[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Molecular Rotation and Proton Transfer in the Solid Forms of 1-Monopalmitin and 1-Monostearin[1]

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Although polymorphism is now known to be a common phenomenon with most long-chain compounds, its presence in the fatty-acid glycerides has led to a great deal of investigation. These compounds exhibit the peculiar property of possessing multiple melting points. Among these are the 1-monoglycerides, as evidenced by the X-ray diffraction and thermal investigations of Malkin and Shurbagy.[3] These investigators have shown that both odd and even members of this series from monodecoin through monostearin exist in three polymorphic forms, α, β' and β, in order of increasing stability and melting point. At temperatures considerably below the α melting points, small arrests corresponding to transitions were observed in the cooling curves of these compounds. X-Ray diffraction measurements indicated that the α form consisted of vertical rotating chains, while the β' and β forms were tilted at an angle of about 59°. More recent X-ray and dilatometer studies on 1-monopalmitin and 1-monostearin by Lutton and Jackson[4] have indicated that, at least in these two members of the series, the α form is also tilted. In addition, the nature of the form designated as sub-α,[5] which appears below the low temperature arrest in the α cooling curves, has been carefully studied. These investigators were unable to isolate the β' form by transformation from the α form, but did succeed in obtaining it by rapid crystallization from solvents.

It has been observed that long-chain compounds capable of hydrogen bonding, show abnormal conductivity in the solid, accompanied by dependence of the dielectric constant upon frequency in the low-frequency range. This phenomenon is especially prevalent in the long-chain alcohols[6,7,8] and to a lesser extent in the long-chain amines,[9] and has been attributed to Maxwell–Wagner polarization between two solid phases with different conductivities and dielectric constants.[8] The abnormally high conductivity in the α forms of the alcohols has been attributed to a proton transfer mechanism, made possible by rotation of the molecules about their long axes. Such rotational freedom is supposed to facilitate the mechanism by offering an optimum configuration conducive to the transfer of protons along the planes of hydroxyl groups located in the crystals. No such behavior has been observed in the rotator phase of the only long-chain bromide thus far found to show rotational freedom.[10] Since the 1-monoglycerides, which possess two free hydroxyl groups near the end of the molecule, are undoubtedly highly hydrogen bonded, evidence of proton transfer in the α forms similar to that in the α forms of the alcohols would not be surprising. It, therefore, seemed of interest to investigate their dielectric properties at low frequencies in order to determine whether peculiar polarization behavior comparable to that of the alcohols is evident. It was also of interest to determine whether molecular orientational freedom about the long axis is possible in the α forms as suggested by Malkin.[3] 1-Monopalmitin and 1-monostearin were chosen for study because of the greater stability of the α forms with increasing chain length and also because they were easily available. During the course of the investigation, the dielectric constants, dielectric losses, and conductivities of these two substances were measured over a considerable temperature and frequency range with varying thermal histories.

Purification of Materials

Purified samples of the two compounds investigated were kindly given to us by the Procter and Gamble Company of Ivorydale, Ohio. Since they were considered to be of at least 98 to 99% purity, no additional purification procedures were attempted. Each compound was placed in a vacuum desiccator for two days to remove possible traces of moisture from the crystals.

Experimental Method and Results

The dielectric constants were measured at 100, 50, 25 and 5 kilocycles with the aid of the impedance bridge previously described.[11] As in previous measurements with this apparatus[12] the average error in determination of the dielectric constant was about ±1%. The specific conductivity was calculated from the relation $k = 0.0885/RC_0$ where R is the resistance in ohms and C_0 the vacuum capacitance of the cell. The dielectric loss factor ϵ'' was calculated by using the relation $\epsilon'' = 1.8 \times 10^{12}k/f$ where f is the frequency in cycles/sec. Since both compounds had a rather high liquid conductivity, values for ϵ'' are reported only in the low temperature regions of the sub-α forms where true dipole dispersion was observed. Even at these temperatures the values may be somewhat high. The temperature measurements were made with a

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[2] Procter and Gamble Fellow in Chemistry, 1949–1950.

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

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

[5] The nomenclature of the polymorphic forms employed by Lutton and Jackson will be used throughout the discussion to facilitate comparison.

[6] Baker and Smyth, THIS JOURNAL, **60**, 1229 (1938).

[7] Higasi and Kubo, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **36**, 286 (1939).

