4. Except at elevated temperatures exchange is incomplete, indicating that recrystallization of the aluminum chloride particles is a very slow process.

5. Whereas complete exchange occurs at 100° in two hours at ratios of aluminum chloride to carbon tetrachloride greater than 10^{-3} m./l. relatively little or no exchange occurs at lower ratios. This observation suggests that exchange can occur only when an aluminum chloride surface is present.

6. Mixtures of gaseous aluminum chloride and carbon tetrachloride can be maintained at 140° for nine hours with no exchange.

7. The characteristics of the exchange between aluminum chloride and carbon tetrachloride cannot be explained by the carbonium ion type of mechanism commonly used to rationalize Friedel–Crafts reactions.

8. Butyl and amyl chlorides exchange chlorine easily with aluminum chloride and this exchange appears to be a convenient general method for tagging organic chlorides with Cl^{36}.

9. Silver chloride precipitated from water consistently retains about 1% by weight of occluded water even after heating in vacuum at 160° for several hours.

10. As little as 10^{-5} mole of water may be quantitatively detected in a vacuum system by collecting and counting the radioactive hydrogen chloride formed by hydrolysis of radioactive aluminum chloride.

MADISON, WISCONSIN RECEIVED MARCH 30, 1950

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Dielectric and Molecular Behavior of 1,3-Dipalmitin, 1,3-Distearin, Tripalmitin, Tristearin and Tetradecyl Palmitate[1]

BY ROBERT W. CROWE[2] AND CHARLES P. SMYTH

The polymorphic behavior of 1-monopalmitin and 1-monostearin has recently been investigated in this Laboratory[3] by dielectric constant measurements, the results of which have been correlated with the X-ray diffraction and thermal studies of Malkin and Shurbagy[4] and the more recent X-ray and dilatometer investigations of Lutton and Jackson.[5] It was found that the α-forms of these compounds possess molecular freedom, probably about their long molecular axes, as suggested by Malkin. Moreover, these α-forms showed an abnormally high conductivity suggesting a proton transfer mechanism enhanced by rotation of the hydrocarbon chains, similar to that occurring in the α-forms of the long-chain alcohols.[6] This similarity in behavior was not surprising in view of the fact that members of both series are highly hydrogen bonded and consist of long chains with hydroxyl groups at one end. It therefore appeared worthwhile to carry out a similar investigation on the corresponding 1,3-diglycerides with one hydroxyl group unesterified and triglycerides, in which hydrogen bonding does not exist. Members of both of these series have been reported to possess "multiple melting points." In this investigation, therefore, dielectric constant measurements were made on 1,3-dipalmitin, 1,3-distearin, tripalmitin and tristearin over a considerable temperature and frequency range. The various polymorphic forms were isolated by varying the previous thermal treatment of the samples. Similar measurements were made on a sample of tetradecyl palmitate, the results of which have been used for comparison purposes.

Preparation and Purification of Materials

Purified samples of the four glycerides investigated were kindly given to us by the Procter and Gamble Company of Ivorydale, Ohio. Since, as in the case of the monoglycerides, they were considered to be of at least 99% purity no attempt was made to purify them further. Moisture was removed before measurement by keeping the solvent-crystallized samples for several hours in a vacuum desiccator. The melting points as observed here are compared with recent literature values in Table I.

Tetradecyl palmitate was synthesized[7] by adding to 0.1 mole of tetradecyl alcohol, dissolved in a large excess of dry pyridine, an equimolar portion of palmitoyl chloride, prepared by the reaction of thionyl chloride with palmitic acid. After the reaction was complete, 100 ml. of benzene was added to the mixture and the pyridine removed by several washings with distilled water. The unreacted palmitic acid was removed by shaking the benzene solution several times with dilute sodium carbonate solution. Finally, the solution was evaporated to approximately half its original volume and about 50 ml. of methanol

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[1] This research has been supported in part by the Office of Naval Research. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

[2] Procter and Gamble Fellow in Chemistry, 1949–1950, this article is based upon a thesis to be submitted by R. W. Crowe in partial fulfillment of the requirements for the degree of Ph.D. at Princeton University.

[3] Crowe and Smyth, THIS JOURNAL, **72**, 4427 (1950).

[4] Malkin and Shurbagy, *J. Chem. Soc.*, 1628 (1936).

[5] Lutton and Jackson, THIS JOURNAL, **70**, 2445 (1948).

[6] Hoffman and Smyth, *ibid.*, **71**, 431 (1949).

