A MATHEMATICAL TREATMENT OF THE ELECTRIC CONDUCTIVITY AND CAPACITY OF DISPERSE SYSTEMS

I. The Electric Conductivity of a Suspension of Homogeneous Spheroids

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Abstract

Conductivity measurements may give values for (1) the specific conductivity, (2) the concentration or (3) eccentricity of form of the suspended particles of suspensions such as biological tissues, blood and cream. *Mathematical theory.* The following relation is derived: $(k/k_1-1)/(k/k_1+x)=\rho(k_2/k_1-1)/(k_2/k_1+x)$, where k, k_1 and k_2 are the specific conductivities of the suspension, the suspending medium and the suspended spheroids, ρ is the volume concentration of the suspended spheroids, and x is a function of the ratio k_2/k_1 and the ratio a/b of the axis of symmetry of the spheroids to the other axis. For the case of spheres, $x=2$ and the formula reduces to that of Lorentz-Lorentz and Clausius-Mossotti. Curves are given showing the variation of x with k_2/k_1 for various values of a/b. Comparison with experimental data of Stewart for the conductivity of the blood of a dog ($k_2=0$, $a/b=1/4.25$, $x=1.05$) shows excellent agreement for concentration from 10 to 90 per cent. Also the observations of Oker-Blom for two suspensions of sand in salted gelatine, give in each case constant values of x for various concentrations.

A. Introduction

THE present theory has been developed as a basis for experiments concerning the electric conductivity and capacity* of colloids and biological cell suspensions, like blood for instance, which for sometime have been carried out in this laboratory. In this paper we shall consider the electric conductivity of a suspension of homogeneous non-polarizable spheroids; in a second paper, the electric capacity of a suspension of polarizable homogeneous spheroids for a current of low frequency; and in a third, the conductivity and capacity for any frequency, of a suspension of spheroids each consisting of a homogeneous interior surrounded by a thin membrane the conductivity of which is different from the conductivity of the interior. The last calculation includes the case of a suspension of homogeneous polarizable spheroids. A series of measurements illustrating the practical and theoretical applicability of

*A suspension is electrically equivalent to a certain resistance in parallel with a certain capacity. We refer to this resistance and to this capacity when we speak of the conductivity and capacity of a suspension.

the theory will be given in separate papers. Preliminary reports of some of the measurements have already been presented at meetings of the American Physical Society.

An investigation of the conductivity of a suspension may serve as a means of determining the conductivity of the single particles of the suspension. Important knowledge of the state of the suspended particles may thus be obtained, as in the case of protected metallic colloids, and especially in the case of suspensions of biological cells the life of which seems to be associated with the existence of a characteristic semi-permeability of the exterior cell wall and of the different interphases of the cell interior. In connection with the latter case we may refer to the researches of Brooks,[1] of Crile, Hosmer and Rowland,[2] of Osterhout[3] and of many other investigators on the changes of the electric conductivity of bacterial suspensions and of different plant and animal tissues under varying conditions.

The determination of the conductivity of a suspension may also furnish a method for obtaining the volume concentration of the suspension when the specific conductivity of the disperse phase and of the suspending medium is known. This method is used practically in the determination of the volume concentration of the red corpuscles of blood. It seems probable that it may have many other practical applications, as for instance, the determination of the butter-fat of cream.

Finally, the measurement of the conductivity of a suspension may lead to a determination of the structural factors of the suspended phase. This is possible because as we shall see later, for a constant volume concentration the conductivity of a suspension is to a certain extent dependent on the form (but not on the size) of the suspended particles. This is especially marked when the suspended particles are non-conductors, the condition which is of the most practical interest. This method may, for instance, find practical application in soil analysis.

