Atomic Polarization of Aliphatic Alcohols in the Liquid state

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The refractive index n and absorption coefficient k of methyl, ethyl, i-propyl, n-butyl,

Table 1.

	methyl alcohol	ethyl alcohol	*i*-propyl alcohol	*n*-butyl alcohol	*i*-butyl alcohol	*tert*-butyl alcohol
ε_0	31.5	24.3	18.0	16.0	16.0	9.90
ε' (3.24 cm.)	5.55	4.08	3.06	3.08	2.94	2.80
ε''(3.24 cm.)	5.12	2.58	1.18	1.08	1.01	0.85
n_D^2	1.76	1.85	1.89	1.95	1.94	1.92

Table 2.

	methyl alcohol	ethyl alcohol	*i*-propyl alcohol	*n*-butyl alcohol	*i*-butyl alcohol	*tert*-butyl alcohol
ε_∞	4.54	3.76	2.96	2.99	2.86	2.70
P_E	8.2	13.0	17.6	22.1	22.2	22.2
M/d	40.7	58.6	79.6	91.9	92.9	94.8
$\frac{\varepsilon_\infty-1}{\varepsilon_\infty+2}\frac{M}{d}$	22.1	28.7	30.4	36.6	35.5	34.3
P_A	13.9	15.7	12.8	14.5	13.3	12.1

i-butyl, and *tert*-buthyl alcohols have been measured at the wave length of 3.24 cm. and at the temperature of 25°C. by the improved free wave method reported previously.[1] From the values of n and k the dielectric constant ε' and the loss factor ε'' have been calculated through the following equation.

$$\varepsilon'-i\varepsilon''=(n-ik)^2 \qquad (1)$$

The calculated values are shown in Table 1 with the static dielectric constant ε_0 and the square of refractive index n_D^2 for D-line.

If we assume a single relaxation time, we have the following relations irrespective of the dielectric model

$$\varepsilon'=\varepsilon_\infty+\frac{\varepsilon_0-\varepsilon_\infty}{1+\omega^2\tau^2}=\varepsilon_\infty+\frac{\varepsilon_0-\varepsilon_\infty}{1+(\lambda_s/\lambda)^2} \qquad (2)$$

$$\varepsilon''=\frac{\varepsilon_0-\varepsilon_\infty}{1+\omega^2\tau^2}\omega\tau=\frac{\varepsilon_0-\varepsilon_\infty}{1+(\lambda_s/\lambda)^2}(\lambda_s/\lambda) \qquad (3)$$

$$\lambda_s=2\pi c\tau \qquad (4)$$

where τ is the relaxation time corresponding to a critical wave length λ_s (Sprungswellenlänge) and λ, ω, and c have their usual significance. ε_∞ is the value of ε' at high frequencies at which the orientation effect of dipole disappears completely. The values of ε_∞ shown in Table 2 (and those of λ_s) have been chosen as to give the best fit with the experimental data through Fqs. (2), (3) and (4). From ε_∞ we can calculate the values of atomic polarization P_A by the following equation:

$$P_A=\frac{\varepsilon^\infty-1}{\varepsilon_\infty+2}\frac{M}{d}-P_E$$

where M is the molecular weight, d the density, $P_E=\frac{n_D^2-1}{n_D^2+2}\frac{M}{d}$ the electronic polarization for D-line. The vaules of $\frac{\varepsilon_\infty-1}{\varepsilon_\infty+2}\frac{M}{d}$, P_E and P_A are shown in Table 2.

We see that the atomic polarization of each alcohol in the liquid state has almost the same value which is about 14 cc. and is much larger than that in the gaseous state which is estimated as less than 10% of the electronic polarization: *i.e.* less than 2 cc.

The large values of atomic polaization of these alcohols in the liquid state are, therefore, attributable to the structure of the liquid and the approximate constancy of these values may be explained by considering that the hydrogen bond plays the most important part in this problem.

Detailed discussion will be published elsewhere.

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(1) M. Yasumi, This Bulletin, **24**, 53 (1951); M. Yasumi, K. Nukazawa and S. Mizushima, This Bulletin, **24**, 60 (1951).