Dielectric Properties of Polyethylene Glycols

Dielectric Relaxation in Solid State

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The dielectric properties of polyethylene glycols have been investigated for the liquid and solid states over a frequency range from 20 cps to 3 Mc at temperatures from −70°C to +60°C. Relatively high dielectric constants of the liquids were ascribed to the end hydroxyl groups and the flexible oxyethylene chain of the molecule. In the solid state, two types of dielectric relaxation were observed separately: The one was the Debye type or the relaxation of orientation polarization, and the other the wedge type relaxation which supposedly resulted from the space change polarization. The general features of the latter are discussed also in connection with low-frequency relaxation found for other materials.

INTRODUCTION

The dielectric properties of low molecular-weight polyethylene glycols have been reported in previous papers[1~3]. In the case of this particalar type of polymer the molecular chain of polyoxyethylene is fairly flexible due to the rotation around the CO bond in the chain skeleton and thus the mean relaxation time is small, being of the order of the magnitude of 10^{-10} sec in the liquid state at room temperature and does not depend much on the molecular weight or the degree of polymerization. These features have been confirmed with higher molecular-weight polymer by Davies, Williams, and Loveluck[4] who worked on the liquids and solutions in benzene of a series of polyethylene glycols with molecular weights of 200 to 29,000.

In the present work an attempt was made to elucidate the dielectric properties of polyethylene glycols (MW = 600 − 6000) in the solid state, since few work was made on the solids and since a small dielectric dispersion was observed for the solids of lower polymers[1]. Also preliminary measurements on solid 'Carbowax' which was made in this laboratory exhibited a considerable dispersion at very low frequencies. It is another point in this work to examine the nature of the low-frequency dispersion.

EXPERIMENTAL

Materials

Polyethylene glycols used were 'Carbowax' polyethylene glycols with molecular weights ranging from 600 to 6000 which were supplied from Union

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Carbide International Company. Although the original samples were fairly
well fractionated, each one was purified by continuous extraction with dry
diethyl ether in order to remove ionic impurities. The molecular weight
was determined from the end hydroxyl groups. The observed molecular
weights were consistent with those designated by the manufacturer except
for Carbowax 4000. Some physical constants of materials are listed in Table
1. The average molecular weight was slightly reduced by the extraction

Table 1. Molecular weights and melting points of Carbowax.

Carbowax	Molecular weight designated	Molecular weight obsebed	Moisture[a] content %	Melting point °C
600	570—630	633	0.80	26.5
600 EE[c]		604	1.52	26.0
1000	950—1050	1003	3.13	39.0
1000 E[b]		937	1.08	39.5
1000 EE[c]		918	0.88	39.0
1000 EEH[d]		918	2.27	36.5
1540	1300—1600	1410	1.92	46.0
1540 EE[c]		1260	1.26	47.0
4000	3000—3700	2920	1.38	56.0
6000	6000—7500	7800	0.58	64.0

[a] Value determined by the Karl Fischer method.   [b] Extracted with dietlyl ether.   [c]
Extracted twice.   [d] After extraction, exposed to saturated water vapor to increase mois-
ture content.

procedure. As shown in Table 1, the original materials contained a small
amount of moisture. Although the moisture content was reduced by extraction
in most cases, no further desiccation was made in this work. Each polymer
melted fairly sharply, showing a well-defined melting point. Diethyl Carbitol
i.e. diethylene glycol diethyl ether from Union Carbide was fractionted twice
under a reduced pressure. Heptaethyle glycol was the same sample as used
before[1].

Measurements

Dielectric measurements were carried out with a TR–1A Ratio Arm Trans-
former Bridge from Ando Electric Co., which is essentially the same as the
admittance bridge by Cole and Davidson[5]. Minor modification was made on
the commercial equipment in order to improve the low-frequency operation
with highly conductive 'unknown'. The bridge normally operates over a
frequency range of 10 cps to 3 Mc   The cell used consisted of concentric
platinum electrodes, the empty capacity of which was about 20 $\mu\mu$F. Although
no guard electrode was used, the stray capacitance was minimized by proper
shielding. The cell was calibrated with several standard liquids.

