each degree increase in temperature.

TABLE II

Effect of Temperature on the Physical Properties of Myristic Acid

Temperature	Surface tension	Interfacial tension against water	Viscosity	Density	Refractive index
°C.	*dynes/ cm.*	*dynes/ cm.*	*centipoises*	*g./cc.*	n_D
60	28.4	8.7	7.93	0.8584	1.4310
75	26.8	9.2	5.06	0.8481	1.4251
90	25.6	9.5	3.67	0.8394	1.4200

Parachor values were determined for the fatty acids, methyl esters, and ethyl esters from the surface tensions and the densities given in Table I. The parachor values found were generally in excellent agreement with those calculated with the aid of Gibling's parachor equivalents (12), which are the best currently available. The experimentally found and the calculated parachors are recorded in Table III.

Interfacial Tension. The interfacial tension between two liquids is generally less than the larger of their surface tensions because the mutual attraction across the interface between the molecules of one liquid and those of the other tends to counteract the inward pull of the molecules in the surface by those of its own kind. The interfacial tension between water and a fatty acid should be quite low since fatty acid molecules contain a polar —COOH group which is strongly attracted to water. It would be expected that the methyl or ethyl ester of a fatty acid would have a greater interfacial tension against water than would the acid. In Figure 2 these relationships are shown quantitatively for the saturated, even-numbered, *n*-fatty acids having six through 18 carbon atoms in their chain and for the methyl and ethyl esters of these acids.

TABLE III

Parachors of Saturated, Even-Numbered, *n*-Fatty Acids and Their Methyl and Ethyl Esters

Carbon atoms in fatty acid chain	Parachor					
	Fatty acid		Methyl ester		Ethyl ester	
	Calc.	Found	Calc.	Found	Calc.	Found
2	260	256	177	......	217	218
4	415	420	254	......	294	296
6	572	578	333	328	373	375
8	734	739	414	414	454	455
10	896	899	494	495	534	536
12	1056	1061	575	576	614	616
14	1221	1223	655	657	695	698
16	1384	1388	737	738	777	781
18	1548	1549	817	819	856	859

This figure also shows the effect of increasing chain length on the interfacial tension between water and the fatty acids, methyl esters, and ethyl esters, respectively. For the fatty acids the interfacial ten-

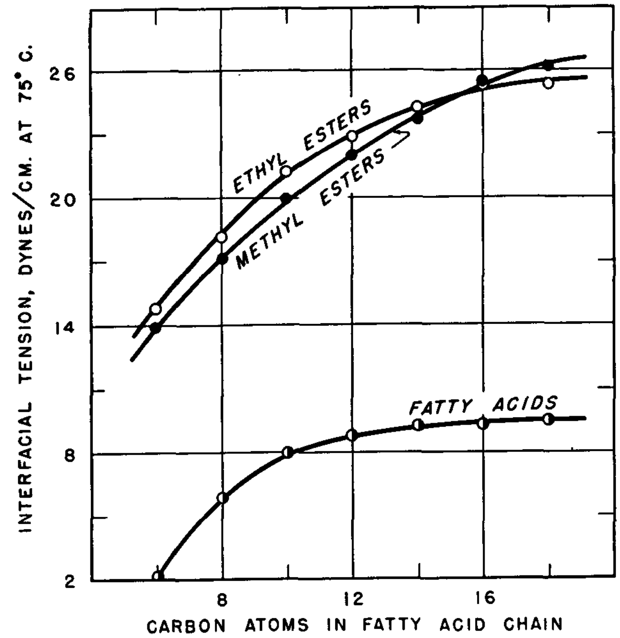

FIG. 2. Interfacial tensions of the *n*-fatty acids and esters against water at 75°C., shown as a function of the number of carbon atoms in the fatty acid chains.

sions which were determined at 75°C., increase from 2.1 dynes/cm. for caproic acid to 9.5 dynes/cm. for stearic acid. For the methyl esters this increase is from 13.9 dynes/cm. for the caproate to 26.2 dynes/cm. for the stearate; and for the ethyl esters the increase is from 14.6 dynes/cm. for the caproate to 25.2 dynes/cm. for the stearate.

The curve for the fatty acids reveals that the interfacial tensions against water are almost identical for myristic, palmitic, and stearic acids. These fatty acid chains are apparently of sufficient length that solubility in water and thermal agitation in water have similar effects on the three fatty acids insofar as it concerns the displacement of their —COOH groups "anchored" at the oil-water interface. The concentration of the hydrophilic —COOH groups at the interface, which is a prime factor in establishing the amount of interfacial tension, is determined by the cross-sectional area of the hydrocarbon chains and is independent of their length for the longer chain length acids.

Interfacial tensions of acetic acid, butyric acid, and the methyl and ethyl esters of these acids against water are not included in Figure 2 because these compounds were either miscible with or markedly soluble in water.