[8] Hoffman and Smyth, THIS JOURNAL, **71**, 431 (1949).

[9] Hoffman and Smyth, *ibid.*, **71**, 3591 (1949).

[10] Hoffman and Smyth, *ibid.*, **72**, 171 (1950).

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

[12] Crowe and Smyth, *ibid.*, **72**, 1098 (1950).

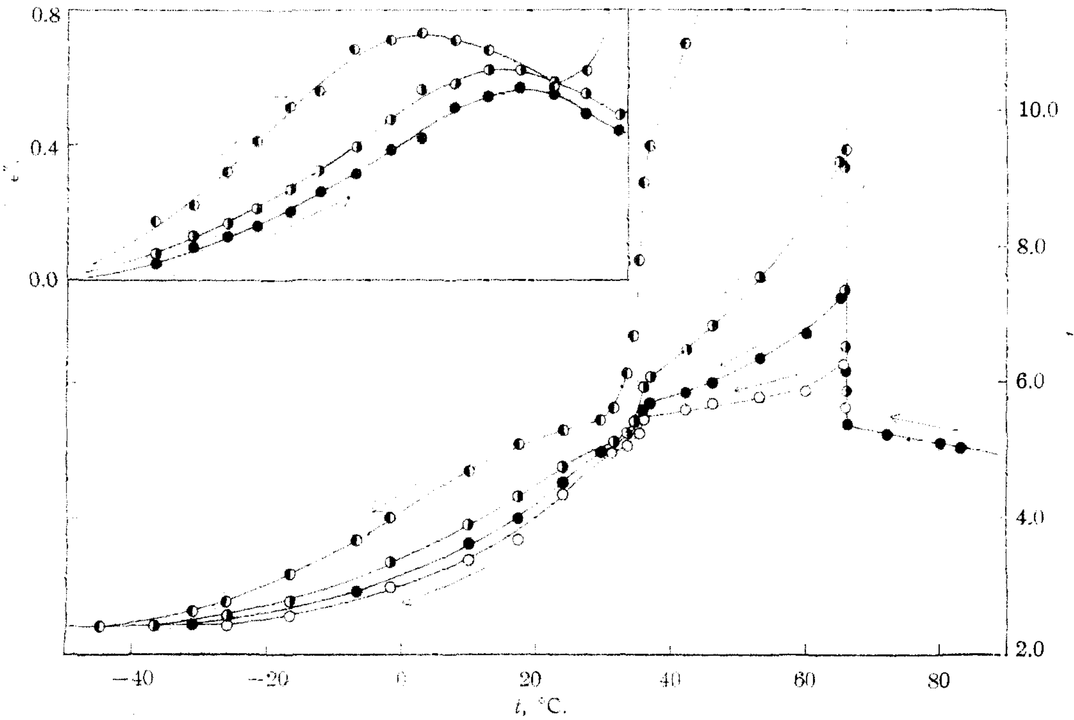

Fig. 1.—The variation of the dielectric constant of 1-monopalmitin with decreasing temperature and loss factor with increasing temperature: ○ represents values at 100 kc.; ●, values at 50 kc.; ◑, values at 25 kc.; and ◐, values at 5 kc.

calibrated platinum resistance thermometer immersed in the sample within the measuring cell. The average rate of cooling and warming was about 0.2° per minute, except in the transition and melting regions where the latent heat involved resulted in a much slower rate.

In Table I are listed a few representative values of the dielectric constant and specific conductivity *k* as observed for the two compounds in the liquid and various solid phases.