RESULTS AND DISCUSSION

Liquid Carbowax

Static or equilibrium dielectric constants and conductivities are listed in

Table 2. Static dielectric constants of liquid Carbowax.

		Dielectric constant ϵ				
		70°	60°	50°	40°	30°
	600		10.38	10.76	11.17	11.60
	600 EE		10.47	10.84	11.22	11.62
	1000		10.74	11.15	11.55	—
	1000 E		9.48	9.76	10.09	—
Carbowax	1000 EE		9.46	9.76	10.09	—
	1000 EEH		10.62	10.95	11.33	—
	1540		9.86	10.19	—	—
	1540 EE		8.95	9.27	—	—
	4000		9.53	9.81*	—	—
	6000	8.20	8.30(65°)	—	—	—
Diethyl Carbitol			5.14		5.52	5.91(20°)

* Supercooled state.

Table 3. Conductivities of liquid Carbowax.

		D. C. Conductivity in 10^{-9} mho cm^{-1}				
		70°	60°	50°	40°	30°
	600		75.6	57.0	40.4	26.7
	600 EE		11.57	8.64	6.08	4.02
	1000		102.3	77.0	54.3	—
	1000 E		20.3	15.60	11.15	—
Carbowax	1000 EE		5.65	4.26	3.04	—
	1000 EEH		9.88	6.85	4.89	—
	1540		16.13	11.86	—	—
	1540 EE		5.08	3.68	—	—
	4000		54.4	39.1*	—	—
	6000	5.70	5.05(65°)	—	—	—
Diethyl Carbitol			0.0887		0.0878	0.0776(20°)
Heptaethylene glycol			4.03	3.05	1.84(35°)	0.961(20°)

*Supercooled state.

Tables 2 and 3, respectively. Since relatively high dielectric constants may be ascribed to the end hydroxyl groups and the flexible oxyethylene chain of the molecule, it is reasonable that the higher molecular-weight Carbowax has the lower dielectrc constant. The contribution of the dipole moment of the oxyethylene chain to the dielectric constant is evident from the high dielectric constant of diethyl Carbitol that has no end hydroxyl groups. The values of dielectric constant of these polyethylene glycols are very consistent with those studied by Davies et al.[1] and also in the previous work on lower polymers[1]. The extracted sample showed a slightly smaller dielectric constant, while the molecular weight was reduced. In this case the dielectric constant was decreased not by a change in the molecular weight but by a decrease in the moisture content. It is clear that a small amount

of water affects the dielectric constant (Table 2). Since the releaxation time of liquid polyethylene is of the order of magnitude of 10^{-10} sec. at room temperature[2,4], no dielectric dispersion was found in the present experimental range of frequency. The apparent increase in dielectric constant due to the electrode polarization took place below about 1 kc. This would be caused by ionic impurities present in Carbowax. The magnitude of the electrode polarization for Carbowax 1000's decreased in proportion to reduction in the conductivity of the sample (Fig. 1). As seen from Table 3, the conductivity
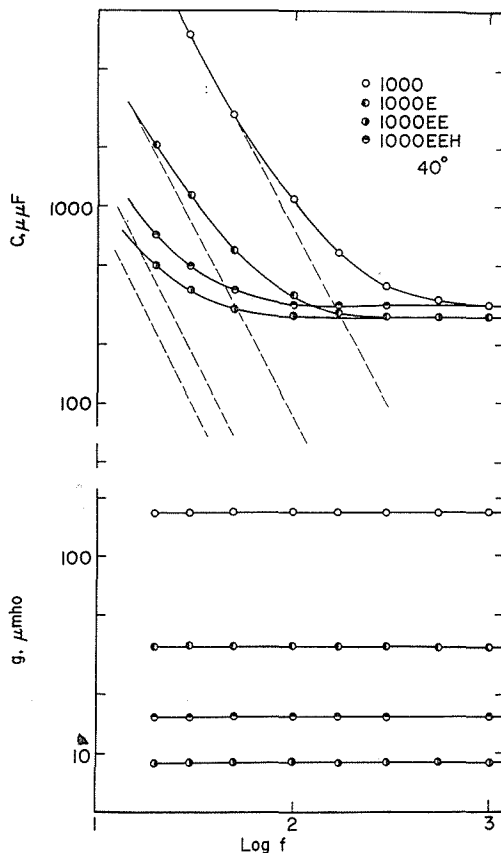
Fig. 1. Frequency dependence of capacitance and conductance
for liquid Carbowax 1000's at 40°C. Broken lines show the
dielectric increment due to electrode polarization.

