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Dielectric Relaxation and Molecular Structure. VIII. Dielectric Relaxation of Alkyl Acetates in Benzene Solution

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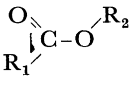
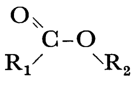
Dielectric constants and losses at the microwave frequency of 96.52 GHz have been measured at 25 °C for methyl, ethyl, *n*-butyl, isobutyl, *s*-butyl, *t*-butyl, *n*-amyl, isoamyl, *n*-hexyl, and *n*-octyl acetates in benzene solutions. Static dielectric constants, refractive indices and densities have also been measured. The effective mean relaxation times of normal alkyl acetates increase with increasing chain length of the alkyl radical, eventually approaching a steady value. The distribution parameters α of all these molecules seem to have appreciable values which may be due to various segment orientations by internal rotation.

According to Wheland[1] the esters of carboxylic acids provide an example with which there appears to be little, if any, freedom of rotation about the bond that links the carbon atom of the carbonyl group to the oxygen atom of the alkoxyl group. If this C–O bond has no freedom of rotation at all, the molecule will have only two planar configurations I (*trans*) and II (*cis*).


I (*trans*)


II (*cis*)

From this viewpoint Marsden and Sutton[2] reached a conclusion from dipole moment measurements that the *trans* form (I) would be more stable than the *cis* form (II).

Williams, Owen, and Sheridan[3] studied the molecular configuration of methyl acetate, *i.e.* $R_1=R_2=CH_3$ by means of microwave spectroscopy and showed that it has the *trans* planar configuration. And methyl and ethyl formates were also shown by microwave spectroscopy[4,5] to exist only in the *trans* planar form. On the other hand Karpovitch[6] suggested the existence of two isomers I and II based on his results of ultrasonic absorption measurements. By use of various spectroscopic methods Ōki and Nakanishi[7] examined the possibility of having two isomers and found that the *cis* conformation, which is very much stabilized in some special cases, does not exist in a great majority of alkyl acetates.

The results of electron diffraction are puzzling because O'Gorman, Shand, and Shomaker[8] showed that the structures of methyl acetate and methyl formate are not perfectly *trans* planar but slightly twisted, that is, the R_2–O bond makes an average dihedral angle 25° with the O=C–R_1 plane of the molecule. They suggested as one of the possibilities that a rather wide oscillation occurs about the completely planar *trans* configuration for these molecules.

The present work was undertaken in order to make a systematic study of dielectric behavior of alkyl acetates in solution and also to examine the aspect of internal motion in these molecules. The molecules examined are ten alkyl acetates, *i.e.* $R_1=CH_3$ and $R_2=C_nH_{2n+1}$, $n=1, 2\cdots 8$.

Experimental

All compounds used in this study were obtained from commercial sources. Further, they were purified by distillation after drying over Molecular Sieve 4A for 24 hours. The apparatus and the experimental technique for dielectric measurements of the free-space method at 100 GHz employed in this work were described in a previous paper.[9] Static dielectric constants at 1 MHz were measured by the heterodyne beat method and refractive indices for sodium D-line were measured with use of a Pulfrich refractometer.

Results

The values of the so-called "slopes" a_0, a', a'', a_D, and b obtained in this experiment for alkyl acetates in benzene solutions are shown in Table 1. The definition of these slopes is given by Eqs. (1) and (2). The dielectric constants ε' and losses ε'' of the dilute solutions are linear functions of the concentration (weight fraction w_2) of the solute.