B. Theory of Electric Conductivity of Suspension of Spheroids

The determination of the electric conductivity of a suspension belongs to a very important group of physical problems all of which depend on the solution of Poisson's equation for a two-phase system, including Poisson's

[1] J. Brooks, J. Gen. Physiol. **5**, 365 (1923); Proc. Soc. Exp. Biol. and Med., **19**, 284 (1922)

[2] G. W. Crile, H. R. Hosmer, and A. F. Rowland, Amer. J. Physiol., **60**, 59 (1922)

[3] W. J. V. Osterhout, Injury, Recovery and Death in Relation to Conductivity and Permeability, Phila., 1922; (see Bibliography).

theory of induced magnetism, the Clausius-Mossotti theory for the dielectric constant, the Lorenz-Lorentz theory for the index of refraction, etc. Applied to the case of electric conductivity, the formula to which these theories lead, reads

$$\frac{(k/k_1)-1}{(k/k_1)+2}=\rho\frac{(k_2/k_1)-1}{(k_2/k_1)+2} \tag{1}$$

in which k, k_1 and k_2 are the specific conductivities of the suspension, the suspending and the suspended mediums respectively; and ρ is the volume concentration of the suspended medium. This formula is true theoretically only for the case of a suspension of spheres. The case of a suspension of infinitely well conducting ellipsoids has been treated theoretically by Poisson[4] in his theory of magnetic induction and also by Lampa[5] in his theory of the dielectric constant of a crystal.

According to its theoretical derivation as presented hitherto, Eq. (1) can be expected to hold only for dilute suspensions. The reason for this is that in the given theoretical treatment the electric field around any usspended particle due to the electric charges on the other particles in the suspension is considered as equal to the average value of this field over the whole space of the suspended medium. For the case of a cubic arrangement of spheres, Lord Rayleigh has shown that the influence of these charges is represented correctly in Eq. (1) only to the first approximation. It seems difficult theoretically to decide whether the formula holds strictly for the case of a random distribution of the suspended particles. That it does is supported by the well known fact that there is usually a very close agreement[7] between the values of the refractive index of a liquid (or dielectric constant, although the agreement here generally is less close)[8] as determined experimentally and as calculated from formula (1) by means of the experimental value of the refractive index for its vapor. Confirmation was obtained for volume concentrations up to 15 per cent by Millikan[9] from his observations of the dielectric constant of emulsions of water in benzol-chloroform. In the following presentation, therefore, we shall take into account the interaction of the suspended particles by means of the procedure employed in deriving formula (1); that is, we shall add to the original field the mean value of the forces due to the charges on the suspended particles throughout the whole space of the

[4] S. D. Poisson, Mem. Acad. Roy. Sci. Inst. France, **5,** 488 (1826)
[5] A. Lampa, Sitz. Math. Nat. Klasse Akad. Wiss. Wien., **104** (IIa), 681 (1895)
[6] Lord Rayleigh, Phil. Mag., **34,** 481 (1892)
[7] W. Brühl, Zeits. Phys. Chem., **7,** 1 (1891)
[8] P. Lebedew, Wied. Ann. **44,** 304 (1891)
[9] R. A. Millikan, Wied, Ann. **61,** 337 (1897)

suspending medium. The exactness of this method is proven by an experimental verification of the formula which we shall derive; to this end we shall in this paper make use of the extensive experimental data which have been accumulated for the electric conductivity of blood.

We shall consider first the general case of a suspension of homogeneous, non-polarizable ellipsoids. The suspension is assumed to be in an electrolytic cell, the dimensions of which are $1 \times 1 \times 1$ cm. The potential between the electrodes is V volts; the current i amperes.

Let us consider a single ellipsoid with half axes a, b, c in this suspension. We shall, for the moment, consider a to be parallel to the direction of the electric force. We shall introduce an orthogonal co-ordinate system with its origin in the center O of the ellipsoid and its axes x, y, z parallel to a, b and c (Fig. 1). We shall designate the electric force at an arbitrary

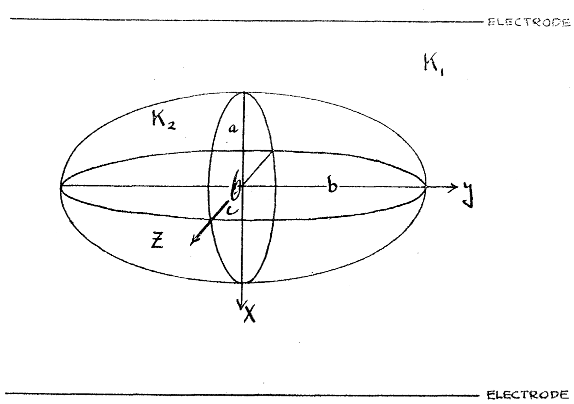

Fig. 1

point of the suspending phase as F; as stated above, this is composed of the original electric force V due to the surface charges on the electrodes and of the mean value of the forces due to the surface charges on the suspended particles throughout the whole space of the suspending medium.

