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Dielectric Properties of the Hydrogen-bonded Liquids. Steric Effects on Dielectric Properties in Glycerol and Acetylated Glycerols

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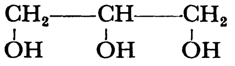
The dielectric constant and the dielectric loss of a monohydroxy molecule (glycerol diacetate) and a dihydroxy molecule (glycerol monoacetate) in the pure liquid state were measured over the frequency range from 23 Hz to 3 MHz in order to elucidate the relation between the steric effects of the acetoxyl group and the dielectric properties of alcohols. For a better understanding, the results of this work were discussed together with those of glycerol and glycerol triacetate. The static dielectric constants decrease in the order of glycerol, glycerol monoacetate, glycerol diacetate, and glycerol triacetate. This order agrees with the order of the decreasing number of hydroxyl groups per molecule. On the other hand, the four curves of a temperature variation of the relaxation times almost form one curve, although the molecular weights and interaction, which are important factors for the determination of relaxation times, differ greatly among the four molecules. Accordingly, it is concluded that the decrease in molecular weight due to the replacement of the acetyl group CH_3CO by a hydrogen atom counteracts the enhanced molecular interaction due to the increased OH···O hydrogen bonds. The experimental Cole-Cole arcs of the complex dielectric constants were well represented by the calculated curve of the Davidson-Cole empirical equation, for glycerol mono- and diacetate as well as for glycerol.

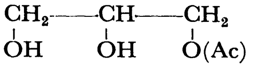
The dielectric properties of a hydrogen-bonded liquid are of interest because such a liquid generally shows abnormal dielectric behavior which is not observed in a non-hydrogen-bonded liquid. With some exceptions, such as acetic acid, the static dielectric constant of a hydrogen-bonded liquid is generally larger than that for a normal polar one, mainly because of the regular alignment of a dipolar molecule in the hydrogen-bonded cluster.[1] The static dielectric constants of alcohols,[2] *N*-methylamides,[3] and cyano compounds[4,5] are particularly large.

Another typical phenomenon with regard to the dielectric properties for a hydrogen-bonded liquid is seen in the distribution of relaxation times. For example, it is well known that a Debye-type semi-circular relaxation is generally observed for a liquid monohydroxy alcohol; on the other hand, a Davidson-Cole-type skewed arc relaxation is observed for liquid polyhydric alcohols, such as diol and triol.[6] As for the relaxation of liquid dielectrics, we have ourselves reported that a Havriliak-Negami-type relaxation, often observed in the α-relaxation of polymers,[7,8] is observed in the relaxation of a non-hydrogen-bonded liquid.[9] This relaxation is not, however, observed in a hydrogen-bonded liquid. A number of dielectric studies have made it clear that the distribution of the relaxation times of organic liquids is associated with both the liquid structure and the molecular structure. In this study we have compared the dielectric properties of glycerol[6] and its acetylated derivatives as follows:



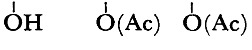
$$\underset{\substack{|\\ \mathrm{OH}}}{\mathrm{CH_2}}-\underset{\substack{|\\ \mathrm{OH}}}{\mathrm{CH}}-\underset{\substack{|\\ \mathrm{OH}}}{\mathrm{CH_2}}$$

glycerol[6]



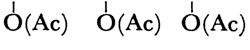
$$\underset{\substack{|\\ \mathrm{OH}}}{\mathrm{CH_2}}-\underset{\substack{|\\ \mathrm{OH}}}{\mathrm{CH}}-\underset{\substack{|\\ \mathrm{O(Ac)}}}{\mathrm{CH_2}}$$

glycerol
monoacetate



$$\underset{\substack{|\\ \mathrm{OH}}}{\mathrm{CH_2}}-\underset{\substack{|\\ \mathrm{O(Ac)}}}{\mathrm{CH}}-\underset{\substack{|\\ \mathrm{O(Ac)}}}{\mathrm{CH_2}}$$

glycerol
diacetate



$$\underset{\substack{|\\ \mathrm{O(Ac)}}}{\mathrm{CH_2}}-\underset{\substack{|\\ \mathrm{O(Ac)}}}{\mathrm{CH}}-\underset{\substack{|\\ \mathrm{O(Ac)}}}{\mathrm{CH_2}}$$

glycerol
triacetate[9]

where Ac is the acetoxyl group.

