The Dielectric Constant of Dispersion of Spherical Particles

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The dielectric constant of emulsions and suspensions and the magnetic permeability of compressed powders have been studied theoretically and experimentally in view of their scientific as well as of their technical importance. Many empirical and theoretical equations have been proposed for disperse systems composed of two different phases. Almost all the empirical formulas assume that some function of dielectric constant ε changes linearly with the volume fraction ϕ.

$$f(\varepsilon)=\phi_1 f(\varepsilon_1)+\phi_2 f(\varepsilon_2) \qquad (1)$$

where suffixes denote the two components constituting the heterogeneous system. The following functions have been proposed.

$f(\varepsilon)=\varepsilon$ (2)
$f(\varepsilon)=1/\varepsilon$ (3) } Wiener's limiting formulas

$f(\varepsilon)=\log\varepsilon$ (4) Lichtenecker

$f(\varepsilon)=(\varepsilon-1)/(\varepsilon+2)$ (5) Clausius-Mosotti

$f(\varepsilon)=(\varepsilon-1)/(\varepsilon+u)$ (6) Wiener

Here u is a constant dependent on the form of the particles. Since earlier works on the problem have already been reviewed by Heymann[1] and Voet,[2] our references to such works need not be comprehensive. The Wiener's limiting formula (2) applies strictly to such heterogeneous systems, in which each single part of the components is cylindrical in shape with the generating line of the cylindrical surface parallel to the electric vector, while the formula (3) to systems in which all the boundary surfaces between the phases are planar and perpendicular to the field. To be sure, the actual heterogeneous systems of interest are very different from these limiting cases. In fact we may expect for instance that an oil-in-water emulsion has a different dielectric constant from that of a water-in-oil emulsion with the same volume fraction of the oil. In fact Goto and Koizumi[3] found that such was actually the case. Therefore we should reject the additive rule of the form (1).

(1) E. Heymann, *Kolloid-Z.*, **66**, 229 (1934).
(2) A. Voet, *J. Phys. Coll. Chem.*, **51**, 1037 (1947).
(3) R. Goto and N. Koizumi, *Rep. Inst. Chem. Research, Kyoto Univ.*, **18**, 121 (1949); R. Goto, *Rev. High Molecules*, **5**, 47 (1951).

and derive a theoretical formula taking into account the non-equivalence of the dispersion medium and the disperse phase. Such an attempt has already been made by Wiener[4] and by Bruggeman.[5] The original paper by Wiener was not available to the writers. His formula for the dielectric constant of a dispersion of concentration ϕ in volume fraction is

$$\frac{\varepsilon-\varepsilon_0}{\varepsilon+2\varepsilon_0}=\frac{\varepsilon_1-\varepsilon_0}{\varepsilon_1+2\varepsilon_0}\phi \qquad (7)$$

for spherical particles of dielectric constant ε_1 dispersed in a medium of dielectric constant ε_0. Piekara[6] derived the same formula with the aid of Wiener's proportionality postulate. That is, he calculated the dielectric constant of dispersion of spherical particles in vacuum and assumed that the same equation holds for a dispersion in a homogeneous medium if in the original equation ε and ε_1 are substituted by $\varepsilon/\varepsilon_0$ and $\varepsilon_1/\varepsilon_0$ respectively. This procedure lacks an adequate theoretical justification. In addition he employed Mosotti's inner field, which has nothing to do with dispersions of particles of greater size than molecular dimensions. Bruggeman proposed the following formula.

$$\frac{\varepsilon_1-\varepsilon}{\varepsilon_1-\varepsilon_0}\left(\frac{\varepsilon_0}{\varepsilon}\right)^{1/3}=1-\phi \qquad (8)$$

He employed Rayleigh's formula,[7] which gave the dielectric constant increment due to the introduction of spherical particles arranged regularly at the lattice points of a simple cubic lattice into a homogeneous phase. Then he ignored higher terms of ϕ. The result is equivalent to that derived from the assumption of Wiener's proportionality postulate, the difference between his theory and Wiener's being that instead of using Mosotti's inner field he integrated a differential equation containing $d\varepsilon/d\phi$. Hence it is not surprising that these two formulas give an identical value for $d\varepsilon/d\phi$ at $\phi=0$.

