The Dielectric Properties of Some Phenols

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Résumé.

L'auteur présente les propriétés diélectriques de quelques phénols, à l'état liquide et en solution, dans le domaine de réquences 0,1 Mcs à 8,5 Gcs. Les systèmes étudiés sont les suivants: le 2-6 diisopropylphénol, le 2-6 diméthoxyphénol et l'éther de diméthylhydroquinone. Les résultats sont discutés en relation avec l'empêchement stérique de rotation du groupe phénolique par les groupements substitués en position ortho.

INTRODUCTION.

An aspect of dielectric absorption which is of particular interest to chemists is that which arises when the polar molecule has a non rigid dipole element. The general anticipation is that such molecules should show two absorptions: one characterised by the relation time of the rigid molecular framework: the other determined by the characteristic time of the rotation, flexure or flapping within the molecule.

Davies and Meakins [1] have produced some examples of such resolved absorptions. Taking two highly hindered phenols in dilute solution they were able to identify component absorptions due to the " rigid framework " rotation and a higher frequency absorption due to the hindered rotation of the hydroxyl group

There is clearly appreciable interest in assessing such rotating elements in other cases, both in relation to the molecular structure and in terms of the energy barrier contolling the process.

Accordingly a study of a number of phenolic and related substances has been commenced. The measurements this far completed have been made from a fraction of a megacycle per second up to 8.5 KMc/s.

APPARATUS.

The Hartshorn Ward set has been used up to 100 Mc/s. From 250 to 920 Mc/s the General Radio slotted line has been adapted in our laboratories by Williams [2] to provide standing wave measurements giving adequate precision in the dielectric parameters for dilute solution work and for high loss materials: the simple conditions and pre-requisites are described in a paper in the March (1959) number of *Journal of Physical Chemistry*.

The top frequencies available are those of 1.3 and 8.5 KMc/s provided by the dielectrometer based on Westphal and Van Hippel's design and constructed by the Central Research Laboratories, Minnesota.

The procedure of operation and calculation have been checked by measurement of well characterised dielectric media. The dielectric constant and the absorption factor can be established within a few per cent.

MATERIALS.

A sample of 2:6 diisopropyl phenol was obtained from Messrs. Lights Ltd. A constant boiling fraction (B.Pt. 121-122° C at 13 mm) was taken. The measured refractive index of 1.5144 (20° C) agreed with the value quoted by Messrs. Lights (1.5145 at 20° C (personal communication)).

2:6 Dimethoxy phenol was recrystallised from water. The product melted at 53.5° C (lit. 55° C) [3].

Hydroquinone dimethyl ether was recrystallised from ethyl alcohol. M.Pt. 55.2-55.8 (lit. 56° C) [4].

Decalin and tetrachloroethylene were purified and fractionally distilled [5]. The decalin fraction distilled at 81° C (23 mm pressure), and the tetrachloroethylene at 119.5-120° C. Analar benzene was dried over calcium sulphate and fractionally distilled B.Pt. 80° C (lit. 80.1° C).

RESULTS.

Some of the systems show the critical frequency (peak absorption) of a Debye type absorption directly. Where the critical frequency is not observed a plot of ε''/w against $\varepsilon'' w$ has been made, and when all the points fall on a straight line, this indicates that only a single relaxation time is involved; this plot defines the value of the relaxation time τ and $(\varepsilon_0 - \varepsilon_\infty)$.

When a distribution of relaxation times appears to be involved the Cole-Cole plots have been used to evaluate the parameters.

The new data available are summarized in table 1.

TABLE 1.

Solute	Solvent	Molar Conc.	$t°$ C	$\tau \times 10^{12}$ sec.	ε' Sol.	ε''_m	$(\varepsilon_0 - \varepsilon_\infty)$
2:6 diisopropyl-phenol	Pure liquid Decalin	0.995	19.0 17.5	46* 32	3.90 2.43	0,51 0.085	1.42 0.17
Hydroquinone dimethyl ether .	Decalin Benzene	0.576 0.960	23.0 21.5	10 12	2.38 2.67		0.19 0.25
2:6 dimethoxy-phenol	$C_2 CL_4$	0.36	18.0	31	2.60	0.12	0.24

* A Cole-Cole distribution parameter of $n = (1 - \alpha) = 0.80$ is found.

