Dielectric Properties of Some Long-Chain Esters in the Solid State[1]

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Abstract

The dielectric properties of a series of long-chain alkyl esters were investigated over a wide temperature range (+25C to −35C) and frequency range (0.05kc to 100kc). The series included esters of all combinations of tetradecanol, hexadecanol, and octadecanol alcohols with tetradecanoic, hexadecanoic, and octadecanoic acids. The thermodynamic parameters were calculated and related to chain length, position of ester group in the chain, and crystal structure.

Introduction

PHYSICAL PROPERTIES OF ANIMAL FATS depend to a large extent on the mechanical properties of the individual molecules which make up animal fats. Little is known about the fundamental mechanical properties of these long-chain molecules. Yet it is these same molecules which are altered chemically to improve their mechanical properties, for example, shortenings, plasticizers, and lubricants. With the present limited knowledge of their physical properties, it is impossible to predict beforehand the results of a particular modification. Successful modifications have been made on a method of trial and error. This is a result of the lack of understanding of the contribution of properties on the molecular level to the over-all macroscopic behavior.

Fats contain long, freely moving molecules; their physical behavior depends on the properties of these long molecules. These physical properties are affected by chain length, the position of various active groups along the chain, and interaction with neighboring molecules. Such physical properties cannot be determined by spectroscopic or chemical methods. They must be determined by some physical method involving larger aspects of the molecule. Dielectric properties constitute one class of physical measurements which are determined by the behavior of the entire molecule. There are a number of publications and books on the theory of dielectric phenomena which are recommended to the reader for background information (5,8).

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TABLE I

Compound	MP (Obs.)	MP (Lit.)
Tetradecyl tetradecanoate	39.1–39.8	
Hexadecyl hexadecanoate	46.4–46.5	
Octadecyl octadecanoate	50.5	
Tetradecyl hexadecanoate	49.5–49.8	48 (7)
Hexadecyl hexadecanoate	51.0	51.6(7)
Octadecyl hexadecanoate	58.3–58.8	59 (7)
Tetradecyl octadecanoate	50.1	50.1(1)
Hexadecyl octadecanoate	57.0–57.6	
Octadecyl octadecanoate	62	62 (7)

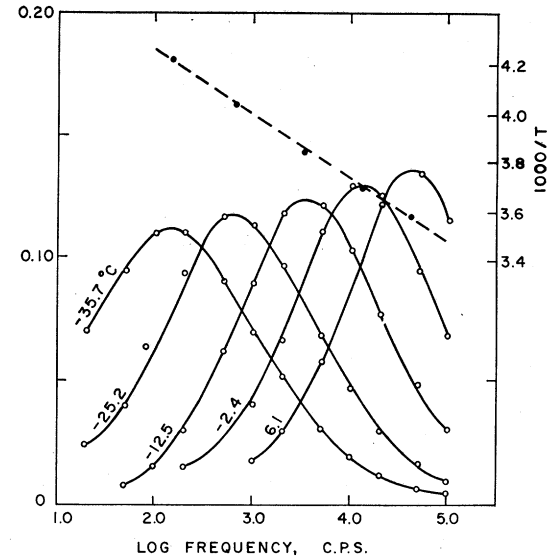

FIG. 1. Temperature dependence of dielectric absorption for tetradecyl tetradecanoate.

Experimental Procedure

Table I shows the experimental and literature values of the melting points of the compounds used in this study. The majority of the samples were purchased from Lachat Chemicals Inc. Two samples (octadecyl tetradecanoate and octadecyl octadecanoate) were synthesized at this laboratory. The commercial samples contained unreacted acids which were removed by washing with a 10% solution of $KHCO_3$. All the samples were then crystallized three times from a hot acetone solution, then their melting points were taken.