Table I

Dielectric Constants and Specific Conductivities of 1-Monoglycerides

		ε′				k (× 10^8)		
Phase	t, °C.	100	50	25	5 kc.	50	25	5 kc.
				1-Monopalmitin				
Liq.	80.1	5.09	5.09	5.09	5.09	11.9	11.9	11.9
	67.1	5.34	5.34	5.34	5.34	9.8	9.8	9.8
α	65.7	6.26	7.13	9.15	22.10	19.7	17.1	12.0
	53.2	5.75	6.33	7.54	14.36	9.2	7.9	4.6
Sub-α	31.4	4.95	5.00	5.08	5.63	0.77	0.67	0.47
	−36.9	2.38	2.40	2.42	2.53	.14	.10	.05
β	57.1	2.60	2.69	2.91	3.98	1.44	.91	.70
	47.2	2.53	2.61	2.71	3.18	0.70	.46	.23
				1-Monostearin				
Liq.	89.1	4.71	4.71	4.72	4.73	9.53	9.53	9.53
	77.1	4.87	4.87	4.87	4.88	8.16	8.16	8.16
α	72.1	5.82	6.80	8.90	22.70	20.1	18.2	13.4
	50.2	5.15	5.48	6.20	10.73	5.20	4.50	2.30
Sub-α	32.4	4.41	4.46	4.50	4.84	0.46	0.46	0.28
	−24.5	2.53	2.62	2.71	3.03	.57	.33	.10
β	71.1	2.64	2.80	3.03	4.37	1.66	1.25	.64
	43.2	2.53	2.58	2.69	3.13	0.60	0.45	.23

Discussion of Results

As can be seen in Fig. 1, the dielectric behavior of 1-monopalmitin with decreasing temperature is remarkably similar to that of the long-chain alcohols.[8] The dielectric constant increases normally in the liquid until the freezing point of the α form at 66° is reached. At this point it increases sharply, its maximum value varying considerably with the frequency of measurement. Even at 100 kilocycles it is above that of the liquid. The effect here is actually more pronounced than it is in the alcohols. The apparent dielectric constant at 0.5 kilocycle was of such a magnitude (above 30) that the bridge could not be balanced. With further decrease in temperature, the dielectric constant began to decrease, slightly at 100 kilocycles, and more rapidly at the lower frequencies. At a temperature of about 36°, the frequency dependence of the dielectric constant decreased rapidly as did the conductivity. This temperature corresponds approximately to that (39°) reported by Lutton and Jackson for the $\alpha \rightleftarrows$sub-α transition temperature. With further cooling, a region of anomalous dispersion was observed, the dielectric constant decreasing gradually to a value of 2.4 at −37°. It should be noted that, just below the transition point, the dielectric constant is still reasonably high (5.0), indicating considerable orientational freedom in this phase. On warming, similar results were obtained, the only significant difference being that the $\alpha \rightleftarrows$sub-α transition now appeared at 39°. It was observed, however, that the dielectric constant just above the α melting point was considerably lower than it had been at the same temperature on cooling.

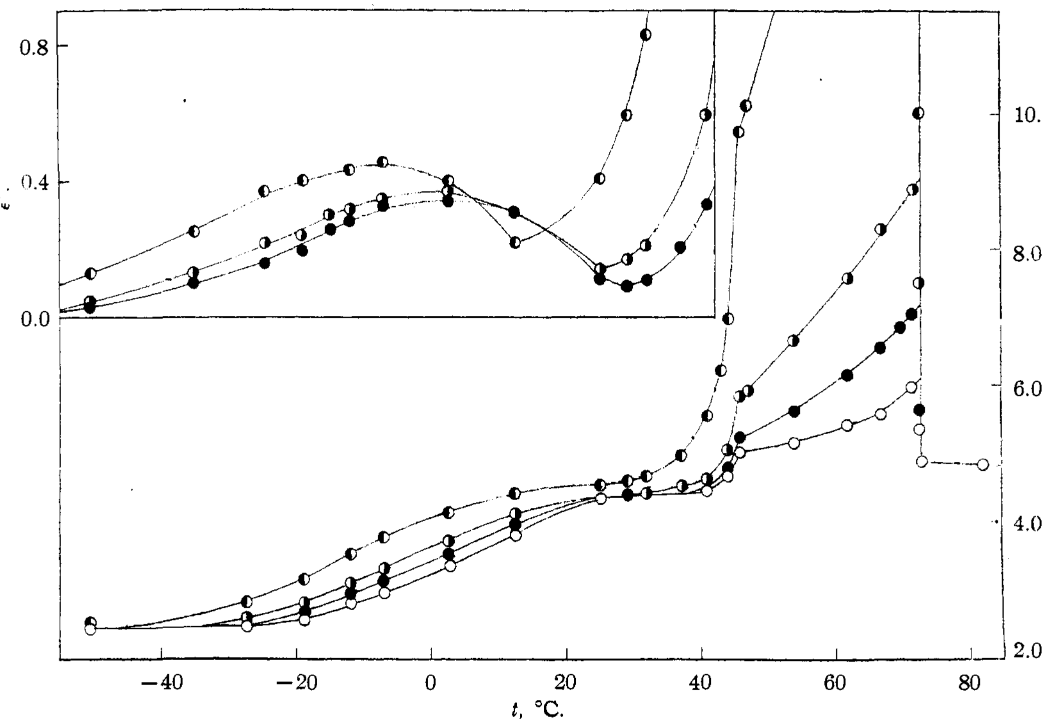

Fig. 2.—The variation of the dielectric constant and loss factor of 1-monostearin with increasing temperature: ○ represents values at 100 kc.; ●, values at 50 kc.; ◑, values at 25 kc.; and ◐, values at 5 kc.

