Dielectric studies. Part XVIII. Dipole moments and relaxation times of some symmetrically substituted alkylbenzenes

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The dielectric absorption at four microwave frequencies of pure liquid benzene and *p*-cymene at 25 °C, *p*-xylene and mesitylene at 25, 40, 50, and 60 °C, and solutions of durene and hexamethylbenzene in mesitylene at 60 °C has been examined. All show measurable loss factors and apparent dipole moments of about 0.1 to 0.2 D. These moments are less in magnitude than those associated with the short relaxation time (τ_2) process for the polar monoalkylbenzenes, *o*-xylene and *m*-xylene. Their relaxation times are too short for molecular reorientation and there is a rough correlation between the number of collisions/molecule s and the reciprocal relaxation time.

Previous papers in this series (1, 2) have reported a small dielectric loss for *p*-xylene. The results revealed that the frequency maximum in the absorption is greater than 70 Gc/s. This corresponds with a relaxation time less than 2×10^{-12} s which is much shorter than would be anticipated for the molecular reorientation of a molecule of this shape and size, e.g. the molecular relaxation of *p*-chlorotoluene in *p*-xylene at 25 °C is 16×10^{-12} s (3).

Whiffen (4) found that the losses of benzene, carbon tetrachloride, and a few other molecules, having no permanent electric dipole moment, were proportional to the frequency in the range 0.3 to 1.2 cm^{-1}. He suggested that the absorption results from dipole moments induced in molecular collisions where, for example, the C—H bond moment in benzene is the inducing dipole. The induced dipole was regarded as changing direction, not by rotation of the molecule containing it, but because of a new distortion produced at another instant by impact with another neighbor. The plots of loss tangent against frequency suggested Debye behavior and a relaxation time of the order of the time between molecular collisions. Similar results have been reported for nonpolar molecules in both liquid (5) and gaseous (6) states. The gaseous measurements have shown that the absorption is proportional to the square of the gas density and are attributed to temporary dipole moments induced during molecular collisions. DiCarlo and Smyth (7) have measured

the dielectric constant and loss at 1.25 and 3.22 cm of several symmetrical molecules. For benzene the dielectric loss at 1.25 cm was about 0.003 at 25 °C, and, in addition, hexamethylbenzene appeared to have a small apparent dipole moment.

The microwave method is well suited to the detection and estimation of small dipole moments, and unlike, for example, the Halverstadt–Kumler approach involves no atomic polarization approximation. It seemed worthwhile determining fairly precise values of apparent dipole moments and relaxation times of some molecules with a center of symmetry, with a view to comparing their magnitude with those obtained for the short relaxation process of the monoalkylbenzenes (8), and also to attempt correlation of the relaxation time for such a process with the number of collisions/molecule s.

Experimental Methods

The apparatus and techniques employed have been described previously (9, 10). The dielectric constant ϵ' and loss factor ϵ'' were determined by the bridge method at frequencies of 70.00, 35.09, 23.98, and 9.313 Gc/s. The static dielectric constant ϵ_0 was measured with a heterodyne beat apparatus at 2 Mc/s.

The compounds were commercially available. Special attention was paid to the purity of the compounds, particularly to the elimination of water. The liquids were treated with sulfuric acid, to remove sulfur compounds, and after preliminary drying with magnesium sulfate, the liquids were allowed to stand over phosphorus pentoxide for 24 h before refluxing and distilling from sodium, using a 30 theoretical plate spinning band column. The

TABLE I

Dielectric loss and apparent dipole moment data for some symmetrically substituted alkyl-benzenes. $\mu_1{}^1$ and $\mu_2{}^1$ are the apparent dipole moments (in debyes) corresponding to mean relaxation times of 2 and 5×10^{-12} s respectively as calculated from eq. [1]. The loss of the solvent (mesitylene) was subtracted in the case of durene and hexamethylbenzene. The pure liquids were measured at 25 °C and the mesitylene solutions at 60 °C