was reduced greatly by the extraction procedure. When the equivalet impedance of the electrode polarization is taken as $Z_0(j\omega)^{-n}$,[6] the dielectric increment $\epsilon_{app}-\epsilon_0$ due to the electrode polarization is given by

$$\epsilon_{app}-\epsilon_0 = \frac{g^2 Z_0}{C_0}\left(\sin\frac{n\pi}{2}\right)\cdot\omega^{-(n+1)}, \tag{1}$$

and the apparent conductance is

$$g_{app} = g + g^2 Z_0\left(\cos\frac{n\pi}{2}\right)\cdot\omega^{-n}, \tag{2}$$

where ϵ_0 is the static dielectric constant, g is the conductance of liquid, C_0 the capacitance of the empty cell, Z_0 the magnitude of the impedance of the electrode polarization, n an empirical constant $(1 \geqslant n \geqslant 0)$ and ω the angular frequency.

The value of n for these polyethylene glycols was about 0.9. The experimental results on the apparent increase of dielectric constant and no appreciable change in the conductivity with respect to frequency are consistent with those expected from Eqs. (1) and (2), since the second term on the right-hand side of Eq. (2) is negligibly small for $n \approx 1$. The extracted Carbowax was still contaminated with a trace of ionic impurity, because the conductivity shown in Table 3 is higher than those of pure low-membered polymers. Further reduction of ionic impurity could be possible by repeated extraction. With diethyl Carbitol no electrode polarization effect was observed in accordance with a low conductivity.

Solid Carbowax

Dielectric constants and losses of these polyethylene glycols in the crystalline solid state were considerably dependent on frequency and temperature. Plots of dielectric constants and losses versus temperature are shown with Carbowax 1000 in Figs. 2 and 3 respectively. Other polyethylene glycols also showed similar results. The temperature and frequency dependence of this kind are found for several solid dielectrics. There are two types of dielectric dispersion and absorption in Figs. 2 and 3: The one appears at higher temperatures and the other at lower temperatures. The
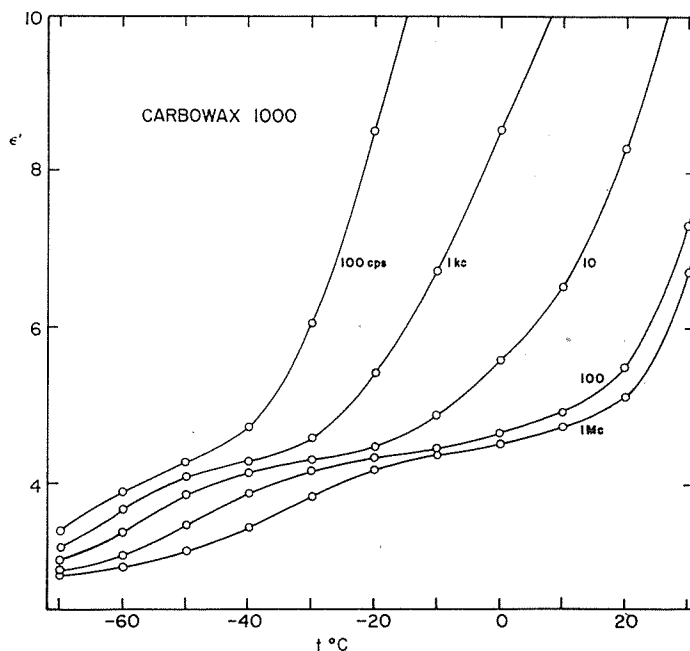

