Dielectric Relaxation of Aliphatic Ethers in Dilute Solutions

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Dielectric relaxation of nine primary aliphatic ethers — seven symmetric ethers of chain length C_6 to C_{32}, one asymmetric ether and one molecule with three ether groups in the chain — has been studied by loss measurements at 11 frequencies between 0.3 and 300 GHz in dilute cyclohexane and mesitylene solutions at 20 °C. The absorption curves are shown not to be symmetrical. The main region has been analysed in terms of a symmetric distribution of relaxation times; the high frequency contribution due to the far infrared absorption was always less than 20%. Symmetric ethers show an increasing mean relaxation time and broadening of its distribution with increasing chain length. The spectra of cyclohexane solutions are found to contain additional short relaxation times. Compared with α, ω-dichlorides the mean relaxation times of symmetric ethers generally are shorter, which suggests a high mobility around C—O bonds becoming more effective in the unsymmetric ethers and even more so in the chain molecule with two methoxy end groups.

Dielectric loss measurements provide a method to investigate dipole reorientation processes of polar molecules in liquids. Aromatic molecules with various substituted polar groups have been intensively studied and the results have been interpreted in terms of molecular and intra-molecular motions [1—4]. Similar work was done with aliphatic molecules, especially with flexible chain molecules [5—14]. Their dipole orientation may involve intramolecular rotation of segments of various size. Aliphatic halides are probably a class of nonassociated molecules whose dielectric absorption has been studied in every detail [5—9]. In previous work [8] on haloalkanes, only a mean relaxation time according to Cole and Cole [15] is evaluated, and it is suggested that reorientation of smaller segments is an important mechanism of dielectric relaxation in these molecules. Absorption data of α, ω-halo-alkanes [9] have been interpreted in terms of a distribution of relaxation times according to Fröhlich [16] associated with the moment component along the short axis in addition to a weak FIR region. On the other hand, a process with longer relaxation time due to the component of the dipole moment parallel to the long molecular axis was observed only in 1-haloalkanes because this component is compensated for α, ω-substitution. Experimental work has also been reported on aliphatic amines [7, 10], ketones [6, 11, 12], and

esters [13, 14] in dilute solution. Aliphatic amines were found by Tay and Crossley [10] to relax predominantly by intramolecular rotation of the polar amino group.

A few aliphatic ethers were studied by Smyth [7, 17] and coworkers in dilute heptane solution. These authors have analysed their absorption data in terms of two discrete relaxation processes. In addition to molecular over all orientation, they suggested an intramolecular process involving rapid coupled rotations or twisting around C–O bonds. However, there is little consistency in the resultant relaxation parameters of such an analysis. Besides, the relaxation spectrum of aliphatic chain molecules is more difficult to interpret on a molecular basis. For these reasons, a more detailed study of the dielectric absorption of aliphatic ethers in dilute solution over a wide frequency range has been undertaken to obtain more information about the various molecular processes of dipole orientation. The chain length of the symmetric ethers selected varied over as wide a range as practible and an asymmetric ether and a molecule with three ether groups in the unbranched chain are included in the investigations.

1. Experimental

Dielectric loss measurements have been made at 11 different frequencies between 0.3 to 300 GHz in dilute solutions at 20 °C. The difference of dielectric loss $\Delta\varepsilon''$ between solution and solvent was measured for several concentrations up to molar fractions x of 5%. $\Delta\varepsilon''$ was found to be proportional to x and this has been used to calculate the increment of loss

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$\Delta\varepsilon''/x$. Similarly, the static dielectric increment $\Delta\varepsilon_s/x$ was obtained at 1 MHz and the high frequency limit of permittivity $\Delta n_D^2/x$ was estimated from the optical refractive index. The equipment and the procedure to determine dielectric loss used in this work have been described elsewhere [19−21]. Although, under favourable conditions an accuracy of 1% can be achieved with all the instruments, the practical accuracy was only about 3% in some cases.

All polar substances for this investigation were obtained as pure grade samples from Fluka AG or Riedel-de-Haen AG. The solvents cyclohexane and mesitylene (1,3,5-Trimethylbenzene) were for synthesis. Solutes and solvents were used without further purification.