Solute	w_2	ε_0		Frequency (Gc/s)			
				70.00	35.09	23.98	9.313
Benzene	1.000	2.278	ε''	0.0059	0.0035	0.0025	0.0003
			$\mu_1{}^1$	0.10	0.08	0.08	0.05
			$\mu_2{}^1$	0.11	0.07	0.06	0.03
p-Xylene	1.000	2.263	ε''	0.0063	0.0054	0.0037	0.0022
			$\mu_1{}^1$	0.12	0.12	0.11	0.11
			$\mu_2{}^1$	0.13	0.10	0.09	0.09
p-Cymene	1.000	2.244	ε''	0.0071	0.0076	0.0060	0.0047
			$\mu_1{}^1$	0.15	0.16	0.15	0.17
			$\mu_2{}^1$	0.16	0.14	0.13	0.15
Mesitylene	1.000	2.275	ε''	0.0074	0.0074	0.0064	0.0034
			$\mu_1{}^1$	0.14	0.15	0.14	0.14
			$\mu_2{}^1$	0.15	0.13	0.12	0.12
Durene	0.430	2.239	ε''	0.0039	0.0030	0.0042	0.0034
			$\mu_1{}^1$	0.17	0.16	0.18	0.22
			$\mu_2{}^1$	0.18	0.14	0.16	0.20
Hexamethylbenzene	0.126	2.237	ε''	0.0004	0.0000	0.0015	0.0011
			$\mu_1{}^1$	0.11	—	0.23	0.25
			$\mu_2{}^1$	0.12	—	0.21	0.23

distillates were stored in amber bottles over sodium wire. Durene and hexamethylbenzene were recrystallized from p-xylene and dried in a vacuum oven over phosphorus pentoxide.

Experimental Results

The errors involved in the dielectric constants for low-loss solutions are such that Cole–Cole plots are difficult to formulate, and it is more realistic to examine the absorption in terms of the dielectric losses. The latter are presented in Table I together with the static dielectric constant (ε_0) and dipole moment (μ) data evaluated from the equation

$$[1] \quad \mu = \left(\frac{27kT}{4\pi Nc} \times \frac{\epsilon''}{(\epsilon_0 + 2)^2} \times \frac{1 + \omega^2\tau^2}{\omega\tau} \right)^{1/2},$$

in which k is the Boltzmann constant, T the absolute temperature, N the Avogadro number, ε'' the dielectric loss, ω the angular frequency, and τ the relaxation time.

Some appreciation of the results and an indication of the respective relaxation times are given by the plots of ε'' against log ω (Fig. 1). These plots give some indication of the errors especially for the very low-loss durene and hexamethylbenzene solutions. The broken line curves on these plots were obtained from ε'' values calculated from eq. [1] by substitution of dipole moments and relaxation times giving ε'' values comparable with the experimental values.

Discussion

The dipole moments listed in Table I, calculated from eq. [1], indicate that the values are relatively insensitive to the choice of relaxation time. For benzene the dipole moment values compare favorably with those of 0.06 and 0.02 D calculated from the results of DiCarlo and Smyth (7) at 24.00 and 9.32 Gc/s respectively, using a relaxation time of 5×10^{-12} s.

