are also consistent with the hypothesis that the mechanism of the acid-catalyzed hydrolysis of esters of tertiary alcohols is different from that of other ester hydrolyses, and involves a rupture of the alkyl-oxygen bond.

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Anomalous Dispersion of Dipolar Ions

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Low frequency measurements of the dielectric constant of amino acids, peptides and other similar dipolar ions in solution in polar liquids indicate polarizations which are the same as those calculated statistically on the assumption of free rotation about the various single bonds of the chain between the charges.[1] These low frequency measurements cannot, as shown by Kuhn,[2] distinguish between polarizations resulting from orientation of the molecule as a rigid body and polarizations resulting from distortion under the influence of the field. The latter possibility is a likely one if the rotation about the bonds is unhindered. If, on the other hand, the rotation is subject to steric hindrance no rotation will occur in the short period of high frequency oscillations. The molecule will then orientate as a rigid body. To distinguish between these two alternatives, we must make observations at frequencies comparable with those corresponding to the relaxation times of the molecules regarded as rigid bodies. If the dipolar ions contribute to the polarization by orientation as rigid bodies a region of anomalous dispersion will be observed at frequencies corresponding to this relaxation time. If, however, free rotation still occurs at these high frequencies, orientation of the dipoles with the electric field may be expected to occur by a deformation of the loose jointed chain. The region of anomalous dispersion would then occur at much higher frequencies.

The two alternatives are illustrated by solutions of the proteins and of decanoic acid polymers.[3] Both molecules have large electric moments, the proteins by virtue of their dipolar structure and the decanoic acid polymers because of the large number of ester linkages. In the case of the proteins relaxation times have been observed at radio frequencies of the order of those calculated by Stokes' law. The solutions of decanoic acid polymers, however, which, as spheres, would be expected to have a relaxation time corresponding to ordinary radio frequencies on the basis of Stokes' law show no dispersion at frequencies as high as 100 megacycles. Moreover, the measured polarizations are the same as those calculated for independent orientation of the polar groups. The present problem is to distinguish between these two alternatives in the case of solutions of amino acids and peptides.

Unfortunately, even for the largest available dipolar ions other than proteins, the relaxation times predicted by Stokes' formula, on the assumption that the ions are rigid spheres, correspond to frequencies of the order of 10^8 cycles. Relaxation times may be calculated from the variation of either the observed dielectric constant or the power absorption, or both, over a frequency range. Measurements at these ultra high frequencies are, however, difficult in view of the importance of distributed inductance and capacitance and the resulting complication of the electrical circuit analysis. A further restriction is the large a. c. conductivity associated with the very power absorption effect we wish to measure.[3a] For the case of concentrated solutions of highly polar solutes, this may be sufficient to make the measurements inaccurate or even impossible. Consideration must also be given to limiting the amount of substance required for an experiment in view of the small amounts of large dipolar ions available.

Very little previous experimental work has been done on this problem of determining the relaxation times of amino acids and peptides. Fricke and Parts[4] made some observations at 4.6 meters (65.6 megacycles) on various amino acids. The

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(1) J. Wyman, Jr., *J. Phys. Chem.*, **43**, 143 (1939).

(2) W. Kuhn, *Z. physik. Chem.*, **A175**, 1 (1935).

(3) J. Wyman, Jr., THIS JOURNAL, **60**, 328 (1938).

(3a) Theoretically the ratio of resistance to reactance at the frequency for which this is a maximum increases without limit with the static value of the dielectric constant.

(4) H. Fricke and A. Parts, *J. phys. Chem.*, **42**, 1171 (1938).

frequency they used is unfortunately too low to give large dispersion or absorption effects and their results must be considered inconclusive. More recently J. B. Bateman and G. Potapenko[5] have made observations at 25.5 cm. (1176 megacycles) on the absorption and dispersion of glycine, α-alanine, β-alanine, and several dipeptides of glycine and alanine. For glycine and alanine they record relaxation times slightly below the values calculated for spheres by Stokes' law. For the dipeptides they observed relaxation times almost twice those calculated by Stokes' law. The latter observations would support the hypothesis of rigid orientation.

In the present study we have developed a cathode ray oscilloscope to compare the impedances of two similar cells, one filled with water and the other filled with an aqueous solution of the peptide under investigation. Both the real and the imaginary components of the unknown impedance corresponding, respectively, to the ordinary dielectric constant and to the a. c. conductivity are determined to a fair degree of accuracy. In evaluating the observed relaxation time the ratio of the imaginary to the real component of the dielectric constant proves much more reliable than the real component alone, representing the ordinary dispersion effect.

The compounds selected for the investigation were lysylglutamic acid, previously synthesized by J. P. Greenstein,[6] and glycine tripeptide synthesized by T. L. McMeekin using the method of Fischer.[7] Both peptides have the advantage of a high molecular weight, resulting in a greater relaxation time. Lysylglutamic acid has a high dipole moment and also a high solubility. The molar dielectric increment observed for this peptide by Wyman[8] was 345. This high molar dielectric increment combined with high solubility makes it possible to prepare solutions with a high dielectric constant and a large absorption effect, thereby permitting a more accurate calculation of the relaxation time. At the concentration used in this experiment (0.23 molar) the dielectric constant of the lysylglutamic acid solution was approximately twice that of water. Triglycine has a lower dipole moment and much smaller solubility. We cannot, therefore, determine its relaxation time as accurately. Most of the other large peptides available have such low solubilities that they are not suitable for measurements of this kind.

