# Microwave Relaxation and Association of 3,5 Dimethyl 3-Hexanol

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The dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) of 3,5 dimethyl 3-hexanol in heptane have been measured for dilute and concentrated solutions at five wavelengths between 25 cm and 2 mm and at 20°, 40° and 60 °C. The data have been analysed and two relaxation times are obtained. The long relaxation time is attributed to the rotation of the whole molecule and the short relaxation time to the relaxation of the OH-group. For the range of concentrations used, the results show that associates are hardly detectable.

## Introduction

Measurements on dilute solutions of molecules having an OH-group like alcohols and phenols are somehow limited to *m*-waves [1, 2]. An attempt was made to study the relaxation properties of the OH-group [3] from absorption measurements on very dilute solutions by mm and cm waves. These measured values were found to depend on the concentration showing that associated molecules are present [4]. A more detailed study is carried out in this communication to give more information about the association of the OH-group when it lies within and not at the end of the molecule.

## Experimental Results and Discussions

Measurements of $\varepsilon'$ and $\varepsilon''$ are carried out at wavelengths 0.216, 1.25, 3.24, 10 and 25 cm and at temperatures 20, 40 and 60 °C to an accuracy

| $x$ mole frac. | $\lambda$ cm | | $t=20$ °C | | | $t=40$ °C | | | $t=60$ °C | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $\varepsilon_0$ | $\varepsilon'$ | $\varepsilon''$ | $\varepsilon_0$ | $\varepsilon'$ | $\varepsilon''$ | $\varepsilon_0$ | $\varepsilon'$ | $\varepsilon''$ |
| 0.1780 | 0.216 | 2.223 | 2.023 | 0.0614 | 2.1924 | 2.014 | 0.0749 | 2.162 | 2.001 | 0.0822 |
| | 1.250 | | 2.148 | 0.0770 | | 2.143 | 0.072 | | 2.098 | 0.0627 |
| | 3.240 | | 2.180 | 0.0514 | | 2.177 | 0.0489 | | 2.159 | 0.041 |
| | 10.000 | | 2.203 | 0.0285 | | 2.190 | 0.0206 | | 2.159 | 0.0152 |
| | 25.000 | | 2.214 | 0.0115 | | 2.203 | 0.0096 | | 2.183 | 0.0071 |
| 0.1261 | 0.216 | 2.125 | 1,999 | 0.0428 | 2.1089 | 1.986 | 0.048 | 2.0686 | 1.957 | 0.0523 |
| | 1.250 | | 2.080 | 0.0516 | | 2.064 | 0.0486 | | 2.043 | 0.0349 |
| | 3.240 | | 2.105 | 0.0362 | | 2.099 | 0.0322 | | 2.069 | 0.0245 |
| | 10.000 | | 2.116 | 0.0185 | | 2.108 | 0.0131 | | 2.068 | 0.0095 |
| | 25.000 | | 2.119 | 0.0089 | | 2.118 | 0.0054 | | 2.089 | 0.0046 |
| 0.0883 | 0.216 | 2.0695 | 1.977 | 0.0315 | 2.0495 | 1.960 | 0.035 | 2.0110 | 1.928 | 0.0355 |
| | 3.240 | | 2.062 | 0.0235 | | 2.041 | 0.0215 | | 2.0097 | 0.0171 |
| | 10.000 | | 2.065 | 0.0118 | | 2.047 | 0.0087 | | 2.010 | 0.0065 |
| | 25.000 | | 2.080 | 0.0040 | | 2.053 | 0.0040 | | 2.0185 | 0.0031 |
| 0.0335 | 0.216 | 1.9886 | 1.947 | 0.0148 | 1.9511 | 1.922 | 0.0146 | 1.9206 | 1.892 | 0.0149 |
| | 3.240 | | 1.988 | 0.0098 | | 1.969 | 0.0081 | | 1.926 | 0.0060 |
| | 10.000 | | 1.986 | 0.0045 | | 1.956 | 0.0033 | | 1.925 | 0.0024 |
| | 25.000 | | 1.986 | 0.0021 | | 1.965 | 0.0019 | | 1.942 | 0.0018 |
| 0.0085 | 0.216 | 1.941 | 1.924 | 0.0040 | 1.9102 | 1.902 | 0.0043 | — | — | — |
| | 3.240 | | 1.938 | 0.0031 | | 1.911 | 0.0023 | | — | — |
| | 10.000 | | 1.941 | 0.0011 | | 1.911 | 0.0009 | | — | — |
| | 25.000 | | 1.941 | 0.0005 | | 1.910 | 0.0004 | | — | — |

Table 1. Static dielectric constant $\varepsilon_0$, dielectric constant $\varepsilon'$ and dielectric loss $\varepsilon''$ at different wavelengths $\lambda$, temperatures $t$ and concentrations $\chi$.

