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The Dielectric Properties of Two-Body Systems

The dielectric constant (ε) or conductivity (σ) of a heterogeneous system containing homogeneous particles uniformly dispersed in a homogeneous medium can generally be represented very well by the well-known theoretical formula[1]

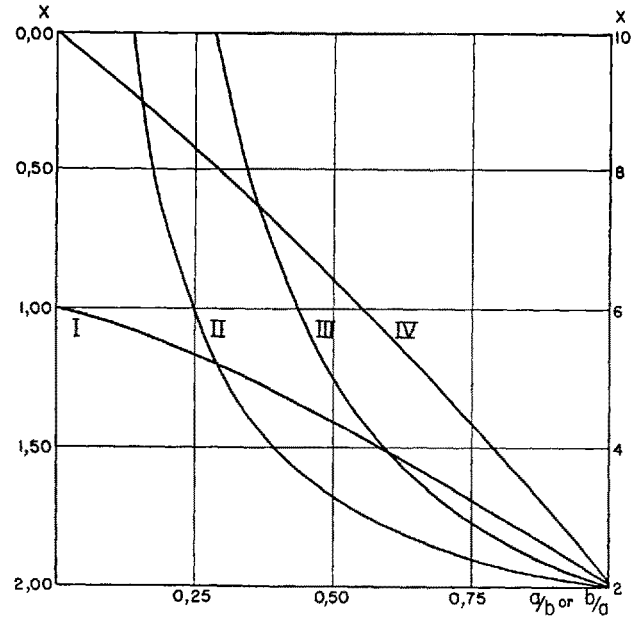
$$\frac{k-k_1}{k+x\,k_1}=\varrho\,\frac{k_2-k_1}{k_2+x\,k_1}\,. \qquad (1)$$

k stands for ε or σ; ϱ is the fractional volume of the suspended phase, and the subindices 1 and 2 refer to suspending and suspended phases respectively. The "form factor" x is independent of ϱ, but depends generally on k_2/k_1. The formula refers to systems in which the conductivities or dielectric constants respectively of the two phases are negligible. When this condition does not apply, the formula is still valid, when

$$\sigma_2/\sigma_1=\varepsilon_2/\varepsilon_1.$$

Otherwise, the calculation of σ and ε is much more complicated, the system showing the MAXWELL-WAGNER type of dispersion. Its dielectric properties were calculated by WAGNER[2] for a dilute suspension of spheres on basis of the same principles as were employed in deriving (1). This note describes a further development of this subject, particularly applicable to biological cellular materials at ultra high frequencies[3].

The general solution of the problem can be stated very simply for, by applying the theoretical procedure used in deriving (1) to a suspension in an alternating field, it will be recognized that this formula is valid also when the k^s are complex e.g. $k=\sigma+j\frac{\varepsilon}{2}n$ (n: cycles per second). The formulae for σ and ε in terms of the σ_p^s and ε_p^s and the practically more important formulae for σ_2 and ε_2 in terms of σ, ε, σ_1 and ε_1 can be obtained therefore by separating the real and imaginary terms in this generalized formula. The value of x is already known[1] for particles of ellipsoidal form, which provides a satisfactory basis for most biological applications.



Form factor x for a suspension of parallel ellipsoids of revolution, half axis a, a, b.

b parallel to electrodes { $b>a$: Curve I, left scale; $b<a$: Curve II, right scale;

b perpendicular to electrodes { $b>a$: Curve III, right scale; $b<a$: Curve IV, left scale.

Since x depends on k_2/k_1, it is generally complex. For our present purpose, we are, however, chiefly interested

$$\sigma/\sigma_1=\frac{A(\sigma_2\,\sigma_1)\,B(\sigma_2\,\sigma_1)+A(\varepsilon_2\,\varepsilon_1)\,B(\varepsilon_2\,\varepsilon_1)\,n^2/_4+(x+1)^2\,\varrho\,\varepsilon_1^2(\sigma_2/\sigma_1-\varepsilon_2/\varepsilon_1)\,n^2/_4;}{[B(\sigma_2\,\sigma_1)]^2+[B(\varepsilon_2\,\varepsilon_1)]^2\,n^2/_4} \qquad (2)$$

$$\varepsilon/\varepsilon_1=\frac{A(\sigma_2\,\sigma_1)\,B(\sigma_2\,\sigma_1)+A(\varepsilon_2\,\varepsilon_1)\,B(\varepsilon_2\,\varepsilon_1)\,n^2/_4-(x+1)^2\,\varrho\,\sigma_1^2(\sigma_2/\sigma_1-\varepsilon_2/\varepsilon_1)}{[B(\sigma_2\,\sigma_1)]^2+[B(\varepsilon_2\,\varepsilon_1)]^2\,n^2/_4} \qquad (3)$$