For the purpose of determining the surface charges of the ellipsoid we shall introduce confocal co-ordinates defining these for a point x, y, z as the three values of θ, λ, μ and ν, which satisfy the equation

$$\frac{x^2}{a^2+\theta} + \frac{y^2}{b^2+\theta} + \frac{z^2}{c^2+\theta} = 1 \, .$$

The potential due to the force F is

$$V_x = -Fx = -F\sqrt{(a^2+\lambda)(a^2+\mu)(a^2+\nu)/(b^2-a^2)(c^2-a^2)} \, .$$

The total potential at a point outside the ellipsoid must be of the form

$$V_{ext} = -F\sqrt{\frac{(a^2+\mu)(a^2+\nu)}{(b^2-a^2)(c^2-a^2)}}\left\{\sqrt{(a^2+\lambda)} + D\sqrt{(a^2+\lambda)}\int_\lambda^\infty \frac{d\lambda}{(a^2+\lambda)\,\Delta\lambda}\right\} \quad (2)$$

while at a point inside the ellipsoid

$$V_{int} = -F\sqrt{\frac{(a^2+\lambda)(a^2+\mu)(a^2+\nu)}{(b^2-a^2)(c^2-a^2)}}\,D_1 \,. \quad (3)$$

where $\Delta\lambda = \sqrt{(a^2+\lambda)(b^2+\lambda)(c^2+\lambda)}$, and D and D_1 are constants which are to be determined by the boundary conditions. The boundary conditions to be fulfilled are

(1) For $\lambda = \infty$, V_{ext} must be equal to the potential of the original field; this condition is fulfilled since the last term becomes zero for $\lambda = \infty$.

(2) At the surface of the ellipsoid ($\lambda = 0$), $V_{int} = V_{ext}$; hence, from Eqs. (2) and (3),

$$D_1 = 1 + D\int_0^\infty \frac{d\lambda}{(a^2+\lambda)\,\Delta\lambda} \quad (4)$$

Hence

$$\int_0^\infty \frac{d\lambda}{(a^2+\lambda)\,\Delta\lambda} = \frac{D_1-1}{D} \equiv L_a \,,$$

if we write L_a for the definite integral.

At the surface of the ellipsoid, $N_{ext}k_1 = N_{int}\,k_2$, N_{ext} and N_{int} being the normal forces at the two sides of the surface of the ellipsoid. The equation indicates that no accumulation of electricity takes place at the surface. Using n for the direction of the normal to the surface of the ell psoid we have

$$N_{ext} = -(dV_{ext}/dn)_{\lambda=0} = -(dV_{ext}/d\lambda)_{\lambda=0}\cdot(d\lambda/dn)_{\lambda=0}$$

and a similar equation for N_{int}.

Consequently our equation of condition becomes

$$+F\sqrt{\frac{(a^2+\mu)(a^2+\nu)}{(b^2-a^2)(c^2-a^2)}}\left[\frac{1}{2a} + \frac{DL_a}{2a} - \frac{D}{a^2bc}\right]k_1$$

$$= +F\,D_1\sqrt{\frac{(a^2+\mu)(a^2+\nu)}{(b^2-a^2)(c^2-a^2)}}\;\frac{1}{2a}k_2 :$$

$$k_1[1+DL_a-2D/abc] = k_2\,D_1. \quad (5)$$

From equations (4) and (5) we obtain:

$$D = \frac{(1-k_2/k_1)}{2/abc+L_a(k_2/k_1-1)}$$

$$D_1 = \frac{2}{2+abcL_a(k_2/k_1-1)}$$

We now obtain for V_{int}

$$V_{int} = -F\sqrt{\frac{(a^2+\lambda)(a^2+\mu)(a^2+\nu)}{(b^2-a^2)(c^2-a^2)}}\cdot\frac{2}{2+abcL_a(k_2/k_1-1)}$$

or, going back to the x, y, z co-ordinate system

$$V_{int} = -\frac{2Fx}{2+abcL_a(k_2/k_1-1)}\,. \tag{6}$$

The values of V_{int} when b or c are parallel to the electric field, are derived by replacing a in Eq. (6) by b or c.