The Present Experimental Method

For the study of the peptides we need a method applicable to a frequency reasonably near the expected critical frequency. In this dispersion region the conductivity due to power absorption will exceed the limits for which the transmission line methods are reliable.[8a] It will also be so great that resonance methods are inaccurate.[8b] The expected critical frequency of about 6 × 10^8 cycles is too low for application of the optical method. There remains a choice between the thermal method of Debye and an extension of impedance measurements to the highest possible frequencies. The former method is objectionable because of the experimental difficulties in maintaining a constant, known power output into the thermometer condenser at ultra high frequencies. The high conductivity restricts the latter methods. A solution to this difficulty was suggested by an impedance measuring method of Cole.[9] This method makes use of a cathode ray oscilloscope as a means of comparing the absolute magnitude and phase of the unknown impedance with that of a standard impedance.

If an alternating current passes through two impedances in series, a potential will be developed across each impedance with phase and magnitude depending on the particular impedance. We may apply these potentials to the vertical and horizontal plates respectively of a cathode ray tube. In general the pattern appearing on the screen will be an ellipse. The tilt of this ellipse will indicate the ratio of the amplitudes of the two potentials and its eccentricity will give the phase difference between the applied potentials. The

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(5) J. B. Bateman and G. Potapenko, *Phys. Rev.*, **57**, 1185 (1940).

(6) M. Bergmann, L. Zervas and J. P. Greenstein, *Ber.*, **65**, 1629 (1932).

(7) E. Fischer, *ibid.*, **36**, 2982 (1903).

(8) J. P. Greenstein, J. Wyman, Jr., and E. J. Cohn, THIS JOURNAL, **57**, 637 (1935).

(8a) The results given below show that the a. c. conductivity of a 0.23 molar solution of lysylglutamic acid at a frequency of 115 megacycles (λ = 2.61 meters) is approximately 1.4 × 10^{-3} mho. The critical frequency is estimated to be about 370 megacycles (λ_0 = 81 cm.).

(8b) A possible exception to this statement is a resonance method, applicable to conducting solutions, described by Hartshorn and Ward [*Proc. Wireless Section I. E. E.* (London), **12**, 6 (1937)]. This method, which is based on the use of a variable reactance and a thermionic voltmeter contained in the resonance circuit, makes it possible to obtain quite accurate determinations of the conductivity of the dielectric medium at moderate frequencies. Unfortunately, at frequencies of 100 megacycles the inductance and resistance of the various leads introduce corrections which are both considerable and difficult to determine when power loss factors of the order found in this paper are involved.

(9) R. H. Cole, *Rev. of Sci. Instruments*, **12** (6), 298 (1941).

oscillograph pattern may thus be used to determine one impedance in terms of the other.

In ordinary cathode ray tubes the horizontal and vertical plates are set at some distance apart. It takes a certain time for the electrons to pass from the center of one set of plates to the center of the next. At radio frequencies such as used by Cole this effect is negligible. At ultra high frequencies this transit time becomes an appreciable part of the period of the oscillations and we may make use of it to determine the phase difference between the potentials applied respectively to the two sets of plates. If the transit time corresponds to the phase difference between the potentials, and the leading potential is applied to the first set of plates, *i. e.*, that nearer the cathode, the ellipse will be flattened to a straight line, easily identifiable on the oscillograph. Therefore, controlling the velocity of the electrons by means of the accelerating voltage until a straight line is observed gives us a simple way of determining the phase difference between the potentials and consequently the difference between the phase angles of the impedances themselves. The basis of this will appear from the following calculations. Assume that the first set of plates is vertical, the second set horizontal. Let

a = distance between the centers of the two sets of plates
V = the total accelerating voltage
e/m = the ratio of charge to mass of an electron
v_0 = initial velocity of the electron (this is discussed in the next section)
T = the period of the alternating current oscillations = $2\pi/\omega$
v = the velocity of the electron at the plates = $\sqrt{2Ve/m} + v_0$

Then the transit time t is given by

$$t = a/(\sqrt{2Ve/m} + v_0)$$

This transit time introduces a difference of phase between the vertical and horizontal displacements on the oscillograph given by the angle

$$\psi = \frac{2\pi t}{T} = \frac{\omega a}{\sqrt{2Ve/m} + v_0}$$

When the accelerating voltage V is adjusted so that the ellipse is reduced to a straight line, we know that this angle ψ is equal to the angle which gives the phase difference between the potentials applied to the vertical and horizontal plates. If we can neglect the effect of the leads to the oscillograph plates this latter angle equals the difference between the phase angles of the corresponding impedances themselves. If the second of these impedances is a pure capacitance, its phase angle is $-\pi/2$. The phase angle ϕ of the other impedance, applied to the first set of plates, is therefore given by

$$\phi = \psi - \pi/2$$

We suppose this impedance to be the condenser containing the absorbing medium under investigation. Owing to absorption the dielectric constant of this medium is complex

$$\epsilon = \epsilon' - i\epsilon''$$

Assuming that the low frequency conductivity is negligible, it may be shown that the phase angle of this condenser is given by

$$\cot \phi = -\epsilon''/\epsilon'$$

Expressing ϕ in terms of ψ we have therefore

$$\tan \psi = \epsilon''/\epsilon' \qquad (1)$$

From this ratio it is possible to determine the relaxation time τ or the critical frequency ν_c on the basis of the Debye theory. For this purpose, since we are dealing with highly polar media, we may assume some linear relation between the dielectric constant and polarization in place of the classical Clausius–Mosotti relation.[10] Then ϵ''/ϵ' may be expressed in terms of the static dielectric constant ϵ_0 and the high frequency dielectric constant ϵ_∞ by the equation

$$\epsilon''/\epsilon' = \frac{(\epsilon_0 - \epsilon_\infty)x\nu}{\epsilon_0 + \epsilon_\infty x^2\nu^2} = \tan \psi$$

where $x = 2\pi\tau = 1/\nu_c$. All that is required therefore for the determination of τ or ν_c on the basis of the simple case just outlined is the measurement of the angle ψ at some known frequency ν within the absorption range. This measurement depends simply on a knowledge of a, the separation of the plates in the cathode ray tube, e/m, the ratio of charge to mass of an electron, and an observed accelerating voltage.