The disks used for dielectric measurement were prepared by compressing the samples in a 2-in. circular mold at about 6,000 lbs/sq. in. Aluminum foil

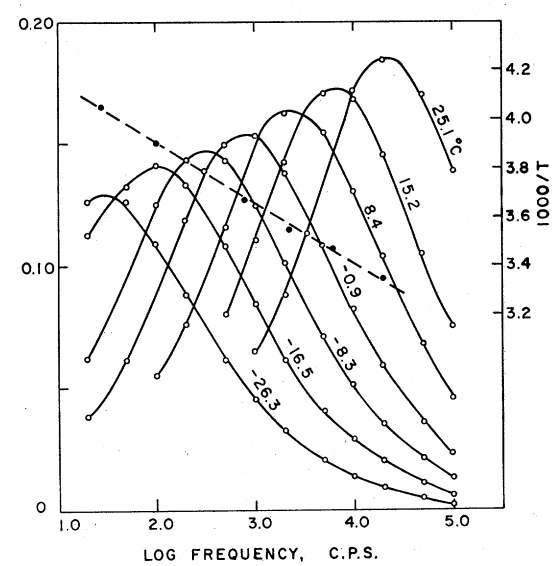

FIG. 2. Temperature dependence of dielectric absorption for hexadecyl tetradecanoate.

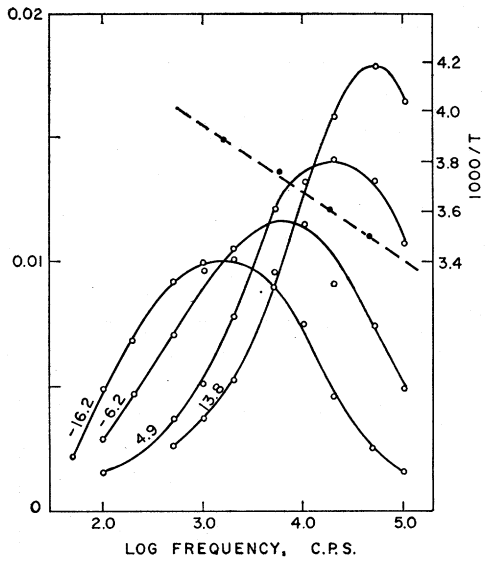

FIG. 3. Temperature dependence of dielectric absorption for octadecyl tetradecanoate.

was placed between the platens of the mold and the sample to insure good contact for the electrodes of the dielectric sample holder and to prevent the sample from adhering to the platen.

A General Radio capacitance bridge, type 716C, energized by a General Radio oscillator, type 1310A, was used to measure capacitance and dissipation of the sample. A substitution method was used, and the signal null was detected by a General Radio tuned amplifier and null detector, type 1232A. The sample holder was a modified General Radio dielectric sample holder, type 1690A. The modification consisted of replacing the present housing with a cored aluminum housing. This cored housing permitted a coolant to be pumped around the electrodes for temperature control. The temperature in the sample holder was measured with a cooper-constantan thermocouple connected to a direct-reading Leeds and Northrup potentiometer, Catalog No. 8692. Dry nitrogen was bled into the sample holder to prevent the accumulation of moisture.

Results and Discussion

Figures 1–7 show the dielectric loss, ϵ'', as a function of the logarithm of frequency at various temperatures. It should be noted that the peaks of the dielectric loss curves decrease with decreasing temperature. This is caused by a wider distribution of relaxation times. Also shown in the figures are the plots of the reciprocal of absolute temperature *versus* logarithm of the frequency at which ϵ'' is at a maximum. These curves are plotted as shown to save space. Normally logarithm of the frequency is plotted *versus* reciprocal of the absolute temperature. Kauzmann (5) has shown that the dielectric dispersion can be treated as a rate process, employing the rate equation:

$$\tau = (h/kT) \exp\ [(\Delta H_\epsilon^\ddagger/RT - (\Delta S_\epsilon^\ddagger/R)])$$

where τ is the relaxation time and equal to the reciprocal of the angular frequency ($2\pi f$) at which ϵ'' is a maximum, h is the Planck constant, k is the Boltzmann constant, and $\Delta H_\epsilon^\ddagger$ and $\Delta S_\epsilon^\ddagger$ are enthalpy and entropy of activation for dipole relaxation respectively. Table II shows the enthalpies and entropies of activation for the various compounds. Two compounds, octadecyl hexadecanoate and tetradecyl octadecanoate, give no dispersion in the frequency and temperature range used. Smyth (1) has shown that tetradecyl octadecanoate does not rotate in the