Fig. 2. Plots of dielectric constant ϵ' versus temperature for Carbowax 1000.
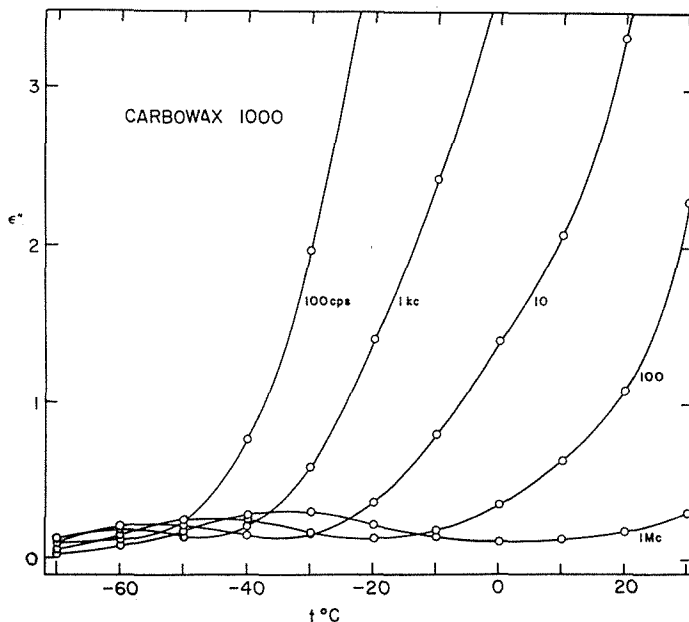
Fig. 3. Plots of dielectric loss ϵ'' versus temperature for Carbowax 1000.

former is what is called the wedge type tentatively in this paper. The latter is an ordinary relaxation of the orientation polarization.

Dielectric Dispersion of the Wedge Type

The frequency dependence of dielectric constant and conductivity at higher temperatures are shown with Carbowax 1000's in Fig. 4, where the dielectric constant decreases with increasing frequency, reaching a limiting value, while the conductivity increases with frequency, levelling off above a certain frequency. Thus, it is evident that $\log \epsilon - \epsilon_0$ and $\log \sigma$ are linear with $\log f$ over a range of frequency.

Now one can put

$$\sigma = A\omega^n, \tag{3}$$

where A and n are empirical constants. Then the dielectric loss ϵ'' is given by

$$\epsilon'' = B\omega^{n-1} = B\omega^{-m}, \quad m = 1 - n, \tag{4}$$

where B and m are also numerical constants. Using Fourier transforations, one can obtain the decay function $a(t)$ from the expression for ϵ''[7],

$$a(t) = \frac{2}{\pi} \int_0^\infty \epsilon''(\omega) \sin \omega t\, d\omega$$

$$= \frac{2B}{\pi} \int_0^\infty \omega^{-m} \sin \omega t\, d\omega$$

$$= \frac{2B}{\pi} \Gamma(1-m) \cdot \cos \frac{\pi m}{2} \cdot t^{m-1}, \quad 1 > m > 0, \tag{5}$$

where $\Gamma(1-m)$ is the Gamma function. Now the real part ϵ' can be derived
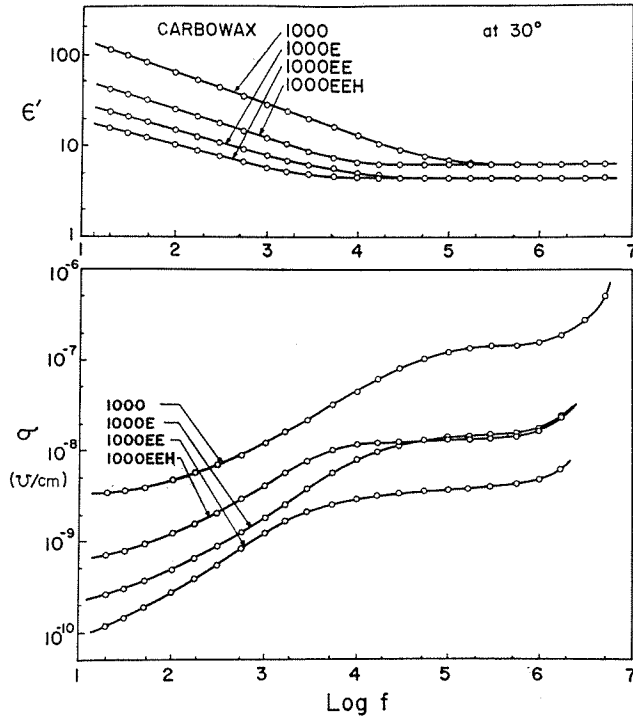
Fig. 4. Frequency dependence of dielectric constant and conductivity in the wedge type relaxation of solid Carbowax 1000's at 30°C.