The value of F is determined by the following equation:

$$\int_{ext} F_x\,dx\,dS + \int_{int} F_x\,dx\,dS = V$$

in which F_x is the component of the electric force parallel to x and dS an element of area perpendicular to x, the first integral is taken over the space outside the ellipsoids, the other over the space inside the ellipsoids.

We obtain, using equation (6) and writing

$$\int_0^\infty \frac{d\lambda}{(b^2+\lambda)\,\Delta\lambda} \equiv L_b\,; \quad \int_0^\infty \frac{d\lambda}{(c^2+\lambda)\,\Delta\lambda} \equiv L_c$$

$$V = F(1-\rho)+\tfrac{1}{3}F\rho\sum^{\alpha=a,b,c}\frac{2}{2+abc\,L_\alpha(k_2/k_1-1)} \tag{7}$$

In order to find the conductivity k of the suspension we shall divide the space between the electrodes (Fig. 1) into an infinite number of volume elements dS, dx.

By Ohm's law we have

$$k_1\int_{int} dx \int_{int} F_x\,dS + k_2\int_{ext} dx\int_{ext} F_x\,dS = i = Vk\,. \tag{8}$$

where the first of the two integrals is taken over the space inside the ellipsoids and the other over the space outside the ellipsoids. This equation is evidently equivalent to

$$k_1\int_{all} dx\int_{all} F_x\,dS + (k_2-k_1)\int_{ext} dx\int_{ext} F_x\,dS = Vk$$

in which the first double integral is taken over the whole space between the electrodes. We obtain

$$Vk_1+(k_2-k_1)\int dS[(V_{int})_{-x}-(V_{int})_{+x}] = Vk$$

$$Vk_1+(k_2-k_1)\frac{2F}{2+abcL_a(k_2/k_1-1)}\int 2x\, dS = Vk$$

$$k_1+\frac{2k_1(k_2/k_1-1)F/V}{2+abcL_a(k_2/k_1-1)}\rho = k \tag{9}$$

ρ being the volume of the ellipsoids.

This equation corresponds to the case in which a is parallel to the direction of the original field. The equations which correspond to the cases in which b and c are parallel to the original field are obtained by replacing a by b and c.

The equation corresponding to an arbitrary orientation of the ellipsoids is the sum of three equations like (9)

$$3k_1+k_1\rho\sum^{a=a,b,c}\frac{2(k_2/k_1-1)F/V}{2+abcL_a(k_2/k_1-1)} = 3k \tag{10}$$

Combining this equation with equation (7) we obtain

$$\frac{F}{V}=\frac{k_2-k}{(1-\rho)\,(k_2-k_1)}$$

Introducing this value of F/V into equation (10), we obtain finally

$$k=k_1+\frac{\frac{1}{3}\rho}{1-\rho}\sum^{a=a,b,c}\frac{2(k_2-k)}{2+abcL_a(k_2/k_1-1)}\,. \tag{11}$$

We shall now confine ourselves to the case of spheroids, that is $b=c$. We have the following two integrals in equation (11) to integrate

$$L_a=\int_0^\infty\frac{d\lambda}{(a^2+\lambda)\,\Delta\lambda}=\int_0^\infty\frac{d\lambda}{(a^2+\lambda)^{3/2}\,(b^2+\lambda)}$$

$$L_b=\int_0^\infty\frac{d\lambda}{(b^2+\lambda)\,\Delta\lambda}=\int_0^\infty\frac{d\lambda}{(b^2+\lambda)^2(a^2+\lambda)^{1/2}}$$

We find by partial integration

$$L_a=\frac{2}{ab^2}-2\int_0^\infty\frac{d\lambda}{(a^2+\lambda)^{1/2}(b^2+\lambda)^2}\,.$$

The integral

$$ab^2\int_0^\infty\frac{d\lambda}{(a^2+\lambda)^{1/2}(b^2+\lambda)^2}\equiv M$$

can easily be calculated.