A comparison of estimates of the frequency of the absorption maximum, in Fig. 1, readily indicates that this frequency decreases with increase in molecular size, and hence, since $\omega\tau = 1$, the observed relaxation time accordingly increases. The different temperature plots for mesitylene and p-xylene indicate that the relaxation times are not detectably dependent upon temperature. For benzene the results may be compared with those obtained by Whiffen at 25 °C (4) and DiCarlo and Smyth at 20 °C (7). The plot shows the agreement between the
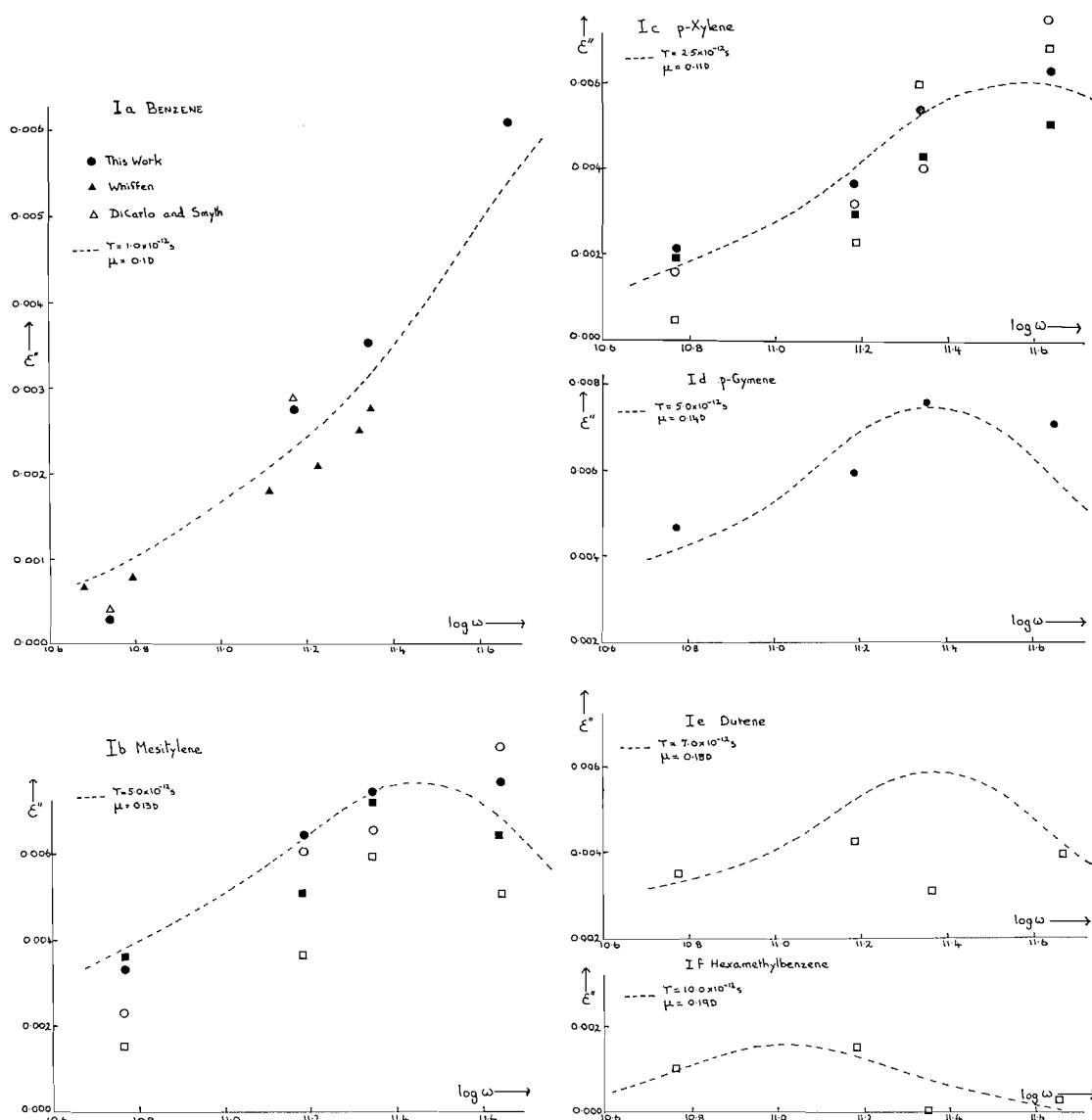
FIG. 1. Plots of ε'' against $\log \omega$ for benzene and some symmetrically substituted benzenes at ($\bullet$) 25 °C, ($\blacksquare$) 40 °C, ($\bigcirc$) 50 °C, and ($\square$) 60 °C. Durene and hexamethylbenzene were measured in mesitylene solution and the loss of the solvent has been subtracted; the remainder were measured as the pure liquid. The broken line indicates a possible loss curve. However, more experimental points would be necessary to establish the true shape.

three sets of results to be remarkably good and supports their validity.

The molecular relaxation times of toluene (8) and bromobenzene in cyclohexane (9) are about 9 and 12 × 10⁻¹² s respectively at 25 °C. Such molecules are of similar shape but of smaller volume than all of the symmetrical alkyl-benzenes. In addition, the mean relaxation times of pure liquid t-butylbenzene (8) and benzo-

trichloride in cyclohexane (11) are about 20 and 23 × 10⁻¹² s respectively at 25 °C, compared with a value of approximately 5 × 10⁻¹² s obtained for p-cymene, a molecule greater in volume than these mono-substituted compounds. Whiffen and Thompson (12) measured the dielectric absorption of p-cymene over a range of temperatures and calculated, using a dipole moment of 0.19 D, relaxation times of 8.0 and

11.0×10^{-12} s at 30 and 10 °C respectively. These values were obtained from measurements at one frequency, and though they are somewhat longer than the value reported in this study, the values are again much shorter than permissible for molecular reorientation.

It is evident that the relaxation times of the symmetrical molecules are not to be attributed to molecular reorientation. Whiffen (4) considered the possibility that the loss tangents are the long wavelength tails of vibrational absorption bands. However, with the exception of benzene, the ε'' against $\log \omega$ plots show a maximum in the loss either in or close to the microwave region, and the absorption does not detectably increase with temperature for p-xylene and mesitylene. Thus, both these features oppose such an assignment.