from the decay function obtained,

$$\epsilon' - \epsilon_\infty = \int_0^\infty a(t) \cos \omega t \cdot dt$$

$$= \frac{2}{\pi} B \Gamma(1-m) \cos \frac{\pi m}{2} \int_0^\infty t^{m-1} \cos \omega t dt$$

$$= B \cot \frac{\pi m}{2} \cdot \omega^{-m}. \tag{6}$$

Combinig Eqs. (4) and (6), the expression in terms of complex dielectric constant, $\epsilon^* = \epsilon' - j\epsilon''$, is given by,

$$\epsilon^* - \epsilon_\infty = \frac{B}{\sin(\pi m/2)} (j\omega)^{-m}, \quad 1 > m > 0. \tag{7}$$

Also

$$\frac{\epsilon''}{\epsilon' - \epsilon_\infty} = \tan \frac{\pi m}{2}. \tag{8}$$

The decay function is related with the distribution function $G(\tau)$ of relaxation times by the equation,

$$a(t) = \int_0^\infty G(\tau) e^{-t/\tau} \frac{d\tau}{\tau}.$$

Thus, one can obtain

$$G(\tau) = \frac{2B}{\pi} \cos \frac{\pi m}{2} \tau^{m-1}. \tag{9}$$

(121)

Therefore $\log G(\tau)$ must be linear with $\log \tau$.

The experimental results shown in Fig. 4 are quite consistent with those expected from the relations derived above. Eq. (4), however, means that the linear relation of $\log \sigma$ with $\log f$ extends to higher frequencies and that there is no levelling-off of the conductivity. The fact that the conductivity attains a limiting value at a certain frequency is connected with the distribution of relaxation times that is somewhat different from prediction of Eq. (9) : There must be the smallest or cut-off relaxation time in the actual system while the function $G(\tau)$ of Eq. (8) has no such a value. It is interesting features that the magnitude of polarization or dielectric constant due to the wedge type relaxation is proportional to the conductivity of the sample in the liquid state (see Table 3). The higher the conductivity, the polarization was the larger and extended to higher frequencies. With Carbowax 1000 the $\log \sigma -$ $\log f$ curve levels also below 50 cps. This may be due to the contribution of d. c. conductivity in the solid state. As temperature was reduced, the d. c. conductivity became smaller and the linear relation of $\log \sigma$ with $\log f$ hold even at lower frequencies. Eq. (8) predicts that the frequency dependence of ϵ^* in a complex plane should be a straight line with the slope of $\tan \pi m/2$. A typical example is illustrated for Carbowax 1540 at 0°C in Fig. 5. The value of m, that is, the slope of $\log (\epsilon' - \epsilon_\infty) - \log f$ and $\log \epsilon'' - \log f$ plots was in a rang of 0.3 to 0.62, depending on individual polymers and temperature.

The decay function of Eq. (5) is essentially the same as that obtained from the absorption current in solid dielectrics by Schweidler[8]. Fricke found the wedge type relaxation for an aqueous dispersion of solid particles or macro-
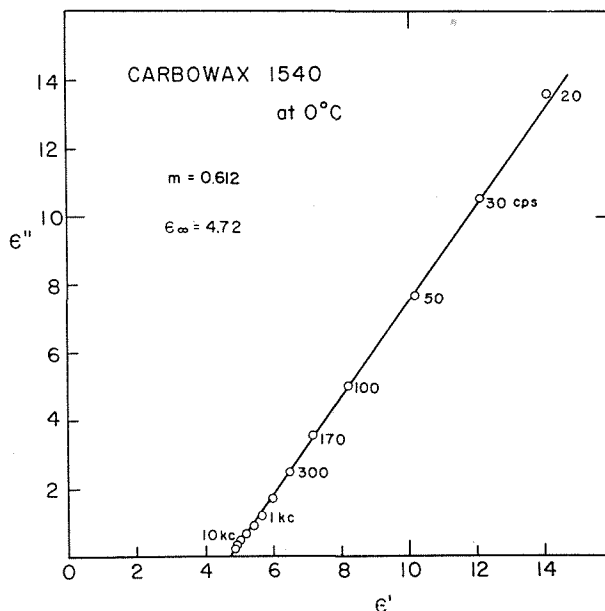

Fig. 5. Complex plane plots of the wedge type relaxation of solid Carbowax 1540 at 0°C.

molecules and he ascribed the effects to the polarization of water molecules bound at or near the dispersed phase[9]. The present authors have found the wedge type relaxation for solid powders dispersed in paraffin[10]. In the case of Carbowax, however, the existence of a small amount of ions as well as the water molesules contained is connected with the mechanism of the wedge type polarization.

