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Intramolecular dipole motion in amines and ethers from dielectric microwave measurements on dilute solutions

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Résumé.

Notre étude porte sur l'absorption de quelques amines, éthers et molécules de structure semblable, en solution diluée dans un liquide non polaire. Les mesures ont été effectuées avec des longueurs d'onde de 3 m, 1,5 cm et 0,7 cm et à 20° C. On peut reproduire la courbe d'absorption ainsi obtenue au moyen de deux termes Debye. L'un de ces termes doit être attribué à la rotation de la molécule entière, ce que l'on démontre en comparant son temps de relaxation à celui d'une molécule rigide de même volume. L'autre terme, possédant un temps de relaxation plus petit, est dû à la mobilité interne du dipôle moléculaire. Nos expériences ont montré entre les amines aliphatiques et aromatiques une différence remarquable concernant la mobilité de rotation du groupe NH_2. De plus, dans le diphényl-éther, sulfite et sélénide, le dipôle moléculaire présente un phénomène d'orientation très rapide. On est conduit à conclure que ce phénomène n'apparaît que si l'un, et un seul, des atomes de la sixième colonne de la classification de Mendélejeff, est lié sans intermédiaire aux deux groupes phényls.

To gain information from the Debye relaxation which is related to the molecule itself, it is recommendable to measure the absorption in dilute solutions. The influence of its surroundings, that is of the solvent molecules, may summarily be regarded as a hindering by friction, whereas in concentrated dipole liquids the specific intermolecular forces have a considerable importance.

In several papers [1] this method was used especially in measuring the dipole loss at *m*-waves on the long wave end of the absorption region. They intended to verify experimentally the predictions of the hydrodynamic theories of Debye [2] and Perrin [3] concerning the relations between molecular size, shape, and relaxation time. Later on rigid molecules are compared with molecules, whose dipole was supposed to possess a rotational degree of freedom. According to Budó [4] the complex dielectric constant

$\Delta\varepsilon = \Delta\varepsilon' - i\,\Delta\varepsilon''$ (Δ means the difference between solution and solvent) should have a frequency dependence:

$$\Delta\varepsilon = (\Delta\varepsilon_0 - \Delta\varepsilon_\infty)\left(\frac{G_1}{1 + i\,\omega\,\tau_1} + \frac{G_2}{1 + i\,\omega\,\tau_2}\right). \qquad (1)$$

The two Debye terms represent the dispersion and absorption resulting from each component of the molecular dipole respectively. G_i stands for its portion of the squared dipole moment; the two relaxation times may be written-

$$\tau_1 = \frac{1}{2\,D_M} \qquad \tau_2 = \frac{1}{D_M + D_G}, \qquad (2)$$

if the molecular shape is approximated by a spheroid of revolution. Index 1 is related to the Dipole component parallel to the interior rotational axis, the motion of which is determinated by a constant of " rotational diffusion " D_M, while the entire molecule is rotating. The component perpendicular to this axis (index 2) has a decreased relaxation time τ_2, because besides D_M the increased rotational mobility D_G around the interior axis is efficacious for it. From absorption at longer waves there is evaluated formally an effective relaxation time $\tau_{\mathrm{eff}} = G_1\,\tau_1 + G_2\,\tau_2$, representing a weighted average over the real distribution. According to these considerations it may be concluded a dipole to possess an intramolecular motion from the fact, that τ_{eff} is found noticeably smaller then expected for rigid molecules of similar size. This has been observed inter alia on primary amines [5], phenyl ether, phenyl sulfide and diphenyl amine [6]. But further statements are only possible with special assumptions upon the moment angle and the relaxation time of the rigid dipole component and have therefore a rather hypothetical character.