2:6 diisopropyl phenol.

For the decalin solutions the agreement between ε'' max and $\frac{1}{2} \times (\varepsilon_0 - \varepsilon_\infty)$ shows that the results are consistent with a simple Debye absorption with a single relaxation time. The dipole moment of the polar element involved in the absorption is found to be 1.1D from the observed value of $(\varepsilon_0 - \varepsilon_\infty)$. The dipole moment calculated from Guggenheim's equation [6] is 1.4D. This difference between the two dipole moments obtained probably arises due to the difference between the values ε_∞ and the square of the solution refractive index $(\varepsilon_\infty = 2.26: (n)^2 = 2.19)$.

Comparison with o-dichlorobenzene in decalin (relaxation time of 11×10^{-12} sec. [1]) on the basis of molecular volumes deduced from Courtauld's models suggest a value of 24×10^{-12} secs. for the relaxation time of the rigid 2:6 diisopropyl phenol. The observed value is 32×10^{-12} secs. It is therefore possible that the molecule behaves as an effectively rigid structure. The isopropyl group, unlike the t-butyl group, still allows the hydrogen atom of the phenolic group to occupy a position in the plane of the benzene ring. This is the prerequisite for partial double bond character in the C-O bond (by delocalization of the $2p_z$ lone pair electrons of the oxy-

gen atom with the π bond system of the phenyl molecules) and it is this which may confer rigidity on the molecule.

The distribution of relaxation times observed in the pure liquid arises probably due to the presence of hydrogen bonding, which is much greater in the pure liquid than in solutions.

Hydroquinone dimethyl ether.

For this solute in decalin and benzene measurement from 1 to 8.5 KMc/s show a single Debye type of absorption although the critical frequency is not reached. The relaxation time and $(\varepsilon_0 - \varepsilon_\infty)$ are estimated from the linearity of the plot of ε''/w against $\varepsilon'' w$. The relaxation times deduced are appreciably more significant than earlier values for this molecule which were confined to lower frequencies [7].

Comparison with o-dichlorophenol in decalin on the basis of van der Waal's models give a value of 12×10^{-12} sec. for the relaxation time of hydroquinone dimethyl ether in decalin. The measured value is 10×10^{-12} sec. Again this suggests that the whole molecule rotates as an effectively rigid structure.

The literature value for the dipole moment of hydroquinone dimethyl ether in benzene is 1.70D [8], while the dipole moment deduced from the $(\varepsilon_0 - \varepsilon_\infty)$ values are 1.4D in benzene and 1.6D in decalin. Again these differences probably arise due to the differences between ε_∞ ($\varepsilon_\infty = 2.42$ for solution in benzene, and 2.19 in decalin solution) and the square of the solution refractive index ($n^2 = 2.25$ for benzene solution; 2.16 in decalin solution).

2 : 6 dimethoxy phenol.

The equality of ε'' max and $\frac{1}{2}(\varepsilon_0 - \varepsilon_\infty)$ confirms the presence of a Debye type absorption with a single relaxation time for this molecule in tetrachloroethylene. The dipole moment deduced from $(\varepsilon_0 - \varepsilon_\infty)$ is 2.2D, while that decued from the Debye theory is 2.5D. The square of the refractive index for this solution is 2.28 which differs from the value of 2.36 obtained for ε_∞.

Comparison with the effectively rigid dibenzothiophene (relaxation time of 30×10^{-12} in tetrachloroethylene [9]) suggests an expected relaxation time of the 2 : 6 dimethoxy phenol of 31×10^{-12} sec. This suggests that the 2 : 6 dimethoxy phenol behaves as an effectively rigid structure in this frequency range.

ACKNOWLEDGEMENT.

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