Table 1. Slopes a', a'' obtained at 96.52 GHz in benzene (25 °C) and a_0, a_D and b

Substance	a_0	a'	a''	a_D	b
Methyl acetate	3.989	1.227	1.321	−0.412	−0.055
Ethyl acetate	3.722	0.757	0.972	−0.410	−0.018
n-Butyl acetate	2.963	0.449	0.563	−0.352	−0.002
Isobutyl acetate	2.951	0.466	0.589	−0.336	0.017
s-Butyl acetate	2.942	0.287	0.460	−0.370	0.021
t-Butyl acetate	3.122	0.264	0.632	−0.363	0.022
n-Amyl acetate	2.648	0.348	0.493	−0.312	0.009
Isoamyl acetate	2.606	0.351	0.470	−0.337	0.019
n-Hexyl acetate	2.347	0.331	0.416	−0.301	0.017
n-Octyl acetate	1.909	0.202	0.311	−0.270	0.024

$$\begin{aligned} \varepsilon' &= \varepsilon_1' + a'w_2 \\ \varepsilon'' &= a''w_2 \end{aligned} \tag{1}$$

in which subscripts 1 and 2 refer to the pure solvent and to the solute, respectively. Similarly, the static dielectric constants, ε_0, the infinite dielectric constants (the dielectric constants at high-frequency limit), ε_∞, the square of refractive indices, n_D, (for the sodium D-line), and the specific volumes, v, are also assumed to be linear with the concentration.

$$\begin{aligned} \varepsilon_0 &= \varepsilon_{10} + a_0 w_2, \quad \varepsilon_\infty = \varepsilon_{1\infty} + a_\infty w_2 \\ n_{\mathrm{D}}^2 &= n_{1\mathrm{D}}^2 + a_{\mathrm{D}} w_2, \quad v = v_1 + b w_2 \end{aligned} \tag{2}$$

The total molar polarization ${}_\infty P_2$, the distortion polarization $P_{\mathrm{A}}+P_{\mathrm{E}}$, the molecular refraction R_{D} and the dipole moment μ together with the literature values are recorded in Table 2. The total molar polarization of the solute at infinite dilution ($w_2 \to 0$) was obtained from the Halverstadt-Kumler equation.[10)]

TABLE 2. TOTAL MOLAR POLARIZATIONS ${}_\infty P_2$, MOLECULAR REFRACTION R_{D}, AND DIPOLE MOMENTS μ OF ALKYL ACETATES IN BENZENE AT 25 °C WITH THE LITERATURE VALUES

Substance	${}_\infty P_2$ [cm^3]	R_{D} [cm^3]	μ[a)] [D]	μ (lit[b)]) [D]
Methyl acetate	79.6	17.8	1.72	1.77
Ethyl acetate	91.2	22.2	1.82	1.83
n-Butyl acetate	104.3	31.1	1.87	1.87
Isobutyl acetate	104.7	32.1	1.86	1.89
s-Butyl acetate	104.6	31.5	1.87	—
t-Butyl acetate	108.6	31.7	1.92	1.93 (22 °C)
n-Amyl acetate	109.6	36.3	1.87	1.93
Isoamyl acetate	108.9	36.0	1.86	1.8
n-Hexyl acetate	113.5	40.8	1.86	—
n-Octyl acetate	121.8	50.0	1.84	—

a) $\mu = 0.0128\sqrt{({}_\infty P_2 - 1.05R_{\mathrm{D}})T}$

b) A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco and London (1963).

$${}_\infty P_2 \simeq M_2 \left\{ \frac{3a_0 v_1}{(\varepsilon_{10}+2)^2} + (v_1+b)\frac{\varepsilon_{10}-1}{\varepsilon_{10}+2} \right\} \tag{3}$$

in which M_2 is the molecular weight of the solute. The distortion polarization $P_{\mathrm{A}}+P_{\mathrm{E}}$ is obtained by using a_∞ and $\varepsilon_{1\infty}$ instead of a_0 and ε_{10} in Eq. (3), respectively.[11)]

$$P_{\mathrm{A}} + P_{\mathrm{E}} \simeq M_2 \left\{ \frac{3a_\infty v_1}{(\varepsilon_{1\infty}+2)^2} + (v_1+b)\frac{\varepsilon_{1\infty}-1}{\varepsilon_{1\infty}+2} \right\} \tag{4}$$