Satisfactory interpretations of the dielectric absorption of nonpolar liquids (4, 5, 13) and the microwave and far infrared spectrum of compressed gases (6, 14, 15, 18) have been obtained on the basis of electric dipole moments induced during molecular collisions. The number of collisions (cm^{-3} s^{-1}) between molecules of the same kind is given by (19)

[2] $$\frac{N^2 d^2}{V^2} \left(\frac{4 \pi k T}{m} \right)^{1/2},$$

in which N is the number of molecules in volume V, d the collision diameter, m the mass of a molecule, k the Boltzmann constant, and T the absolute temperature. To gain some insight into collision processes eq. [2], which strictly is applicable to gases, will be applied to our liquid and solution systems.

For a temperature increase 25–60 °C the collision frequency will be increased by a factor $(333/298)^{1/2}$ which is only slightly greater than unity. Similarly, the number of molecules per cc will not be appreciably affected, since the densities of the symmetrical and monoalkylbenzenes show only an approximate 5% decrease over such a temperature range. Thus, a collision process, for which the relaxation time may be governed by the frequency between collisions, would explain the apparent temperature independence shown by the frequency corresponding to the absorption maximum for p-xylene and mesitylene. Similarly, the indication that the enthalpy of activation ($\Delta H_2^{\neq}$) for the τ_2 process of a number of monoalkylbenzenes was in-

distinguishable from zero (11) may also be explained.

In order to obtain an estimate of the number of collisions per second experienced by the various alkylbenzenes in question, in the pure liquid state at 25 °C, numerical values have been substituted into eq. [2]. The collision diameter was taken to be 4 Å in every case, since the van der Waals radius of the phenyl group is about 2 Å. The results are compared with the corresponding reciprocal relaxation times in Fig. 2.
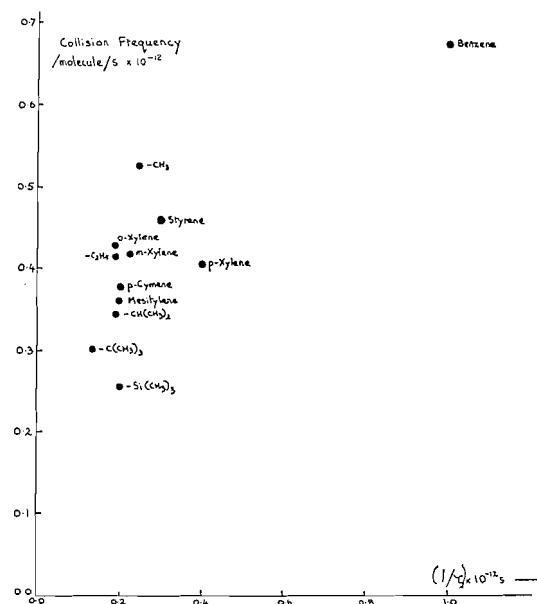

FIG. 2. Plot of number of collisions/molecule s against the reciprocal of relaxation time ($1/\tau_2$) for some alkylbenzenes as the pure liquid at 25 °C. For the low-loss (nonpolar) compounds the τ_2 values are only very rough estimates.

An exact relationship between $1/\tau_2$ and the number of collisions/molecule s is not anticipated because of the inaccuracy of the former and the very approximate estimate of the latter. In addition, it is probable that a favorable orientation of the colliding molecules may be required for a collision to be fruitful. Nevertheless, the plot in Fig. 2 indicates a rough correlation and is in favor of the τ_2 process being dependent on molecular collisions.

The collision frequencies were based on the values for the pure liquid, i.e. the number of molecules per cc; in solution N will decrease and it might be expected that the frequency of

collision between solute molecules would also decrease. However, the solute molecules will collide with solvent molecules and such collisions could be fruitful, especially so for the durene and hexamethylbenzene which interact with mesitylene.

The τ_2 values for toluene in the pure liquid, carbon tetrachloride, and cyclohexane at 25 °C are 4.3, 3.5, and $\sim 2 \times 10^{-12}$ s respectively (8). The molecular interaction of toluene with itself or of toluene with carbon tetrachloride would be appreciably greater than that of toluene with cyclohexane and this may be a factor in determining the magnitude of τ_2.

For the halobenzenes which have dipole moments about 1.5 D for an induced moment (μ_2) of 0.4 D, and from $C_1/C_2 = \mu_1{}^2/\mu_2{}^2$, where μ_1 is the molecular dipole moment, a C_2 value < 0.1 would be predicted. Thus, the zero distribution coefficients observed for these compounds in p-xylene solution (2) are not unexpected, since such a small C_2 value would lead to an α tending to zero and this would be even more so for benzotrichloride (in Part XVII) which has a molecular dipole moment of about 2.2 D as opposed to a value of ~ 1.5 D for the monohalobenzenes.

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