THE RADIO-FREQUENCY DIELECTRIC DISPERSION
IN SOLID ETHYL STEARATE

D. W. DAVIDSON

ABSTRACT
The dielectric properties of solid ethyl stearate were studied between -100° and the melting point at frequencies between 100 cycles/sec and 80 Mc/sec. The circular-arc locus lying within this frequency range in the β (tilted) form consists of a time-dependent and a time-independent part. It is more likely to arise from rotational disorder of tilted molecules than from regions of vertically stacked molecules. The width of the relaxation-time distribution function appears to decrease somewhat more rapidly with increasing temperature than would be expected for a temperature-independent distribution of heights of rotational-energy barriers.

In spite of the common occurrence of dielectric-relaxation effects in the solid forms of polar derivatives of long-chained aliphatic compounds (I) there remains considerable doubt about their origin. One such compound is ethyl stearate, for which a number of experimental studies (2-4) have been published. In the most recent report (4), the radio-frequency dispersion in the β form of ethyl stearate has been attributed to the presence of metastable regions of vertically stacked molecules.

The present report gives some recent results which bear on this question.

EXPERIMENTAL METHODS
Two samples of ethyl stearate were used: one (EK) was the Eastman Kodak White Label product, the other (PRL) a purified product provided by Dr. Burton M. Craig of the Prairie Regional Laboratory. Melting points determined by the capillary-tube method were 31.9 and 30.0° for the EK sample and 33.1 and 30.7° for the corresponding forms of the PRL sample. The latter are in close agreement with the values of Smith (33.3 and 30.9°, respectively) (5).

Measurements were made at frequencies between 0.1 and 800 kc/sec with a capacitance bridge, and at frequencies between 80 and 80,000 kc/sec by the voltage-resonance method of Hartshorn and Ward (6). Measurements were made to below -100° with the bridge and to -35° with the Hartshorn-Ward apparatus. In the latter the micrometer head containing the sample was enclosed in a Lucite box through which cold air was circulated.

All solid samples were prepared by cooling the melts in the dielectric cells. For examination at low temperatures the samples were rapidly cooled so as to "freeze-in" a sufficient number of defects to ensure sufficient dispersion for accurate measurement.

RESULTS
In Fig. 1 the dielectric constant of the EK sample is plotted vs. temperature for two separate cycles, starting from the liquid, at cooling and heating rates of ca. 3° per hour. In the first cycle freezing into the α phase (ε = ~ 2.95) was followed by conversion into the β phase, which was complete at 20°. The shape of the curve in the α → β transformation region depends on the rate of cooling and on the purity of the sample, the transformation being more rapid for the PRL than for the EK sample. In the second
cycle the α form was melted before an appreciable amount of the β form had been formed. It is apparent that the melting point of the α form is lower by about 2° than that of the β form.

Figure 2 shows the dependence on time of the dielectric loss of the PRL sample at 24°, measured at a frequency near that of the loss maximum of the β form. The zero of time was taken at the first appearance of solid (α form) in the melt. At 24°, conversion to the β form starts within 30 minutes of freezing and is thereafter rapidly completed.

Typical complex plane loci for the PRL sample are illustrated in Fig. 3. Except for an upward turn at low frequencies (particularly marked for these rapidly cooled samples),
these loci are circular arcs, with centers below the real axis. Data obtained with the resonance device (like those shown at 272.6° K) give more uncertain arcs than bridge data. This arises primarily from the inaccuracy of the $\varepsilon$ values, as may be seen from the results shown in Fig. 4. Analysis of the resonance results was based on $\varepsilon''$ values alone.