2. Results and Discussion

The measured increments of dielectric loss $\Delta\varepsilon''/x$ are plotted over the frequency on a double logarithmic scale which allows the shape of the absorption curves to be compared independently of the static dielectric increment [18] (see Fig. 1, 2, 4, 5). All curves are broader than a Debye curve due to a single relaxation time and they are unsymmetrical. At the high frequency side the slope is noticeable flatter and the curves are slightly convexe towards the abszissa. Similar shapes have already been observed in dilute solutions of alkyl halides [9] and rigid polar molecules [2].

In a first approximation we shall ignore this contribution of the weak far infrared absorption (FIR). The predominant main absorption region then only corresponds to the symmetrical part of the absorption curve and can be approximated by a shape according to Fröhlich [16]:

$$\frac{\Delta\varepsilon''}{\Delta\varepsilon_s - \Delta n_D^2} = \frac{G}{p}\arctan\left[2\left(\sinh\frac{p}{2}\right)\frac{\omega\tau}{1 + (\omega\tau)^2}\right], \quad (1)$$

where G is the weight fraction of this absorption region in relation to the total dispersion range $(\Delta\varepsilon_s - \Delta n_D^2)/x$. $\tau = \sqrt{\tau_a \tau_b}$ is the mean relaxation time of the Fröhlich distribution with limiting values τ_a and τ_b. The width of this distribution is given by the parameter $p = \ln(\tau_a/\tau_b)$.

The best fit of the above Eq. (1) to the experimental data was obtained by a least squares approximation using a digital computer. Agreement

between calculated and experimental points in the symmetric part of the curve is within 2%.

2.1. Symmetric ethers $(C_nH_{2n+1})_2O$

Selected absorption curves of symmetric ethers in cyclohexane and mesitylene solutions are shown in Fig. 1 and 2. With increasing chain length their maxima shift to lower frequencies and the width of the curves increases continuously.

The relaxation data of the analysis are given in Tables 1 and 2. It should be pointed out that these relaxation times are average values only describing different processes whose time constants are distributed between two limiting values. The
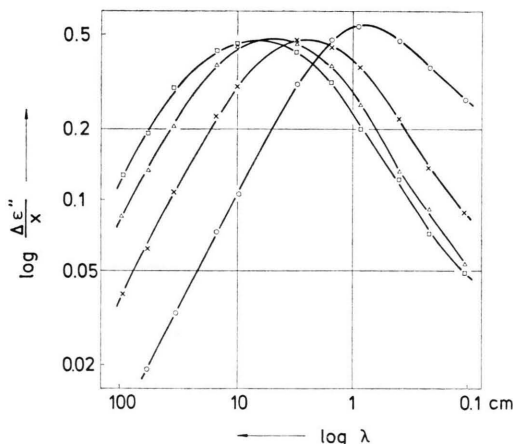

Fig. 1. Dielectric loss of symmetric ethers in cyclohexane solution at 20 °C: ○ dipropyl-, × dihexyl-, △ didecyl-, □ dihexadecyl ether.
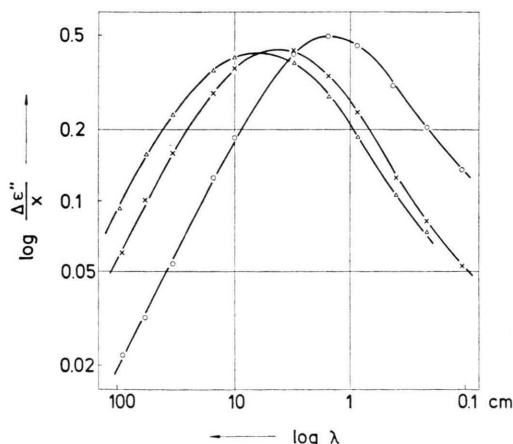

Fig. 2. Dielectric loss of symmetric ethers in mesitylene solution at 20 °C: ○ dibutyl-, × dioctyl-, △ didodecyl ether.

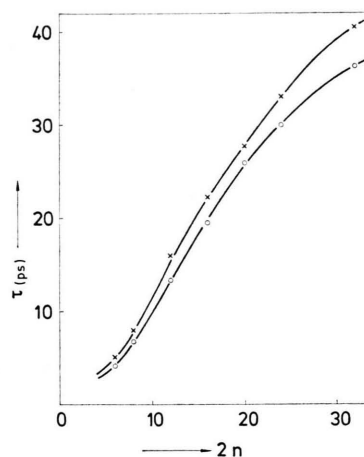Table 1. Relaxation parameters for cyclohexane solutions at 20 °C [see Eq. (1)].

