DIELECTRIC ABSORPTION STUDY OF HYDROGEN-BONDED PENTACHLOROPHENOL-TRIBUTYLAMINE COMPLEX

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Dielectric permittivities and losses of solutions of the pentachlorophenol-tributylamine complex in CCl_4 were studied over the frequency range from 90 Mc/s to 22 Gc/s. Two relaxation times (1.01×10^{-9} and 1.38×10^{-10} s) were found. A possibility of the proton jumping effect as responsible for the second absorption band is suggested.

The existence of a double minimum potential function in hydrogen bonding was confirmed by several independent methods [1–5]. In dielectric response the proton transfer through the potential barrier was found in the anomalous dielectric saturation phenomenon [3, 4]. Field-induced proton displacement can be achieved even for significant distance between two energy levels if a high field strength is applied. It would be interesting to determine the relaxation time of proton jumping directly from dielectric absorption studies. However, the marked dielectric losses can be observed only for systems where the distance between the two minima is small. This condition arises from the relation [6]

$$\varepsilon_0-\varepsilon_\infty=\frac{1}{2}\varepsilon''_{\max}=\frac{3\varepsilon_0}{2\varepsilon_0+n^2}\frac{4\pi N_0\mu\mu^*}{3kT}4w(1-w)$$

which can be expressed in simpler form as

$$\varepsilon''_{\max}=\frac{C}{T}\left(1+\cos h\frac{\Delta U}{kT}\right)^{-1}$$

where C is a constant depending on the square of dipole moment in the absence of dipole coupling, and ΔU is the difference of energy between the two minima.

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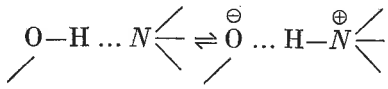
Earlier dipole moment measurements [5] indicate that this condition is probably satisfied by the phenol-amine systems, where the equilibrium



should be taken into account.

In the present study the pentachlorophenol (PCP)-tributylamine (TBA) system in CCl_4 was examined. From IR-spectra and dielectric titration studies it follows that at the concentration used complexes of the 1 : 1 ratio are formed, the formation constant being equal to 1.9×10^4. Therefore, the participation of free noncombined molecules and more complicated species can be neglected. The choice of PCP and TBA as the components of the system was justified by the fact that the relaxation time of the reorientation of the whole molecules should not be low even in the solvent of small viscosity.

The ε^* measurements in the range from 90 MHz to 3 GHz were carried out on the slotted lines. At the frequencies 7 GHz, 10 GHz and 22 GHz appropriate wave guides were used. VSWR-values were measured for various thicknesses of the sample, and the Roberts-von Hippel calculation procedure was used. The accuracy in permittivity (ε') was ±0.01, and in dielectric losses (ε'') ±0.02. Concentration of the complex was $c = 0.194$ M at $T = 298°$K.

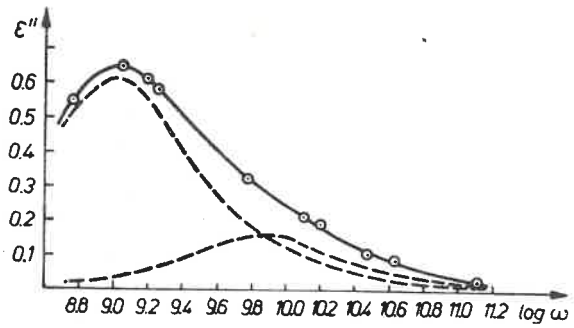


Fig. 1. Experimental curve ε'' *versus* log ω (solid line) and its resolution into two absorption curves of Debye type (dashed lines)

The details concerning the technical aspects and procedure of the measurements will be published elsewhere [7].

The results obtained are presented in Fig. 1 (solid line). The experimental curve shows two absorption regions, both with single relaxation time. The total losses were resolved by using the digital computer into two components, illustrated by the dashed curves. An iteration method was elaborated which optimalizes both $\Delta\varepsilon'$ and τ values for a number of overlapping Debye dispersion regions. The corresponding characteristics of the two dispersion regions (denoted by indices 1 and 2) are: $\Delta\varepsilon'_1 = 1.224$, $\Delta\varepsilon'_2 = 0.292$, $\tau_1 = 1.01\times10^{-9}$ s, $\tau_2 = 1.38\times10^{-10}$ s. Here, $\Delta\varepsilon' = \varepsilon_0 - \varepsilon_\infty$, ε_0 being the static and ε_∞ the optical permittivity and τ is the relaxation time. ε_∞ for the first absorption domain was estimated from the Cole-

Cole arc. The dipole moments ascribed to both absorptions were calculated from the equation [8]

$$\mu^2 = \frac{9\,kT(2\varepsilon_0+\varepsilon_\infty)\,(\varepsilon_0-\varepsilon_\infty)}{4\pi n\varepsilon_0(\varepsilon_\infty+2)^2}$$

and are equal to 7.23 and 3.72 D, respectively. n is the number of molecules per c. c.

The first absorption domain can be ascribed without any doubt to the reorientation of whole molecules of the complex. One could suppose that the second domain is due to the proton jumping effect.

It is rather difficult to ascribe this absorption to some other relaxation phenomena. The concentration of free PCP and TBA is negligibly low and, moreover, a high μ_2 — value presumably excludes an intramolecular rotation of phenolate groups along the hydrogen bridge or phenyl ring along the C—O bond as responsible for the second absorption band. In both cases only a small change of dipole moment should be expected. The rotation of the phenolate group can raise the change of dipole moment due to the steric hindrance and appearance of nonequivalent arrangements with respect to butyl chains. The rotation of the phenyl ring can really lead to the change of mesomeric moment; however, it was shown that this moment usually does not exceed 1 D [9].

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