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[1] E. FISCHER, Z. Naturforsch. **4 a**, 707 [1949]; **8 a**, 168 [1953]; **9 a**, 360 [1954].

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of 2%. The apparatus used have been described before [5–8]. The static dielectric constant $\varepsilon_0$ has been measured at 10 kHz using "General Radio Low frequency bridge" type 1615 A to an accuracy of 1%.

Pure grade 3,5 dimethyl 3-hexanol was obtained from Aldrich Chemical Co. Inc. For further purification, it has been distilled under low pressure. Five concentrations between 0.0085 and 0.1780 mole fraction in pure n-heptane solution are used. The measurements are given in Table 1.

The values of $\varepsilon_0$ are plotted versus the concentration $X$ for the three temperatures used and the relation between them, as shown in Fig. 1, is found to be linear. The extrapolation of the curves to zero concentration gives the corresponding values of the dielectric constant of heptane.

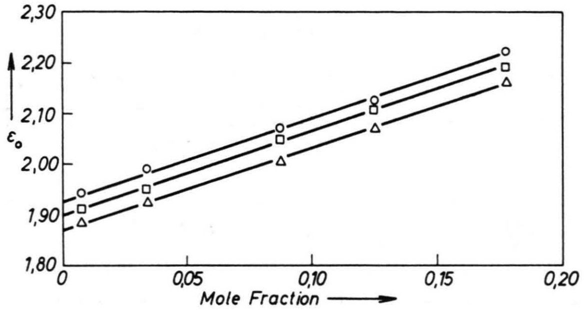

Fig. 1. The static dielectric constant ($\varepsilon_0$) versus the concentration ($x$) in mole fraction for 3,5 Dimethyl 3-Hexanol in heptane at the different temperatures (○ 20 °C, □ 40 °C, △ 60 °C).

Unfortunately the refractive index $n_D$ of the solutions is not measured to be able to find the dispersion step $(\varepsilon_0 - n_D^2)$. Since the molecule of the 3,5 dimethyl 3-hexanol has approximately the same size as the molecule of heptane, so the difference in $n_D^2$ between both of them is aproximately zero and the value of $n_D^2$ of heptane could be a good approximation for $n_D^2$ of 3,5 dimethyl 3-hexanol. So, for the first approximation the measured values of $n_D^2$ of heptane namely: 1.9265 at 20 °C, 1.8867 at 40 °C and 1.8692 at 60 °C are used. Knowing $(\varepsilon_0 - n_D^2)$, the reduced absorption values

$$\eta'' = \varepsilon''/(\varepsilon_0 - n_D^2)$$

could be calculated.

An attempt has been done to analyse the data of $\eta''$ into two Debye terms using the iteration method. This attempt was successful and the values of $\tau_1$, $\tau_2$ and $G$ obtained from the analysis are given in Table 2. Figures 2 and 3 show the sum of the two

| Concentration in Mole Fraction | $t$ °C | $\tau_1$ $\times 10^{12}$ sec | $\tau_2$ $\times 10^{12}$ sec | $G$ |
|---|---|---|---|---|
| 0.1780 | 20 | 7.70 | 0.36 | 0.55 |
| | 40 | 7.30 | 0.40 | 0.60 |
| | 60 | 6.98 | 0.41 | 0.65 |
| 0.1261 | 20 | 7.51 | 0.34 | 0.55 |
| | 40 | 6.98 | 0.32 | 0.60 |
| | 60 | 6.23 | 0.34 | 0.65 |
| 0.0883 | 20 | 7.14 | 0.35 | 0.55 |
| | 40 | 6.68 | 0.34 | 0.60 |
| | 60 | 6.29 | 0.32 | 0.65 |
| 0.0335 | 20 | 6.82 | 0.36 | 0.60 |
| | 40 | 6.54 | 0.36 | 0.65 |
| | 60 | 6.24 | 0.39 | 0.65 |
| 0.0085 | 20 | 6.98 | 0.45 | 0.55 |
| | 40 | 6.45 | 0.46 | 0.65 |

Table 2. $\tau_1$ and $\tau_2$ are the relaxation times obtained from the analysis using two Debye terms. $G$ is the weight of $\tau_2$ for the different concentrations of 3,5-dimethyl 3-hexanol in heptane at the different temperatures ($t$).

