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Dielectric Relaxation Spectra of Alkyl Chlorides in Diluted Solutions

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In several papers [1] the question is raised, whether the internal mobility of the aliphatic chain contributes to dipole orientation in low-molecular compounds and dilute solutions. In relation to this problem, we have measured the loss factor ε'' at m -waves and microwaves with methods already described [2], selecting a series of chlorides with different chain length up to seven carbon atoms and different position of the dipole within the chain. The solvents were benzene and n -heptane. For all molecules, the position of the absorption curve versus frequency and its shape are discussed to obtain some information about their relaxation spectra.

I. CHLORIDES WITH THE DIPOLE AT CHAIN END

Since 1-Chlorides show absorption curves most flattened relative to Debye curves, their dipole orientation must be determined by several relaxation times. At first, we have tried to approximate the absorption by that from empirical relaxation spectra. Here Froehlich's distribution [3], frequently used, fails, for although through the microwave points a corresponding curve may be drawn, it yields absorption values, at m -waves, which are 25-50% above those measured. Therefore, it seems to us that general caution is necessary in deducing the features of a relaxation spectrum, if measured values are available only from a small frequency region.

Another possibility to analyse the absorption curve empirically employs two discrete relaxation times, as demonstrated earlier [4]. This gives as a rough approximation of the relaxation spectrum a short relaxation time τ_2 , with a weight G_2 of about 0.3, whereas the second, τ_1 , has the weight 0.7 hence and is longer by a factor 5-6.

It is difficult to interpret these relaxation spectra in terms of molecular structure, following the known theoretical conceptions. There are two possibilities:

i) τ_1 and τ_2 are caused by the spheroidal shape of the molecules, which rotate like rigid particles, τ_1 belonging to dipole component parallel and τ_2 to that perpendicular to the chain. But if the obtained values of τ_2 are compared with results on unbranched ketones possessing a dipole strictly perpendicular to the chain they are too short. Moreover Perrin's equations [5] representing the Brownian motion of spheroidal particles predict a ratio of only 1.5 for the two relaxation times.

ii) They result from intrinsic mobility of the CH_2Cl -group and may be treated according to Budó's model [6] of a free rotating polar group, τ_1 belonging to the moment component in direction of the rotation axis and τ_2 perpendicular to it. From the wellknown angle of the dipole against the C-C rotation axis calculations give a weight $G_2 = 0.77$ to the shorter relaxation time, much greater than observed. Furthermore, the measurements and their analysis with two Debye terms give values of τ_2 , which increase with chain length so rapidly, that the effective mobility of the group formally depends on the molecular volume.

Therefore, we may conclude, that the molecules are not rigid, τ_2 being too short for that; but on the other hand the polar end group can not rotate freely, because G_2 is not great enough. We suggest Hoffman's model [7] may be applicable for the group, concerning a rotator with three equilibrium positions. The height of its potential barriers would be dependent on the instantaneous configuration of the chain and in some cases it may be so great that the rotational mobility of the group is smaller than that of the whole rigid molecule and therefore it is ineffective. In such a way the existence of three relaxation times is possible, the shortest of them being independent of chain length. But this discussion calls special attention to the fact, that the shape of the absorption curve will depend only insignificantly on details of the relaxation spectrum, so that experimental errors of 2% prevent discrimination between an analysis with two and with three relaxation times.

II. CHLORIDES WITH THE DIPOLE WITHIN THE CHAIN

We approximate the low frequency tail of absorption at m -waves by a Debye curve and call the relaxation time so obtained τ_L . For 2- and

3-Chlorides this value is smaller than for 1-Chlorides with equal volume; moreover τ_L increases with a greater slope against chain length for 1-Chlorides. Discussing τ_L values only, no positive statements on intrinsic mobility of the CH_2Cl -group are possible, they may almost mislead into denying any mobility. In addition to τ_L we must consider the shape of the absorption curve, which, according to microwave measurements, is less flattened the more the molecular dipole is removed from chain end.

Here in all investigated molecules, we succeed in representing empirically the measured absorption values at microwaves and at m -waves by a Froehlich spectrum. On the other hand an analysis by two Debye terms is possible too, it yields two approximately equal weights and a ratio between 2 and 3 of the two relaxation times.

The relations of these results to molecular structure are not fixed definitely. The relaxation spectrum, narrower than that of the 1-Chlorides, may be caused by the spheroidal shape of the molecules, or several configuration forms of the flexible molecules, or by further possibilities of internal motion within the chain. It is significant that it contains no such short relaxation times, which we have attached to intrinsic mobility of the polar end group.

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