[7] Prepared by Mr. D. A. Pitt.

was added to precipitate the ester. The crude product was recrystallized five times from an ether–methanol mixture, and finally dried for 24 hours in a vacuum desiccator; m. p. 47.0°.

TABLE I

MELTING POINTS OF GLYCERIDES

Glyceride	This research α	This research β-a	This research β-b	Literature α	Literature β-a	Literature β-b
1,3-Dipalmitin	..	71.7	72.8	68^{8}	71.8^{9}	72.9^{9}
1,3-Distearin	..	77.7	78.5	74^{8}	77.2^{9}	78.2^{9}
	α	β'	β	α	β'	β
Tripalmitin	44	..	65.8	44^{10}	55.5^{10}	65.5^{10}
Tristearin	54	(65)	72.5	54^{10}	64^{10}	73.1^{10}

Experimental Method and Results

The dielectric constant measurements were made with the impedance bridge previously described.[11] Except in cases where no frequency dependence of the dielectric constant was observed, measurements were made at 50, 5 and 0.5 kilocycles. None of the compounds investigated showed enough conductivity or loss to be measured with accuracy. It is estimated that the error in measurement of the dielectric constant never exceeded ±1%. As in the case of the monoglycerides, the rate of cooling and warming was 0.2° per minute, except in melting regions where the energy involved resulted in a much slower rate.

In Table II are listed a few representative values of the dielectric constants of the four glycerides and tetradecyl palmitate with temperatures and frequencies of measurement. In the case of the α-forms of the triglycerides and of tetradecyl palmitate, values are listed at 50, 5 and 0.5 kilocycles at a temperature near the middle of their dispersion regions in order to represent the extent of the frequency dependence of the dielectric constant.

TABLE II

DIELECTRIC CONSTANTS OF GLYCERIDES

Phase	t, °C.	ε' (5 kc.)	Phase	t, °C.	ε' (5 kc.)
1,3-Dipalmitin			1,3-Distearin		
Liquid	76.0	3.49	Liquid	82.0	3.29
	72.0	3.52		78.0	3.32
β-a	26.5	2.50	β-a	21.5	2.40
	60.1	2.55		70.1	2.43
β-b	44.2	2.55	β-b	14.7	2.39
	64.1	2.57		68.6	2.44
Tripalmitin			Tristearin		
Liquid	70.0	2.895	Liquid	80.0	2.751
	60.0	2.927		70.0	2.785
α	−140.0	2.327	α	−147.0	2.283
	41.3	2.737		52.2	2.684
β	20.6	2.292	β	16.7	2.313
	60.0	2.320		65.1	2.340

	Phase	t, °C.	ε' 50 kc.	ε' 5 kc.	ε' 0.5 kc.
Tripalmitin	α	−60	2.456	2.488	2.515
Tristearin	α	−60	2.382	2.403	2.431
Tetradecyl palmitate	Solid	0	2.235	2.357	2.407

Discussion of Results

In Fig. 1 are plotted the dielectric constants of 1,3-dipalmitin, measured at 50 kilocycles, as functions of increasing and decreasing temperature. On cooling, this compound solidified reproducibly with little super-cooling at 70.1°, as indicated by a sharp drop in the dielectric constant to a value approaching the square of the refractive index. It must, therefore, be assumed that virtually no freedom of orientation exists in the solid first formed from the liquid. On warming immediately after solidification, rapid increases in the dielectric constant were observed in the vicinities of 71.7 and 72.8°, corresponding to the melting points of the β-a- and β-b-forms,[9] respectively. After the sample had been maintained at a temperature just below its melting point for three hours and then warmed, only a slight increase was observed at the lower temperature, indicating a nearly complete transformation to the more stable β-b-form.

In Fig. 2 are plotted similar data for 1,3-distearin. This substance froze reproducibly at 76.7°. On warming immediately, the entire sample melted at 77.7°, which corresponds to the melting point of the β-a-form (Table I). After being maintained for ten hours just below the melting point, part of the sample melted at 77.7° and the remainder at 78.5° (β-b melting point). After being kept for thirty hours just below the melting point, almost the entire sample melted at 78.5°, there being only a slight break in the curve at 77.7°.