Similarly, the molecular refraction for the D-line is given by

$$R_{\mathrm{D}} \simeq M_2 \left\{ \frac{3a_{\mathrm{D}} v_1}{(n_{1\mathrm{D}}^2+2)^2} + (v_1+b)\frac{n_{1\mathrm{D}}^2-1}{n_{1\mathrm{D}}^2+2} \right\} \tag{5}$$

The dielectric relaxation times $\tau(1)$, $\tau(2)$, and τ_0 and the distribution parameter α are shown in Table 3. The relaxation times $\tau(1)$ and $\tau(2)$ were calculated from the following equations[12)]

$$\tau = \frac{1}{\omega}\frac{a''}{a'-a_\infty} \equiv \tau(1) \tag{6}$$

$$\tau = \frac{1}{\omega}\frac{a_0-a'}{a''} \equiv \tau(2) \tag{7}$$

on the assumption of a single Debye relaxation. On the other hand, if the system is not of the single relaxation but of the multi-relaxation times which follow Cole-Cole's[13)] rule, Eq. (8) will become valid instead.

$$a^* = a' - ja'' = a_\infty + \frac{a_0 - a_\infty}{1+(j\omega\tau_0)^{1-\alpha}} \tag{8}$$

The probable relaxation time τ_0 and the distribution parameter α are estimated by measurements of a' and a'' at a single frequency.[14)]

$$\tau_{\mathrm{o}} = \frac{1}{\omega}\left\{ \frac{A^2+B^2}{C^2} \right\}^{(1-\alpha)/2} \tag{9}$$

$$1 - \alpha = \frac{2}{\pi}\tan^{-1}\left(\frac{A}{B}\right) \tag{10}$$

where

$$\begin{aligned} A &= a''(a_0 - a_\infty) \\ B &= (a_0 - a')(a' - a_\infty) - a''^2 \\ C &= (a' - a_\infty) + a''^2 \end{aligned} \tag{11}$$

The term a_∞ which we find in Eqs. (6) and (11) may be estimated in the following way. Assuming the familiar assumption of $P_{\mathrm{A}}+P_{\mathrm{E}} \simeq 1.05R_{\mathrm{D}}$ for the dipole moment work to be valid, we shall obtain probable but tentative values of a_∞ from Eqs. (4) and (5). That is,

$$a_\infty = \frac{(\varepsilon_1'+2)^2}{3v_1}\left\{ \frac{1.05R_{\mathrm{D}}}{M_2} - (v_1+b)\frac{\varepsilon_1'-1}{\varepsilon_1'+2} \right\} \tag{12}$$

where $\varepsilon_{1\infty} \simeq \varepsilon_1'$ for non-polar solvent is assumed. The probable relaxation time τ_0 is found to be nearly equal to the geometrical mean, $\sqrt{\tau(1)\tau(2)}$, of $\tau(1)$ and $\tau(2)$. (See Table 3.)

TABLE 3. DIELECTRIC RELAXATION TIMES $\tau(1)$, $\tau(2)$ AND τ_0 AND DISTRIBUTION PARAMETERS α AND a_∞ OBTAINED FROM Eq. (12) ON THE ASSUMPTION OF $P_{\mathrm{A}}+P_{\mathrm{E}} \simeq 1.05\,R_{\mathrm{D}}$

Substance	a_∞	$\tau(1)$ [ps]	$\tau(2)$ [ps]	$\sqrt{\tau(1)\tau(2)}$ [ps]	τ_0 [ps]	α
Methyl acetate	−0.382	1.4	3.5	2.2	2.1	0.28
Ethyl acetate	−0.377	1.4	5.0	2.7	2.7	0.35
n-Butyl acetate	−0.315	1.2	7.4	3.0	2.8	0.46
Isobutyl acetate	−0.296	1.3	7.0	3.0	2.9	0.43
s-Butyl acetate	−0.334	1.2	9.5	3.4	3.1	0.49
t-Butyl acetate	−0.325	1.8	7.5	3.6	3.7	0.34
n-Amyl acetate	−0.272	1.3	7.7	3.2	3.0	0.44
Isoamyl acetate	−0.296	1.2	7.9	3.1	2.9	0.47
n-Hexyl acetate	−0.260	1.2	8.0	3.0	2.8	0.48
n-Octyl acetate	−0.228	1.2	9.1	3.3	3.0	0.49

