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On the Average Dielectric Relaxation Time Obtained by Means of Cole Plots

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IT is known that for polydisperse substances different types of "average" molecular weights can be obtained by different procedures. An analogous situation arises in systems exhibiting a distribution of dielectric relaxation times. In these cases it is convenient to obtain an "average" relaxation time, τ_0 , by means of a "Cole plot"^{1,2}; i.e., a plot of the imaginary against the real components of the dielectric constant, ϵ'' against ϵ' , corresponding to angular frequencies ω . The distances from any point P on the Cole plot to the intersections ϵ_0 and ϵ_∞ of the plot with the ϵ' axis may be termed v and u , respectively. The method of determining τ_0 consists then of finding the point P_m for which

$$(v/u)P_m = 1. \quad (1)$$

The angular frequency ω_m corresponding to the point P_m then yields τ_0 according to the equation

$$\tau_0 = 1/\omega_m. \quad (2)$$

At P_m one has

$$\epsilon' - \epsilon_\infty = (\epsilon_0 - \epsilon_\infty)/2. \quad (3)$$

Equations (2) and (3), together with the relations

$$\sum_i x_i = 1, \quad (4)$$

where x_i is the fraction of dipoles with the relaxation time τ_i , and

$$\epsilon' - \epsilon_\infty = (\epsilon_0 - \epsilon_\infty) \sum_i x_i / (1 + \omega^2 \tau_i^2) \quad (5)^{1,2}$$

yield upon rearrangement

$$\sum_i x_i (\tau_0^2 - \tau_i^2) / (\tau_0^2 + \tau_i^2) = 0. \quad (6)^\dagger$$

It is noteworthy that Eq. (6) does not depend on the actual shape of the Cole plot. Thus, it would be as valid for an arc of an ellipse as for a circular arc.

Equation (6) can be extended to mixtures of different dipoles, provided that ϵ_∞ be essentially independent of composition. Setting, then, $(\epsilon_0 - \epsilon_\infty) = \Delta_i$ for any dipole species, one obtains

$$\sum_i x_i \Delta_i (\tau_0^2 - \tau_i^2) / (\tau_0^2 + \tau_i^2) = 0. \quad (7)$$

Although Eq. (7) would be strictly applicable only in exceptional cases, it will hold approximately wherever the Δ_i 's are large in comparison to the ϵ_∞ 's.

Application to ice NH₄F solutions.—The peculiar values of τ_0 , obtained for ice NH₄F solutions³ (with the aid of Cole plots) might be mainly attributed, at first sight, to the small fraction of molecules present in the vicinity of the ions. To show that this is not the case one may apply Eq. (6) to the simple case of only two relaxation times, τ_1 and τ_2 . Equation (6) then becomes

$$\frac{n_1(\tau_0^2 - \tau_1^2)}{\tau_0^2 + \tau_1^2} + \frac{n_2(\tau_0^2 - \tau_2^2)}{\tau_0^2 + \tau_2^2} = 0$$

which yields

$$\tau_0 = \left[\frac{(\tau_1^2 - \tau_2^2)(x_1 - x_2)}{2} + \left(\frac{(\tau_1^2 - \tau_2^2)^2(x_1 - x_2)^2}{4} + \tau_1^2 \tau_2^2 \right)^{\frac{1}{2}} \right]^{\frac{1}{2}}.$$

Table I shows the variation of τ_0/τ_1 with different values of x_2

TABLE I. Effect of τ_2 on τ_0 in the case of only two relaxation times.

τ_2/τ_1	x_2	τ_0/τ_1
0.1	0.99	0.10
0.1	0.90	0.11
0.1	0.50	0.32
0.1	0.10	0.90
0.1	0.01	0.99
0.01	0.50	0.10
0.01	0.40	0.45
0.001	0.50	0.032
0.001	0.40	0.45

and τ_2/τ_1 , where τ_2 may correspond to molecules affected by NH₄⁺ and/or F[−] ions in ice. It is apparent that unless the relaxation time of half or more of the molecules is decreased at least ten times or more, it would be impossible to obtain the threefold to twenty-fold decrease in τ_0 that actually was observed upon introduction of 0.002% NH₄F into pure ice.³ This means that, on the average, an ion must affect the rotation of at least

$$\frac{50\%}{0.002\%} = 25,000$$

ice molecules; i.e., addition of NH₄F to ice can increase the rate of rotation of molecules separated by a distance of 30 Å or more from any ion.

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¹ K. S. Cole and R. H. Cole, J. Chem. Phys. **9**, 341 (1941).

