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Autor(en): **Maier, W.**

Objekttyp: **Article**

Zeitschrift: **Archives des sciences [1948-1980]**

Band (Jahr): **12 (1959)**

Heft 8: **Colloque Ampère : Maxwell-Ampère conference**

PDF erstellt am: **12.07.2024**

Persistenter Link: https://doi.org/10.5169/seals-739090

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Dielectric relaxation in dilute solutions

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Résumé.

Les temps de relaxation de l'orientation des dipôles ont été étudiés dans des solutions diluées de Benzol (20° C) en mesurant ε_0 (à 1,2 MHz), ε' et ε'' (λ = 13,82 cm, 3,48 cm et 1,46 cm) et calculés d'après Debye. Pour le 2-Cl-anisol, le 4-Cl-anisol et le 2,6-dichloranisol, on obtient des valeurs correspondant approximativement aux valeurs estimées à partir du volume moléculaire pour une molécule dipolaire rigide.

Par contre, les temps de relaxation mesurés sur l'anisol et le 2,4,6-trichloranisol sont notablement plus petits que ceux que l'on pourrait attendre d'une molécule dipolaire rigide.

Nous en concluons qu'il doit exister une mobilité du groupe methoxy pour toutes les molécules examinées. Cette mobilité peut ne pas être sensible pour les anisols mono- et di-substitués; parce que pour ces molécules le temps de relaxation, très long, des dipôles C-Cl liés de manière rigide au cycle du phénol, est prédominant.

Pour le diphényléther et le 2-méthyldiphényléther et le 2-hydroxydiphényléther, les temps de relaxation mesurés sont respectivement de $\tau \,.\, 10^{11} = 0{,}37$; 0,66 et 2,0 sec. Pour des molécules rigides, il faudrait s'attendre à des valeurs de l'ordre de 2,0 sec. La valeur notablement plus faible des deux premières substances n'est pas attribuée à la mobilité des moments dipolaires atomiques de 0, mais expliquée par un mouvement particulier des deux cycles diphényl n'exigeant qu'un très faible espace et au cours duquel le moment dipolaire est retourné de 180°.

Les ponts internes d'hydrogène bloquent ce mécanisme dans la troisième substance.

The existence of internal mobilities in dipole molecules may be revealed by the observation that the relaxation time τ_{exp} (determined by dielectric measurements on dilute solutions of the dipole molecule in a nonpolar solvent) is distinctly lower than the theoretical value τ_{rig} (calculated from the molecular dimensions assuming the whole dipole moment to be rigidly fixed to the molecule). In this manner we have studied first the mobility of the methoxygroup in 2,6-dichloroanisole and 2,4,6-trichloroanisole and secondly the well known unusual small relaxation time of diphenylether.

The measurements were performed on dilute solutions in benzene (mole fractions from 0,002 to 0,01) at 20° C. They include the static value ε_0 (by a standard method) and the complex permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ at wavelengths of 13,82 cm (coaxial resonator), 3,48 cm (rectangular wave-guide absorptioncell of fixed length, standing wave pattern by slotted line) and 1,46 cm (method of Poley [1] simplified for $\varepsilon'' \ll \varepsilon'$, absorptioncell with movable short). With the small concentrations used in our measurements the differences $\Delta\varepsilon$ between solution and solvent are proportional to the mole fraction $\varkappa$. The quantities $a_0 = \Delta\varepsilon_0/\varkappa$, $a' = \Delta\varepsilon'/\varkappa$ and $a'' = \Delta\varepsilon''/\varkappa$ (averaged over a great number of single measurements on different concentrations) then obey the same equations as ε_0, ε' and ε''. We first assumed a frequency dependence of the simple Debye type

$$\left(a' = a_\infty + \frac{a_0 - a_\infty}{1 + \omega^2 \tau^2} \text{ and } a'' = (a_0 - a_\infty) \frac{\omega \tau}{1 + \omega^2 \tau^2}\right)$$

and calculated the best fitting values of the three parameters a_0, a_∞ and τ by minimizing the mean squared deviations. With these values we drew the Coleplot and inserted into this diagramm the experimental points with their limits of the mean squared errors as they resulted in determining the quantities a. If the error-rectangles did not deviate distinctly from the Cole-plot we regarded the values of a_0, a_∞ and τ as valid. This was the case with the substances reported here; the results are given in tables 1 and 2:

TABLE 1.