This was caused by the presence of a small amount of the more stable β' or β form, probably formed during the α melting process. It appeared in the form of small white patches of solid dispersed throughout the molten glyceride. After melting, the temperature was raised slightly to 67° and held there until recrystallization into the more stable form was complete. Approximately two hours were required for complete crystallization, which lowered the dielectric constant from 5.16 to 2.65.

In Fig. 2 are plotted dielectric constant values for 1-monostearin at different frequencies as functions of increasing temperature. Here again both warming and cooling runs were quite similar. The same general type of behavior was observed for this compound, except that the α form was more stable than it was in the case of 1-monopalmitin. Although a trace of a higher melting form may have been present after melting of the α form, it could not be observed. Its absence is indicated by the fact that essentially the same liquid values of the dielectric constant were obtained on warming as on cooling. The α melting point as observed here was 73° and the $\alpha \rightleftarrows$ sub-α transition point appeared at 46°, as compared to 74 and 49°, respectively, reported by Lutton and Jackson.

Since the α forms of these two substances are relatively unstable near their melting points, it is possible that at least a trace of the β' or β form is always present during the measurements, and that the considerable difference in dielectric constant and the large difference in conductivity between the two phases gives rise to interfacial or Maxwell–Wagner polarization. Malkin and Shurbagy[3] actually observed both the vertical long spacings and the tilted β long spacings in some of their X-ray diffraction patterns of the α forms. However, the present investigation indicates that, at least in the case of 1-monostearin, the gradually cooled sample could be melted completely at the α melting point, even though a relatively slow rate of warming was employed. Only after the sample was allowed to stand for several hours near the α melting point was there any evidence of transformation to a higher melting form. It, therefore, appears that the observed dependence of the dielectric constant upon frequency is not the result of the coexistence of two solid phases.

As in the case of the alcohols, it is reasonable to assume that the abnormally high conductivities of the α forms of the 1-monoglycerides are the result of the transfer of protons through the sheets of hydroxyl groups in the crystals. If one looks upon the solid as consisting of a large number of these crystals of various sizes and shapes, it can be seen that the application of an electric field would induce a relatively large displacement of charge in each due to displacement of protons. When the field changes direction, this displacement would be reversed. Each crystal, then, acts as a macroscopic "dipole." Obviously the average extent of the separation of charges in these "dipoles" will be dependent upon the time the field remains in one direction, and, therefore, upon the frequency. As the frequency is increased, this separation of charges decreases, thus resulting in a corresponding decrease in the apparent dielectric constant. At a sufficiently high frequency, the displacement becomes so slight that only orientation of the molecules themselves can contribute to the dielectric constant. Actually, the observed effects should be dependent to some extent upon the sizes and shapes of the crystals. This spatial polarization mechanism is similar to that of ordinary Maxwell–Wagner polarization and should give similar results. The similar behavior of the long-chain alcohols might also be explained in this manner. The dielectric constants and the considerable conductivities (Table I) for the liquid phases show no dependence upon frequency because the liquid gives no opportunity for the accumulation of interfacial charges.