It is well known that solid long-chain alcohols exhibit very high dielectric constants and conductivyies in the α-phase between melting and transition points and that the dielectric constant is considerably dependent on frequency[11]. Hoffman and Smyth[12] interpreted the dispersion of the dielectric constant in terms of the Maxwell-Wagner effect for the mixture of two solid phases, the α- and β-phases, which have different dielectric constants and conductivities. Asai et al.[13] proposed that very high dielectric constant of higher alcohols at low frequency may be attributable to the electrode polarization of the conductive proton in the α-phase. He noticed that the polarization was increased markedly by adding foreign ions. The frequency dependence of the dielectric constant for octadecyl alcohol[14] examined in this laboratory was fitted with the relation for the wedge type relaxation.

The exacts mechanism of this type of relaxation have not been established yet. Possibly the relaxation of the space charge in solids would give rise to such frequency dependence.

Relaxation of Orientation Polarization

The wedge type relaxation diminishes with decreasing temperature and the Debye type relaxation of orientation polarization predominates below $-40°C$. The dielectric loss for Carbowax 1000EE at low temperatures are plotted against $\log f$ in Fig. 6. The $\epsilon'' - \log f$ are not symmetrical about the frequency for the maximum ϵ'', i. e. the critical frequency, showing a shoulder on the low-frequency wing. No contribution of the wedge type polarization are found at these indicated temperatures. It is evident in Fig. 6 that there
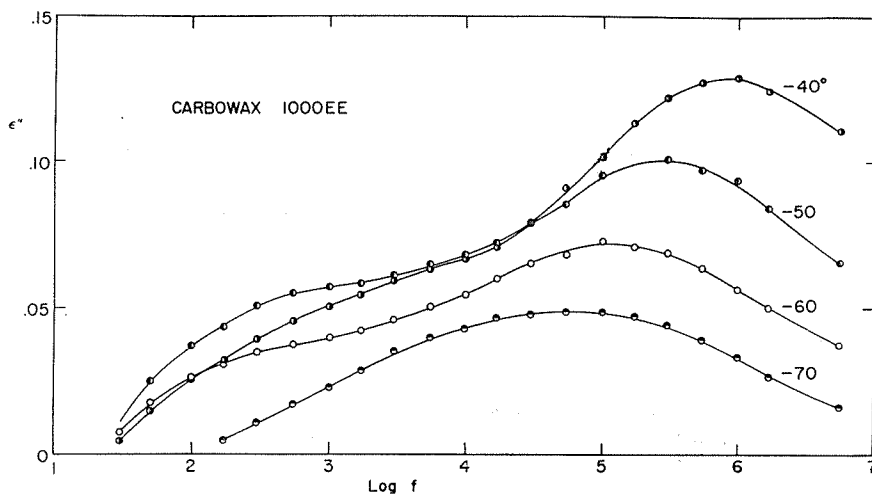

Fig. 6. Frequency dependence of ϵ'' for solid Carbowax 1000 EE.

exist two absorption regions: The one appears at 100 kc to 1 Mc and the other between 1 and 10 kc. The absorption in the high-frequency region may be ascribed to the end hydroxyl groups, because the heat of activation obtained from the temperature dependence of the critical frequency[15] was about 10 kcal/mole for these Carbowax. The low-frequency absorption might be due to the motion of polyoxyethylene chain. Unfortunately no confirmation was possible on account of limited results.