The present writers have taken a different method of approach avoiding the use of the Wiener's proportionality postulate and obtained an entirely different theoretical formula. The basic assumptions underlying the writers' derivation are as follows. Each particle of the disperse phase is spherical in shape. The radius of the sphere is very small compared with the dimension of the whole heterogeneous system, enabling us to ignore the effect of boundary of the whole system. But it is very great in comparison to the molecular dimensions so that the disperse phase and the dispersion medium can be considered to be homogeneous media characterized by their respective dielectric constants alone. The particles are assumed to have no net charge. If the particles are not so finely dispersed, the effect of polarization will be more important than that of charges at the boundary surfaces. The system may be polydisperse, i. e., the radius of the particles may not be uniform. For the time being, let us assume that all the particles have a radius a.

Suppose a dispersion containing n particles of disperse phase per unit volume. The volume fraction ϕ is given by

$$\phi=\frac{4\pi}{3}a^3n. \qquad (9)$$

Let us imagine $\Delta\nu$ spheres of radius a in unit volume. The number of spheres is so small that the distance between them is very great compared with the radius a. Take out the matter in the spheres and substitute it with a medium of dielectric constant ε_1. If such substitution were made on a homogeneous medium of dielectric constant ε, we could give an expression for the dielectric constant increase. We assume that the same formula for the dielectric constant change is approximately valid for the result of substitution applied on an already existing dispersion containing n particles per unit volume. This means that the heterogeneous system can well be represented by a homogeneous system of the same dielectric constant. Actually the system under consideration is not perfectly static, i. e., the particles already present are moving with respect to the newly inserted spheres. Hence the averaging may be justified to a certain extent. The assumption would be exact if the particles already present were much smaller in size than those introduced. In our case, however, the representation of a heterogeneous system by an average homogeneous phase is an approximation. It will be worthwhile to mention that Brinkman[8] applied the same idea to the theory of viscosity of concentrated suspensions and solutions and obtained a good viscosity formula.

When a sphere of dielectric constant ε_1 is introduced into a homogeneous medium of dielectric constant ε subjected to a uniform

(4) O. Wiener, *Abh. Königl. sächs. Ges. Wiss. Math. Phys. Kl.*, **32**, 509 (1912).
(5) D. A. G. Bruggeman, *Ann. Physik*, (5) **24**, 636 (1935).
(6) A. Piekara, *Kolloid-Z.*, **59**, 12 (1932).
(7) Rayleigh, *Phil. Mag.*, (5) 34, 481 (1892).
(8) H. C. Brinkman, *J. Chem. Phys.*, **20**, 571 (1952).

electric field E_0, the field is distorted in such a way[9] that outside the sphere, its effect is equivalent to a dipole at the center pointing to the field direction, which we shall call x-direction, with its moment equal to

$$m=\frac{\varepsilon_1-\varepsilon}{\varepsilon_1+2\varepsilon}a^3E_0. \tag{10}$$

The potential outside the sphere is given by

$$V=-E_0x+\frac{m}{r^2}\cos\theta \tag{11}$$

where r is the distance between the dipole and the point P in question and θ is the angle between r and the x-direction. On the other hand the sphere is uniformly polarized with a modified field given by

$$F=\frac{3\varepsilon}{\varepsilon_1+2\varepsilon}E_0. \tag{12}$$

Outside the sphere the x-component of the field due to a dipole m is given by

$$\begin{aligned}F_x&=\left(-\frac{\partial V_m}{\partial r}\right)\cos\theta-\left(-\frac{1}{r}\frac{\partial V_m}{\partial\theta}\right)\sin\theta\\&=\frac{m}{r^3}(3\cos^2\theta-1)\end{aligned} \tag{13}$$

where V_m denotes the dipole potential given by the second term in the right-hand side of equation (11). The x-component of the induced moment in a volume element at P is