Bhide and Bhide[13] have measured the dielectric constant of 1-monomyristin and 1-monostearin at 1,000 and 5,700 kilocycles, and, in general, the results obtained were similar to those reported here. They found, however, that 1-monostearin solidified at 70.8° when cooled gradually, while a rapidly chilled sample melted at 74.5°. The form obtained by rapid chilling was called the true α form, but little mention was made of the nature of the form obtained by slow cooling except that its dielectric constant was somewhat higher than that of the liquid. In the present investigation, no such variation in melting point with rate of solidification was observed, and there is no reason to doubt that the α form was obtained in both cases. Moreover, Bhide and Bhide consistently obtained higher dielectric constant values at 5,700 kc. than at 1,000 kc., even for the molten glyceride. This discrepancy could easily arise from failure to correct for the effects of inductance at the high frequencies. However, since the dielectric constant of the α form is higher than that of the liquid at 5,700 kc., their results justify the conclusion that the apparent dielectric constant values obtained here at 100 kc. are only slightly higher than the true values for the α phase. Actually, this same conclusion is indicated by the smallness of the difference between the values at 100 kc. for the solid and the liquid in Figs. 1 and 2. Part of the difference between the solid and liquid values is, presumably, due to the increase in density on solidification, which results in an increase in the number of dipoles between the condenser plates. It would, therefore, appear that the molecules possess orientational freedom in the α forms comparable to that of the liquid. The rather high dielectric constant in the higher temperature regions of the sub-α forms also indicates freedom of orientation, the possible mechanism of which will be discussed later in this paper.

In previous work,[8,9,10] orientational freedom for long-chain molecules about their long axes has been observed only in a vertical phase, that is, a phase in which the long axes of the molecules are perpendicular to the planes of the terminal groups. However, Lutton and Jackson were unable to observe vertical long spacings in the α forms of the monoglycerides and Malkin and Shurbagy were also unable to obtain them except near the melting points of these forms, and not at all in the case of 1-monopalmitin. These latter authors have suggested that the α form is stable only near its melting point and that, at lower temperatures, the solid consisted of aggregates of molecules in all intermediate stages from vertical rotating to tilted rigid, possessing the mobility of the liquid crystalline rather than the crystalline state. Malkin[14] suggested that the vertical rotating form is typical of liquid crystals and reported evidence of liquid crystalline behavior just below the α melting point. In any event, one would expect a decrease in the frequency dependence of the dielectric constant with decreasing temperature, since conductivity normally decreases under these conditions. As indicated in Table I, the conductivity decreases quite rapidly with cooling in the α form. A similar decrease in the case of the alcohols[8] was shown to be partially due to a gradual and irreversible transformation to the more stable β_2 form. This cannot be the case with the 1-monoglycerides since the phenomena are reversible and reasonably reproducible on warming through the same temperature region.

After the two monoglycerides had been maintained near their α melting points for a considerable length of time (2 hr. for 1-monopalmitin and 48 hr. for 1-monostearin), they were found to have transformed into the more stable forms. Subsequent dielectric constant measurements on these forms (Fig. 3) indicate that molecular orientation is greatly restricted or no longer possible until the melting point is approached. It is not possible, from these measurements, to determine whether the β' form or the β form was present under these conditions. The frequency dependence of the dielectric constant below the region of melting may, in this case, be attributable to Maxwell–Wagner polarization, resulting from the presence of at least a trace of a second phase. The observed melting points (77° for monostearin and 74.5° for monopalmitin), however, agree well with the values 78 and 74.5° reported for the β' forms, which could not be isolated from the α forms.[4] It was observed in the present investigation that slow decomposition, caused by prolonged treatment at elevated temperatures, resulted in a gradual decrease in the α melting points and also in the $\alpha \rightleftarrows$sub-α transition points of these substances. This decomposition may have introduced sufficient impurity either to stabilize

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[13] Bhide and Bhide, *J. Univ. Bombay*, **8**, 220 (1939).

[14] Malkin, *Trans. Faraday Soc.*, **29**, 977 (1933).