The effect of temperature on the interfacial tension between water and the fatty acids or their monoesters is comparatively small. The surface tensions of the fatty materials and water, which is a factor in their interfacial tension, both decrease with increasing temperature and their actual difference remains about constant. Data presented in Table II show the effect of temperature on the interfacial tension between myristic acid and water. An increase in temperature from 60° to 90°C. increased the interfacial tension only 0.8 dyne/cm.

Viscosity

The viscosity of each of the fatty acids together with that of most of their methyl and ethyl esters was determined at 75°C. The results obtained are recorded in Figure 3. Viscosity measurements were also made on myristic acid at different temperatures, and these results are recorded in Table II.

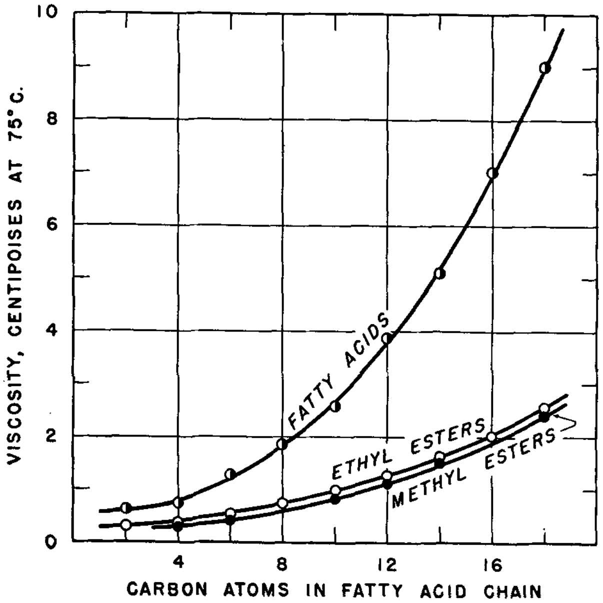

FIG. 3. Absolute viscosities at 75°C. of the n-fatty acids and esters as a function of the number of carbon atoms in the fatty acid chains.

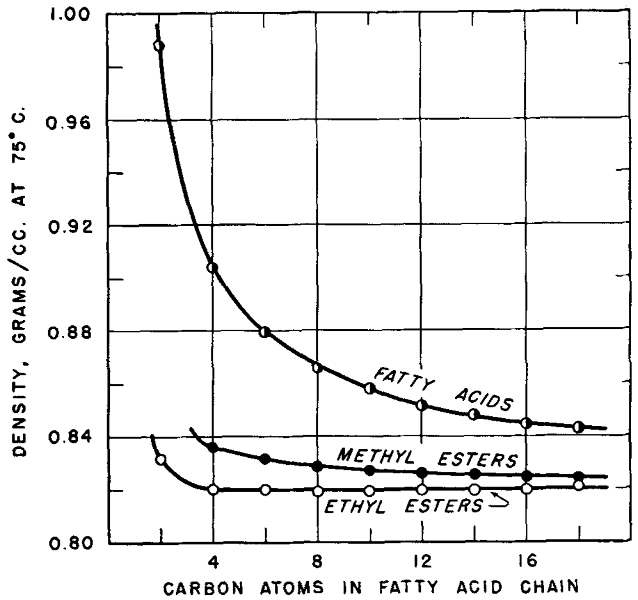

FIG. 4. Densities at 75°C. of the n-fatty acids and esters as a function of the number of carbon atoms in the fatty acid chains.

It is shown in Figure 3 that the viscosities of the fatty acids and esters increase with increasing chain length. For the fatty acids the viscosities increase from 0.662 centipoise for acetic acid to 9.040 centipoises for stearic acid. For the ethyl esters the viscosity increases from 0.269 centipoise for ethyl acetate to 2.269 centipoises for ethyl stearate. The methyl ester possesses a viscosity about 0.15 centipoise lower than that for the corresponding ethyl ester.

The fact that the viscosity of a given fatty acid is higher than that of its methyl or ethyl ester is, of course, generally recognized and is attributed mainly to hydrogen bonding. The carboxyl groups of the fatty acid molecules tend to associate and form dimers which impede flow to a greater extent than would single molecules.

Work by Thorpe and Rodger (19) showed that in an homologous series each additional CH_2 group contributes an increment to the viscosity; but the increment is not constant, depending upon such factors as the number of CH_2 groups already present, end groups, and temperature. Beyond this generalization little of a mathematical nature is known concerning the relationship between molecular structure and viscosity.

In comparing the viscosities it must be recognized that there is a fundamental difference between viscosity and physical properties like surface tension, interfacial tension, density, and refractive index. The latter may be considered as approximately linear functions of the temperature when the acids and esters are in the liquid state, but viscosity is an exponential function of the absolute temperature. The relative differences in viscosity between the fatty acids and their esters shown in Figure 3 will change with temperature. At 75°C. the viscosity of stearic acid is quite sensitive to changes in temperature, but that of lower melting components like acetic and butyric acid is not. However at all temperatures a given fatty acid is more viscous than its ethyl ester, which in turn is more viscous than the methyl ester.