If there is an appreciable direct current conductivity the ϵ'' due to absorption which occurs in the Debye expression will be only a part of the observed ϵ''_{obs}. The contribution to ϵ''_{obs} due to the direct current conductivity is given by

$$\epsilon''_{\text{obs}} - \epsilon'' = (4\pi\kappa/\omega)\, 9 \times 10^{11}$$

where κ gives the d. c. conductivity in mhos. This simple correction is to be applied before making use of Debye's expression.

The oscillograph pattern also allows us to determine the real part of the dielectric constant and from this an independent value of the critical

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[10] J. Wyman, Jr., *Chem. Rev.*, **19**, 236 (1936).

frequency. This is based on the measurement of the slope of the major axis of the elliptical oscillograph pattern with reference to a line generated by the vertical plates, which we shall denote by λ. The real part of the dielectric constant decreases with increasing frequency through a considerable frequency range, from the static value ϵ_0 to ϵ_∞. If the two sets of cathode ray tube plates are mutually perpendicular and we neglect the difference in "magnification" (see below) for the two sets of plates, λ is equal to the ratio of the maximum deflections produced by the plates. This in turn equals the ratio of the amplitudes of the potentials applied to the plates and therefore the ratio of the amplitudes of the impedances. If the impedances are perfect condensers of equal capacitance in air, λ will equal the ratio of the dielectric constants of the media filling the capacitors.

In practice we fill one condenser with a standard liquid such as water which shows no appreciable absorption at the experimental frequencies and the other with the liquid to be measured. This latter will in general be absorbing and we cannot regard the condenser as a perfect one. There will be a shorting resistance r between the plates arising from the a. c. conductivity due to the absorption. If C is the capacity of the condenser, then the impedance z is given by $(r - jr^2\omega C)/(1 + r^2 \omega^2C^2)$. The phase angle ϕ is therefore given by $\tan \phi = - r\omega C$, and the impedance amplitude $\bar{z}$ by

$$\bar{z} = \frac{r}{\sqrt{1 + r^2\omega^2C^2}}$$

From these equations it follows that

$$\omega C = \omega\epsilon' C_0 = - \sin \phi/\bar{z}$$

At the same time $\bar{z}$ is given in terms of the impedance amplitude of the standard condenser $(= 1/\omega\epsilon_s C_0)$ by the slope of the oscillograph pattern λ. Consequently

$$\epsilon' = - \epsilon_s\lambda \sin \phi = \epsilon_s\lambda \cos \psi \tag{2}$$

On the other hand, we have on the basis of the Debye theory

$$\epsilon' = \epsilon_0 + \frac{\epsilon_0 - \epsilon_\infty}{1 + x^2\nu^2}$$

where, if we again assume a linear relation between dielectric constant and polarization, x has the definition given above. In the past the relaxation time has been studied chiefly in terms of the real part of the dielectric constant. However, ϵ' is less sensitive to changes in the critical wave length than the phase angle and in our results discussed below far more weight is given the critical frequency calculated from the latter.

Certain modifications of the simplified theory given above are required to give an accurate representation of the actual apparatus used. At ultra high frequencies the inductance of all leads and the resistance of the longer leads must be taken into account. Moreover, at such frequencies the oscilloscope deflection plates themselves have an appreciable reactance. In effect these and the leads to them constitute two new impedances in parallel with each of the original impedances. We ought further to complicate our analysis by the introduction of parallel capacitances to represent the stray capacitance between leads. If we assume lumped inductance, capacitance and resistance in view of the small dimensions of the circuit compared with the wave length, the complete equivalent circuit becomes that shown in Fig. 1.

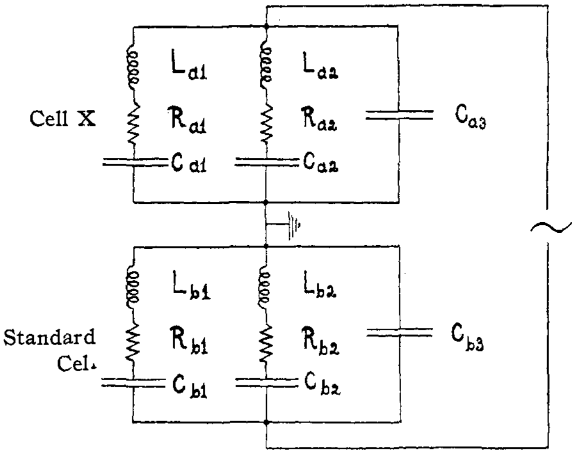

Fig. 1.

L, C and R denote inductance, capacitance and resistance, respectively. Subscript a_1 refers to the cell filled with the unknown liquid, b_1 to the cell filled with standard liquid and subscripts a_2 and b_2 to the oscilloscope deflection plates and associated leads connected with cells a_1 and b_1, respectively. C_{a_3} and C_{b_3} represent the stray capacitances of the leads. In view of the dimensions of the apparatus we neglect the resistance of the leads associated with the two cells, and assume that R_{a_1} and R_{b_2} simply represent equivalent series resistances arising from the conductivity of the unknown and standard liquids. The analysis of this circuit leads to the expression

$$\frac{\bar{E}_{a_2}\, e^{j\phi_{a_2}}}{\bar{E}_{b_2}\, e^{j\phi_{b_2}}} = \gamma \frac{Z_{a_1}}{Z_{b_1}} \tag{3}$$

where $\bar{E}_{a_2}$ and $\bar{E}_{b_2}$ are the amplitudes of the potentials across the deflection plates C_{a_2} and C_{b_2} of the cathode ray tube. ϕ_{a_2} and ϕ_{b_2} are the phase angles of these potentials. γ, a factor dependent on the electrical constants of the entire circuit, is in general a complex number, but for impedances and frequencies of the order used in this experiment (see results below) the imaginary part may be neglected with the introduction of an error of less than 0.1%. We shall, therefore, consider γ a real number. It will be recalled that $\phi_{a_2} - \phi_{b_2}$ is the same as the oscillograph angle ψ.