Variation of the relaxation time with molecular weight was not made clear, whereas the critical frequency for the loss maximum scattered for polymers with different molecular weights as shown in Fig. 7. The reason for this would be due to the interaction between water molecules present and the end hydroxyl groups or the oxyethylene group.
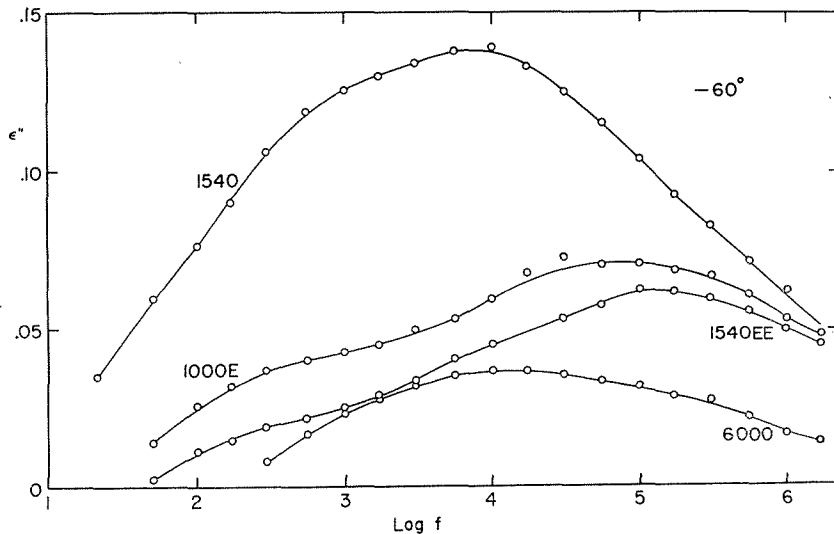

Fig. 7. Plots of ϵ'' versus frequency for Carbowax at $-60°$C.

The Cole-Cole plots of low temperature data give very flat circular arcs, showing a quite broad distribution of relaxation times[16]. Corresponding to the existence of two dispersion regions the $\epsilon''-\epsilon'$ curve may be divided into two circular acrs, as shown in Eig. 8. Another example for Carbowax 1540
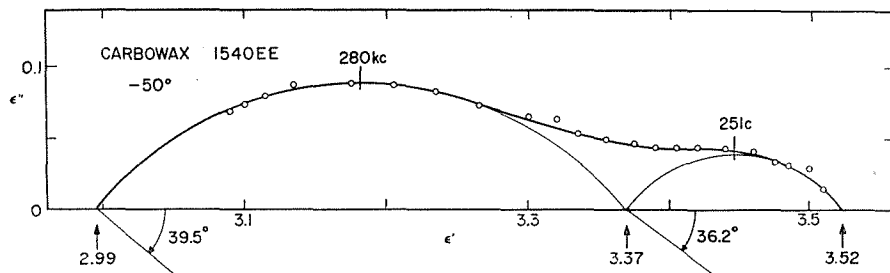

Fig. 8. Cole-Cole plots for solid Carbowax 1540 EE at $-50°$C.
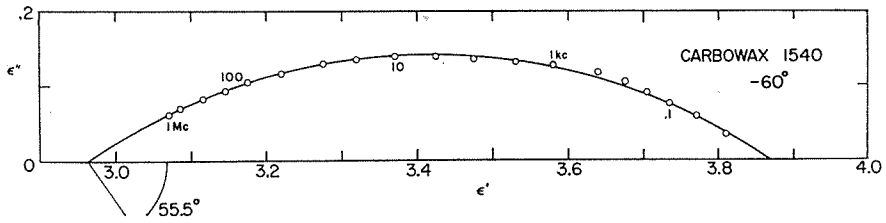
Fig. 9. Cole-Cole plots for solid Carbowax 1540 at −60°C.

at −60° in Fig. 9 shows a much depressed arc. But this would not be a single arc either, possibly consisted of two dispersion region which can be expected from the $\epsilon'' - \log f$ plot in Fig. 7.