$$\sigma_2/\sigma_1=\frac{C(\sigma\,\sigma_1)\,D(\sigma\,\sigma_1)+C(\varepsilon\,\varepsilon_1)\,D(\varepsilon\,\varepsilon_1)\,n^2/_4+(x+1)^2\,\varrho\,\varepsilon_1^2\,(\sigma/\sigma_1-\varepsilon/\varepsilon_1)\,n^2/_4;}{[D(\sigma\,\sigma_1)]^2+[D(\varepsilon\,\varepsilon_1)]^2\,n^2/_4} \qquad (4)$$

$$\varepsilon_2/\varepsilon_1=\frac{C(\sigma\,\sigma_1)\,D(\sigma\,\sigma_1)+C(\varepsilon\,\varepsilon_1)\,D(\varepsilon\,\varepsilon_1)\,n^2/_4-(x+1)^2\,\varrho\,\sigma_1^2(\sigma/\sigma_1-\varepsilon/\varepsilon_1);}{[D(\sigma\,\sigma_1)]^2+[D(\varepsilon\,\varepsilon_1)]^2\,n^2/_4} \qquad (5)$$

$$A(k_2\,k_1)=(k_2+x\,k_1)+x\,\varrho(k_2-k_1); \qquad B(k_2\,k_1)=(k_2+x\,k_1)-\varrho\,(k_2-k_1);$$

$$C(k\,k_1)=x(k-k_1)+\varrho\,(k+x\,k_1); \qquad D(k\,k_1)=-(k-k_1)+\varrho\,(k+x\,k_1).$$

[1] J. C. MAXWELL, *Treatise on Electricity and Magnetism* (Clarendon Press, Oxford, 1937), p. 313. – O. WIENER, Abh. Königl. Sächs. ges. Wiss. Math. Phys. K. *32*, 509 (1912). – H. FRICKE, Phys. Rev. *24*, 575 (1924); Physics *1*, 106 (1931).

[2] K. W. WAGNER, Ann. Phys. *40*, 817 (1913); Arch. Elektrotech. *2*, 371 (1914).

[3] B. RAJEWSKY and H. SCHWAN, Naturwissenschaften *35*, 315 (1948). – H. F. COOK, Nature *168*, 247 (1951); Brit. J. Appl. Phys. *2*, 295 (1951).

[1] H. FRICKE, Phys. Rev. *24*, 575 (1924); Physics *1*, 106 (1931).

in cases for which x is real. We obtain, then, the formulae 2–5.

These formulae are valid for particles of spherical form, in which case $x = 2$[1]. They are valid also if the form is non-spherical, provided the particles are all oriented in the same direction. If the particles are ellipsoids (half axis: a, b, c) the value of x can be obtained in a similar manner to that used earlier in treating the case of random orientation[2]. When a is perpendicular to the electrodes, the solution is:

$$x = \frac{2 - abcL_a}{abcL_a}$$

where

$$L_a = \int_0^\infty \frac{d\lambda}{(a^2+\lambda)\sqrt{(a^2+\lambda)(b^2+\lambda)(c^2+\lambda)}}.$$

The Figure records x for ellipsoids of revolution of different axis ratios, arranged with the axis of revolution either parallel with or perpendicular to the electrodes. A limiting case is that of cylinders arranged parallel to the electrodes, for which $x = 1$.

In the ultrahigh frequency range of particular biological interest, the effect of the conductances is small and we have then:

$$\sigma_2/\sigma_1 = \frac{C(\varepsilon\,\varepsilon_1)}{D(\varepsilon\,\varepsilon_1)} + \frac{(x+1)^2\,\varrho\,\varepsilon_1^2\,(\sigma/\sigma_1 - \varepsilon/\varepsilon_1)}{[D(\varepsilon\,\varepsilon_1)]^2}; \qquad (7)$$

$$\varepsilon_2/\varepsilon_1 = \frac{C(\varepsilon\,\varepsilon_1)}{D(\varepsilon\,\varepsilon_1)}. \qquad (8)$$

Since now x depends on $\varepsilon_2/\varepsilon_1$ only and therefore is real, these formulae are valid also for non-spherical particles of random orientation. For ellipsoids, the value of x can be calculated by means of the formulae given earlier[2], using $k_2/k_1 = \varepsilon_2/\varepsilon_1$. This paper gives also numerical values of x in graphical form for ellipsoids of rotation of different axis ratios and different values of $k_2/k_1 = \varepsilon_2/\varepsilon_1$.

Examination of formulae (2) and (3) will show that, whether $\varepsilon_2/\varepsilon_1 \lessgtr \sigma_2/\sigma_1$, ε decreases and σ increases with increasing frequency (σ_p and ε_p of the two phases being taken to be independent of frequency) and the curves representing $(\sigma/\sigma_1)\ n = \infty/(\sigma/\sigma_1)\ n = 0$ and $(\varepsilon/\varepsilon_1)\ n = 0/(\varepsilon/\varepsilon_1)\ n = \infty$ plotted against $\varepsilon_2/\varepsilon_1$ (or σ_2/σ_1) for a fixed value of σ_2/σ_1 (or $\varepsilon_2/\varepsilon_1$) have a minimum at $\varepsilon_2/\varepsilon_1 = \sigma_2/\sigma_1$, where the two quantities are unity. (These statements follow also directly from the well known theorem, that the lines of electric force through a conducting heterogeneous system, are distributed in such a manner that the energy consumed is minimum.) When the difference between $\varepsilon_2/\varepsilon_1$ and σ_2/σ_1 is not very large, the error resulting from calculating the electric conductivity of the suspension by means of formula (1), is therefore relatively small.