The results obtained for these two compounds differ in two respects from those of Malkin, *et al.*,[8] but are in nearly complete agreement with the more recent investigations of Baur, *et al.*[9] Malkin observed melting points for all members of this series from didecoin through distearin corresponding to the typical α-forms (no alternation of melting points). However, never in the course of the present investigation, did the two members studied show the slightest indication of an α melting point, even after rapid solidification. The freezing points, although somewhat lower than the observed β-a melting points, are considerably higher than the reported α melting points (Table I). If such forms do exist, they must be extremely unstable and transform very rapidly to the β-a-forms. In addition, Malkin observed that the intermediate melting β-a-form (called β' by him), found in the lower members, did not exist above dipentadecoin. Figures 1 and 2, however, definitely establish its presence in dipalmitin and distearin. Baur, *et al.*, ob-

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(8) Malkin, Shurbagy and Meara, *J. Chem. Soc.*, 1409 (1937).

(9) Baur, Jackson, Kolp and Lutton, THIS JOURNAL, **71**, 3363 (1949).

(10) Lutton, *ibid.*, **67**, 524 (1945).

(11) Smyth and Hitchcock, *ibid.*, **54**, 4631 (1932); **55**, 1830 (1933).

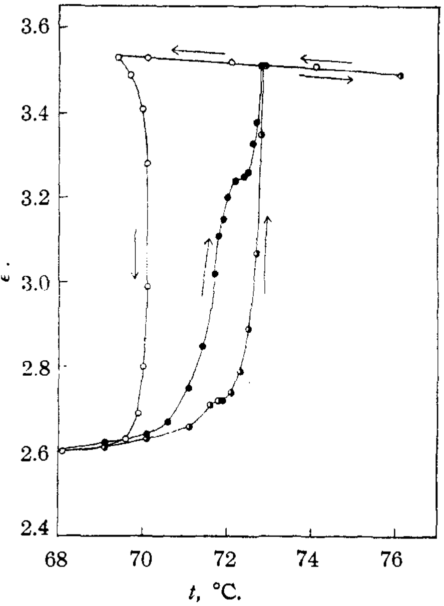

Fig. 1.—Temperature dependence of the dielectric constant of 1,3-dipalmitin at 50 kc. Hollow circles represent values obtained on cooling; filled circles, values obtained on warming immediately after solidification; half-filled circles, values obtained on warming after 3 hr. at 69°.

tained characteristic long and short spacings for both β-a and β-b-forms, but were somewhat uncertain as to whether a difference in melting point existed for the two forms. They found that the solvent-crystallized β-a appeared to melt as high as β-b. Actually they are very close together but reproducibly different in the present investigation. The β-a melting points listed in Table I are in quite close agreement with the "rapid complete melting points" obtained by Baur, *et al.*, using a "thrust-in" technique.

It is of interest to note that the high conductivity and polarization observed in the solid forms of the long-chain alcohols[6] and 1-monoglycerides are almost non-existent in the 1,3-diglycerides. No solid rotator forms exist in the latter, and, consequently, little or no proton transfer is possible, even though hydroxyl groups are present. The presence of weak Maxwell–Wagner polarization was observed for both substances for several degrees below the melting points, however. This is shown in Fig. 3 for 1,3-distearin of various thermal histories. The upper and lower sets of curves are the results of dielectric constant measurements on the relatively pure β-b- and β-a-forms, respectively, which show very little Maxwell–Wagner polarization. The middle set of curves represents the results obtained on a sample treated in such a manner that considerable amounts of both β-a and β-b were present. Here the effect, though small, is definitely greater than before. Since both solid forms evidently possess approximately the same dielectric constant and small conductivity, it is not surprising that the effect observed here is small. It is, however, of sufficient magnitude to confirm the presence of two different crystalline forms. The discontinuity in the properties of

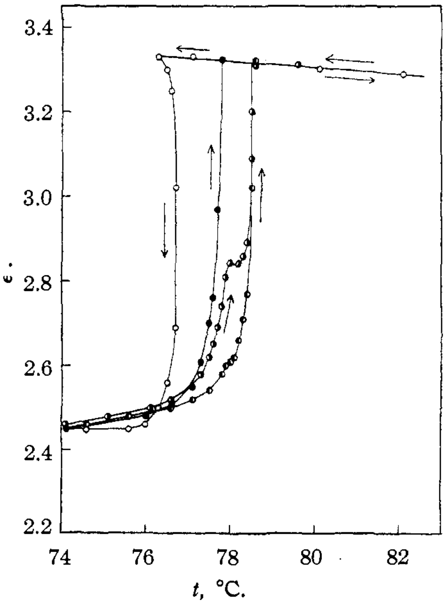

Fig. 2.—Temperature dependence of the dielectric constant of 1,3-distearin at 50 kc. Hollow circles represent values obtained on cooling; filled circles, values obtained on warming immediately after solidification; ◑ values obtained on warming after 10 hr. at 75°; ◐ values obtained on warming after 30 hr. at 75°.