Ether	$(\Delta\varepsilon_S - \Delta n_D{}^2)/x$	τ ps	p	G
Dipropyl-	1.46	4.1	1.7	0.84
Dibutyl-	1.45	6.7	2.1	0.88
Dihexyl-	1.40	13.3	2.5	0.83
Dioctyl-	1.41	19.5	2.6	0.84
Didecyl-	1.43	25.9	2.7	0.85
Didodecyl-	1.43	29.9	2.8	0.90
Dihexadecyl-	1.44	36.4	3.0	0.88
Ethylbutyl-	1.61	3.9	1.8	0.83
Bis(2-methoxy-ethyl)-	3.87	2.8	1.8	0.91

Table 2. Relaxation parameters [see Eq. (1)] for mesitylene solutions at 20 °C.

Ether	$(\Delta\varepsilon_S - \Delta n_D{}^2)/x$	τ ps	p	G
Dipropyl-	1.27	5.1	1.8	0.87
Dibutyl-	1.28	7.8	1.9	0.88
Dihexyl-	1.29	15.7	2.0	0.78
Dioctyl-	1.29	22.2	2.4	0.82
Didecyl-	1.24	27.7	2.5	0.81
Didodecyl-	1.29	33.1	2.8	0.84
Dihexadecyl-	1.18	40.5	2.8	0.87
Ethylbutyl-	1.42	4.9	1.8	0.84
Bis(2-methoxy-ethyl)-	3.46	4.3	1.3	0.80

Fig. 3. Symmetrical ethers. Relaxation time τ from maximum of dielectric loss vs. number of carbon atoms (2 n). ○ cyclohexane and × mesitylene solutions.

relaxation time τ of the symmetric ethers increases with increasing molecular size from dipropyl- to dihexadecylether, as already obvious from the shift of the absorption maxima. A plot of τ versus $2n$ the number of C-atoms in the molecule shows a characteristic behaviour (Figure 3). Starting from the lowest value τ at first increases more than proportional with increasing chain length from dipropyl- to dihexyl-ether. Then, for molecules with more than 20 C-Atoms the slope falls off again. The latter fact is caused by the flexibility of the chain which prevents the relaxation time to increase as for rigid molecules of the same size. Cooperative rotations around different bonds may become effective to reorient a dipole inside a longer hydrocarbon chain faster than by over all rotation of the molecule. Simultaneously, coiling of the longer chains may be important.

Furthermore, it seems striking that the relaxation time τ of every molecule from Tables 1 and 2 is shorter in cyclohexane solution than in mesitylene solution by an average factor of 0.87 for symmetric ethers, despite of the slightly higher viscosity of cyclohexane. Similar behaviour, however, has been found for rigid polar molecules, the relaxation times of which also are shorter in cyclohexane than in other solvents like benzene, heptane or carbon-tetrachloride, if related to their viscosity [22]. This has thought to be a special property of the solvent cyclohexane. On the other hand, viscous flow perhaps will only be of reduced importance to the relaxation in these flexible molecules.

The *Froehlich parameter* p which describes the width of the continuous distribution of relaxation times in logarithmic scale between limiting values τ_a and τ_b also increases with increasing chain length. Similar behaviour is shown by all symmetric ethers in both solvents cyclohexane and mesitylene. The upper limit τ_a of relaxation times nearly is a linear function of chain length. Increase in chain length adds more larger segments to the relaxation process and τ_a corresponds to the largest unit taking part in it. — The lower limit τ_b of the Froehlich distribution, on the other hand, is not independant on chain length, but also increases slowly. This is to be expected, since in symmetric ethers there are no polar end groups leading to a constant relaxation time as in the homologous series of α, ω-diethylesters [14], where free intramolecular rotation is possible.

With regard to the two solvents used, the absorption curves in mesitylene are narrower than in cyclohexane resulting in a smaller parameter p. The high limits τ_a of the distribution practically do

not differ in both solvents, but the low limits τ_b are appreciably shorter in cyclohexane, in the average by a factor 0.79. This is in agreement with the special behaviour of cyclohexane, where the relaxation times of rigid polar molecules were found to be the more reduced the smaller the molecules [22]. This then applies also to small absolute values of relaxation times.