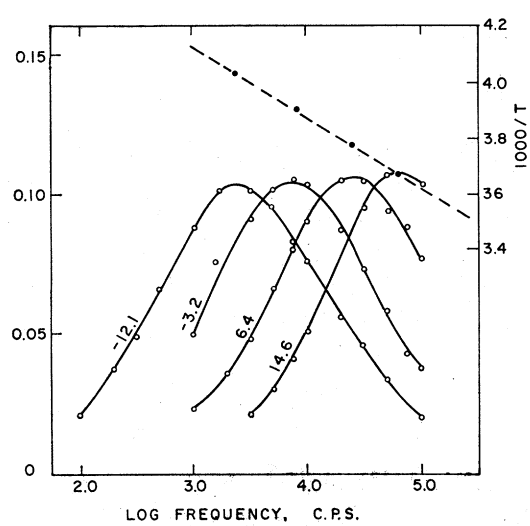

FIG. 4. Temperature dependence of dielectric absorption for tetradecyl hexadecanoate.

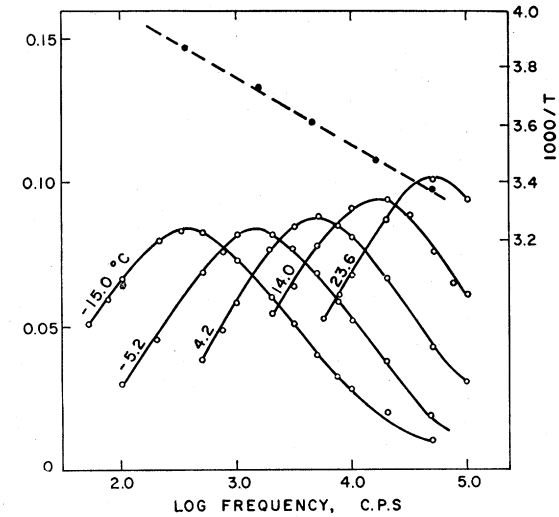

FIG. 5. Temperature dependence of dielectric absorption for hexadecyl hexadecanoate.

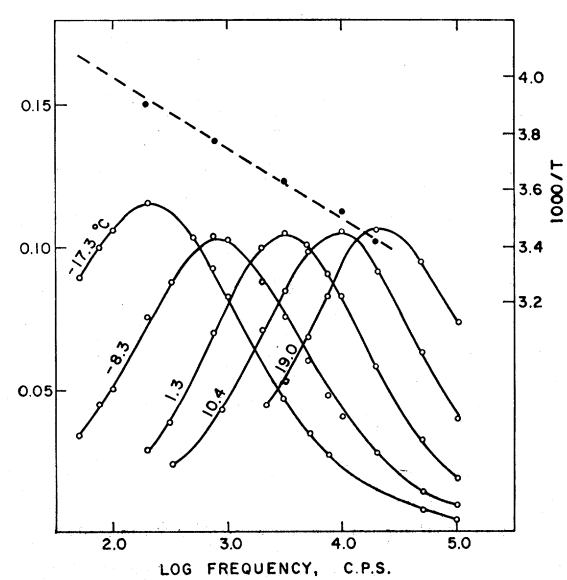

FIG. 6. Temperature dependence of dielectric absorption for hexadecyl octadecanoate.