$$\begin{aligned}&\chi F_x r^2\sin\theta dr d\theta d\phi\\&=\frac{(\varepsilon-1)m}{4\pi r^3}(3\cos^2\theta-1)r^2\sin\theta dr d\theta d\phi\end{aligned} \tag{14}$$

where χ denotes the electric susceptibility or polarizability per unit volume. If we integrate (13) over θ from 0 to π, and over r from a to infinity, the integral over θ vanishes,

$$\int_0^\pi(3\cos^2\theta-1)\sin\theta d\theta=0 \tag{15}$$

while that over r becomes infinity.*

$$\int_a^\infty\frac{dr}{r}=\Big|\ln r\Big|_a^\infty. \tag{16}$$

From the physical point of view, it is unlikely that the effects of volume elements far from the center of the sphere are appreciable. Let us assume that the dipole field smaller than a certain value F_c can contribute to the induced moment only in a negligible magnitude. Since the dipole field is given by

$$\begin{aligned}F_m&=\left[\left(-\frac{\partial V_m}{\partial r}\right)^2+\left(-\frac{1}{r}\frac{\partial V_m}{\partial\theta}\right)^2\right]^{1/2}\\&=\frac{m}{r^3}(3\cos^2\theta+1)^{1/2}\end{aligned} \tag{17}$$

the integration over r should be extended to

$$b=\left(\frac{m}{F_c}\right)^{1/3}(3\cos^2\theta+1)^{1/6}. \tag{18}$$

Therefore the increase of moment due to the introduction of the sphere is

$$\begin{aligned}\Delta M_{\text{out}}&=\iiint\chi F_x r^2\sin\theta dr d\theta d\phi\\&=\iiint\frac{(\varepsilon-1)m}{4\pi r^3}(3\cos^2\theta-1)r^2\sin\theta dr d\theta d\phi\\&=\frac{\varepsilon-1}{2}m\int_0^\pi(3\cos^2\theta-1)\left[\int_a^b\frac{dr}{r}\right]\sin\theta d\theta.\end{aligned} \tag{19}$$

Owing to the logarithmic form of (16) and the relation (15), the constant b does not affect the integral. In other words the absolute value of the ambiguouly chosen F_c is not important. Then we have

$$\begin{aligned}\Delta M_{\text{out}}&=\frac{\varepsilon-1}{2}m\int_0^\pi(3\cos^2\theta-1)\frac{1}{6}\\&\qquad\times\ln(3\cos^2\theta+1)\sin\theta d\theta\\&=\frac{\varepsilon-1}{2}m\frac{1}{6}\int_{-1}^1(3x^2-1)\ln(3x^2+1)dx.\end{aligned} \tag{20}$$

The integration by parts gives

$$\begin{aligned}\Delta M_{\text{out}}&=-(\varepsilon-1)m\int_0^1\frac{x^4-x^2}{3x^2+1}dx\\&=-(\varepsilon-1)m\left|\frac{x^3}{9}-\frac{4x}{9}+\frac{4\sqrt{3}}{9\times3}\arctan\sqrt{3}\,x\right|_0^1\\&=\frac{\varepsilon-1}{3}m\left(1-\frac{4\pi}{9\sqrt{3}}\right)\\&=\frac{(\varepsilon_1-\varepsilon)(\varepsilon-1)}{3(\varepsilon_1+2\varepsilon)}ca^3E_0\end{aligned} \tag{21}$$

where

$$c=1-\frac{4\pi}{9\sqrt{3}}=0.1939. \tag{22}$$

(9) Cf. R. Becker, "Theorie der Elektrizität". I. Teubner, Leipzig and Berlin, 1933, p. 77.

* Higasi[10] in his theory of the solvent effect on dipole moments considered that the product of the two integrals vanishes.

(10) K. Higasi, *Sci. Pap. Inst. Phys. Chem. Research*, **28**, 284 (1936).