Typical dielectric parameters are listed in Table I. For the bridge measurements,

![Fig. 3. Cole-Cole plots for β-phase ethyl stearate.](image)

<table>
<thead>
<tr>
<th>Phase</th>
<th>$T$ (°K)</th>
<th>$\tau_0$ (sec)</th>
<th>$\varepsilon_0$</th>
<th>$\Delta\varepsilon$</th>
<th>$\alpha$</th>
<th>$\varepsilon''_{\text{max}}$</th>
<th>Method</th>
</tr>
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<tbody>
<tr>
<td>β</td>
<td>204.7</td>
<td>$3.29 \times 10^{-3}$</td>
<td>2.517</td>
<td>.326</td>
<td>.37</td>
<td>.084</td>
<td>Bridge</td>
</tr>
<tr>
<td></td>
<td>215.6</td>
<td>$7.04 \times 10^{-3}$</td>
<td>2.461</td>
<td>.312</td>
<td>.34</td>
<td>.088</td>
<td></td>
</tr>
<tr>
<td></td>
<td>226.9</td>
<td>$1.47 \times 10^{-3}$</td>
<td>2.469</td>
<td>.326</td>
<td>.31</td>
<td>.095</td>
<td></td>
</tr>
<tr>
<td></td>
<td>244.6</td>
<td>$1.85 \times 10^{-3}$</td>
<td>2.486</td>
<td>.330</td>
<td>.29</td>
<td>.102</td>
<td></td>
</tr>
<tr>
<td></td>
<td>255.2</td>
<td>$5.04 \times 10^{-3}$</td>
<td>2.467</td>
<td>.311</td>
<td>.25</td>
<td>.104</td>
<td></td>
</tr>
<tr>
<td></td>
<td>272.6</td>
<td>$7.58 \times 10^{-3}$</td>
<td>$\sim 2.50$</td>
<td>.27</td>
<td>$\sim 21$</td>
<td>.097</td>
<td>Resonance</td>
</tr>
<tr>
<td></td>
<td>297.2</td>
<td>$7.40 \times 10^{-3}$</td>
<td>$\sim 2.50^*$</td>
<td>.27*</td>
<td>$\sim 12$</td>
<td>.109*</td>
<td></td>
</tr>
</tbody>
</table>

For Cole–Cole arcs (7), $\log \nu/\mu = (1 - \alpha) (\log f + 2\pi \tau_0)$. Figure 5 shows such a plot of the data at 215.6° K.

For the resonance data, $\Delta\varepsilon$ was determined from the area of the $\varepsilon''$ vs. $\log f$ plot (8) and $\alpha$ from tan $(1 - \alpha) \pi/4 = 2 \varepsilon''_{\text{max}}/\Delta\varepsilon$ (7).
The results given for bridge measurements in Table I refer to the same solid sample; no dependence on time was observed at these temperatures. The amplitude, but not the frequency characteristics, of the dispersion–absorption region varied considerably with the thermal history of the sample. At room temperature the magnitude of the dispersion decreased slowly with time, as is shown by the decay of the loss in Fig. 6. The decay was approximately exponential, with a time constant of some 24 hours. After several days the loss had fallen to about one half of its initial value and no further reduction was apparent.

The linear dependence of log \( \tau_0 \) on \( 1/T \) (Fig. 7) formally gives an activation energy of 13.7 kcal/mole, in agreement with the value 13 kcal/mole reported by Dryden and Dasgupta (3) from measurements in the vicinity of room temperature and with the 12.7 kcal/mole value obtained by Broadhurst and Fitzgerald (4) for temperatures between ca. \(-80\) and \(-30^\circ\).
Fig. 6. Time dependence of $\varepsilon''$ of $\beta$-phase ethyl stearate at 24° and 15 Mc/sec.

Fig. 7. Dependence of relaxation time on temperature.
DISCUSSION

Variation of Width of the Distribution Function of Relaxation Times with Temperature

Broadhurst and Fitzgerald reported (4) a value of 0.39 for the distribution parameter $\alpha$, a value obtained from measurements at $-65^\circ$ (private communication from Professor Fitzgerald). As is evident from Fig. 8, our results indicate that $\alpha$ decreases rapidly with increasing temperature. Such a trend is to be expected from the presence of a finite distribution in heights of the energy barriers to orientation of dipoles. It is of interest to attempt to estimate quantitatively the temperature-dependence of $\alpha$ in such a case.