For brevity let us set

$$\alpha = \frac{1}{\gamma}\frac{\overline{E}_{a_2}}{\underline{E}_{b_2}}$$

Equation (3) then becomes

$$\alpha e^{j\psi} = \frac{Z_{a_1}}{Z_{b_1}} = \frac{R_{a_1} + j(\omega L_{a_1} - 1/\omega C_{a_1})}{R_{b_1} + j(\omega L_{b_1} - 1/\omega C_{b_1})}$$

Taking the real part

$$R_{a_1} = \alpha \cos \psi(R_{b_1}) - \alpha \sin \psi(\omega L_{b_1} - 1/\omega C_{b_1})$$

Taking the imaginary part

$$\frac{1}{\omega C_{a_1}} = \alpha \cos \psi((1/\omega C_{b_1}) - \omega L_{b_1}) - \alpha \sin \psi\, R_{b_1} + \omega L_{a_1}$$

We may simplify these last two equations by assuming $R_{b_1} = 0$, the case when the conductivity of the standard liquid is negligible. Then

$$R_{a_1} = -\alpha \sin \psi \left(\omega L_{b_1} - \frac{1}{\omega C_{b_1}}\right) = \frac{\alpha \sin \psi}{\omega C_{b_1}}(1 - \omega^2 L_{b_1} C_{b_1}) \quad (4)$$

and

$$\frac{1}{\omega C_{a_1}} = \alpha \cos\psi \left(\frac{1}{\omega C_{b_1}} - \omega L_{b1}\right) + \omega L_{a_1}$$
$$= \frac{\alpha \cos \psi}{\omega C_{b_1}}\left(1 - \omega^2 L_{b_1} C_{b_1} + \frac{\omega^2 L_{a_1} C_{b_1}}{\alpha \cos \psi}\right) \quad (5)$$

Setting

$$A = (1 - \omega^2 L_{b_1} C_{b_1})$$
$$B = \left(1 - \omega^2 L_{b_1} C_{b_1} + \frac{\omega^2 L_{a_1} C_{b_1}}{\alpha \cos \psi}\right)$$
$$R_{a_1}\omega C_{a_1} = \tan \psi\ (A/B) \quad (6)$$

and

$$C_{b_1}/C_{a_1} = \alpha \cos \psi\ (B) \quad (7)$$

We have represented the cell containing the unknown in terms of the series resistance R_{a_1} and the series capacity C_{a_1}. We know, therefore, that its phase angle ϕ is equal to $\cot^{-1}(-R_{a_1}\omega C_{a_1})$. This phase angle ϕ is, however, as we have pointed out above, equal to $\cot^{-1}(-\epsilon''/\epsilon')$. Consequently equation (6) becomes

$$\tan \psi\ (A/B) = -\cot \phi = \epsilon''/\epsilon' \quad (8)$$

At the same time we know that the equivalent series capacity is given in terms of the phase angle and the impedance amplitude by $-1/\omega Z \sin \phi$. However, we have already shown that the true parallel capacity, in which we are interested as giving a measure of ϵ', is equal to $-\sin \phi/\omega Z$.

Consequently, if we call this parallel capacity C_x, we have

$$C_x = C_{a_1} \sin^2 \phi = \frac{C_{a_1}}{1 + \tan^2 \psi\ (A^2/B^2)} \quad (9)$$

Since the standard liquid has negligible conductivity, the parallel capacity C_s is the same as the series capacity C_{b_1}. Introducing this and making use of equation (9), equation (7) becomes

$$\frac{C_x}{C_s} = \frac{\cos \psi}{\alpha B\ (\cos^2 \psi + \sin^2 \psi\ (A^2/B^2))} \quad (10)$$
$$= \cos \psi \frac{\gamma}{B\left(\cos^2 \psi + \sin^2 \psi \frac{A^2}{B^2}\right)} \frac{\overline{E}_{b_2}}{\overline{E}_{a_2}} = \frac{\epsilon' C_{x_0}}{\epsilon_s C_{s_0}}$$

The ratio $\overline{E}_{b_2}/\overline{E}_{a_2}$ is directly equal to the observed slope of the oscillograph pattern subject to two relatively simple correction factors due to the construction of the cathode ray tube itself, which we shall now consider.

As we have already mentioned, the deflection plates are placed at different distances from the screen. This will result in a greater deflection sensitivity or "magnification" for the more distant set of plates. The slope of the pattern, therefore, is not directly equal to the ratio of the voltage amplitudes. It is, however, proportional to it. Thus

$$\lambda = \frac{\text{maximum vertical deflection}}{\text{maximum horizontal deflection}} = R\frac{\overline{E}_{b_2}}{\overline{E}_{a_2}}$$

where R is the proportionality constant. Second, difficulties of manufacture make it impractical to construct the two sets of plates exactly perpendicular to each other. If the angle between the two sets of plates is 90° $- \delta$, it can be shown that the slope

$$\lambda = \frac{\overline{E}_{b_2}}{\overline{E}_{a_2}} \frac{R \cos \delta}{(1 - R\ (\overline{E}_{b_2}/\overline{E}_{a_2})\sin \delta)} = \frac{\overline{E}_{b_2}}{\overline{E}_{a_2}} D$$

Thus, as a result of both corrections we can represent the slope λ as proportional to the ratio of the voltage amplitudes. The proportionality factor, which we have called D, will itself vary slightly with the voltage amplitude ratio.