We have tried to control these preliminary results by measuring the absorption region near its maximum, so that we obtain besides τ_{eff} the approximate shape of the absorption curve for further information. For that purpose the absorption $\Delta\varepsilon''$ has been determined at three wavelengths in the 3 m-, 1.5 cm- and 0.7 cm-band. We have employed an interferometric method with two shunted waveguide paths at 1.5 cm wavelength. In the mm-region the transmitted power was measured behind a liquid layer of variable thickness. In modifying the arrangement of Lane and Saxton [7] the solution ascended in the inclined waveguide and the tuned crystal diode remained fixed at its termination.

The following theoretical aspects arise for the analysis of the observed absorptions curves: With only a single relaxation time the well-known Debye curve will be found with the maximum absorption value $\Delta\varepsilon'' = \frac{1}{2}$ $[\Delta\varepsilon_0 - \Delta\varepsilon_\infty]$. If several relaxation times exist the curve flattens and broadens, the maximum value, therefore, decreases. The investigated absorption being of the relaxation type, the curve will nowhere show a greater slope than the Debye absorption curve; so knowing τ_{eff} and the real maximum absorption value together with its corresponding frequency, its course at lower frequencies may already be fixed without further measurements.

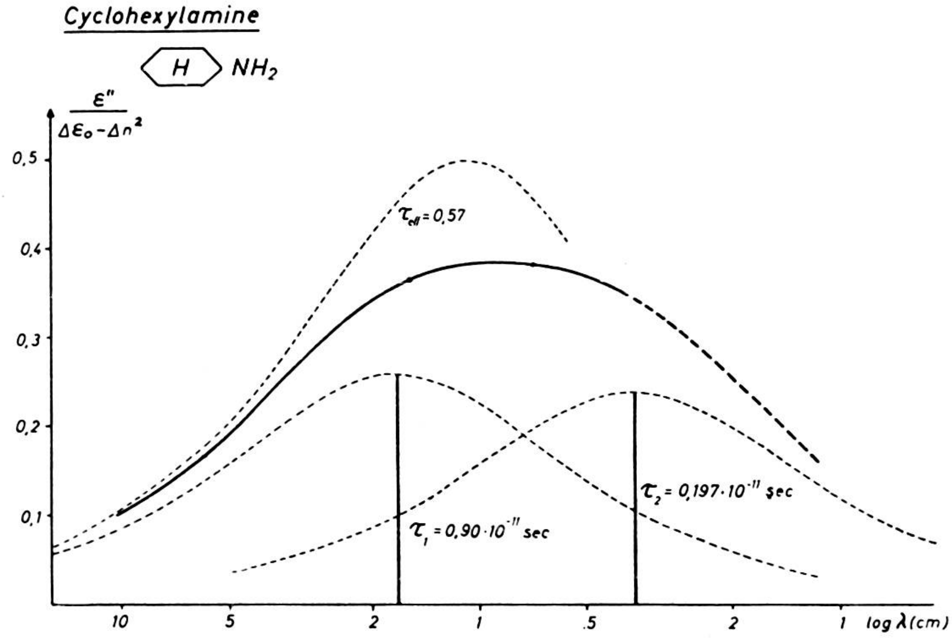

Fig. 1.

Cyclohexylamine in benzene.
Analysis of the absorption curve by two Debye terms.
The threshold Debye curve with τ_{eff} is got from absorption at 3 m wavelength.

If our observed absorption values yielded such a flattening, we therefore, have approximated the curves analytically with two Debye terms corresponding to (1) (fig. 1). For a physical interpretation the model of a rotating polar group seems convenient, provided that it is allowed by molecular structure; then the mobility D_M of the whole molecule D_G of the rotating group may be computed from the two relaxation times, using (2).