The increase of moment inside the sphere is obviously

$$\Delta M_{\text{in}}=\left(\frac{\varepsilon_1-1}{4\pi}F-\frac{\varepsilon-1}{4\pi}E_0\right)\frac{4\pi a^3}{3}$$
$$=\frac{(\varepsilon_1-\varepsilon)(2\varepsilon+1)}{3(\varepsilon_1+2\varepsilon)}a^3E_0. \quad (23)$$

Hence for $\Delta\nu$ such spheres far apart from each other, the increase of polarization is

$$\Delta P=(\Delta M_{\text{out}}+\Delta M_{\text{in}})\Delta\nu$$
$$=\frac{(\varepsilon_1-\varepsilon)[(2+c)\varepsilon+(1-c)]}{3(\varepsilon_1+2\varepsilon)}a^3E_0\Delta\nu. \quad (24)$$

The increase of the dielectric constant of the whole system is therefore

$$\Delta\varepsilon=\frac{4\pi\Delta P}{E_0}$$
$$=\frac{(\varepsilon_1-\varepsilon)[(2+c)\varepsilon+(1-c)]}{(\varepsilon_1+2\varepsilon)}\left(\frac{4\pi a^3}{3}\right)\Delta\nu. \quad (25)$$

By the removal of $\Delta\nu$ spheres of the initial dispersion of concentration ϕ, followed by substitution with the medium of disperse phase, we take out $\phi\Delta\nu$ particles on the average and add $\Delta\nu$ particles anew. Hence the increase in the number of particles of the disperse phase is

$$\Delta n=(1-\phi)\Delta\nu. \quad (26)$$

Combining these two equations, we have

$$\frac{\Delta\varepsilon}{\Delta n}=\frac{(\varepsilon_1-\varepsilon)[(2+c)\varepsilon+(1-c)]}{(\varepsilon_1+2\varepsilon)(1-\phi)}\left(\frac{4\pi a^3}{3}\right) \quad (27)$$

or

$$\frac{\varepsilon_1+2\varepsilon}{(\varepsilon_1-\varepsilon)[(2+c)\varepsilon+(1-c)]}d\varepsilon=\frac{d\phi}{1-\phi}, \quad (28)$$

Therefore

$$\int_{\varepsilon_0}^{\varepsilon}\frac{\varepsilon_1+2\varepsilon}{(\varepsilon_1-\varepsilon)[(2+c)\varepsilon+(1-c)]}d\varepsilon=\int_0^{\phi}\frac{d\phi}{1-\phi} \quad (29)$$

where ε_0 denotes the dielectric constant of the pure dispersion medium. The integration can be evaluated immediately and we have

$$\frac{3\varepsilon_1}{(2+c)\varepsilon_1+(1-c)}\log\frac{\varepsilon_1-\varepsilon}{\varepsilon_1-\varepsilon_0}$$
$$-\frac{(2+c)\varepsilon_1-2(1-c)}{[(2+c)\varepsilon_1+(1-c)](2+c)}\log\frac{(2+c)\varepsilon+(1-c)}{(2+c)\varepsilon_0+(1-c)}$$
$$=\log(1-\phi) \quad (30)$$

where the base of the logarithm may be either e or 10. This equation gives the relation between ε and ϕ, if ε_0 and ε_1 are known. It will be remarked that in this derivation the radius a of particles has been eliminated completely. Therefore the absolute value of the radius is trivial and the uniformity of the particle size is not a necessary condition for the derivation of this equation. For conducting particles we may put $\varepsilon_1=\infty$. Then we have

$$-\frac{1}{2+c}\log\frac{(2+c)\varepsilon+(1-c)}{(2+c)\varepsilon_0+(1-c)}=\log(1-\phi). \quad (31)$$

This relation is applicable to metal sols of spherical particles.

Equations in magnetostatics are similar in form to those in electrostatics. If magnetic permeabilities are approximately equal to unity, the second term of the left-hand side of the equation (30) vanishes. This condition is satisfied for dia- or paramagnetic solid powder in air. Then the following simple relation holds for the magnetic permeability μ

$$\frac{\mu_1-\mu}{\mu_1-\mu_0}=1-\phi. \quad (32)$$

That is, the magnetic permeability of a heterogeneous system changes linearly with the volume fraction. Linearity holds also between the magnetic susceptibility and the volume fraction. This relation is used for the measurement of the magnetic susceptibilities of solids by the powder method.