By combining this result with equation (10) we obtain finally as the expression for the real part of the unknown dielectric constant

$$\epsilon' = \epsilon_s\, \lambda \cos \psi \frac{C_{s_0}\, \gamma}{C_{x_0}\, BD\ (\cos^2 \psi + \sin^2 \psi\ (A^2/B^2))} \quad (11)$$

We retain the ratio C_{s_0}/C_{x_0} of the air capacities of the two cells to provide for slight inequalities of construction.

Equations (8) and (11) may be compared with the simpler equations (1) and (2) given earlier. The various multiplying factors in these new equations are real and can be computed for any observed ψ and λ if we know the resistances, capacitances, and inductances of all the circuit elements. At ultra high frequencies, however, these "constants" are both difficult to compute and may vary with many factors. It is therefore more reliable to collect the various factors in each of the two equations (8) and (11) into a simple factor and evaluate them by empirical means. This can be done by making up model solutions of potassium chloride and glycine which have known values for the dielectric constant and the conductivity at wave lengths as low as one meter. Cell X may then be filled with a model solution and compared with the standard cell. Determinations of λ, the slope of the oscillograph pattern, and ψ, which is the transit phase time for the electrons when the elliptical oscillograph pattern becomes a straight line, give us the factors directly.

Apparatus

The cathode ray tube selected was an RCA 905. It has the advantage of short direct leads to the deflection plates. The potential applied to the anode was continuously variable from 340 volts to 1740 volts. A ten megohm wire wound resistor in series with a 5000 ohm wire wound resistor was placed in parallel with the anode. The voltage developed across the 5000 ohm resistor was measured by a Leeds and Northrop Type K potentiometer. This indicated the total anode voltage.

To calculate the total accelerating potential acting on the electrons in the region of the deflection plates a small correction must be applied to the anode potential for the voltage drop in a leakage resistor between the deflection plates and the grounded anode. The amount of this voltage drop increases with increasing anode current. It reduces the accelerating potential below the anode potential.

Another small correction must be applied because of the initial velocity of the electron. Since the emitted electrons do not reach the anode instantaneously the space between cathode and anode will develop a negative space charge. This charge will repel the emitted electrons causing the slower electrons to return to the cathode. In this manner a space charge potential is set up which will be negative to the cathode in the region where the electrons are statistically at rest. The magnitude of this potential will vary with the potentials of the grids and the anode. It will tend to increase the accelerating potential above the anode potential.

The sum of these corrections may be determined empirically for various grid potentials by using a known phase difference between the plates and comparing the observed anode potentials with accelerating potentials V calculated from the formula

$$\psi = \frac{\omega a}{\sqrt{2e/mV}}$$

given above. This amounts to determining the equivalent initial velocity of the electrons v_0. The best method is to use identical impedances and adjust the accelerating voltage to give a shift of 180° in phase between the two sets of deflection plates. Under these conditions the elliptical pattern will become a straight line with a slope perpendicular to the "in phase" condition, and thus we determine the effective accelerating voltage. We have done this for various values of the grid biases.

Since very high accelerating potentials are required in order to produce low values of ψ it is more convenient to measure small phase angles in terms of a 180° phase difference. This is easily accomplished by making the sum of the phase angle and the angle equivalent to the transit time equal to 180°. This condition is shown by a degeneration of the elliptical pattern to a straight line. There is a further advantage in this procedure if the second harmonic is present. It can easily be shown that for a large phase difference this second harmonic will cause the elliptical pattern to assume the shape of a figure eight. If the phase difference is precisely 180° this figure eight will be symmetrical. We have then only to adjust the accelerating voltage until the crossing point of our figure eight is at the center of the pattern. The use of this simple criterion greatly increases the accuracy of the results.

The experimental cells consisted of two holes drilled in a brass block 2 cm. × 1 cm. × 1.5 cm. A concentric no. 14 gage copper wire, insulated by glass supports from the block, formed the inner electrode of each cell. These wires were bent over above the cells and dipped into mercury cups. The entire length of each wire was 3.5 cm. Both cell and leads were gold plated. The volume of each cell was approximately 0.6 cc. The standard solution, always distilled water, was placed in one cell and the unknown solution in the other cell.

Considerable power input is required to develop a potential across the experimental cell large enough to deflect the electron beam sufficiently and thus give a reasonably large oscillograph pattern. The oscillator employed two TZ 20 tubes in a push pull tuned plate, tuned cathode, resonant line circuit. The frequency was adjusted to 2.605 meters by a heterodyne beat frequency meter shortly before measurements were made. Frequency variations were never greater than 0.1%. The power output was approximately 30 watts. Even in 0.01 molar salt solutions this power caused boiling within a few minutes. To prevent such excessive heating it is necessary that the oscillator be off most of the time. It is also required that the oscillator deliver a constant amount of power throughout the interval in which it operates in order that the oscillograph pattern be sharp. To accomplish both these requirements a rectangular impulse voltage is applied to the grid of the oscillator, thus turning it off and on. The rectangular impulse was generated by a method described by H. Klemperer.[11] The duration of the 60-cycle rectangular impulse could be varied at will. This allowed variation of the power applied to the experimental cell and thus provided an effective

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(11) H. Klemperer, *Rev. Scientific Instruments*, **10**, 69 (1939).

means of temperature regulation. Optimum results were obtained when the oscillator operated 10% of the 60-cycle period. The equilibrium temperature was measured by a conventional copper-nickel thermocouple embedded in the cell, but removed during observations of the oscillograph pattern.

The slope λ was measured with a protractor of conventional design.

Accuracy of the Method

Determinations of the observed phase angle ψ for the lysylglutamic acid solution showed an average deviation of 5% from the mean. Errors in the calibration amounted to another 5%. The measurements of the true phase angle ϕ were, therefore, subject to an over-all error of about ± 10%. This leads to an error of about ± 12% in the calculation of the critical wave length and the relaxation time.