$$M\,(a<b) = \frac{(\varphi - \frac{1}{2}\sin 2\varphi)}{\sin^3\varphi}\cos\varphi \quad \text{where } \cos\varphi = a/b\text{, and}$$

$$M\,(a>b) = \frac{1}{\sin^2\varphi'} - \frac{1}{2}\,\frac{\cos^2\varphi'}{\sin^3\varphi'}\log\left(\frac{1+\sin\varphi'}{1-\sin\varphi'}\right), \quad \text{where } \cos\varphi' = b/a$$

consequently by (11),

$$k = k_1 + \frac{k_1\rho\beta}{(1-\rho)}\;\frac{(k_2-k)}{(k_2-k_1)} \tag{12}$$

or

$$\left(\frac{k-k_1}{k_2-k}\right)\left(\frac{k_2}{k_1}-1\right) = \frac{\beta\rho}{1-\rho} = \beta\rho_1 \tag{13}$$

where $\rho = \rho_1/(1+\rho_1)$

and

$$\beta = \tfrac{1}{3}\left[\frac{2}{1+(k_2/k_1-1)\frac{1}{2}M} + \frac{1}{1+(k_2/k_1-1)\,(1-M)}\right]\left(\frac{k_2}{k_1}-1\right)$$

In Figs. 2 and 3 we have plotted β against k_2/k_1 (or k_1/k_2) for different values of a/b.

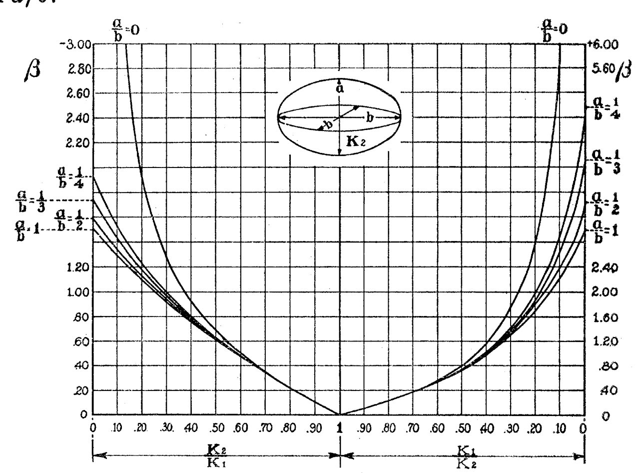

Fig. 2. Graphical representation of β for the case of the oblate spheroid.

The influence of the geometrical factors of the suspended particles is expressed in equation (13) solely in β. Therefore we conclude from the expression for β and from Figs. 3 and 4, that for a constant volume concentration, the conductivity of a suspension is independent of the size of the suspended particles and also nearly independent of the form of the particles when the difference between the conductivities of the suspended and the suspending phases is not very large. This is especially true for suspensions of prolated spheroids which are less conducting than the suspending medium.

Putting

$$x = -\frac{(k_2/k_1-1) - (k_2/k_1)\beta}{(k_2/k_1-1)-\beta}$$

we obtain from equation (13) the following analogue to equation (1)[10]

$$\frac{(\mathrm{k}/\mathrm{k}_1)-1}{(\mathrm{k}/\mathrm{k}_1)+\mathrm{x}} = \rho \cdot \frac{(\mathrm{k}_2/\mathrm{k}_1)-1}{(\mathrm{k}_2/\mathrm{k}_1)+\mathrm{x}} \tag{14}$$

x is plotted in Figs. 4 and 5.

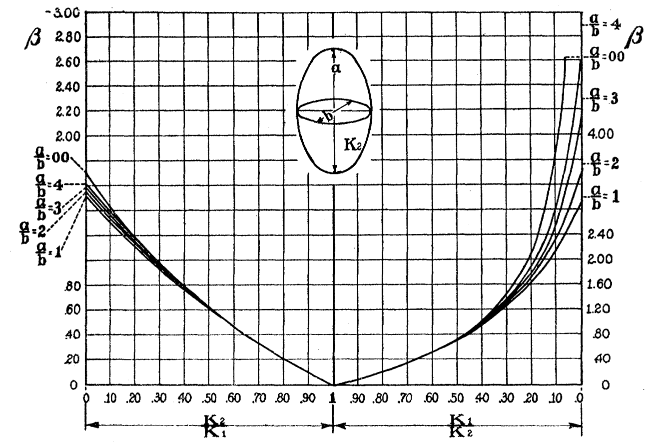

Fig. 3. Graphical representation of β for the case of the prolate spheroid.