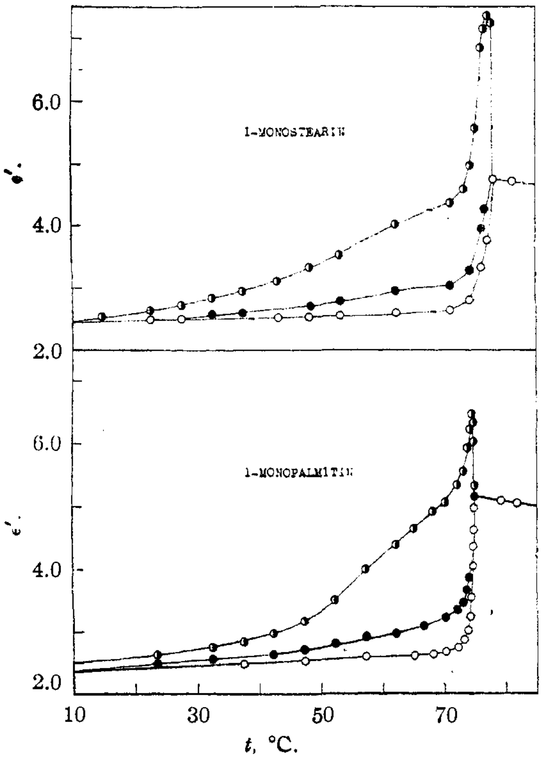

Fig. 3.—The variation of the dielectric constants of 1-monopalmitin (lower) and 1-monostearin (upper) with increasing temperature after prolonged treatment just below the α melting points. Hollow circles represent values at 100 kc.; filled circles, values at 25 kc.; and half-filled circles, values at 5 kc.

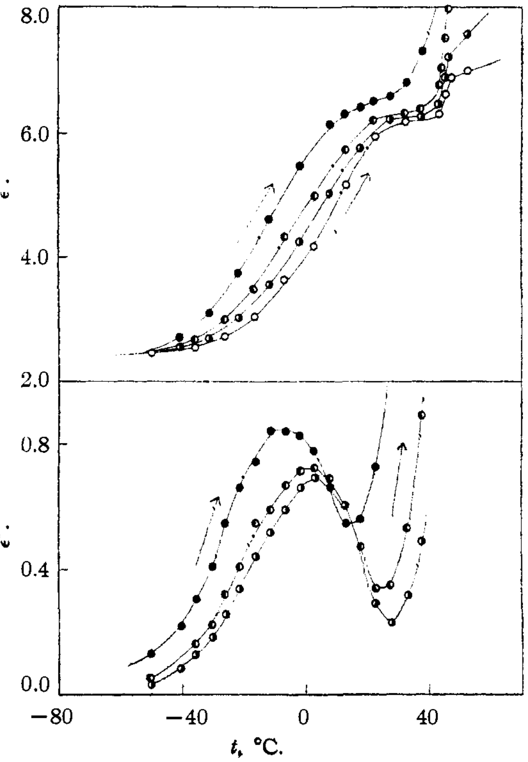

Fig. 4.—The variation of the dielectric constant and loss factor of a rapidly chilled sample of 1-monostearin with increasing temperature: ○ represents values at 100 kc.; ◑, values at 50 kc.; ◐, values at 25 kc.; and ●, values at 5 kc.

the β' forms considerably or result in an even more pronounced decrease in the β melting points. However, neither β' nor β is expected to possess molecular freedom.

As previously mentioned, Lutton and Jackson[4] have made a careful dilatometer study of the sub-α forms of the two substances studied here. They found that rapid cooling resulted in a sub-α form with nearly the same density as that of the α form. However, after increasing the temperature to within a few degrees of the α melting point and then recooling, the density was considerably greater (even greater than that of the β form). An analogous change in dielectric properties was also observed in the present work. The sample of 1-monostearin was cooled rapidly to room temperature and then more slowly to low temperatures. Dielectric constant and loss measurements were then made with increasing temperature. The results plotted in Fig. 4 are, in most respects, similar to those obtained with a gradually cooled sample (Fig. 2). However, the magnitude of the dielectric constant just below the transition point is considerably higher (6.2 compared to 4.4 for the slowly cooled sample). After warming to just below the α melting point and recooling, results identical with those in Fig. 2 were obtained. It would appear, from these measurements, that greater molecular freedom exists after rapid cooling, probably due to larger volume. The phenomenon evidently depends both upon the rate of solidification of the α form and upon its subsequent cooling rate. The behavior of the sub-α form does not change with successive warming and cooling above and below the transition point until the vicinity of the α melting point is approached in warming. It seems, therefore, that the somewhat less rigid environment at elevated temperatures may permit changes in the alignment of the chains which persist to a large extent on recooling. Although the data are not reproduced here, it was found that 1-monopalmitin behaved in an analogous manner when rapidly solidified.

In the lower members of the series, it has been shown[3] that the arrests in the α cooling curves are associated with transitions into the β' and β forms, while in the intermediate members they corresponded almost entirely to transitions into the β' forms. Above monopentadecoin, they appeared in both cooling and warming curves and, as indicated in our research, were completely enantiotropic. The forms existing below the transitions were reported to be vitreous in nature.[8] The more recent X-ray investigations of Lutton and Jackson, however, indicate that these sub-α

forms are highly ordered structures, even more so than the α forms.