Hitherto, there have been a number of studies of the dielectric properties of aliphatic mono- and polyhydric alcohols,[10] such as ethanol and pentanediol, however, little is known about the dielectric properties of the substituted alcohols.

Experimental

Purification of Glycerol Monoacetate and Diacetate. The glycerol monoacetate (Eastman Kodak Co.) and the glycerol diacetate (Merck Co.) are both commercial products, and both are mixtures composed of glycerol monoacetate, diacetate, and triacetate. Therefore, it is necessary to separate the mixtures into pure fractions. The fractional distillation under reduced pressures was, however, ineffective for this purpose. Next, a chromatographic column method was tested and adopted. Here, the packing gel was Wako Gel C-200 (Wako Chemical Co.), and the mobile phase used as the developer was a mixture of benzene and methanol, in a ratio which was continuously changed. The results of separation were examined by means of GLPC.

Dielectric Measurement. The dielectric constant and dielectric loss were measured with a ratio-arm transformer bridge (Ando Electric Co., TR-1BK type) over the frequency range from 23 Hz to 3 MHz. The dielectric cell for the liquid studied was a platinum concentric glass cell.

Results and Discussion

Static Dielectric Constant. The dielectric properties of glycerol and glycerol triacetate have been studied by Davidson and Cole[6] and by Ikada and Watanabe[9] respectively.** For comparison, the data have been cited from each reference. The temperature dependence of the static dielectric constant of all four molecules in the liquid state is represented by the linear relation shown in Fig. 1. We, however, recognize a marked variation in the values with the number of hydroxyl

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Ras and Bordewijk also studied the dielectric properties of glycerol triacetate, tripropionate, and tributyrate (A. M. Ras and P. Bordewijk, *Recl. Trav. Chim. Pays-Bas*, **90, 1055 (1971)).

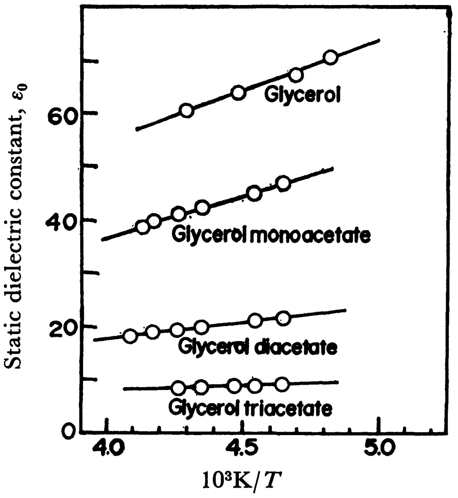

Fig. 1. Temperature dependence of the static dielectric constants of the four liquids. The data of glycerol and glycerol triacetate were cited from Ref. 6 and Ref. 9, respectively.

group per molecule, as the static dielectric constants for glycerol, *ca.* 60, are very large, while, on the other hand, those for glycerol triacetate are less than 10. Doubtless, this step-by-step variation in the static dielectric constant depends mainly on the number of intermolecular hydrogen bonds in each liquid structure, although the detailed conformation of the hydrogen-bonded cluster is not yet known. Strictly speaking, it is necessary to determine the dipole moment *in vacuo* of these molecules for a quantitative estimation of the local ordering due to hydrogen bonds in the liquid structure.[10] However, we can easily see a gradual decrease in the intermolecular hydrogen bonds with an increase in the replacement of a hydroxyl group by a non-hydrogen bonding acetoxyl group. For example, the static dielectric constants of glycerol diacetate are smaller than those for a monohydroxy aliphatic alcohol with the same main chainlength, such as 1-propanol. This decrease in the static dielectric constant of glycerol diacetate proves that the molecular association is destroyed by the hindrance of the large acetoxyl group on forming the hydrogen-bonded cluster.