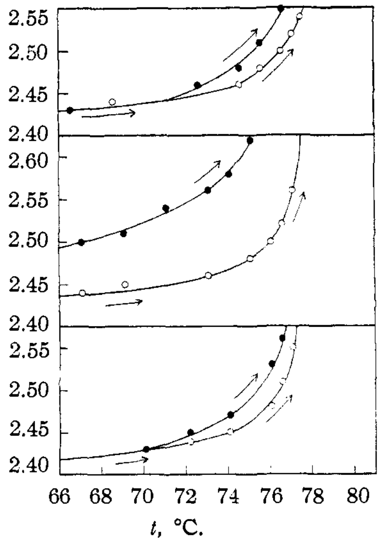

Fig. 3.—Sets of curves showing Maxwell–Wagner dispersion in 1,3-distearin of various thermal histories below its melting point. Hollow circles represent dielectric constants at 50 kc.; filled circles, dielectric constants at 0.5 kc. Lower, β-a-form; middle, mixture of β-a- and β-b-forms; upper, β-b-form. Arrows indicate direction of temperature change.

these higher members reported by Malkin, *et al.*, would appear, therefore, not to exist.

Clarkson and Malkin[12] have reported that the triglycerides exist in four forms, γ, α, β' and β in order of increasing melting point and stability. The γ-form, obtained by rapid solidification, was considered to possess the characteristics of a glass rather than of a true crystal. The α-form was characterized both by its vertical long spacings and its lack of alternation of melting point from odd to even members. The β'- and β-forms, which showed a definite alternation of melting point, were found to consist of tilted chains, the latter at an angle of approximately 65°. X-Ray examinations by Lutton[10] agreed with these results in the case of the stable β-form. Lutton found, however, that the lowest melting form, designated as γ by Clarkson and Malkin, actually gave a diffraction pattern corresponding to the α-form, while the form designated by Clarkson and Malkin as the α-form gave the β' pattern. He found no glassy or γ-form[13] and no melting point corresponding to that of the β'-form reported by Clarkson and Malkin.

In Fig. 4 are plotted the dielectric constants of tripalmitin obtained from several runs with increasing and decreasing temperature. On cooling, the sample nearly always remained in the liquid phase, if not seeded, until the vicinity of the α freezing point was reached. However, as soon as a trace of the α-form appeared, it transformed rapidly into a more stable modification (probably β' initially) with the evolution of considerable thermal energy resulting in a rather rapid increase in sample temperature. The dielectric constant decreased rapidly during this process. This rapid transformation could also be observed by dipping the bottom of the cell containing the molten glyceride at a temperature slightly below the β melting point into a cool bath until a small amount of the α-form crystallized out. If the cell was then returned to its original temperature, small white patches appeared in the α-form before it could melt. These grew quite rapidly and soon filled the entire cell. However, when the sample was chilled rapidly from the melt, it froze entirely into the α-form which was apparently quite stable at room temperature. After such treatment, dielectric constant measurements were made with increasing temperature. The results of these measurements are plotted in Fig. 5 and in part in Fig. 4. Below −140° the dielectric constant had a low value of about 2.32 and was independent of frequency. Between −140 and −10° (Fig. 5) a region of anomalous dispersion was observed, the dielectric constant increasing gradually to a value of 2.63. With further increase in temperature, it continued to rise gradually and again became independent of frequency. However, as soon as the α melting point at 44° was reached, the compound transformed very rapidly to the β-form, resulting in a rapid decrease in dielectric constant and increase in temperature. The spontaneous rise in temperature was so rapid that readings were uncertain in this range. As the transformation neared completion, the temperature of the sample decreased again to that of its surroundings (Fig. 4). After complete transformation, the sample always melted between 65.4 and 65.8°, corresponding to the melting point of the β-form. No evidence of the β' melting point was observed for this compound. This is not surprising, however, since Lutton found that it has a very short existence at its temperature of formation.

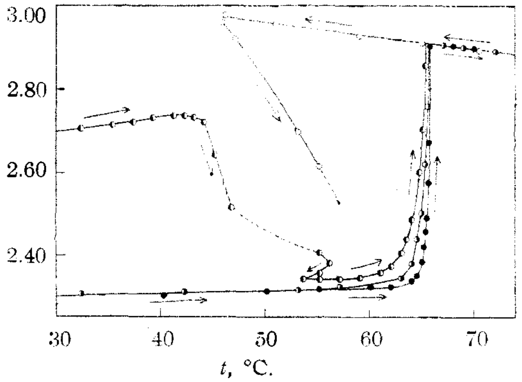

Fig. 4.—Temperature dependence of the dielectric constant of tripalmitin at 5 kc.: ○ are for cooling; ◐ for α-form on warming; ◑ for β-form on warming after 4 hr. at 60°; ● for β-form on warming after 24 hr. at 60°.