Discussion

Among the observed dipole moments of ten alkyl acetates in benzene solutions recorded in Table 2, those for *s*-butyl acetate (1.87 D), *n*-hexyl acetate (1.86 D) and *n*-octyl acetate (1.84 D) are new values; and all the moments (1.72—1.92 D) are in good agreement with literature values.

The dielectric relaxation time of methyl acetate in benzene has been given by Krishna[15)] to be 2.2 ps at 28 °C, by Cripwell and Sutherland[16)] 3.73 ps at 18.5 °C and Whiffen and Thompson[17)] 3.1 ps at 19 °C. The average relaxation time of methyl acetate τ_0 obtained in this study is 2.1 ps, which is near to Krishna's value. The observed relaxation time for ethyl acetate $\tau_0 = 2.7$ ps in benzene solution is smaller than 4.4 ps in liquid at 20 °C by Smyth *et al.*[18)]

Three relaxation times, $\tau(1)$, $\tau(2)$, and τ_0 of normal alkyl acetates are plotted against the carbon number

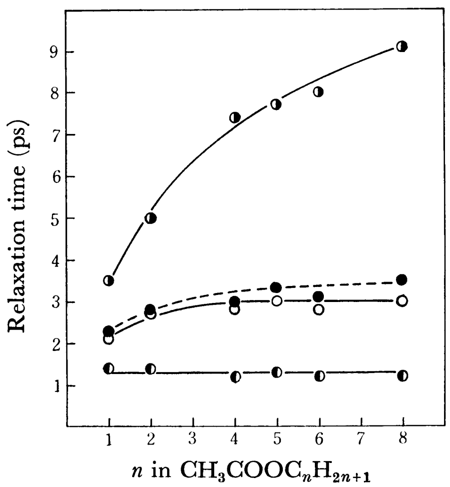


Fig. 1. The dependence of the relaxation times $\tau(1)$, $\tau(2)$, τ_0 and τ_0' upon the carbon number (n) of the alkyl radical (R_2) in normal alkyl acetates.
◐: $\tau(1)$, ◑: $\tau(2)$, ○: τ_0, ●: τ_0'.

(n) of the alkyl radical, R_2. (See Fig. 1.) The increase in the carbon number (n) of the alkyl radical is accompanied with a large increase in $\tau(2)$ while it gives little effect upon $\tau(1)$. The most probable relaxation time τ_0 from the Cole-Cole equation based on the assumption $P_A+P_E\simeq1.05\,R_D$ are also plotted in Fig. 1. For the sake of comparison the values τ_0' calculated on $P_A+P_E\simeq1.10\,R_D$ are shown in the same figure by a broken line—the latter relaxation times are denoted by τ_0' in order to distinguish from τ_0 based on $P_A+P_E\simeq1.05\,R_D$. Both τ_0 and τ_0' values increase with increasing chain length of the alkyl radical and eventually approach steady values of 3.0 and 3.5 ps, respectively. The above tendency, if it is true, could be explained by supposing that with long alkyl chains the dipole can rotate more or less freely without much affecting the other end of the chain to which it is attached.

