

# The Room Temperature Dielectric Spectrum of 2,2-Dimethyl-1-butanol

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The dielectric spectrum of the title substance ('neohexanol') in its pure liquid state is reported for 293 K up to 71 GHz and, for a restricted frequency range, also for lower temperatures (down to 253 K). The room temperature spectrum resembles that of alicyclic alcohols, in particular cyclopentanol, with respect to spectral shape, main relaxation time and the relation of the latter to viscosity, which similarity may be connected with the fact that these alcohols are able to form 'plastic crystals'.

Certain substances consisting of globular molecules are capable of forming 'plastic crystals', i.e. *orientational* disordered (ODIC) phases where only *positional* order exists. Examples are alcohols such as 2,2-dimethyl-1-butanol (neohexanol) and alicyclic alcohols [1], in contrast to e.g. *n*-alkanols. However, for longer chain lengths also rotator phases are observed [2]. Dielectric relaxation spectroscopy probes, in principle, the rotational tumbling motion of molecules, and therefore the finding is not implausible that in those phases the dielectric behaviour of neohexanol resembles that of cycloalcohols.

Concerning these alcohols, the question may arise whether the similarity of the dielectric relaxation in the ODIC phases corresponds to a similar relaxation behaviour in their liquid state. Although there is a wealth of experimental material on the dielectric relaxation of liquid alcohols, data for the substances in question are scarce, in particular around room temperature. Relaxation parameters for pure liquid cycloalcohols C<sub>5</sub> to C<sub>8</sub> are available [3, 4], whereas the dynamic dielectric properties of neohexanol in its liquid state have been reported only for lower temperatures (above its melting point of 241 K up to 268 K [5] and between 248 and 273 K [6]). The primary purpose of the present communication is therefore to describe the relaxation spectrum of neohexanol at 293 K over a frequency range up to about 70 GHz, which covers the absorption region at that temperature. Data for

some lower temperatures are included, which, however, are obtained by measurements up to 13 MHz only. The results shall briefly be compared with those for alicyclic alcohols as well as some alcohols which do not form ODIC phases.

Neohexanol was prepared by Dr. Jan Boksa from the Institute of Pharmacology, Cracow, Poland. The water content, determined after the dielectric measurements, was  $\approx 0.15\%$  (Karl Fischer), thus negligible with respect to its influence on dielectric data. Measurements of complex permittivity between 253 and 268 K up to 13 MHz were carried out using a Hewlett-Packard 4192A impedance analyzer [6]. For measurements at 293 K, several apparatus were employed, covering the range from 5 MHz to 71 GHz by 13 spot frequencies. Of main interest is the dielectric loss  $\epsilon''$ , which is obtained with an uncertainty of some percent.

Figure 1 shows the absorption (dielectric loss) spectrum at 293 K. We note that the high frequency side is not linear in the double log representation but reveals a weak shoulder. Therefore the spectrum cannot simply be described by a single one of the widely used spectral functions, as, for instance, the Cole-Davidson (CD) function, but an additional spectral component (at least) is required. A satisfactory fit of the data is obtained employing three superimposed Debye type spectral components. Their parameters, viz. relaxation times  $\tau_i$  and relaxation strengths  $S_i$ , are given in Table 1. That table contains also data for lower temperatures. Since in these cases the measurements cover the absorption region not always completely, the absorption can be characterized by a single CD term. Its

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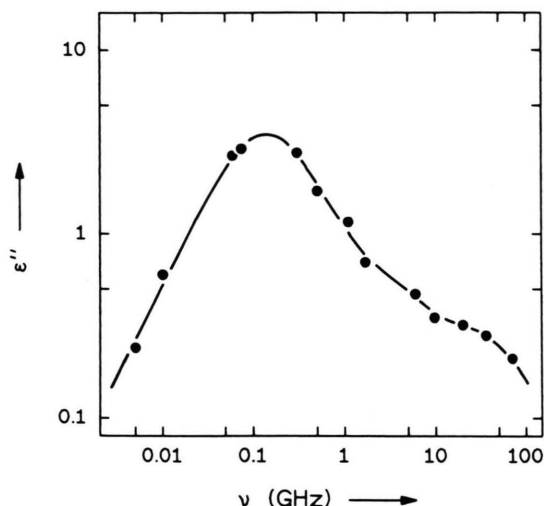


Fig. 1. Absorption spectrum ( $\epsilon''$  vs. frequency  $\nu$ ) of liquid neohexanol, 293 K (log-log plot).