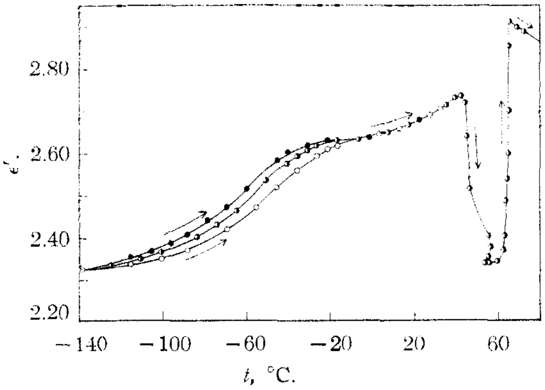

Fig. 5.—Variation of the dielectric constant of the α-form of tripalmitin with increasing temperature. Hollow circles are for measurements at 50 kc.; half-filled circles for measurements at 5 kc., and filled circles for measurements at 0.5 kc.

The results of dielectric constant measurements for tristearin are shown in Figs. 6 and 7. As can be seen, they are quite similar to those obtained for tripalmitin, except that some evidence of the

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[12] Clarkson and Malkin, *J. Chem. Soc.*, 666 (1934); 985 (1948).

[13] The nomenclature employed by Lutton is used throughout this discussion for purposes of comparison; *cf.* Bailey, Jefferson, Creeger and Bauer, *Oil & Soap*, **22**, 10 (1945).

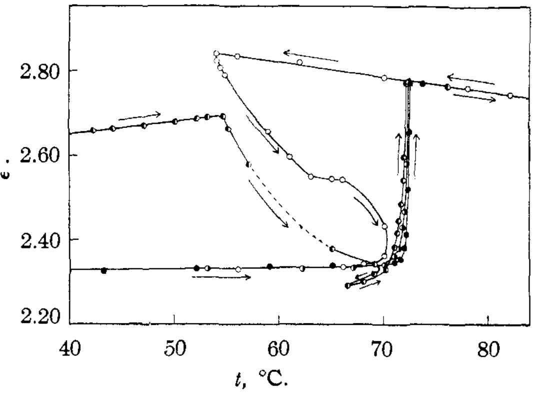

Fig. 6.—Temperature dependence of the dielectric constant of tristearin at 5 kc.: ○ are for cooling; ◐ for α-form on warming; ◑ for β-form on warming after 2 hr. at 60°; ● for β-form on warming after 8 hr. at 60°.

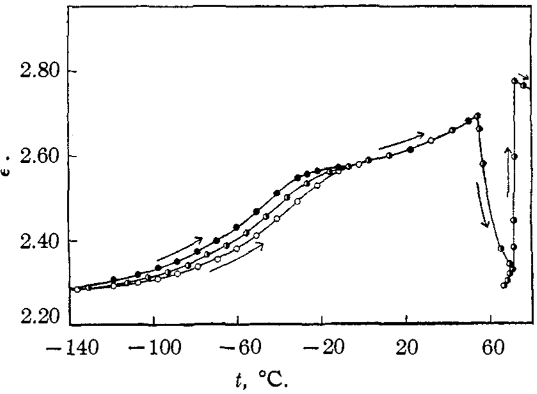

Fig. 7.—Variation of the dielectric constant of the α-form of tristearin with increasing temperature. Hollow circles are for measurements at 50 kc., half filled circles for measurements at 5 kc., and filled circles for measurements at 0.5 kc.

β' melting point was observed. The flat portion of the cooling curve at about 65° (Fig. 6) suggests a simultaneous melting of the β'-form and its rapid transformation to the more stable β-form, but no actual rise in dielectric constant associated with melting could be detected at this temperature. Bhide and Bhide[14] have measured the dielectric constant of tristearin at 930 and 4,400 kilocycles and have obtained results similar in some respects to those reported here. They found, however, that the substance froze completely at 55° when cooled gradually. They also found that the α-form (called glassy by them), obtained by rapid solidification, transformed near its melting point to the β'-form (called α by them), which then melted completely at 66°. It is highly probable that the apparently greater stability of these lower melting forms resulted from the presence of impurity. This belief is supported by the fact that the dielectric constant of the stable β-form began to increase markedly on warming several degrees below the melting point. In addition, the melting point of this form, 71.5°, was somewhat lower than that reported here, 72.5°. It was also found that their dielectric constant values at 4,400 kilocycles were consistently higher than those measured at 930 kilocycles. Since there is no theoretical basis for this, it seems probable that failure to correct for the effect of inductance upon their measurements may be responsible for the discrepancy. Our liquid values agree more closely with those obtained at 930 kilocycles.