Dielectric Relaxation. As for the relaxation mechanism of liquid normal alcohols, which has been discussed by many investigators and summarized in many books,[1,10] the explanation is explicit and seems to be well recognized. The proton jump along a hydrogen-bonded chain of monohydric alcohols clarifies the absence of any distribution of the relaxation times. On the other hand, the relaxation mechanism in such polyhydroxy compounds as glycerol appears to remain undetermined, partly because of difficulty in the structural analysis of liquid polyols. The contribution of the hydrogen bond to the dynamic properties of the polyhydric alcohol is apparent in the comparatively high viscosities of the liquids. In other words, the long relaxation times in polyols are due to the accompanying breaking and reforming of the hydrogen bonds on the molecular relaxation. Moreover, the fact that almost all the polyhydric aliphatic compounds show merely the Davidson-Cole-type relaxation in the liquid state makes us imagine a rather similar relaxation mechanism for the molecular motion in these molecules. However, the relaxation mechanism of polyol compounds has not yet been thoroughly clarified in detail. Almost all of the polyols show empirically the Davidson-Cole-type relaxation:[6]

$$\varepsilon^* - \varepsilon_\infty = \frac{\varepsilon_0 - \varepsilon_\infty}{(1+j\omega\tau_0)^\beta}$$

where ε^* is the complex dielectric constant, ε_0 and ε_∞ are the limiting low- and high-frequency dielectric constants respectively, ω is the angular frequency, τ_0 is the mean relaxation time, j is $\sqrt{-1}$, and β is the distribution parameter. As has been described above, Davidson and Cole reported that glycerol shows a Davidson-Cole-type relaxation.[6] On the other hand, glycerol triacetate, a completely acetylated glycerol, does not show this relaxation, but a Havriliak-Negami-type relaxation:[9]

$$\varepsilon^* - \varepsilon_\infty = \frac{\varepsilon_0 - \varepsilon_\infty}{[1+(j\omega\tau_0)^{1-\alpha}]^\beta}$$

where $1-\alpha$ is also the distribution parameter of the relaxation times. The distribution of the relaxation times of glycerol triacetate is wider than that for glycerol, as may be seen in Table 1. The broadening of the relaxation times results from the lack of a hydrogen bond in the liquid structure. The same broadening may be seen in a comparison of the dielectric properties of ethylenediamine and 2-aminoethanol.[12]

Table 1. Distribution parameters ($1-\alpha$) and β in the Davidson-Cole and the Havriliak-Negami-type relaxations

	T/°C	$1-\alpha$	β	ε_∞	ε_0
Glycerol monoacetate[a)]	−31.0		0.517	3.55	38.57
	−33.6		0.500	3.02	40.00
	−38.4		0.498	3.40	40.95
	−43.3		0.513	3.73	42.41
	−52.9		0.500	3.78	45.20
	−58.1		0.464	3.45	46.83
Glycerol diacetate[a)]	−28.5		0.504	3.78	18.16
	−33.4		0.520	4.10	18.78
	−38.4		0.464	3.64	19.33
	−43.4		0.512	4.12	19.95
	−53.4		0.511	3.96	21.20
	−58.3		0.503	3.96	21.70
Glycerol triacetate[b),c)]	−39.1	0.982	0.484	3.65	8.56
	−43.5	0.954	0.483	3.53	8.73
	−49.5	0.967	0.494	3.53	8.89
	−53.3	0.964	0.497	3.53	9.03
	−58.1	0.915	0.523	3.49	9.20
Glycerol[a),d)]	−40.0		0.608	4.20	60.50
	−50.0		0.603	4.10	63.40
	−60.0		0.593	4.16	67.40

a) The distribution parameter of the Davidson-Cole-type relaxation. b) The distribution parameter of the Havriliak-Negami-type relaxation. c) The data from Ref. 9. d) The data from Ref. 6.

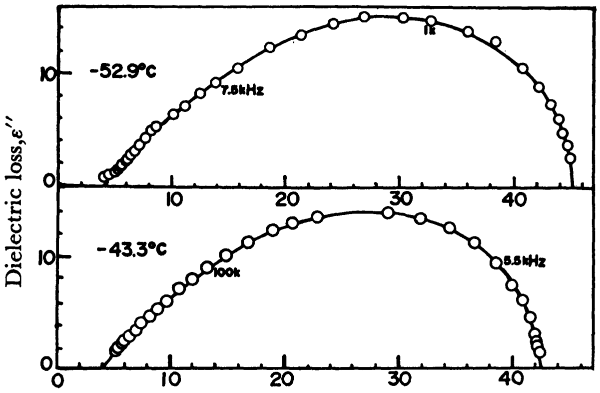

Fig. 2. Cole-Cole plots of glycerol monoacetate.