The distribution function (7) for relaxation times $G(s)ds$, where $s = \ln_e (\tau/\tau_0)$, may be replaced by a distribution in barrier heights $B$, where $B$ is related to the relaxation time by $\tau/\tau_0 = \exp (B/T)$:

$$H(B)dB = \frac{\sin \alpha \pi}{2\pi T \cosh (1-\alpha)B/T - \cos \alpha \pi} dB.$$  

If the distribution of barrier heights does not depend on temperature, the integral

$$\int_{-\infty}^{B} H(B)dB = 0.5 + \frac{1}{(1-\alpha) \pi} \tan^{-1} \left[ \tanh \left( \frac{(1-\alpha)B}{2T} \right) \tan \left( \frac{(1-\alpha)\pi}{2} \right) \right]$$

is independent of temperature. If $\alpha$ is known at some temperature, $\alpha$ may then be computed for some other temperature for various assumed values of $B$. The value so obtained is found to be somewhat dependent on $B$, which implies that the assumption of a temperature-independent distribution of barrier heights is not strictly compatible with maintenance of the circular-arc locus as the temperature is changed. However, the variation of $\alpha$ with $B$ is small for $B$'s which contribute appreciably to the relaxation behavior.

It is evident from Table II that over-all values of $\alpha$ of 0.31 at 250° and 0.265 at 300° K lead to approximately the same integral distribution in $B$ as that given by the experimental value of $\alpha$ (0.38) at 200° K. The experimental values of $\alpha$ (Fig. 8) decrease somewhat more rapidly than these “predicted” values. This suggests that the breadth of the barrier distribution function decreases as the temperature is raised.

Fig. 8. Variation of $\alpha$ with temperature: ● bridge, ○ resonance measurements.
TABLE II

Integrated distribution function \( I(B) = \int_{-\infty}^{B} H(B) dB \)

<table>
<thead>
<tr>
<th>( B )</th>
<th>( \alpha = 0.38, T = 200^\circ )</th>
<th>( \alpha = 0.31, T = 250^\circ )</th>
<th>( \alpha = 0.265, T = 300^\circ )</th>
</tr>
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<tr>
<td>-2000</td>
<td>0.001</td>
<td>0.001</td>
<td>0.002</td>
</tr>
<tr>
<td>-1000</td>
<td>0.022</td>
<td>0.025</td>
<td>0.029</td>
</tr>
<tr>
<td>-600</td>
<td>0.078</td>
<td>0.081</td>
<td>0.086</td>
</tr>
<tr>
<td>-346</td>
<td>0.179</td>
<td>0.178</td>
<td>0.182</td>
</tr>
<tr>
<td>-290</td>
<td>0.268</td>
<td>0.263</td>
<td>0.265</td>
</tr>
<tr>
<td>-100</td>
<td>0.366</td>
<td>0.383</td>
<td>0.384</td>
</tr>
<tr>
<td>0</td>
<td>0.500</td>
<td>0.500</td>
<td>0.500</td>
</tr>
</tbody>
</table>

For positive values of \( B \), \( I(B) = 1 - I(-B) \).

It is worth noting that the range of barrier heights corresponding to the distribution of relaxation times is small in comparison with the actual magnitude of the barriers. Thus at 200°K half the relaxation occurs across barrier heights which lie within \( BR = \pm 0.5 \) kcal/mole of the 14 kcal/mole value of the most probable barrier height given by the energy of activation.

The variations with temperature of bridge values of \( \Delta \alpha \) and \( \epsilon''_{\text{max}} \) for the same rapidly cooled sample are shown in Fig. 9. The fall in \( \epsilon''_{\text{max}} \) with decreasing temperature, observed also by Broadhurst and Fitzgerald, reflects the increase in \( \alpha \), since \( \Delta \epsilon \) is approximately constant.