² C. J. F. Böttcher, *Theory of Electric Polarization* (Elsevier Publishing Company, Inc., New York, 1952), p. 363.

[†] Equation (6) was first derived by the writer in a more involved manner. Thanks are due to Professor R. H. Cole for suggesting the simple derivation presented here.

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Nuclear Spin-Lattice Relaxation Times of Aromatic and Aliphatic Protons

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THE spin-lattice relaxation times (T_1) of some structurally distinguishable proton groups in organic compounds have been measured at 40 Mcps using commercially available high-resolution nuclear induction equipment.¹

One or both of the following methods described elsewhere^{2,3} were used.

*Method I.*²—The rate of increase of signal from each group of protons was observed following introduction of the sample into the magnetic field. The value of T_1 for a group could be easily calculated from the rate constant describing the exponential increase in the corresponding resonance signal. A small rf field intensity H_1 and large sweep amplitude were used but when necessary a correction was applied for the effect of the finite values of H_1 and of the sweep amplitude.⁴ Also, the ratio of transmitter "leakage" to resonance signal was kept high to maintain proportionality of resonance signal to nuclear polarization.

*Method II.*³—This method utilized the reversal of polarization produced by adiabatic rapid passage through resonance (large H_1). The triangular voltage output of a Hewlett-Packard Model 202A function generator was applied to the sweep coils to sweep back and forth through resonance. The position of a resonance signal on the forward sweep was so adjusted that the one on the reverse sweep was zero. The time interval between the resonance signal on the forward sweep and the "zero signal" on the reverse sweep was then used to calculate T_1 . Because of the signal broadening by the large H_1 required, this method is not generally applicable unless the resonance signals are well separated from one another. This was true for the present set of measurements.

The results of some preliminary measurements at room temperature ($\sim 25^\circ\text{C}$) are summarized in Table I.

TABLE I.

Sample	Ring protons	T_1 (sec)	CH ₃ protons
Benzene	19.3
Toluene	16	9	7½
p-Xylene	14	7½	5
Mesitylene	10	5	...
Benzene in CS ₂ (11%v)	60	...	10
p-Xylene in CS ₂ (11%v)	37

Dissolved oxygen was removed from each sample by a freeze-pump thaw technique. Unless this was done, T_1 was found to be about 2 or 3 sec for both groups of protons. The T_1 values quoted for the pure liquids are believed accurate to about 1 sec. In the dilute solutions an unfavorable signal-to-noise ratio reduced the accuracy considerably. No correction has been made to allow for the differences in viscosity.

The value quoted for benzene is in excellent agreement with that reported⁵ recently. It is noteworthy that in the pure liquids, T_1 for the ring protons is of the order of twice that for the methyl group protons. Furthermore, in the diluted samples the T_1 for both groups is increased, probably more for the ring protons than for the methyl group protons. These results are interpreted on the basis of an intramolecular (concentration independent) and an intermolecular contribution to T_1 . A rough calculation using the BPP theory² and reasonable proton-proton distances indicates that in the CS_2 solutions the major contribution to T_1 arises from intramolecular interactions. In the pure liquids a comparison of the theoretical calculations with the experimental results indicates that, for the ring protons, the larger contribution to T_1 arises from intermolecular interactions and that, for the methyl group protons, such interactions may be relatively less important. More careful measurements of T_1 as a function of concentration are being made. From these it is expected to determine $(1/T_1)_{\text{intra}}$ and $(1/T_1)_{\text{inter}}$ for such structurally distinguishable protons.

¹ Varian Associates, Palo Alto, California.

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Proton Magnetic Resonance of Hydrocarbons

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THE chemical shift of the proton resonance line in an external magnetic field has been measured for a wide range of compounds.¹ These shifts, which distinguish between chemical groups containing the proton, have usually been interpreted in terms of varying ionic character of the bond. The series of standard C—H bonds in simple hydrocarbons do not fit well into this scheme, however. If the shift is measured in terms of a parameter δ defined as $10^6 (H_r - H_c)/H_r$, where H_r is the resonant field for H_2O as reference, and H_c the field for the compound investigated, the average values for $-\text{CH}_3$, $=\text{CH}_2$, aromatic H and $\equiv\text{CH}$ are¹ -0.4 , $+0.05$, $+0.19$, and -0.25 . Other properties of the C—H bond, such as vibrational stretching frequencies, which are expected to correlate with ionic character, indicate that ethylenic and aromatic hydrogens should be of similar polarities and intermediate between $-\text{CH}_3$ and $\equiv\text{CH}$.

