Dielectric Relaxation of Liquid Alicyclic Alcohols

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The dielectric spectra of liquid cyclopentanol, cyclohexanol, cycloheptanol and cyclooctanol are reported for frequencies up to 72 GHz and temperature 20 (cyclohexanol solid), 30 and 40 °C. The absorption spectra are peculiar in exhibiting a remarkably developed high frequency shoulder which is attributed to single molecule and internal motion, while the principal absorption is due to association as with other alcohols.

Although numerous dielectric relaxation studies on different kinds of liquid alcohols have been reported, alicyclic ones have received only little attention. Cyclohexanol has been examined in nonpolar solvents [1], which work was extended recently to some very high spot frequencies (≤ 670 GHz) [2]. On ther other hand, the solid state dielectric properties have attracted attention. These, for example, have been measured at frequencies covering the solid state absorption region (at ≤ 13 MHz [3, 4]) over a very broad temperature and pressure range. Those studies yielded also some results on the liquid state [5]. An investigation of pure liquid cycloalcohols by Shinomiya [6] was restricted to frequencies covering the principal absorption region (≤ 4.5 GHz). It seems therefore worthwhile to reconsider the dielectric properties of pure cycloalcohols (at normal pressure) and to extend measurements over a broader frequency band in order to gain information also on possible higher frequency relaxation contributions. Here we report dielectric relaxation data of four alicyclic alcohols, cyclopentanol (C_5) to cyclooctanol (C_8), as measured up to 72 GHz. In relation to the literature quoted, our results complement the hitherto known lower frequency part of the dielectric spectrum of pure cycloalcohols [5, 6] and also the solution results for cyclohexanol [2].

Substances obtained from Fluka and Merck were used without further purification. Residual water contents < 0.5 percent should, according to experiences with various alcohol-water systems [7], not yet significantly influence the relaxation parameters. The complex permittivity was determined by use of various apparatus at 15 fixed frequencies, ranging between 2 MHz and 72 GHz, at temperatures 20, 30 and 40 °C. At 20 °C, C_6 is solid. However, the dielectric data will be reported, too. On the other hand, C_8 was still liquid at that temperature, although a somewhat higher melting point has been reported (20.2 ... 24.3 °C [4, 6]). We shall consider the results in terms of dielectric loss $\varepsilon''(\omega)$, viz. the (negative) imaginary part of permittivity as already corrected for the conductivity contribution (if significant).

Two examples of absorption spectra are represented in Figure 1. It should be emphasized that, contrary to

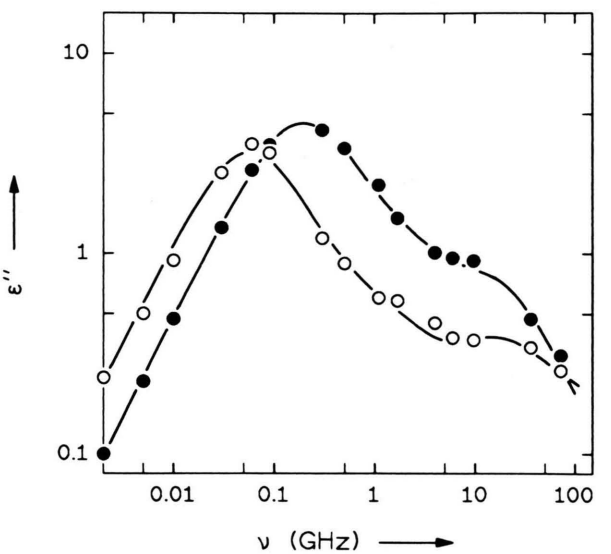

Fig. 1. Typical absorption spectra, dielectric loss ε'' against frequency ν (log-log plot): Cyclopentanol (full symbols) and cyclooctanol (open symbols), both 30 °C. Fitting curves with parameters according to Table 1. (For cyclooctanol, the fit includes an additional minor term with $\tau_4 = 1.5$ ps, $S_4 = 0.25$ which is not given in Table 1.)

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Table 1. Relaxation times τ_i, relaxation strengths S_i and activation enthalpies $\Delta H_{\tau 1}$ (averaged from liquid state values) for pure cycloalcohols.