The measurement of the real part of the dielectric constant of the lysylglutamic acid solution is subject to a total error of 6.5%. The determination of the empirical factor in equation (11) accounts for 3.5% of this error and the remainder comes from errors of observation. Since the dispersion effect is not very sensitive to a change in the relaxation time at wave lengths much different from the critical value, an uncertainty of 40% in the critical wave length may result from the possible 6.5% error. Therefore, we must attach far more significance to the value calculated from the absorption effect.

The absorption effect in solutions of triglycine was about one-fifth as great as with lysylglutamic acid. As a result the error in the calculation of the critical wave length increased several fold to ± 40%. At the same time the dispersion effect at the frequency used was negligible, a result expected in view of the much lower critical wave length of triglycine.

Results

From calibration experiments with solutions of glycine and potassium chloride we obtain the empirical factor of equation (11). It varies slightly with the phase angle ψ but not appreciably with the slope of the oscillograph pattern. Its value is close to 0.800.

The empirical factor A/B of equation (8) is found to be 0.832 ± 5% for values of λ around 2.24. It increases to approximately 0.88 for values of λ near 1.73.

Since the different measurements were made at slightly different temperatures, values of the dielectric constant of water, the dielectric increment of glycine, the conductivity of potassium chloride, and the low frequency conductivity of the peptides as functions of temperature were necessary. The dielectric constant of water is given by the empirical relation[12]

$$\epsilon_{H_2O} = 78.54\,[1 - 4.579 \times 10^{-3}(t - 25) + 1.19 \times 10^{-5}(t - 25)^2 - 2.8 \times 10^{-8}\,(t - 25)^3]$$

The dielectric constant of glycine for this temperature range was taken from Wyman's unpublished data. His results are summarized by the empirical relation

$$\Delta\epsilon = 22.89[1 - 2.61 \times 10^{-3}(t - 25) + 3.2 \times 10^{-6}(t - 25)^2]$$

The low frequency conductivity of the peptides is probably due largely to salt contamination, and was regarded as that of a mono-mono-valent salt similar to potassium chloride. Its temperature correction was taken from tables for potassium chloride given in the chemical handbook.

The static dielectric constant of the lysylglutamic acid solution was calculated from the results of Wyman.[8] As these results were obtained at a wave length of about 4.2 meters, a correction for dispersion on the basis of the observed critical wave length given in the data below was required. This correction amounted to about 4.4% of the dielectric increment. The high frequency dielectric constant, ϵ_∞, of the solution was estimated on the assumption that the volume occupied by the peptide had a negligible optical dielectric constant. The results on lysylglutamic acid culminating in values of the relaxation time are summarized in Table I.

A similar procedure in the case of triglycine leads to the results summarized in Table II. The static value of the dielectric constant was taken from the data given by Wyman and McMeekin[13] without correction for frequency. The high frequency dielectric constant was calculated as in the case of lysylglutamic acid.

Conclusions

The values of the relaxation times of lysylglutamic acid calculated on the basis of the Debye theory from observations of the absorption, given basically by ψ, and of the dispersion, given basi-

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[12] J. Wyman, Jr., and E. N. Ingalls, THIS JOURNAL, **60**, 1182 (1938).

[13] J. Wyman, Jr., and T. L. McMeekin, *ibid.*, **55**,908 (1933).

TABLE I

RESULTS ON LYSYLGLUTAMIC ACID DISSOLVED IN WATER

Concn. = 0.230 M, frequency = 1.1508 × 10^8; ϵ_0 = 164.64; ϵ_∞ = 0.9603 ϵ_{H_2O}. Data to left of double line give absorption results; data to right of double line give dispersion results.

Temp., °C.	ϵ_s	$\kappa \times 10^4$, mhos.	ψ	A/B	ϵ''obs./ϵ'	ϵ''/ϵ'	$\tau \times 10^{10}$, sec.	λ	$\epsilon'/\epsilon_s\lambda$	ϵ'/ϵ_s	ϵ'	$\tau \times 10^{10}$ sec.
[31.0	76.42	5.37	14.28°	0.8324	0.2118	0.1498	4.06	2.256	0.793	1.790	136.8	8.28]
25.6	78.33	2.99	13.1°	.8324	.1937	.1605	4.38	2.267	.800	1.814	142.1	7.43
25.9	78.21	3.01	12.6°	.8324	.1860	.1523	4.12	2.246	.801	1.800	140.8	7.69
26.2	78.11	3.02	12.9°	.8324	.1906	.1570	4.23	2.278	.800	1.822	142.3	7.32
22.3	79.52	2.78	12.4°	.8324	.1830	.1522	4.12	2.236	.801	1.791	142.4	7.64
25.5	78.36	2.96	12.6°	.8324	.1860	.1531	4.15	2.267	.801	1.816	142.3	7.37
24.4	78.76	2.60	13.06°	.8324	.1931	.1645	4.47	2.278	.799	1.820	143.3	7.22
24.0	78.90	2.58	13.1°	.8324	.1937	.1652	4.50	2.267	.799	1.811	142.9	7.37
23.5	79.08	2.55	13.9°	.8324	.2060	.1780	4.87	2.278	.798	1.818	143.8	7.16
23.3	79.16	2.84	12.0°	.8324	.1770	.1459	3.96	2.278	.803	1.825	144.5	7.00
Av. 24.5							4.31					7.36

The bracketed observation was omitted in calculating the mean critical wave length because of the high temperature at which the observations were made.

TABLE II

RESULTS ON GLYCYLGLYCYLGLYCINE DISSOLVED IN WATER

Concn. 0.25 M, frequency 1.1508 × 10^8, ϵ_0 = 110.5, ϵ_∞ = 0.9647 ϵ_{H_2O}. Data to left of double line give absorption results; data to right of double line give dispersion results.