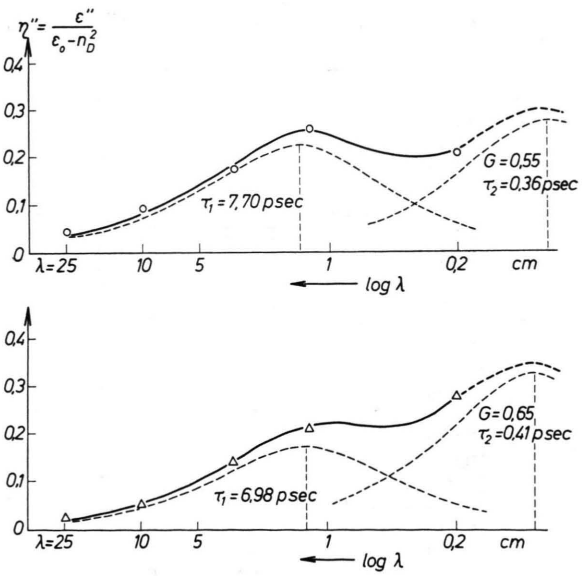

Fig. 2. Absorption curves of 3,5 dimethyl 3-hexanol in heptane for the concentration 0.1780 mole fraction obtained from the sum of two Debye terms having relaxation times $\tau_1$ and $\tau_2$ at the different temperatures (○ 20 °C, △ 60 °C).

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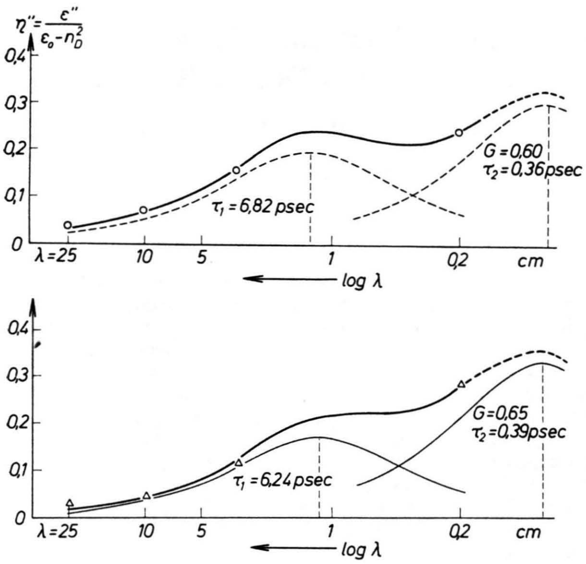

Fig. 3. Absorption curves of 3,5 dimethyl 3-hexanol in heptane for the concentration 0.0335 mole fraction obtained from the sum of two Debye terms having relaxation times $\tau_1$ and $\tau_2$ at the different temperatures (○ 20 °C, △ 60 °C).

Debye terms for 0.1780 and 0.0335 mole fraction at two temperatures. The analyses represent the experimental data very well. It is clear that the measurements at $=0.22$ cm are very important as they help in defining the shape of the curve. Unfortunately, after measuring $\varepsilon''$ at $\lambda = 1.25$ cm for 0.1780 and 0.1261 mole fraction, the apparatus became unstable and it was difficult to complete the measurements at this wavelength. Anyhow, this had no effect on the analyses.

The value of $\tau_1$ which ranges between 7.70 and 6.8 *p* sec at 20 °C for 0.1780 and 0.035 mole fraction respectively could be attributed to the orientation of the molecule as a whole. The increase in $\tau_1$ with the increase in concentration as seen from Table 2 may be due to the increase in the viscosity of the solution by the addition of the solute.

The short relaxation time $\tau_2$ as shown in Table 2 lies around 0.35 psec. The value 0.45 psec obtained for the lowest concentration is somehow high with respect to the others. Referring to Table 1, the measured $\varepsilon''$ values for this concentration are very small and so not so accurate as the other concentrations. This may be the cause for this difference. $\tau_2$ is found to be insensitive to a change in temperature and concentration, i. e. independent upon the viscosity of the medium. This means that it represents the orientation of a small group. So, it can be concluded that $\tau_2$ is that for the relaxation of the free hydroxyl group.

Referring to Table 2, *G* the weight of $\tau_2$ is almost the same (within the approximation given in the analysis) for the different concentrations at the same temperature but increases with increasing temperature showing that the contribution from the faster relaxation process increases with increasing temperature. For n-decanol in heptane at 20 °C, it was found by KILP [9] that $G = 0.68$ and $\tau_2 = 0.5$ psec which is in good agreement with the values obtained here.

The dipole moment $\mu$ of 3,5-dimethyl 3-hexanol in heptane is calculated at the different temperatures, for the mole fraction 0.035, using the Debye equation adapted for dilute solutions and is found to be 1.58 D.

From the order of magnitude of $\tau_1$ at the different concentrations used, together with the linear relation between $\varepsilon_0$ and concentration (Fig. 1), it could be concluded that the association in 3,5 dimethyl 3-hexanol in heptane solutions is very low, that it is hardly detectable. This means that 3,5 dimethyl 3-hexanol is shielded against the intermolecular interaction due to the presence of the OH-group within the molecule.

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[9] H. KILP, private communication, Mainz.