A point of considerable interest is the variation in the sharpness and magnitude of the β melting points of the triglycerides (especially tripalmitin). The recently formed β-forms always melted lower and less sharply than they did after tempering below the melting point for several hours. This phenomenon was observed by Lutton[10] for several members of the series, although no significant change in X-ray diffraction pattern was evident. He suggests that differences in crystal size may be the cause. Similar behavior has been observed in some of the mixed triglycerides.[15] It is difficult to believe that variations in crystal size alone could cause such large variation in melting point. It may be that we are dealing with small variations in the actual crystal structure or a difference in the perfection of the chain alignment in the crystal.

The values of the dielectric constants of the α-forms of the two triglycerides show the existence of a certain amount of dipole orientational freedom. In the case of the monoglycerides, it is reasonable to attribute dipole orientation to rotation of the molecules about their long axes,[3] but such rotation would appear to be impossible in the triglycerides. In the crystal lattice of the diglycerides,[8] X-ray analysis suggests that the two acid chains form the sides of a greatly elongated U, while, in the triglycerides,[16] the third acid chain converts the U to the shape of an elongated tuning fork. The data in this paper for the diglycerides show the absence of rotational freedom for these closely packed U-shaped molecules in the crystal, an absence which would seem almost inevitable in view of the molecular shape. For the triglyceride molecules, rotation would seem to be even more completely out of the question. It would seem, therefore, that the orientation must be that of molecular segments as has been assumed in the case of high polymers.[17,18,19] The polar COO groups are present in the triglyceride molecules as they are in the polymers of ω-hydroxydecanoic acid,[17] where they orient freely without loss at frequencies higher than those used in the present measurements. It is evident that the use of a much higher fre-

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[14] Bhide and Bhide, *J. Univ. Bombay*, **7**, 97 (1938).

[15] Lutton, Jackson and Quimby, THIS JOURNAL, **70**, 2441 (1948).

[16] Lutton, *ibid.*, **70**, 248 (1948).

[17] Bridgman, *ibid.*, **60**, 530 (1938).

[18] Fuoss, *ibid.*, **63**, 369, 378 (1941).

[19] Kirkwood and Fuoss, *J. Chem. Phys.*, **9**, 329 (1941).

quency on tripalmitin and tristearin would push the dispersion region to temperatures above the α melting points in Figs. 5 and 7, so that no orientation polarization would be observed. The absence of any considerable dipole orientation in the two diglycerides may be due to the restriction of motion by closer packing of the two COO groups in the crystal. It is possible, however, that all three COO groups or merely the central COO group in the vertical α-forms of the triglycerides are less closely packed than those of the diglycerides. In any case, the dispersion regions for the triglycerides are decidedly different from those usually encountered in crystalline compounds and organic glasses.[20] It has been observed[21] that in materials which approximate Debye behavior, the orientation process can be represented approximately in terms of a single relaxation time. In such materials, the dielectric constant ϵ' decreases from a value equal to the static dielectric constant to one equal to the optical dielectric constant as the frequency is increased in the dispersion region, nearly all of the decrease taking place within a hundred-fold increase in frequency. However, it is seen in Figs. 5 and 7 that the decrease is only about one-fifth of this amount at any given temperature in the dispersion region. One must assume, then, that the dipole orientation process in the triglycerides involves a wide distribution of relaxation times, which could easily result from orientation of various segments of the molecules. The same conclusion was reached from similar dispersion behavior in the sub-α-forms of the monoglycerides.[3]

The dielectric constant of tetradecyl palmitate (Fig. 8) drops sharply at the freezing point, but remains sufficiently high to show the existence of dipole orientation, probably by rotation of the molecules about their long axes as supposed in the case of n-docosyl bromide.[22] The curves in the dispersion region in Fig. 8 show that the maximum drop in dielectric constant for a hundred-fold increase in frequency is close to that which corresponds to a single relaxation time for the dipole orientation process. The dispersion region for this compound covers a 50° range of temperature for a single frequency. In the case of the triglycerides the corresponding region covers about 130°. This unusually large temperature range may be accounted for by the suggested distribution of relaxation times, but it is also possible that the process requires an unusually low activation energy, which causes only a gradual decrease in relaxation rate with decreasing temperature.