Temp., °C.	ϵ_s	$\kappa \times 10^4$, mhos.	ψ	A/B	ϵ''obs./ϵ'	ϵ''/ϵ'	$\tau \times 10^{10}$ sec.	λ	$\epsilon'/\epsilon_s\lambda$	ϵ'/ϵ_s	ϵ'
24.0	78.90	0.835	2.61°	0.88	0.04011	0.02814	1.35	1.746	0.800	1.397	110.2
24.3	78.79	.837	2.44°	.88	.03750	.02539	1.21	1.732	.800	1.386	109.2
24.5	78.72	.842	2.61°	.88	.04011	.02816	1.35	1.767	.800	1.414	111.3
25.8	78.25	.874	2.82°	.88	.04335	.03082	1.48	1.760	.800	1.408	110.2
26.3	78.07	.882	2.97°	.88	.04566	.03289	1.59	1.746	.800	1.397	109.1
26.1	78.14	.879	2.09°	.88	.03212	.01955	0.93	1.767	.800	1.414	110.5
26.0	78.18	.840	2.26°	.88	.03472	.02257	1.08	1.746	.800	1.397	109.2
27.3	77.71	.860	2.89°	.88	.04443	.03207	1.54	1.767	.800	1.414	109.9
26.4	78.04	.846	2.31°	.88	.03549	.02343	1.12	1.775	.800	1.420	110.8
Av. 25.6							1.29				110.0

cally by λ, show a discrepancy probably in excess of the experimental error. In so far as this is so, the discrepancy must arise from inadequacy of the theory.

Various modifications of the original Debye theory have been proposed which might account for this disagreement. One consists in treating the molecules not as spheres, but as rigid ellipsoids. If these are ellipsoids of revolution, this treatment results in the introduction of two relaxation times, one for orientation about the long, the other for orientation about the short, axis, both greater than the relaxation time of a spherical molecule of equal volume.[14] This modification of the Debye theory has been used successfully in the interpretation of data on the real component of the dielectric constant of certain protein solutions, notably zein.[15] However, it is found to be impossible to obtain a satisfactory fit for the data for lysylglutamic acid on this basis.

Another modification of the theory is due to Fuoss and Kirkwood.[16] This amounts to the introduction of a distribution of relaxation times in place of the single relaxation time employed by Debye. The effect of this modification is to flatten the classical Debye curves in which the real and imaginary components of the dielectric constant are plotted as functions of frequency. The use of this theory in place of the simple Debye theory might remove the inconsistency in the relaxation times calculated from the two sets of data for lysylglutamic acid. Our experimental results, however, are not sufficiently extensive to afford a real decision as to the applicability of this theory, and we have not attempted to apply it to them.

Still another approach is to adopt the empirical procedure of Cole and Cole.[17] These authors point out that in a large number of cases a plot of the imaginary against the real part of the dielec-

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(14) J. Perrin, *J. phys. radium*, **5** (7), 497 (1934).

(15) M. A. Elliott and J. W. Williams, THIS JOURNAL, **61**, 718 (1939).

(16) R. M. Fuoss and J. G. Kirkwood, *ibid.*, **63**, 385 (1941).

(17) K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9** (4), 341 (1941).

tric constant does not give the semicircle required by the simple Debye theory, but a circular arc with the center depressed below the axis of abscissas, and thus a curve involving one additional parameter. No explanation is given for this behavior, and it is not consistent with any of the proposed molecular theories. Nevertheless, in many cases the circular arc proves highly successful as a means of describing the data and estimating a value of the relaxation time. Our data on lysylglutamic acid furnish only three points for the construction of such an arc, namely, the high and low frequency dielectric constants, and one intermediate complex dielectric constant. Since it is always possible to draw a circular arc through any three points, our data do not establish the applicability of this treatment. However, by proceeding in this way, we automatically eliminate the discrepancy in the results, and obtain from the use of both real and imaginary components of the dielectric constant a value of the relaxation time equal to 4.54×10^{-10} sec. It should be noted that this value is not significantly different from the value 4.31×10^{-10} sec. given in Table I calculated from the simple Debye theory on the basis of the absorption data alone.

These values should be compared with the relaxation time of lysylglutamic acid calculated from Stokes' law, which assumes that the molecules are spheres:

$$\tau_{\mathrm{sph}} = 8\pi\eta r^3/2kT$$

In this expression r is the radius of the molecule, which may be obtained from the molecular weight and apparent molal volume, and η denotes the viscosity of the solution. Taking the relative viscosity of a 0.23 molar solution of lysylglutamic acid on the basis of the data of Daniel and Cohn,[18] we obtain $\tau_{\mathrm{sph}} = 2.45 \times 10^{-10}$ sec.

In the case of triglycine the only value of the relaxation time given is that calculated from the absorption data. The average value of this is 1.29×10^{-10} sec. (see Table II). As would be expected from this value, the real part of the dielectric constant is so close to the static value that it cannot be used as a basis for an independent determination of the relaxation time. The value 1.29×10^{-10} sec. is to be compared with the value 1.4×10^{-10} sec. calculated from Stokes' law on the basis of an estimated viscosity.

Fortunately, a decision as to the exact value of the relaxation time is not essential in order to settle the main point at issue. The observed dispersion certainly arises from the orientation of the dipolar ions. If these behave like rigid bodies, the relaxation times will be at least as great as those calculated from Stokes' formula. Certainly the relaxation time of both peptides calculated from the present data on any basis would be so great that the molecules must be regarded as orienting essentially as rigid bodies in response to the field. This means that there can be no significant transition of the molecules from one configuration to another in intervals less than that corresponding to the critical frequencies, that is, in intervals in the neighborhood of 10^{-9} sec. or less.[18a] This must be regarded as the main conclusion of the investigation, and provides an answer to the problem raised at the outset of this paper.

The authors wish to express their indebtedness to the Laboratory of Physical Chemistry of the Harvard Medical School for the use of the two peptides studied in this investigation.