In symmetric ethers the molecular dipole points perpendicular to the chain. In this respect, they are similar to α, ω-dichlorides with two partial moments on the ends of the chain; therefore is it reasonable to compare their dielectric behaviour. Recently, results have been reported on 1,10-dichlorodecane in mesitylene solution [9]. The chain length of this molecule equals approximately that of dihexyl ether. Its main absorption region was analysed by a Froehlich curve with $\tau = 19.7$ ps and $p = 1.7$. The corresponding ether has a mean relaxation time of 15.7 ps, shorter by nearly 25%, and a broader absorption curve ($p = 2.0$). The high limits τ_a of both relaxation spectra do not differ much, but the short time limit is lower by approximately 40% in the ether. That seems to be a property characteristic of an ether molecule.

Further comparisons as above can be made taking relaxation times of 1,4-dichlorobutane (6.9 ps) and 1,6-dichlorohexane (9.8 ps) in benzene solutions at 20 °C [9]. These time constants are longer than those of the corresponding molecules dipropylether (5.1 ps) and dibutylether (7.8 ps) in mesitylene (Table 2), although benzene has a somewhat lower viscosity. Moreover, in n-heptane solution the dichlorides mentioned above show relaxation times about 15% shorter only than the ethers of Table 1 in cyclohexane, despite a much larger viscosity difference between cyclohexane (0.97 cP) and n-heptane (0.41 cP).

All these results support the conclusion that the molecular dipole in ethers may relax faster than the molecular dipole in α, ω-substituted carbon chains of equal length. This is possibly due to a greater rotational mobility around O–C bonds which enables the ether dipole to reorient within the chain. Likewise, the potential barrier to rotation around C–O bonds is considerably lower than the barrier of 3.0 kcal mole^{-1} in saturated hydrocarbons [23].

The *dipole moments* for all the seven symmetric ethers investigated are constant in both the solvents (1.18 D) within the limit of experimental error.

The *relative contribution* G to the total absorption does not follow any systematic trend. The average value of G for all symmetric ethers is 0.86 in cyclohexane and 0.84 in mesitylene. A second absorption region at higher frequencies is to be expected not only from these values but also from the measured loss which exceeds the fitted Froehlich curve in the mm wave range (Fig. 1 and 2). The weight factor $1 - G$ of this so called FIR absorption region is in good agreement with the value of 0.13 found in chloroalkanes, also independant of chain length [9]. For ethers the time constant of the FIR contribution can be estimated to be in the order of 0.1 ps.

Finally, it should be mentioned that fitting the whole absorption curves to a superposition of three Debye terms [7, 17] is formally possible, however, with decreased accuracy. Since we did not find any reasonable trend in the weight factors G_i going from dipropyl- to dihexadecylether, it seems difficult to assume the existence of exactly two discrete time constants for the main absorption region instead of a continuous distribution. The reorientation by rotation around C–O bonds may be of greater importance than other processes, but the experimental data do not suggest a discrete relaxation region for this process.

2.2. Asymmetric ether $C_2H_5OC_4H_9$

Ethylbutyl ether has been chosen to study the influence of molecular asymmetry, if any. The molecule is similar in size to dipropyl ether and the asymmetry is not large. Nevertheless, the absorption
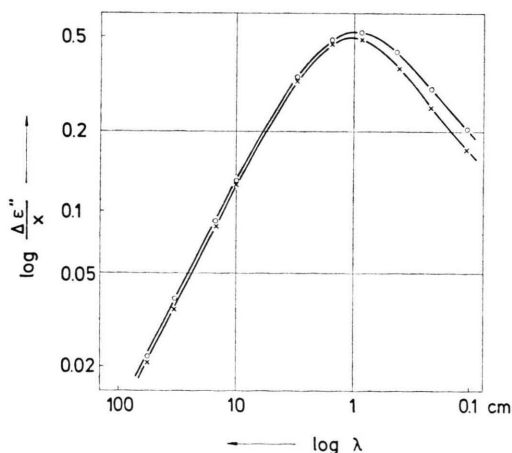

Fig. 4. Dielectric loss of ($\times$) dipropyl- and ($\circ$) ethylbutyl ether in mesitylene solution at 20 °C.

curves of both molecules in mesitylene solution (Fig. 4) differ noticeably. The absorption peak of the asymmetric ether is slightly higher and shifted towards the high frequency side. The same tendency is observed in cyclohexane solution. It follows that the relaxation times of ethylbutyl ether are clearly shorter than the respective values of dipropylether (Tables 1 and 2). — The widths of the distribution p tend to be somewhat larger for ethyl butyl ether.