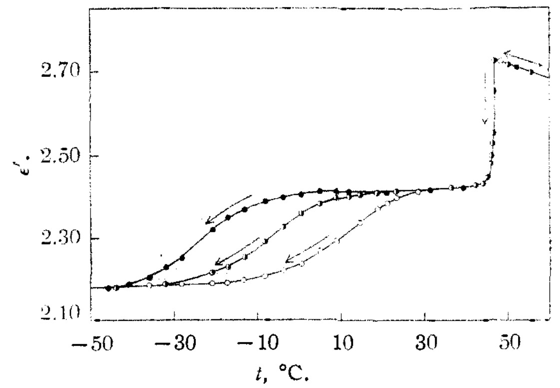

Fig. 8.—Variation of the dielectric constant of tetradecyl palmitate with decreasing temperature. Hollow circles are for measurements at 50 kc., half-filled circles for measurements at 5 kc., and filled circles for measurements at 0.5 kc.

The question may be raised as to why dipole orientation is attributed to segment orientation in the triglycerides and to rotation of the whole molecule in tetradecyl palmitate and the monoglycerides. The cylindrical symmetry indicated by X-ray analysis for long-chain molecules in the α-phase is interpreted as indicating rotational freedom around the long axes. The magnitude of the dielectric constant of the vertical phase is that which should be given by rotational orientation about the long axis. This does not mean, however, that segment orientation cannot occur at the same time. It was concluded in microwave investigations on liquid alkyl bromides[23] that, with increasing length of the hydrocarbon chain in the long molecules, dipole orientation probably occurred to an increasing extent by twisting around the carbon–carbon bonds of the chain, that is, by segment orientation. An accompanying increase in the distribution of relaxation times was observed. It seems rather probable that, in the monoglycerides, molecular rotation ceases when the α-form changes to sub-α, but that segment orientation continues in the latter. The resemblance of the sub-α dispersion region to that observed in the triglycerides can thus be accounted for.

Summary

The dielectric properties of 1,3-dipalmitin, 1,3-distearin, tripalmitin, tristearin and tetradecyl palmitate have been investigated over a wide range of temperature at frequencies from 0.5 to 50 kilocycles. The diglycerides were found to exist in two solid forms, β-a and β-b, as recent X-ray diffraction measurements have indicated, and were found to show no appreciable amount of dipole orientation. The α-forms of tripalmitin and tristearin showed dipole orientational freedom down to relatively low temperatures, the orientation being attributed to movement of molecular segments. The dipole orientation showed an exceptionally wide dispersion region which indicated a wide distribution of relaxation

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[20] Baker and Smyth, THIS JOURNAL, **61**, 2063 (1939).

[21] Kauzmann, *Rev. Modern Phys.*, **14**, 12 (1942).

[22] Hoffman and Smyth, THIS JOURNAL, **72**, 171 (1950).

[23] Hennelly, Heston and Smyth, *ibid.*, **70**, 4102 (1948).

rates for the process. Previously reported variations in the β melting points of the triglycerides have been observed by dielectric constant measurements. Tetradecyl palmitate resembles the monoglycerides in showing apparent freedom of rotation of the molecules around their long axes for some distance below the freezing point.

PRINCETON, NEW JERSEY RECEIVED MAY 8, 1950

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Thermodynamics of 1-Butyne from Calorimetric and Spectroscopic Data

BY J. G. ASTON, S. V. R. MASTRANGELO[1] AND G. W. MOESSEN

A study of the thermodynamic properties of 1-butyne and other compounds of the unsaturated type such as the butadienes, butenes, dialkylacetylenes, etc., is of particular interest because it yields additional information about the potential function hindering internal rotation. This paper presents the experimental data and potential barrier for one of these compounds, 1-butyne.