A comparison of the relation (30) with the Bruggeman's formula will be of interest. If we substitute E_0 in the first line of (23) by F, a procedure which is not justified of course, and let $\Delta M_{\text{out}}=0$ or $c=0$, we have

$$\frac{\varepsilon_1+2\varepsilon}{3\varepsilon(\varepsilon_1-\varepsilon)}d\varepsilon=\frac{d\phi}{1-\phi} \quad (33)$$

instead of (28). Integration gives

$$\log\frac{\varepsilon_1-\varepsilon}{\varepsilon_1-\varepsilon_0}-\frac{1}{3}\log\frac{\varepsilon}{\varepsilon_0}=\log(1-\phi) \quad (34)$$

which is identical with the Bruggeman's formula (8).

Though at first sight our theoretical formula and those by Wiener and Bruggeman seem to cover the whole volume fraction range from 0 to 1, the volume fraction of a disperse phase can never be higher than $\pi/3\sqrt{2}=74.0$ %. It is expected that these theories will become inadequate when the volume fraction approaches this limiting value.

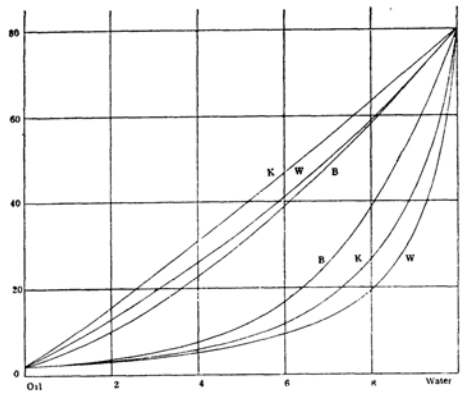

Fig. 1.—The dielectric constants of an oil-in-water type emulsion (upper three curves) and a water-in-oil type emulsion (lower three curves) after the theories of Wiener (W), Bruggeman (B) and the present writers (K)

As an example we have drawn in Figure 1 the dependence of dielectric constant upon the volume fraction for dispersions of water-in-oil and oil-in-water types, taking the dielectric constants of water and oil to be equal to 80 and 2 respectively. For comparison, curves from the formulas of Wiener and Bruggeman are also given. It will be seen that though the functional forms of the three theoretical formulas are entirely different, the curves are similar to each other in their general trend. Namely, the dielectric constant of an oil-in-water type emulsion is higher than that of the water-in-oil type emulsion of the same volume fraction. The curve for the oil-in-water type emulsion is slightly convex to the abscissa, while the deviation from linearity is considerable for the water-in-oil type emulsion. These theoretical conclusions are in conformity with experiments.[11] Most of the experiments which have hitherto been made[12] deal with dilute dipsersions, in which the disperse phase has higher dielectric constant than that of the dispersion medium. In this case the three theories give nearly coincident results. Up to the present, the Bruggeman's formula has been tested and is supposed to be fairly satisfactory. A quantitative comparison of the three theoretical formulas will be made in the succeeding paper.

Summary

The dielectric constant of the dispersion, in which spherical particles of dielectric constant ε_1 are dispersed in a medium of dielectric constant ε_0, has been worked out theoretically without employing Wiener's proportionality postulate. The following equation has been derived for the relation between the dielectric constant ε of the dispersion and the volume fraction ϕ of the disperse phase.

$$\frac{3\varepsilon_1}{(2+c)\varepsilon_1+(1-c)}\log\frac{\varepsilon_1-\varepsilon}{\varepsilon_1-\varepsilon_0} - \frac{(2+c)\varepsilon_1-2(1-c)}{[(2+c)\varepsilon_1+(1-c)](2+c)}\log\frac{(2+c)\varepsilon+(1-c)}{(2+c)\varepsilon_0+(1-c)} = \log(1-\phi)$$

where $c=1-4\pi/9\sqrt{3}$

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(11) R. Goto and N. Koizumi, loc. cit.

(12) A. Voet, loc. cit. F. Wachholtz and A. Franceson, *Kolloid-Z.*, **92**, 158 (1940); A. Piekara, ibid., **49**, 97 (1929); **58**, 283 (1932).