Substance	$\tau_{exp} \cdot 10^{11}$ sec	$\tau_{rig} \cdot 10^{11}$ sec	μ in D
Anisole $C_6H_5 . OCH_3$	0,7	1,24	1,24
4-Chloroanisole $Cl . C_6H_4 . OCH_3$	1,78	1,90	2,32
2-Chloroanisole $C_6H_4Cl . OCH_3$	1,23	1,50	2,44
2, 6-Dichloroanisole $C_6H_3Cl_2 . OCH_3$	1,99	1,91	2,63
2, 4, 6-Trichloroanisole $Cl . C_6H_2Cl_2 . OCH_3$	1,2	2,25	1,40

TABLE 2.

Substance	$\tau_{\text{exp}} \cdot 10^{11}$ sec	$\tau_{\text{rig}} \cdot 10^{11}$ sec	μ in D
Diphenylether $C_6H_5 . O . C_6H_5$	0,37	1,54	1,20
2-Methyldiphenylether $C_6H_4CH_3 . O . C_6H_5$	0,66	1,85	1,03
2-Hydroxydiphenylether $C_6H_4OH . O . C_6H_5$	2,0	1,83	1,60

The fourth columns of these tables bring the dipole moments calculated from $a_0 - a_\infty$, that is the dipole moments connected with the relaxing polarisation studied by our measurements.

Table 1 shows the well known internal mobility of the methoxydipole of anisole [2] revealed by the clearly lowered τ_{exp}-value. A similar situation is found with trichloroanisole and this proves the mobility of the methoxygroup for all chlorosubstituted anisoles. That the latter cannot be pointed out for the other three substances of table 1 may be clearly understood by the existence of a great dipole component fixed to the phenylring and therefore connected with the great relaxation time τ_f preponderating very strong in the measured τ_{exp} which is an effective one. In trichloroanisole the C-Cl-dipoles compensate each other nearly completely and so the influence of the movable part of the dipole moment with its small value τ_r is predominant. Regarding the results of table 2, attention is called upon the unusual small τ-value of diphenylether (found for the first time by Fischer [3]) which has been explained by a special mechanism of dipole orientation based on the mobility of the atomic dipole moment of the oxygen atome, connected with torsional motions of the phenylrings round the C-O-bond [4]. This explanation requires the assumption that only a part of the total dipole moment orientates in this quick manner, whereas the rest should be combined with the " normal " relaxation time. It is difficult to understand that the highly movable dipole component should be predominant to such an extent as to give the observed small τ-value. We have performed a great number of measurements and we find that our results fit well to a single relaxation time. Of course we cannot exclude the possibility of two relaxation times, but our experiments do not require them. Beyond it we think it not necessary to assume the above mentioned explanation and we propose another one: The whole dipole of the diphenylether molecule can be turned in the opposite direction by an internal motion around the molecular axis of greatest length. With this motion the oxygen atom describes an arc of 180° without changing appreciably its valence angle, whereas the orientation of the two phenylrings varies only within some 20° to 30° (no rotation by 180° !). In the course of this turning over of the dipole the conjugation between the lone pair 2p-electrons of the oxygen and the π-electrons of the two benzenerings is somewhat changed. But the total conjugation energy remains nearly constant because the decreasing resonance with the one ring is compensated by the increasing resonance with the other ring. So there is no essential intramolecular electronic potential barrier for this motion. The external hindering should be smaller than for the rotation of a single phenylring (fluorobenzene: $\tau < 0{,}5 \cdot 10^{-11}$ [5]). The results for 2-Methyl- and 2-Hydroxyphenylether are in agreement with our explanation without, to be sure, excluding the atomic dipole interpretation: The relaxation time of 2-Methyldiphenylether is somewhat increased by the asymmetry causing a small fixed dipole component with greater relaxation time. The relaxation time of 2-Hydroxy-diphenylether is that of the rigid molecule because the hydrogen bond between the two oxygen atoms prevents our internal motion.

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