Figure 2 gives a selection from the results so obtained on *primary amines.* It shows the mobilities D_M and D_G in logarithmic scale, the weights G_2 are noted under the points by numbers. Chlorobenzene, chlorocyclohexane, tert. butylchloride, 1-chloronaphthalene, 4-bromobiphenyl and benzophenone yield in the limits of experimental error Debye curves, their dielectric behaviour being determined by a single relaxation time. These are rigid molecules which others may be compared with and so they are inserted into the figure. It is to be seen, that the amines and the rigid molecules of similar size and shape give quite the same molecular mobility D_M, except benzidine and tolidine. This may be taken as a symptom, that the analysis with the two Debye terms only formally performed has a physical meaning. In various solvents D_M is nearly inversely proportional to viscosity.

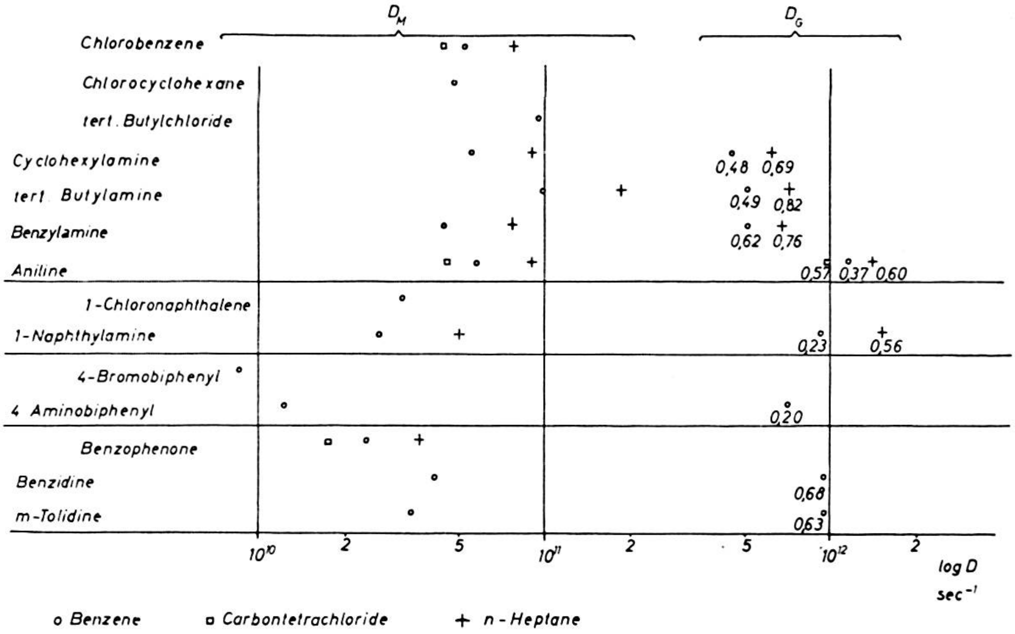

Fig. 2.
Rotational mobilities D_M and D_G of primary amines.

D_G is related to the rotational mobility of the NH_2-group, and in all *aliphatic* compounds it has almost the same value 5×10^{11} sec^{-1} in benzene or 7×10^{11} sec^{-1} in heptane. But it is striking, that the weights G_2 depend on solvent. It is believed the properties of the molecule itself in heptane can be observed, because $G_2 = 0.75$ leads to the expected angle of dipole moment against C — N — axis 60°. The decreased values in benzene seem to indicate an interaction with the solvent. In *aromatic* amines, however, the mobility of the group is nearly twice that mentioned above, and G_2 is decreased. Benzidine and *m*-tolidine are special molecules for the components of the moment parallel to the interior axis cancel. It is interesting, that nevertheless, at least two contributions to relaxation surely are to be derived from measurements, the smaller mobility D_M being increased compared with benzophenone.