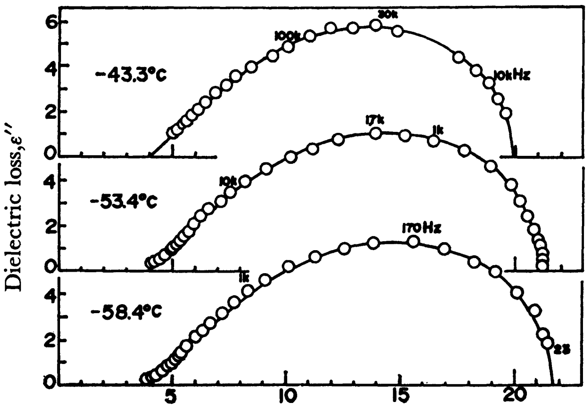

Fig. 3. Cole-Cole plots of glycerol diacetate.

Figure 2 shows the Cole-Cole plots of glycerol monoacetate. The experimental arcs agree well with the curves calculated according to the Davidson-Cole equation. It may, therefore, be concluded that the liquid structure of glycerol monoacetate is not so different from that of glycerol and that the steric hindrance of large CH_3CO–group in this molecule for hydrogen bonding is not so clearly seen. Figure 3 shows the Cole-Cole plots of glycerol diacetate. As may clearly be seen in this figure, these relaxations are expressed by the Davidson-Cole empirical equation. According to our expectations, glycerol diacetate, a monohydric alcohol, should show a Debye-type semicircular relaxation. The result fell short of our expectations, however. Judging from the small static dielectric constants, the hydrogen bonds in glycerol diacetate are much fewer in number than in normal alcohol. On the other hand, glycerol triacetate shows a Havriliak-Negami-type relaxation. The hydrogen bond in glycerol diacetate also contributes to the narrowing of the relaxation times.

Relaxation Times. Empirically, it is considered to be correct that the dielectric relaxation time of an organic molecule in the liquid state depends on the molecular size and weight. Figure 4 shows the relaxation times against the reciprocals of the absolute temperatures. The esterification of the hydroxy group by acetic acid in glycerol leads to a large increase in the molecular size and weight. Nevertheless, the relaxation times do not increase, as is seen in Fig. 4, so much as would be expected from the molecular weight increase.

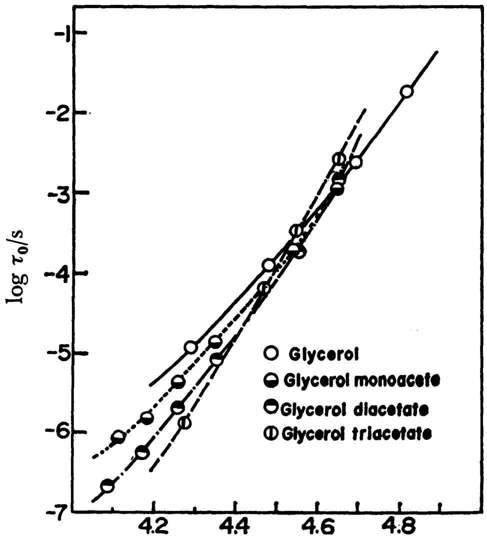

Fig. 4. Arrhenius plots of the relaxation times of the four glycerols. The unit of relaxation times is second.

Another important factor determining a relaxation time is a molecular interaction such as an intermolecular hydrogen bond. The dielectric relaxation of a hydroxy compound in the liquid state generally appears at low frequencies because of this comparatively strong interaction. Thus, the esterification should also lead to a decrease in the intermolecular hydrogen bonds in the liquid structure, and consequently to a decrease in the relaxation times. Figure 4, however, does not show this anticipated tendency; Rather, it shows the four molecules to have almost the same values of relaxation times. The hidden effect due to the change in two important factors, *i.e.*, the molecular weight and the interaction, explains why the relaxation times of the four molecules do not change very much, although the two factors change markedly upon the replacement. The answer is thus given that the two effects counteract each other; therefore, apparently the relaxation times do not differ largely.

References

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