Density. The densities of the fatty acids and their methyl and ethyl esters determined at a temperature of 75° C. are plotted in Figure 4 as a function of chain length. It is evident that the densities of the fatty acids are greater than those for the corresponding methyl esters, whose densities in turn are greater than those for the corresponding ethyl esters. The differences between the densities of the acids, methyl esters, and ethyl esters are most marked at the shorter chain lengths. The densities of the fatty acids decrease relatively rapidly as the chain length increases, particularly at the shorter chain lengths. The ethyl ester series shows perhaps the most remarkable trend: there is no detectable decrease in density with increasing chain length beyond ethyl butyrate.

The density of fatty acids and their methyl and ethyl esters is a linear function of temperature. A typical effect of temperature on density is shown in Table II. Calculations based on the data recorded in this table reveal that the density of myristic acid decreases 0.0063 gram/cc. for each degree increase in temperature over the temperature range of 60° to 90°C.

Refractive Index. The refractive indices determined at 75°C. for the fatty acids and their methyl and ethyl esters are plotted as a function of chain length in Figure 5. It is evident that in all cases the refractive index increases rapidly with increasing chain length, but the increase is most rapid for the shorter chain lengths. The refractive index of a fatty acid is greater than that for the corresponding methyl and ethyl ester. The refractive indices for the methyl and ethyl esters of a given fatty acid are quite similar for the shorter chain lengths and are practically identical for the longer chain lengths.

The last column in Table II shows the variation of refractive index of myristic acid with temperature. The refractive index decreases in a linear manner as the temperature increases for the temperature range shown.

Summary

1. Determinations of surface tension, interfacial tension against water, viscosity, density, and refractive index were made at 75°C. for the saturated, even-numbered, *n*-fatty acids from C_2 through C_{18} and for the corresponding methyl and ethyl esters. The typical effect of temperature on the various physical constants was demonstrated for one of the fatty acids, myristic acid.

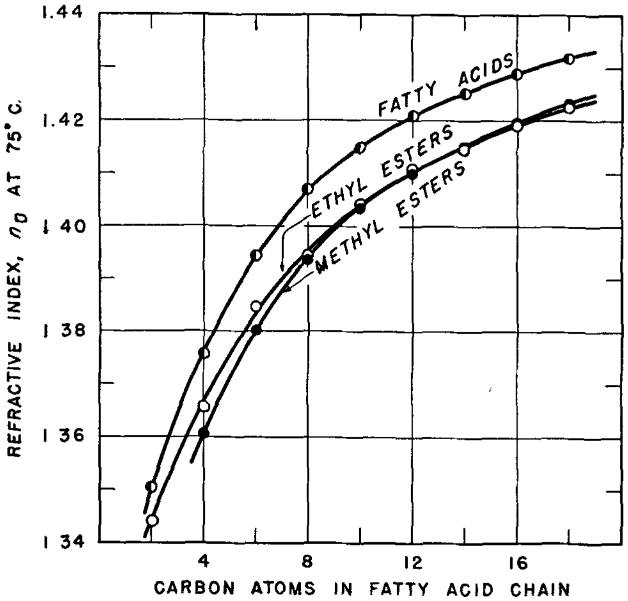

FIG. 5. Refractive indices at 75°C. of the *n*-fatty acids and esters as a function of the number of carbon atoms in the fatty acid chains.

2. Surface tensions of the fatty acids were found to increase from 19.6 dynes/cm. for acetic to 27.7 dynes/cm. for stearic as the length of the carbon chain increased. Surface tensions for the ethyl esters were about 2.5 dynes/cm. lower than those for the corresponding acids, while the surface tensions for the methyl esters were about 2 dynes/cm. lower.

3. The interfacial tensions of the fatty acids and esters against water increased with increasing length of the fatty acid chain. The interfacial tension values for the acids were lower than those for the corresponding esters. For the longer chain length acids, increase in chain length had very little effect on the interfacial tension.

4. The viscosities of the fatty acids and esters increased as the number of carbon atoms in the fatty acid chain increased. Because of molecular association the acids were most viscous, and their viscosity increased most rapidly with increasing chain length. Only small and consistent differences were found in the viscosities of corresponding methyl and ethyl esters.

5. The densities of the fatty acids and esters decreased with increasing chain length, the decrease being most marked for the fatty acids and least marked for the ethyl esters. No decrease in density of the ethyl ester series was detectable beyond the butyrate.

6. The refractive indices of the fatty acids and esters increased rapidly with increasing chain length. The refractive indices of the acids were greater than those for the corresponding esters, and at the longer chain lengths the refractive indices for corresponding methyl and ethyl esters were almost identical.

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