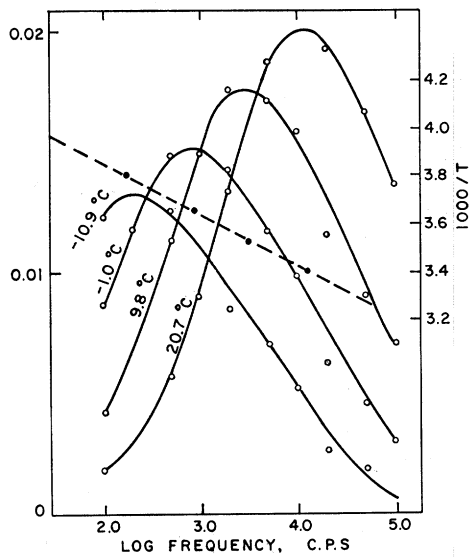

FIG. 7. Temperature dependence of dielectric absorption for octadecyl octadecanoate.

solid state which is in agreement with the data. The interesting thing about these two compounds is that they are of the same crystal form as hexadecyl tetradecanoate, that is, the molecules are almost parallel to the long axis as ascertained by x-ray diffraction data (6). The other compounds listed in Table II have their molecules tilted in the crystal.

It can be noted, by inspecting Table II, that three things affect the dielectric properties of these compounds: chain length, the location of the polar group in the molecule, and the crystal form of the compound.

Tetradecyl tetradecanoate, hexadecyl hexadecanoate, and octadecyl octadecanoate show the effect of chain length. Since the relative location of the ester group in these three compounds is the same in each molecule, any variation in the enthalpy and relaxation time should be a function of the chain length alone; all other effects are assumed equal. One can see from these three compounds in Table II that an increase in chain length can cause an increase in the enthalpy and the relaxation time. This is to be expected if the entire molecule is responding and not the polar group alone.

TABLE II

Compound	$\Delta H\ddagger$[a] ϵ	$\Delta S\ddagger$[b] ϵ	$\tau_0 \times 10^6$[c]	No. of carbons
Tetradecyl tetradecanoate	17,912	31	0.71	28
Hexadecyl tetradecanoate	18,868	31	7.11	30
Octadecyl tetradecanoate	17,038	31	0.4	32
Tetradecyl hexadecanoate	18,760	32	7.96	30
Hexadecyl hexadecanoate	19,649	32	4.49	32
Octadecyl hexadecanoate	.....	....	.....	34
Tetradecyl octadecanoate	.....	....	.....	32
Hexadecyl octadecanoate	18,994	32	8.2	34
Octadecyl octadecanoate	20,783	32	8.92	36

[a] Confidence limits ± 200 cal.
[b] Confidence limits ± 1 cal.
[c] Confidence limits ± 0.5×10^{-6} sec.

The second effect is shown by noting compounds of the same chain length and crystal forms but with the location of the polar group in different relative positions, such as octadecyl tetradecanoate and tetradecyl octadecanoate, also octadecyl hexadecanote and hexadecyl octadecanoate. It is noted that reversing the position of polar groups causes dispersion in one case but, in the other, dispersion does not exist. It is meant by this that octadecyl tetradecanoate has a dispersion region whereas tetradecyl octadecanoate does not; conversely octadecyl hexadecanoate has no dispersion region but hexadecyl octadecanoate does. Daniels and Stark (3) explain symmetrical ketones and Smyth (2) explains esters in the following way: if the polar groups in the molecule are located in the same plane in the crystal, then there is no dipole rotation.

If the interaction in hexadecyl tetradecanoate and tetradecyl hexadecanoate are assumed to be the same, the effect of crystal form can be noted. It can be surmised, qualitatively, that it takes less energy in the perpendicular form to reach the active state than in the tilted state, also that it takes less time to return to the ground state in the perpendicular form than in the tilted form. A mechanism used to explain this phenomenon is the following: if the molecules in the crystal with a perpendicular form are free to rotate in the ground state and in the active state, then it would require less energy to reach the active state and less time to return to the ground state.

In conclusion, generally there is an increase in the enthalpy and the relaxation time with the increase in chain length when the ester group is in the center of the molecule. However what is not known for certain is why some esters rotate while others do not. There appear to be some structural factors, as yet unknown, which influence the dielectric properties of these compounds. Perhaps a more complete investigation of all the crystal forms, both by x-ray and mechanical properties, may give a more complete picture. Also odd-chain alcohol esters, for C_{15} and C_{17}, alcohols of the acids investigated should be studied. The odd-chain alcohol esters are presently being considered as the next step in the investigation.

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