For the case of the sphere, $x=2$, making Eq. (14) identical with Eq. (1). For the case when $k_2=0$, Eq. (13) becomes

$$\left(1-\frac{k_1}{k}\right) = \frac{\beta\rho}{1-\rho} = \beta\rho_1 \; ; \tag{15}$$

also

$$x = -1/(\beta+1) \; ; \; \beta = -(x+1)/x \; , \tag{16}$$

and Eq. (14) becomes

$$-\frac{\rho}{x} = \frac{k-k_1}{k+k_1x} \; ; \quad \left[1-\frac{k_1}{k}(1-\rho)\right]x = -\rho \tag{17}$$

C. Comparison of Theory with Experimental Data

In this section we shall apply the formula which we have derived to the very accurate and extensive experimental data for the conductivity

[10] Compare O. Wiener, Abh. K. Sächs. Ges. Wiss. Math. Phys. Kl. **32**, 509 (1912)

of blood which have been accumulated by Stewart,[11] Bugarszky,[12] Fraenckel[13] and others. According to these investigators for a current of low frequency the red corpuscles of blood are perfect insulators so that the ratio of the conductivity of blood to that of its serum is dependent only on the volume concentration of the red corpuscles but independent of the absolute value of the conductivity of the serum. Determinations of this ratio are made for volume concentrations up to 90 per cent. For the

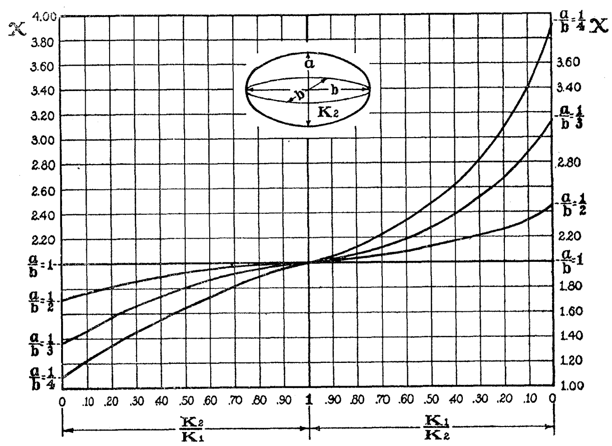

Fig. 4. Graphical representation of x for the case of the oblate spheroid.

same value of the volume concentration, this ratio is very nearly the same for the blood of man, horse, dog and cow.[13] The most exact methods for determining the volume concentration have been used by Stewart and Fraenckel. Stewart has used two independent methods, a colorimetric and Hoppe-Seyler's chemical method. Fraenckel has used Bleibtreu's chemical method. The agreement between the results of Stewart and those of Fraenckel is very good. However, as has been stated also by Fraenckel, one would expect that Stewart's methods would give the most exact results. We shall, therefore, restrict ourselves to a comparison of the results of Stewart with those secured by the formula. In Table I is given a series of measurements made by Stewart (l.c.[11] p. 369) for the blood of a dog. The volume concentration of the normal blood was determined twice by the colorimetric method and twice by Hoppe-Seyler's method. The results were 41.16, 40.72, 41.52 and 40.99 per cent, the average ratio being 40.98 per cent. A series of red corpuscle suspensions of varying volume concentration was made up by concentration or

[11] G. N. Stewart, J. Physiol., **24,** 356 (1899)
[12] S. Bugarszky, Zentr. Physiol., **11,** 297 (1897-98)
[13] P. Fraenckel, Zeits. klin. Med., **52,** 470 (1904)

dilution of the normal blood. The volume concentration for each of these suspensions was determined volumetrically using the value of the volume concentration of the original blood. These volume concentrations are

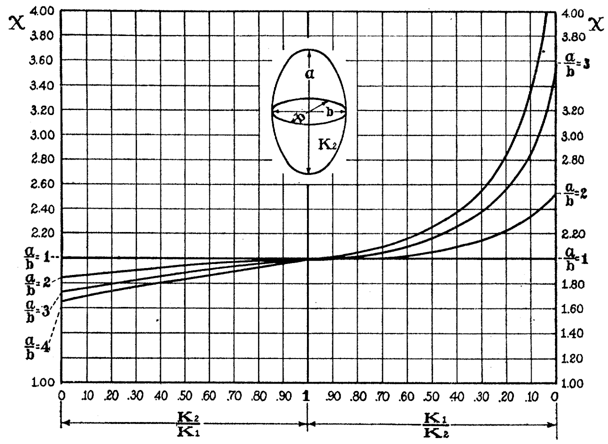

Fig. 5. Graphical representation of x for the case of the prolate spheroid.

given in Table I under ρ (obs.). The ratio of the conductivity of the serum to that of the blood is given under k_1/k.