Summary

The static values of the moments of amino acids, peptides, and similar dipolar ions are the same as those calculated on the assumption of free rotation about the various simple bonds of the molecule. The question arises whether such molecules orient as rigid bodies in an electric field or whether polarization results from rotations within the molecule. An answer to this is to be sought in a study of the relaxation times of these molecules.

In order to investigate this problem we have developed a new oscillograph method free of many of the objections to previous methods at high frequencies. By making use of the transit time of the electrons, controlled by the anode voltage, it is possible to determine phase angles at ultra high frequencies. By this device, together with observations of the oscillograph pattern, both the real and imaginary parts of the dielectric constant can be determined, and from these the relaxation times may be calculated on the basis of the Debye theory.

Observations by this method on the two peptides lysylglutamic acid and triglycine at a frequency of 115 megacycles give relaxation times

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(18) J. Daniel and E. J. Cohn, THIS JOURNAL, 58, 415 (1936).

(18a) The critical frequency of lysylglutamic acid for a relaxation time of 4.31×10^{-10} sec. is 3.7×10^{8} cycles and the corresponding period is 2.7×10^{-9} sec. That of triglycine for a relaxation time of 1.29×10^{-10} sec. is 12.3×10^{8} cycles and the corresponding period is 0.8×10^{-9} sec.

of 4.31×10^{-10} sec. and 1.29×10^{-10} sec., respectively. Values calculated from Stokes' formula by assuming that the molecules are rigid spheres are 2.45×10^{-10} sec. and 1.4×10^{-10} sec., respectively. From the general agreement of these two sets of values we conclude that the molecules orient as rigid bodies in response to the applied electric field, and that there is no significant internal rotation in either molecule in periods shorter than those corresponding to the critical frequencies.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Heats of Dissociation of Some Hexaarylethanes[1]

BY RALPH PRECKEL AND P. W. SELWOOD

The purpose of this investigation was to measure the equilibrium constants, the heats, and the entropies of dissociation of several hexaarylethanes, with the primary object of testing experimentally some of the current theories of free radical stability. The data presented were obtained from measurements of magnetic susceptibilities on the ethanes in solution at several temperatures and at several dilutions.

The applicability of the magnetic method to free radical studies has been amply demonstrated by Müller,[2] by Marvel,[3] and by others,[4] including work done[5] in this Laboratory. There appears, however, to have been only one previous attempt to obtain the heat of dissociation of a hexaarylethane by magnetic measurements. Müller[6] obtained a value of 11.6 kcal. for the heat of dissociation of hexaphenylethane, in agreement with the photometric determination of Ziegler,[7] and in fair agreement with the colorimetric determination of Wooster.[8]

Current theories of free radical stability are discussed by Bachmann.[9] Among the theories of most interest at the present time are the "steric" theory, the "resonance" theory, and the attempt by Conant to predict the heats of dissociation of several substituted ethanes. The steric theory has been shown to be inadequate to explain, for instance, the instability of tricyclohexylmethyl. The resonance theory[10,11] has yielded encouraging results with respect to major stability differences among various free radicals, but has been shown[12] to be unable to explain many relatively minor differences in stability. Conant's[13] theory is based on the assumption that the entropy change during dissociation is independent of substituent. The present work lends little support to the resonance theory; it suggests that the differences in stability among the radicals studied are due to steric effects; and it shows that the entropy change is not independent of substituent.

Experimental

Preparation of Materials.—The quantities of triarylmethyl chlorides required for this investigation were obtained, for the most part, through the courtesy of Professor C. S. Marvel and Mr. C. M. Himel of the University of Illinois. The sample of triphenylmethyl chloride was prepared by Dr. J. D. Malkemus, formerly of this University. All of these materials were supplied in a high state of purity, as attested by sharp melting points and their appearance as nearly white powders or crystalline solids. They were obtained vacuum sealed into glass ampoules which, upon being opened, were either immediately evacuated and resealed or stored in a vacuum desiccator.

"Molecular" silver was prepared by internal electrolysis, substantially as described by Gomberg.

Toluene was prepared from "C. P." toluene by repeated extraction with pure concentrated sulfuric acid until the extract no longer showed color. Subsequently this extracted toluene was shaken with successive portions of dilute sodium hydroxide solution and distilled water, dried over phosphorus pentoxide, shaken with C. P. mercury and distilled from sodium, the middle half being collected.

The radical solutions were prepared by shaking a solution of triarylmethyl chloride with a tenfold excess of molecular silver under an atmosphere of toluene vapor at the vapor pressure of the solution. The shaking was continued for a

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[1] Presented at the Symposium on Magnetism and Molecular Structure at the Atlantic City Meeting of the American Chemical Society, September 8-12, 1941.

[2] Müller, Müller-Rodloff and Bunge, *Ann.*, **520**, 235 (1935), *et seq.*

[3] Roy and Marvel, THIS JOURNAL, **59**, 2622 (1937), *et seq.*

[4] Michaelis and Fetcher, *ibid.*, **59**, 2460 (1937), *et seq.*

[5] Selwood, *ibid.*, **61**, 3168 (1939), *et seq.*

[6] Müller and Müller-Rodloff, *Ann.*, **521**, 89 (1935).

[7] Ziegler and Ewald, *ibid.*, **473**, 163 (1929).

[8] Wooster, THIS JOURNAL, **58**, 2156 (1936).

[9] Bachmann in Gilman, "Treatise on Organic Chemistry," Vol. 1, John Wiley and Sons, New York, N. Y., 1938, p. 489.

[10] Pauling and Wheland, *J. Chem. Phys.*, **1**, 362 (1933).

[11] Wheland, *ibid.*, **2**, 474 (1934).

[12] Marvel, Mueller and Ginsberg, THIS JOURNAL, **61**, 2008 (1939).

[13] Conant, *J. Chem. Phys.*, **1**, 427 (1933).