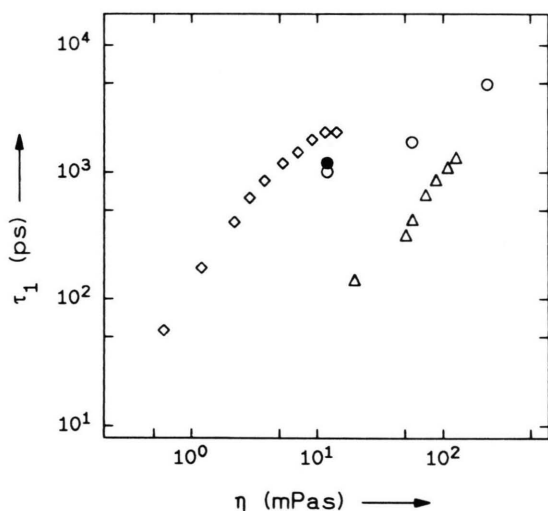


Fig. 2. Main relaxation time  $\tau_1$  and viscosity  $\eta$  of some pure liquid alcohols at 293 K. ● neohexanol, ○ cycloalkanols ( $C_5$ ,  $C_7$ ,  $C_8$ ;  $C_6$  not displayed since solid at 293 K), ◇ *n*-alkanols ( $C_1$  to  $C_{10}$ ), △ dihydric alcohols.

Table 1. Relaxation times  $\tau_i$  and relaxation strengths  $S_i$  of neohexanol. For the four lower temperatures, according to a Cole-Davidson fit of results up to 13 MHz; for 293 K, according to a fit with 3 Debye terms of results up to 71 GHz.

<i>T</i> K	$\tau_1$	$\tau_2$ ps	$\tau_3$	$S_1$	$S_2$	$S_3$
253	$62 \cdot 10^3$			16.15		
258	$35 \cdot 10^3$			14.75		
263	$24 \cdot 10^3$			12.85		
268	$20 \cdot 10^3$			10.90		
293	1180	42	4.5	7.20	0.48	0.42

parameters are given as lower frequency term in Table 1. Here  $\tau_1$  means  $\tau_{CD} \beta$ . The skewness parameter  $\beta$  is close to unity,  $\beta > 0.97$ .

The temperature dependence of  $\tau_1$  can be approximately expressed by an activation enthalpy  $\Delta H_{\tau_1}$  according to an Arrhenius law, though this is not strictly obeyed. The average value for the temperature interval studied is  $\Delta H_{\tau_1} = 60$  kJ/mol. (For comparison, 48.5 kJ/mol are estimated in [7] for 293 K, referring to data from [5], and 51.1 kJ/mol in [6]). The decrease of relaxation strength  $S_1$  with increasing temperature is steeper than  $\sim 1/T$ , which is not unexpected for an associating liquid where relaxation strength and relaxation time of the main spectral component reflect the fraction of hydrogen-bonded clusters and their dynamics, respectively.

To compare the dielectric relaxation behaviour of neohexanol with that of other alcohols, we restrict ourselves to 293 K data. It is informative to regard first the overall shape of the spectral function. Its most remarkable feature is the indication of a resolvable relaxation contribution at high frequencies. In this respect there is a close similarity to cycloalkanols [4]. On the other hand, many alcohols, such as *n*-alkanols, exhibit a differing spectral shape inasmuch as the high frequency side, up to frequencies used here, appears approximately linear in a double log representation. Second, focussing on the main spectral component, we will consider its relaxation time  $\tau_1$  in relation to the viscosity  $\eta$ . It is known that the alcohols fall into 'families' in this regard [8], so it may be informative to see what 'family' neohexanol belongs to. For that purpose Fig. 2 shows  $\tau_1$  vs.  $\eta$  for neohexanol together with values for alicyclic alcohols, *n*-alkanols and some dihydric alcohols. According to Fig. 2, neohexanol appears intimately related to the cycloalcohols, having nearly the same relaxation time and viscosity as cyclopentanol.

In conclusion, the dielectric relaxation behaviour of neohexanol in its liquid state can be classified as closely similar to that of cycloalcohols, especially cyclopentanol, which is in accordance with the solid state dielectric properties. This may mostly be a consequence of the similarity in size and form of the molecules concerned.

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