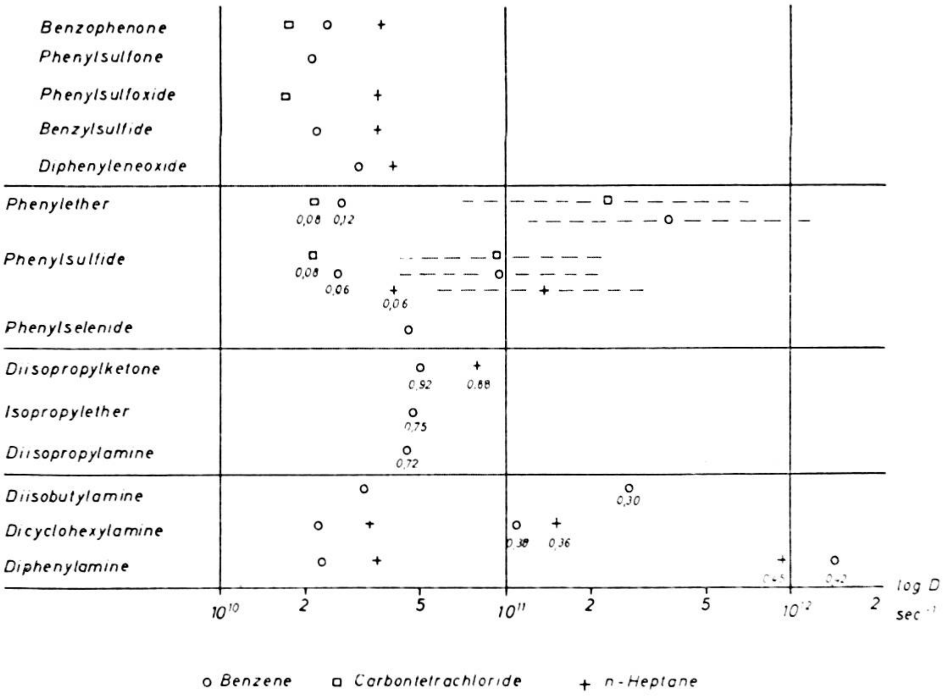

Fig. 3.
Molecules with a plane of symmetry.
Rotational mobilities D_M and D_R.
Further explanation will be found in the text.

Another series of substances are put together in fig. 3. These molecules have a *plane of symmetry* and the model of the rotating group seems to be unapplicable to them. The first five ones have rigid dipoles, for their absorption is fit to be approximated by a Debye curve, the relaxation time corresponding to molecular volume. But the *diphenyl* compounds with the central atom from the 6th column of the periodic system show a quite different behaviour. In phenyl ether the relaxation cannot be divided in two Debye terms, if the higher relaxation time shall be correlated to the rotation of the whole molecule. It is rather necessary to choose a distribution of relaxation times for the faster portion, for which we took formally that specified by Froehlich [8]. The points drawn in the figure mark its maximum absorption, its width being outlined by a dashed line. This relaxation process also depends on solvent, and G_1 being diminutive, most of the dielectric polarisation is connected with it. The absorption curves of the two other substances (sulfide and selenide) gradually approach the Debye slope, but the relaxation times remain still decreased compared with rigid molecules of similar size.

On the other hand the relaxation of the equivalent *aliphatic* molecules is essentially determined by molecular rotation, because G_1 becomes nearly 1. Ketone, ether and amine show quite a similar behaviour. We got no Debye curves for the three isopropyl compounds mentioned in fig. 3, but the deviations are too small, so we must wait for further measurements at higher frequencies to make conclusions on the existence of a fast relaxation process.

The last four substances are secondary amines. It is *diphenyl* amine again, which shows a considerable portion of relaxation with its main absorption to be expected in the lower *mm*-wave region. Therefore, from our measurements only a centre of that region may be predicted, and it remains unknown whether a process of relaxation or resonance belongs to it.

It seems obvious to interpret the interior dipole motion in the aromatic molecules with a plane of symmetry by an inversion. Eq. (1) and (2) are applicable to such a process, too, and they give an approximation of the real absorption curve—except for phenyl ether and sulfide—which may be perhaps somewhat inaccurate, but which enables to gain some quantitative information on the intramolecular dipole motion.

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