In applying our formula, we take $k_2=0$, and assume $a/b=1/4.25$; consequently (see Fig. 2) $x=1.05$ and $\beta=-1.95$, and either (15) or (17)

TABLE I

Conductivity of blood of dog

k_1/k	ρ(obs.) (per cent)	ρ(calc.) (per cent)	Difference (per cent)
15.62	90.7	88.2	+2.7
9.08	82.1	80.5	+2.0
6.56	74.5	74.0	+0.7
5.06	67.8	67.5	+0.4
4.14	61.6	61.6	−0.0
3.51	56.1	56.2	−0.2
3.063	51.0	51.4	−0.8
2.726	46.4	46.9	−1.0
2.436	42.2	42.3	−0.2
2.348	41.0	40.8	−0.5
2.225	38.4	38.5	−0.4
1.903	31.9	31.6	−0.8
1.697	26.4	26.3	−0.0
1.539	21.8	21.6	+1.0
1.428	18.1	18.0	+0.5
1.342	15.3	14.9	+2.4
1.232	11.4	10.7	+6.1

may be used to calculate the values of the volume concentration ρ for the observed values of k_1/k. These are given under ρ (calc.). The deviations ρ (obs.) $-\rho$ (calc.) given in the fourth column are probably always within the experimental errors.*

It may be of interest to apply our formula also to some measurements of sand suspensions which have been made by Oker-Blom.[14] and are often cited in connection with work on the conductivity of blood. Two different kinds of sand were used. The suspensions were prepared by adding the sand to a hot salt solution containing 3 per cent gelatine and cooling this mixture to gelatination under continuous rotation. No information is

TABLE II

Conductivity of suspensions of sand

k_1/k(obs.)	ρ(obs.) (per cent)	β	x
2.488	40.	2.22	.820
2.220	36.4	2.14	.876
2.075	33.3	2.15	.870
1.952	30.8	2.14	.876
1.866	28.6	2.17	.854
1.790	26.7	2.17	.854
1.725	25.0	2.18	.848
1.6835	23.5	2.22	.820
	Average values:	2.17	.854

given concerning the form of the sand particles except for the statement that the particles of the sand which were used in the second series of experiments (Table III) were more nearly spherical than those which were used in the first series (Table II). Our theory is therefore best

TABLE III

Conductivity of suspensions of sand

k_1/k(obs.)	ρ(obs.) (per cent)	β	x
1.190	10	1.710	1.410
1.426	20	1.705	1.420
1.734	30	1.712	1.405
2.156	40	1.732	1.367
2.715	50	1.715	1.400
3.613	60	1.74	1.35
	Average values:	1.72	1.392

*The red corpuscles of mammalians according to the most generally accepted data are biconcave in shape but their dimensions especially in the dog have not been accurately measured. The value 1/4.25 for a/b which secures the best agreement in the present case is in good agreement with the observed values for the dimensions. Determinations of the conductivity of the blood of different animals with simultaneous measurements of the dimensions of the red corpuscles will be made in this laboratory; these investigations will include studies of the blood of different non-mammalian vertebrates in which the red corpuscles are approximately ellipsoids.

[14] M. Oker-Blom, Arch. Ges. Physiol., **79**, 510 (1900)

applied by using Oker-Blom's observed values of k_1/k and ρ and calculating the value of x by means of Eq. (17) since $k_2=0$. Our calculated results are given in Tables II and III, one for each of the two kinds of sand used by Oker-Blom The calculated values for x in each case are constant within experimental errors. It hardly seems probable, however, that the sand particles could have been as flat as these values for x would indicate; it is more probable that the large values for x are due to the fact that the sand particles became more or less completely orientated by the rotation. Eq. (14) with a different value for x holds also in this case.

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