The Material.—We were kindly supplied with an A. P. I.-N. B. S. standard source; sample of 99.90 ± 0.07% purity (A. P. I. R. P. 45-O. S. U.) by Dr. F. D. Rossini. However, since this material was not too difficult to prepare, we prepared our own sample and purified it as a precaution against accidents to the standard sample in the many manipulations required. The sample of 1-butyne was prepared by the action of sodium acetylide on redistilled ethyl iodide.[2a,b] The acetylene was treated following the method of Hurd,[3] by passing tank acetylene through two traps immersed in a Dry Ice and acetone mixture and then condensed in an end trap maintained at liquid air temperatures. The glass apparatus was baked at 150° for three hours before use. A liter of liquid ammonia was condensed from a tank of anhydrous ammonia and placed in a three-necked, three-liter flask with a mercury seal stirrer and condenser refrigerated with solid carbon dioxide and attached to a liquid air trap. The flask was immersed in a bath of Dry Ice, acetone, carbon tetrachloride and chloroform freezing mixture. The temperature of this mixture reached −75°. The stirrer was started and 1.0 g. of hydrated ferric nitrate added to the liquid ammonia. Two grams of sodium was then added. When the blue color turned to gray, the rest of the 115 g. of sodium was added as rapidly as possible over a period of twenty minutes. The reaction was completed after half an hour as indicated by a large decrease in the rate of evolution of hydrogen gas. The solution was blue at this point. After an hour the solution turned gray. An excess of acetylene was then bubbled into the reaction mixture and after the addition, the solution stirred for two hours. Ethyl iodide was then added and shortly after, rapid refluxing was observed.

The reaction mixture was warmed up and the gases were passed through 4 l. of water in a 5-liter flask before condensing in three traps maintained at a temperature of −25 to −30° by careful addition of Dry Ice and finally through a mercury bubble counter to the atmosphere. Approximately 300 cc. of liquid was condensed in this way and purified by passing through 10% sulfuric acid, a tower of sodium hydroxide and finally through a tower of anhydrous calcium chloride. The yield of purified product was 54%.

The sample was finally purified through the laboratory low temperature column and a middle cut of about 50 cc. was used for this calorimetric study.

The Heat Capacity Measurements.—The apparatus and method used for these measurements has been described previously.[4a,b] Standard thermocouple S-7 was used as the primary temperature standard and standard thermocouple S-4 was used as a check. The two thermocouples deviated from one another by not more than 0.05°K. in the range from 10 to 20°K. For the range from 20 to 200°K. the deviations were less than 0.02°K. and at higher temperatures the deviations were somewhat less than 0.03°K.

The time of energy imput in the range from 30 to 275°K. was measured by means of the laboratory automatic timer, which was checked against Arlington time signals. During the second coverage, starting from 13°K., the current from a Type No. 816-B 60 cycle Vacuum-Tube Precision Fork generator (The General Radio Co., Cambridge, Mass.) was amplified to run an electric clock graduated in 0.1 sec. (Standard Electrical Time Co., Springdale,

TABLE I

THE MOLAL HEAT CAPACITY OF 1-BUTYNE

Mol. wt. 54.088; 0.47790 mole, 99.967 mole % pure; 0.0°C. = 273.16°K.; 1 cal. = 4.1833 int. joules.

Temp., °K.	C_p, cal./deg./mole	Temp., °K.	C_p, cal./deg./mole	Temp., °K.	C_p, cal./deg./mole
Crystal:		111.07	14.88	Liquid:	
Series III		115.68	15.34	Series II	
13.30	0.736	120.94	15.84	149.88	27.31
16.72	1.363	126.28	16.24	155.93	27.31
19.29	1.961	131.96	16.81	163.01	27.33
21.69	2.473	137.31	17.29	169.47	27.42
24.74	3.199	142.36	17.89	176.03	27.55
28.43	4.048	Series V		181.83	27.66
33.46	5.169	61.25	9.742	187.38	27.74
37.25	5.941	66.04	10.374	192.85	27.80
Series IV		71.14	11.005	198.67	27.96
14.65	0.988	76.75	11.659	204.10	28.17
19.16	1.921	83.04	12.281	209.72	28.28
24.83	3.210	89.73	12.906	215.61	28.43
32.18	4.924	Series VI		220.93	28.51
39.34	6.320	31.35	4.698	262.28	28.71
45.16	7.452	36.54	5.790	232.47	28.97
50.56	8.330	41.74	6.807	239.03	29.32
Series I		46.45	7.673	246.11	29.76
66.05	10.39	51.10	8.401	253.38	30.23
72.64	11.21	55.94	9.088	260.15	30.42
78.96	11.92	60.73	9.678	265.53	30.89
83.94	12.38	65.50	10.349	270.58	31.08
95.07	14.43	70.20	10.900	275.09	31.14
100.12	13.88				
105.46	14.36				

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[1] Phillips Petroleum Fellow, 1946–1949.

[2] (a) Picon, *Compt. rend.*, **158**, 1184 (1914); (b) **156**, 1077 (1913).

[3] Hurd, THIS JOURNAL, **69**, 239 (1947).

[4] (a) Aston and Messerly, *ibid.*, **58**, 2354 (1936); (b) Messerly and Aston, *ibid.*, **62**, 886 (1940).