**Origin of the Dispersion**

There can be little doubt that the dispersion and absorption effects observed at radio frequencies are related to defects in the crystal structure. The amplitude of these effects, but neither the most probable relaxation time nor the width of the distribution of relaxation times, depends appreciably on the thermal history of the sample. Measurements in the vicinity of room temperature indicate that the amplitude of absorption ultimately
reaches a steady value, rather than falling to zero. This suggests that in general the absorption is the sum of two terms, one arising from the presence of defects intrinsic in the sample at the temperature of measurement, and the second from the presence of defects in excess of the "equilibrium" number by an amount which depends on the thermal history. At low temperatures the rate of disappearance of excess defects is so slow that they are effectively "frozen-in". The loss observed is then considerably higher than that corresponding to the "equilibrium" number of defects. In Fig. 9 the lowest curve is an extrapolation from higher temperatures of the equation for the equilibrium value of \( \epsilon''_{\text{max}} \) reported by Dryden and Dasgupta (3). For a sample maintained several days at room temperature, however, our \( \epsilon''_{\text{max}} \) agreed with the equilibrium value given by their equation (0.08) (but not with the value shown in their Fig. 1).

It is apparent that the dispersion cannot arise from the presence of regions of vertically stacked molecules of the type originally produced on freezing of the sample, since the latter phase shows no dispersion in this frequency range. The possibility has been considered (4) that a second vertical form may be responsible for the dispersion. This suggestion is not supported by a number of factors:

1. The X-ray photographs of freshly frozen samples show (9) a single long spacing which is quite rapidly replaced completely by a second, somewhat shorter, long spacing. The size of the contribution of the dispersion to the static dielectric constant (0.2 to 0.4 or more at room temperature) is an appreciable fraction of the contribution of the rotating dipoles in the liquid state (0.8 to 0.9, extrapolated to room temperature). This seems to indicate that an appreciable fraction (of the order of one third) of the molecules in the \( \beta \) phase at room temperature are capable of contributing to the polarization, despite the X-ray evidence for the absence of a vertical form. This does not necessarily imply that, according to the model of vertical packing, about one third of the molecules need exhibit vertical packing, since one defect might affect the ability of several molecules to orient. However, the case in which the effective defect population is least, that of single, or small groups of, defect molecules, is precisely the case which is least attractive thermodynamically for defects which consist of molecules whose long axes are considerably inclined to the long axes of neighboring molecules.

2. It appears unlikely that parts of the sample can remain indefinitely frozen into a vertical structure, when a good part of the dispersion disappears at a finite rate.

3. Broadhurst and Fitzgerald (4) found that the dispersion shown by the solidified form of a 10% solution of ethyl stearate in heneicosane was similar to that shown by pure ester, except for the magnitude of the dispersion, which was only about 10% as great. These workers have inferred, since heneicosane exists only in vertical modifications, that ethyl stearate in the solid solution occurs in a vertical form. However, the effect of the ester on the crystal form of the hydrocarbon is not known. Moreover, one should have expected the dispersion, per ethyl stearate molecule, to be much greater in the solution (where all the molecules are vertically packed) than in the pure ester (where groups of vertically packed molecules constitute defects in a tilted form).

Perhaps the most satisfactory model is one which takes the defects to consist of molecules whose carbon chains lie in planes which make appreciable angles with the planes of neighboring molecules, that is, which have been considerably rotated about their long axes from their most stable positions. Positions of relative stability would occur at angles of rotation determined by the crystalline field but separated from coplanarity with neighboring molecules by a high rotational barrier. Dryden and Meakins (1) suggest that positions of relative stability exist for angles of rotation of about 90°.
Considerable uncertainty about the nature of the dispersion process remains. A vertical-type defect is not definitely excluded. It is possible that a detailed X-ray or wide-band nuclear magnetic resonance study would prove useful.

Interfacial polarization in the microcrystalline solid is probably responsible for the low-frequency effects (see Fig. 3), which seem to depend even more on rate of cooling than does the radio-frequency dispersion.

ACKNOWLEDGMENTS

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REFERENCES