Some of these chemical shifts can be better understood in terms of a more detailed picture of the diamagnetic current set up in the molecule by an external field. Consider first the relative shifts of ethylenic and aromatic hydrocarbons. On grounds of ionic character and hybridization these would be expected to be similar. The principal magnetic difference lies in the fact that in an aromatic compound, currents can flow round a closed conjugating path. Consider benzene with a magnetic field H perpendicular to the plane of the molecule. Then the mobile electrons will precess in a field of approximate circular symmetry with the Larmor angular velocity $eH/2\text{ mc}$. Six electrons then give a total current $3e^2H/2\pi\text{ mc}$ which is equivalent to a circular magnetic shell or approximately to a magnetic dipole $3e^2Ha^2/2\text{ mc}^2$ at the center of the hexagon. a is the radius of the circle which may be taken as the C—C distance. This dipole has its axis parallel to and opposed to the applied field (a diamagnetic moment). This model is known to give a satisfactory description of the diamagnetic susceptibility of benzene.² The secondary magnetic field due to the magnetic

dipole at the proton positions is $3e^2Ja^2/2\text{ mc}^2(a+b)^3$ where b is the C—H length. The direction is the same as the applied field so the diamagnetic circulation will give rise to a positive shift. When averaging over all directions, this must be multiplied by a factor $\frac{1}{2} (= \langle \cos^2\theta \rangle_{\text{av}}$ where θ is the angle between the hexagonal axis and the field). This gives

$$\delta(\text{benzene}) - \delta(\text{ethylene}) = 10^6 \frac{e^2 a^2}{2 \text{ mc}^2 (a+b)^3}$$

Substituting $a = 1.4 \times 10^{-8}\text{ cm}$ and $b = 1.1 \times 10^{-8}\text{ cm}$ this gives $+0.17$ in good agreement with the observed difference of $+0.14$. A future publication will deal with the application of this model to polycyclic hydrocarbons.

The relative positions of ethylenic and acetylenic protons cannot be compared directly because of the change of hybridization. However, part of the negative shift of $\equiv\text{CH}$ can be interpreted qualitatively in terms of a similar diamagnetic precession about the axis. This will occur without restriction if the applied field is parallel to the axis. There will be a diamagnetic moment in the opposite direction, but in this case the secondary magnetic field due to this moment acts *against* the applied field at the proton positions and consequently gives a negative shift.

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Luminescence of Ice Subjected to Ionizing Radiation*

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(Received March 7, 1956)

ICE subjected to ionizing radiation exhibits fluorescence¹⁻⁵ and thermoluminescence.^{4,5} The emission spectrum of fluorescence of ice has been studied for a limited temperature range near liquid-nitrogen temperature.²⁻⁵ Some work on the spectral distribution of thermoluminescence and of fluorescence at higher temperatures is reported here.

For thermoluminescence measurements, ice prepared from degassed quadruply distilled water was irradiated at -196°C with Co^{60} gamma rays. Heating at a rate of $10^\circ\text{C}/\text{min}$ after irradiation of about 10^{18} ev/g , gave glow curves similar to those reported previously,^{4,5} with the predominant peak at about -115° . However, after an irradiation of 10^{21} ev/g the predominant peak appeared at -155° and had 100 times the intensity of the -115° peak. The emission intensity at -115° was the same for the two different irradiations.

Spectral distribution of the thermoluminescence was studied by intermittently inserting a Corning No. 3389 glass color filter between the sample and the cooled 1P28 photomultiplier used as a photon counter. This filter transmits light only of wavelength greater than 4000 Å and thus provides a simple method for distinguishing between visible and ultraviolet emission. The emission at -155° was found to be 90% ultraviolet while emission at -115° was nearly all in the visible region.

The estimated yield for thermoluminescence is one photon emitted per 10^{10} ev absorbed in the case of the 10^{18} ev/g irradiation, and one photon per 10^{11} ev in the case of the 10^{21} ev/g irradiation. The yield for light emission during irradiation (fluorescence) has been estimated² as one photon per 10^6 ev absorbed.

Light emission during irradiation was studied by means of the monochromator from a Beckman model DU spectrophotometer and a cooled 1P28 photomultiplier used as a photon counter. Emission from ice during irradiation with Co^{60} gamma rays was found to have a continuous spectrum identical with the emission from liquid water. Any radiation characteristic of the ice was completely masked by the more intense Čerenkov⁶ radiation which would be produced by electrons having energy greater than 300 kev. During irradiation with 50 kv x-rays, ice at -196° gave an