In the case of pure heptaethylene glycol, $\epsilon' - \log f$ and $\epsilon'' - \log f$ plots in Figs. 10 and 11 show typical relaxation of the Debye type which corresponds
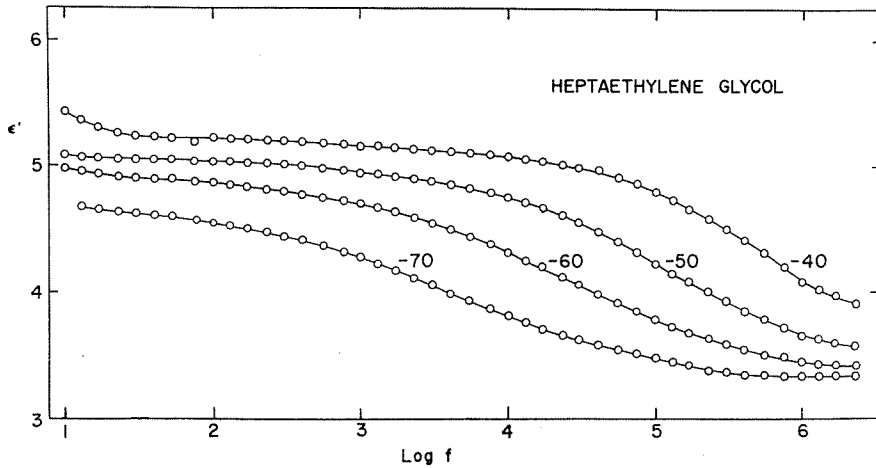

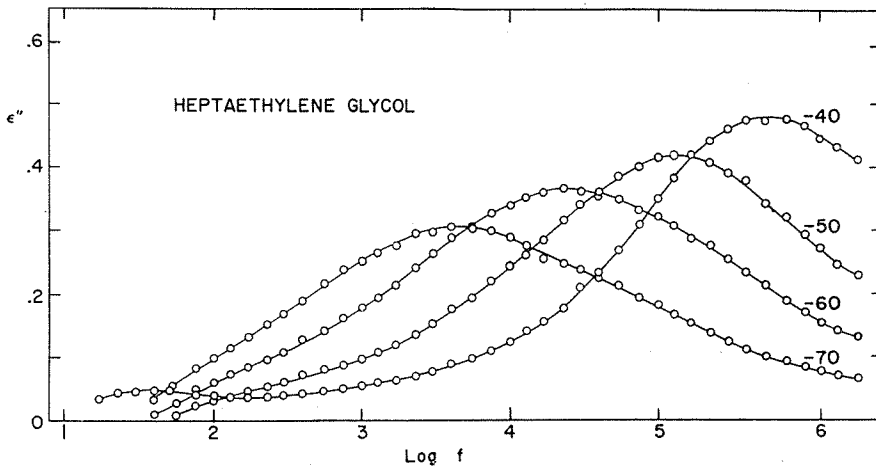Fig. 10. Plots of ϵ' versus frequency for solid heptaethylene glycol.

Fig. 11. Plots of ϵ'' versus frequency for solid heptaethylene glycol.

to a small dielectric dispersion noticed before[1]. A slight increase in dielectric constant below 30 cps at $-40°C$ might be from the wedge type polarization. No shoulder was found with the $\epsilon'' - \log f$ curve, but a small peak of ϵ'' near 30 cps could be corresponding to the low-frequency absorption observed for high polymers. The heat and entropy of activation for relaxtion of heptaethylene glycol was about 15 kcal/mole and 36 e. u., respectively. These values are higher than those for higher polymers. It is likely that hindrance in the orientation of the hydroxyl groups is greater for heptaethylene glycol.

The dielectric constant of solid diethyl Carbitol was as small as 2.6 near $-60°C$. Neither the wedge type relaxatio nor the Debye type was observed. This means that the oxyethylene groups has no freedom of orientation in solid diethyl Carbitol.

CONCLUSION

It was found that the wedge type relaxation for solid Carbowax s closely related to the existence of ions and water molecules. Although the exact mechanism have not been established yet, the space charge polarization of ions co-operated with water molecules would be responsible for relaxation of this type. No particular attention was paid usually to the wedge type relaxation which is common to solid dielectric material at high temperatures and low frequencies, since this type of relaxation seems to be trivial for the dielectric study of the molecular structure. However in the particular cases such as long-chain alcohols, analysis of the dielectric dispersion would be important in connection with the proton transfer mechanism in the α-phase.

The Debye type relaxation found for solid Carbowax would be due to the hydrogen-bonded hydroxyl groups, whereas the heat of activation obtained is sligher higher than those for many other cases.

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