In the earlier calculations (from ultrahigh frequency observations) of the interior conductivity of the red blood cell[3] which were carried out in this manner, the greatest difference between $\varepsilon_2/\varepsilon_1$ and σ_2/σ_1 —which in this case represent the ratios of respectively dielectric constants and conductivities of cell interior to those of suspending fluid—was only about 10% (for corpuscles in plasma), and the values given require corrections of less than 2% from the standpoint of the present theory.

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Zusammenfassung

Es wird darauf hingewiesen, dass die Formel

$$\frac{k-k_1}{k+xk_1} = \varrho\,\frac{k_2-k_1}{k_2+xk_1}$$

(k: dielektrische Konstante bzw. Leitfähigkeit) für die elektrischen Eigenschaften einer Suspension auch dann gilt, wenn die k komplex sind. Verschiedene Anwendungen dieser verallgemeinerten Formel werden besprochen, die für elektrische Messungen an zellularen Substraten biologischer Herkunft bei Ultrahochfrequenzen von Interesse sind. Diese umfassen Suspensionen orientierter Rotationsellipsoide. In Weiterführung früherer Arbeiten[1] werden Kurven angegeben, die x für solche Systeme darstellen.

[1] H. FRICKE, Phys. Rev. *24*, 575 (1924); Physics *1*, 106 (1931).

Significance and Rearrangements of Quinol Models of Tyrosine Metabolites[1]

Labile metabolites in the breakdown of amino acids are of fundamental interest[2]. The transformation of tyrosine to homogentisic acid involving the apparent migration of an acetic acid side chain has led the biochemists to the assumption of a *labile quinol intermediate* as early as 1907[3]. The oxidation of p-alkylphenols with CARO's acid offers welcome analogies to the biochemical oxidation of tyrosine. Whereas under neutral conditions (in the presence of $MgCO_3$) p-cresol is converted to p-toluquinol[4] (yield, 5–10%, possibly some o-hydroxylation to *homo*-catechol) the oxidation in acidic medium (1·8N H_2SO_4)[5] leads directly to toluhydroquinone (about 15%, no catechol). These results prompted FRIEDMAN[3], NEUBAUER[6], and DAKIN[7] to attempt unsuccessfully the preparation of quinols corresponding to tyrosine (DAKIN), p-hydroxyphenylpyruvic (NEUBAUER) and p-hydroxyphenylacetic acids (FRIEDMANN, DAKIN). Our own ex-

[1] J. C. MAXWELL, *Treatise on Electricity and Magnetism* (Clarendon Press, Oxford, 1937), p. 313.

[2] H. FRICKE, Phys. Rev. *24*, 575 (1924); Physics *1*, 106 (1931).

[3] B. RAJEWSKY and H. SCHWAN, Naturwissenschaften *35*, 315 (1948). – H. F. COOK, Nature *168*, 247 (1951).

[1] *On the Mechanism of Oxidation.* VII. Preceding paper in this series: Ber. dtsch. chem. Ges. *85*, 3. H. WIELAND, Festschrift (1952).

[2] Cf. Paper V in this series: Exper. *8*, 36 (1952).

[3] E. FRIEDMANN, Beitr. chem. Physiol. Pathol. *11*, 304 (1908). – In 1901, E. MAYER [Dtsch. Arch. Klin. Med. *70*, 443 (1901)] called attention to the similarity of the reaction tyrosine → homogentisic acid to the rearrangement of p-tolylhydroxylamine to toluhydroquinone [E. BAMBERGER, Ber. dtsch. chem. Ges. *28*, 245 (1895)], at a time when the isolation of the intermediate quinol had not been reported yet by BAMBERGER [Ber. dtsch. chem. Ges. *33*, 3600 (1901)].

[4] E. BAMBERGER, Ber. dtsch. chem. Ges. *36*, 2028 (1903).

[5] T. KUMAZI and R. WOLFFENSTEIN, Ber. dtsch. chem. Ges. *41*, 297 (1908).

[6] O. NEUBAUER, Dtsch. Arch. Klin. Med. *95*, 211 (1909).

[7] H. D. DAKIN, J. Biol. Chem. *8*, 13 (1910). In the light of these precedents, it is surprising to find the following statement by DAKIN in his book *Oxidation and Reduction in the Animal Body* (Longmans, Green & Co., London, New York, Toronto, 1922), p. 93: "The Chemical analogy for the wandering of the $-CH_2-CO-COOH$ group is lacking". The recent findings by S. WEINHOUSE and R. H. MILLINGTON, J. Biol. Chem. *175*, 995 (1948) and by B. SCHEPERTZ and S. GURIN, ibid. *180*, 663 (1949), using tyrosine labeled with C_{14} in various positions, are clear evidence of the intramolecular migration of the side chain.