	T °C	τ_1 ps	τ_2 ps	τ_3 ps	S_1	S_2	S_3	$\Delta H_{\tau 1}$ [a] kJ/mol
Cyclo-	20	1010	95	8	12.9	0.9	0.6_5	
pentanol	30	770	70	10	9.3	0.8	1.1	32 [37.2]
	40	440	23	9	8.2	0.7	1.0_5	
Cyclo-	20	5520	690	9	11.0	1.8_5	0.7 (solid)	
hexanol	30	1830	75	10	10.7	0.4	0.7_5	37 [42.8]
	40	1140	30	11	8.8	0.4	0.7_5	
Cyclo-	20	1940	125	10	9.4	0.8	0.6_5	
heptanol	30	1350	90	10	7.0	0.7_5	0.8_5	38 [45.2]
	40	720	36	10	5.5	0.5_5	1.0_5	
Cyclo-	20	4810	240	11	8.5	0.7_5	0.5	
octanol	30	2640	115	9	6.7	0.5	0.6	44 [45.5]
	40	1550	80	10	5.3	0.4	0.7	

[a] For comparison, $\Delta H_{\tau 1}$ values from [6] are given in brackets.

most other alcohols, they exhibit a considerable asymmetry on the log ω scale, shaped as a well-developed high frequency shoulder. This becomes the more obvious the larger the aliphatic ring, since the overall high frequency contribution (notwithstanding its resolution discussed below) seems to stay nearly unchanged on the frequency scale, while the principal absorption is shifted towards lower frequencies.

A formal description is obtained by fitting a sum of Debye type spectral components

$$\varepsilon''(\omega) = \sum_i S_i \frac{\tau_i \omega}{1 + \tau_i^2 \omega^2}$$

to the data. Three terms are required for the frequency range covered experimentally. In a few cases (for C_8) the fit is improved by allowing for a further, minor, high frequency component. The relaxation parameters τ_i and S_i are recorded in Table 1 except for the last mentioned component, since its absorption maximum is already beyond the experimental frequency limit. While the principal absorption is fairly well defined by the (τ_1, S_1) component, the parameters of the two subsequent components, which describe the shoulder, are less certain since they are variable in opposing sense within a relatively broad range. Table 1 gives also the mean activation enthalpy $\Delta H_{\tau 1}$ of the principal relaxation process, which was calculated according to an Arrhenius dependence of τ_1 on temperature.

The parameters for the principal relaxation agree well with [6]. Our $\Delta H_{\tau 1}$ values are somewhat smaller (by 15 ... 5 percent for C_5 to C_8, respectively) than those given in [6], which is understandable since that quantity is sensitive to fitting details (note that three fitting terms are used in both studies for the coverage of, however, quite different frequency intervals). The high frequency shoulder corresponds to the predominant feature in the dilute solution spectra of C_6 yet studied [2], which also show how the principal relaxation region develops at the expense of the high frequency one as concentration is increased. An extrapolation of the solution data to pure C_6 is again in accordance with the present results.

In a general sense, the spectra of the alicyclic alcohols are of interest inasmuch as the novel finding of a resolvable shoulder shows quite clearly that a description by one of the widely used continuous relaxation time distributions is not possible, so that the conceptual distinction between different relaxators appears to be appropriate. We feel that this is an inference which should be applicable to other alcohols, too, even if these exhibit spectra much closer to the Debye type.

Although a direct assignment of the formally obtained spectral components to distinguishable physical processes may be questionable, at least some qualitative conclusions can be drawn. The principal absorption region can certainly not relate to single molecule motion but may be attributed to stochastic alterations or internal fluctuations of hydrogen bonded aggregations, as customarily considered to cause the principal relaxation of alcohols. The non-monotonic increase of τ_1 with the size of the ring parallels the alteration of viscosity (as already noticed in [6]), which both show an "inverted" order of C_6 and C_7. This may be due to the more symmetric conformation of cyclohexanol (with merely equatorial or axial C–H directions) in comparison to cycloheptanol, which may allow for mutual arrangements making the formation of hydrogen bonds more probable.

The (τ_2, S_2) component, on the other hand, may originate in the tumbling motion of single molecules. This conclusion appears qualitatively from the alteration of τ_2 with the ring size and semi-quantitatively from its comparison to the relaxation times of rigid or quasi rigid molecules, taking into account the molecular size (effective radius) as well as the viscosity [8, 9]. Consequently the (τ_3, S_3), and possibly further spectral components may be due to internal motion (ring flexibility and rotation of OH group). Future experiments may reveal the shape of the respective absorption up to still higher frequencies and may than allow for a more thorough discussion.

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