According to the analysis[19] of the systems with two Debye dispersions, $\tau(1)$ obtained at a very high frequency *e.g.* 100 GHz is slightly larger than the shorter relaxation time, while $\tau(2)$ is a weighted mean of the two relaxation times and then the longer relaxation time becomes important. Although the present system seems to have more than two dispersions, the above results can be used in a qualitative manner. It is striking to notice that $\tau(1)$ for all the alkyl acetates have values between 1.2—1.4 ps which correspond to the relaxation time for a very small rotating unit. Contrary to $\tau(1)$, the other average relaxation time $\tau(2)$ regularly increases with increasing chain length, which may suggest that molecular rotation as a whole could occur to a certain extent. As shown before the probable relaxation time τ_0 approximates a geometrical average of $\tau(1)$ and $\tau(2)$ and its distribution parameter α increases with increasing chain length (see Table 3).

The free energy of activation ΔF^{*} can be calculated from the relaxation time τ by the following equation

$$\Delta F^{*} = 2.303RT\log\frac{kT\tau}{h} \tag{13}$$

where R is the gas constant and T is the absolute temperature and k, h are Boltzmann and Planck constants. Assuming τ is equal to τ_0, ΔF^{*} are estimated to have 1.5—1.9 kcal/mol for all the alkyl acetates. (See Table 4.)

Table 4. Free energy of activation ΔF^{*} and heat of activation ΔH^{*} on the assumption of $\tau=\tau_0$ and $\Delta S^{*}=-1$ e.u.

Substance	ΔF^{*} (kcal/mol)	ΔH^{*} (kcal/mol)
Methyl acetate	1.52	1.22
Ethyl acetate	1.66	1.36
n-Butyl acetate	1.69	1.39
Isobutyl acetate	1.70	1.40
s-Butyl acetate	1.76	1.46
t-Butyl acetate	1.85	1.55
n-Amyl acetate	1.74	1.44
Isoamyl acetate	1.71	1.41
n-Hexyl acetate	1.70	1.40
n-Octyl acetate	1.73	1.43

The heat of activation is given by

$$\Delta H^{*} = \Delta F^{*} + T\Delta S^{*} \tag{14}$$

The values ΔH^{*} recorded in Table 4 are obtained from ΔF^{*} on a very tentative assumption[20] $\Delta S^{*}=-1$ e.u. for all the acetates—it will be expected that ΔS^{*} will increase with increasing chain length, thus ΔH^{*} will become much larger. If $\tau(1)$ is used instead of τ_0, ΔF^{*} would become 1.2—1.3 kcal/mol and $\Delta H^{*}=0.9$—1.0 kcal/mol.

The observed dipole moments of alkyl acetates are 1.72—1.92 D, which are between those calculated for the *trans* 1.64 D and the *cis* 3.51 D. Consequently we may infer that the *cis* configuration is not completely ruled out but there are a small amount (3—10%) of the *cis* isomers present. Smyth[21] favored a view that a wide oscillation occurs about the *trans* position. From this viewpoint it is found that the average twisted configuration out of the *trans* position would have a dihedral angle 20—38°. Lastly there is the remaining possibility that the *trans* planar configuration alone exists with the observed polarity.[2]

From the probable dielectric relaxation times τ_0 and the distribution parameters α obtained in this work, we shall be able to say that all the alkyl acetates have multiple relaxation times and they have flexible and nonrigid configurations. The small value $\tau(1)=1.2$—1.4 ps suggests a small unit of rotation or a very small barrier for the rotating polar group. Estimated values of both ΔF^{*} and ΔH^{*} (using τ_0) are also small in magnitude compared with the size of the molecule.

In the present work a_∞ is very tentatively estimated on the assumption of $P_A+P_E\simeq1.05\,R_D$. Alternatively, if the assumption of single Debye dispersion is valid, we can calculate a_∞ from[9]

$$a_\infty = a_G = a' - \frac{(a'')^2}{a_0-a'} \tag{15}$$

and if Eq. (15) is used in acetates, we shall find both $\tau(1)$ and τ_0 to be equal to $\tau(2)$ and hence $\alpha=0$. However, the use of $a_\infty=a_G$ would result in a considerably large atomic polarization which is inconsistent with experimental data. It seems that Eq. (15) is invalid and the dielectric system of acetates in benzene has multi-relaxation times.

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