The change in τ and p causes the lower limit τ_b of the distribution to be approximately 8% smaller than in the symmetric ether whereas τ_a differs only insignificantly. To understand the first fact, it reasonably has to be assumed that the OC_2H_5 group rotates around the adjacent C–O bond with a small time constant belonging to the lowest part of the Froehlich spectrum. This process will be faster than the corresponding one in the symmetric molecule.

The dipole moment obtained for ethylbutylether (1.25 D) is higher than the average value 1.18 D for symmetric ethers. A similar difference was observed previously [7] between dodecylmethyl ether (1.24 D) and dibutyl ether (1.18 D). Dimethyl ether has a dipole moment of 1.70 D [24], which obviously is reduced by partial moments induced in adjacent hydrocarbon groups of higher ethers.

2.3. Aliphatic Chain with Three Ether Groups

Bis-(2-methoxy ethyl)-ether consists of a chain COC_2OC_2OC. If we assume an ether group as spatially equivalent (at least not larger) to a single CH_2 group, then this molecule may be compared with dibutyl ether. The absorption curves of these two molecules in cyclohexane solution are reproduced in Fig. 5 showing the absorption peak of bis-(2-methoxy ethyl)-ether at higher frequencies than that of the simple ether.

The analysis gives the relaxation time τ of 2.8 ps which is much shorter than the 6.7 ps for dibutyl ether (Table 1) and even shorter than the 4.1 ps for dipropylether. The data of Table 2 show the same tendency in mesitylene solution. Furthermore, the overall dipole moment is increased by the two additional oxygen atoms to 1,94 D. The reorientation of these two end substituted methoxy groups constitutes decisively to the relaxation of the whole molecule reducing the observed mean relaxation time to 2.8 ps. A similar short relaxation time was also observed in pure liquid for 1,2-di-
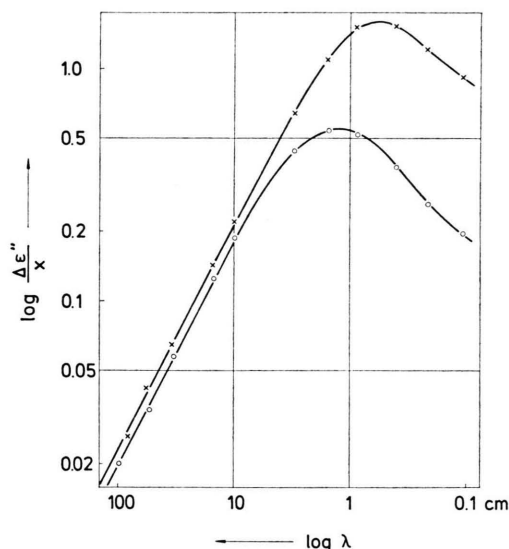

Fig. 5. Dielectric loss of (○) dibutyl ether and (×) bis (2-methoxy-ethyl)-ether $(CH_3OC_2H_4)_2O$ in cyclohexane solution at 20 °C.

alkoxy-ethanes [25] and was attributed to the presence of end substituted alkoxy groups. In our case the lower limit τ_b of the distribution of relaxation times is 1.2 ps in cyclohexane and 2.2 ps in mesitylene.

3. Conclusions

From the above discussion, it can be concluded that dielectric relaxation of aliphatic ethers is due to multiple intramolecular processes. In a first approximation their relaxation times are continuously distributed over a range increasing with chain length. This increase is related to the movement of segments of different size. Rotation around C–O bonds is faster than any segmental motion. However, no distinct relaxation time is separable from those of other processes, but the mean relaxation time becomes shorter than that of α, ω-chloroalkanes of equal size.

Acknowledgement

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