It should be pointed out that low frequency anomalous dispersion, somewhat similar to that observed here for the sub-α forms of the monoglycerides, is normal in organic glasses,[15,16] and may also occur in crystalline compounds.[17,18,19] According to the Debye theory,[20] most of the anomalous dispersion of the dielectric constant with frequency at a given temperature covers a range of only two decades of frequency, that is, when ϵ' begins to decrease with increasing frequency, most of the drop from a value equal to that of the static dielectric constant, ϵ_0, to one equal to the optical dielectric constant, ϵ_∞, should occur within a one hundred-fold increase in frequency. Correspondingly, in this same frequency range, the loss factor, ϵ'', should pass from a low value through a maximum value, $\epsilon''_m = (\epsilon_0 - \epsilon_\infty)/2$, to a low value once more. If the dipole orientation process requires more than the one relaxation time assumed in the Debye theory, the dispersion region extends over a greater range of frequency and the maximum value of the loss factor is less than that given by the above expression.[21] In the cases of several organic glasses,[15,16] the maximum loss factor is not far below that calculated on the basis of a single relaxation time, ϵ' drops from ϵ_0 almost to ϵ_∞ for an increase of frequency from 0.5 to 50 kc. in the dispersion region, and, for a given frequency at the beginning of the dispersion region, a temperature decrease of 25 to 30° causes almost the entire dispersion region to be traversed. Figures 1 and 2 show that a temperature decrease of about 75° is necessary to cause traversal of the entire dispersion region for a given frequency for the sub-α forms for 1-monopalmitin and 1-monostearin. Figure 1 shows that ϵ_0 for 1-monopalmitin is about 5.0 at the beginning of the lower dispersion region, for which ϵ'' is plotted in the insert, and ϵ_∞ is about 2.4. The maximum value reached by ϵ'' should, therefore, be about $(5.0 - 2.4)/2 = 1.3$, instead of about 0.7 as observed. Similarly, Fig. 2 shows that ϵ_0 for 1-monostearin at 30° is about 4.5 and ϵ_∞ about 2.5. The maximum value of ϵ'' should, therefore, be about $(4.5 - 2.5)/2 = 1.0$, instead of the observed 0.4. It is evident, then, that there is a wide distribution of relaxation times for these polarization processes in the sub-α forms of the monoglycerides, although X-ray analysis indicates that their structures are highly ordered. A possible explanation for this unusual behavior is that rotational freedom of the molecules about their long axes ceases below the $\alpha \rightleftarrows$sub-α transition point and that the observed orientation polarization in the sub-α forms is due to orientation of various molecular segments, a process which could easily lead to the observed distribution of relaxation rates.

Summary

The dielectric properties of 1-monopalmitin and 1-monostearin have been investigated at 100, 50, 25 and 5 kilocycles over a wide temperature range. Both compounds were observed to possess orientational freedom in both the α and sub-α forms. Strong frequency dependence of the dielectric constant and abnormally high conductivity, similar to that reported for the long-chain alcohols, were observed in the α forms of these compounds. The high conductivity has been attributed to a proton transfer mechanism facilitated by rotation of the chains about their long axes. The frequency dependence of the dielectric constant has been discussed in terms of a spatial polarization mechanism. The more stable β' or β forms, isolated by special thermal treatment, possessed dielectric constants low enough for them to be considered as non-rotators. The sub-α forms have been studied and their dielectric behavior has been observed to vary considerably with previous thermal treatment. In order to account for the distribution of relaxation times observed in these forms, it has been suggested that the dipole orientation process is that of segment orientation. The results obtained here have been compared with previous X-ray diffraction and thermal studies.

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(15) Baker and Smyth, THIS JOURNAL, **61**, 2063 (1939); *J. Chem. Phys.*, **7**, 574 (1939).

(16) Turkevich and Smyth, THIS JOURNAL, **64**, 737 (1942).

(17) White and Morgan, *ibid.*, **57**, 2078 (1935).

(18) White and Bishop, *ibid.*, **62**, 8 (1940).

(19) White, Biggs and Morgan, *ibid.*, **62**, 16 (1940).

(20) Debye, "Polar Molecules," Chemical Catalog Co., Reinhold Publ. Corp., New York, N. Y., 1929, Chap. V.

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