THE THEORY OF THE DIELECTRIC CONSTANT OF POLYDISPERSE EMULSIONS

By E. S. Rajagopal
(*Physics Department, Indian Institute of Science, Bangalore-3*)

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Abstract

The distortion of a homogeneous dielectric liquid sphere placed in a uniform electric field is investigated theoretically. The results agree with those of Thacher and O'Konski, obtained by a different procedure. The effect of this distortion on the static dielectric constant of polydisperse emulsions is considered and it is shown that the effect increases if the particle sizes are increased. The exact shape assumed by the liquid drop in the electric field is investigated and shown to be a surface of revolution of a higher transcendental curve.

1. Introduction

The dielectric constant of emulsions is one of the physical properties which could be easily measured. The electrostatic problem of evaluating the specific inductive capacity of a homogeneous fluid containing imbedded particles having an inductive capacity different from that of the dispersing medium (e.g., emulsions) has been solved by Rayleigh, Wiener, Bruggeman and others. Their results indicate (Kobo and Nakamura, 1953) that the static ("mixture" contribution) dielectric constant of the emulsion depends only on the total volume concentration of the dispersed phase and is independent of the size of the individual particles. Actual experiments, however, have shown a slight dependence of the dielectric constant on the size of the particles. Thacher (1952) suggested that this might be due to the distortion of the liquid droplets by the applied electric field. Assuming that the spherical droplets become prolate spheroids in the electric field, O'Konski and Thacher (1953) have discussed this effect for monodisperse systems. In view of the importance of the distortion of the spherical shape of the droplets by the electric fields in such phenomena like the birefringence of the emulsion in an electric field and the dielectric relaxation effects, the influence of an electric field on the shape of a perfect dielectric liquid sphere is studied *ab initio*. The results are applied to polydisperse emulsions, limiting the discussion to the "mixture" contribution to the dielectric constant, i.e., double layer effects are not considered.

2. Theoretical Considerations

It is known that an electric field sets up stresses in homogeneous dielectric media. Using the rationalised MKS units, the force on a dielectric substance, (Panofsky and Philips, 1955), can be written as

$$F_v = \nabla p = -\frac{\epsilon_0 E^2}{2} \nabla \epsilon + \frac{\epsilon_0}{2} \nabla \left(E^2 g \frac{d\epsilon}{dg} \right) \qquad (1)$$

where ϵ is the inductive capacity and g the density of the dielectric. For simplicity, consider an ideal dielectric body placed in free space, the physical boundary being at $x=a$. In order to calculate the pressure on the surface, one assumes as usual a smooth but rapid variation of the inductive capacity from $x=a$, into the body of the medium $x=b$. In such a case

$$\int_{p'}^{p} dp = \int_{a}^{b} \left[-\tfrac{1}{2} \epsilon_0 E^2 \frac{d\epsilon}{dx} + \tfrac{1}{2} \epsilon_0 \frac{d}{dx} \left(E^2 g \frac{d\epsilon}{dg} \right) \right] dx \qquad (2)$$

Since the tangential field E_t and the normal induction ϵE_n are continuous across the boundary, the first term on the right hand side is easily shown to be

$$-\tfrac{1}{2} \epsilon_0 (\epsilon - 1)(E_t^2 + \epsilon E_n^2)$$

If one assumes the Clausius-Mosotti relation,

$$[1/g](\epsilon - 1)/(\epsilon + 2) = \text{constant},$$

and notes that the outside medium is free space, the second term is found to be $\frac{1}{6} \epsilon_0 (\epsilon - 1)(\epsilon + 2) E^2$. It must be noted that the quantities E, E_n and E_t refer to the fields inside the dielectric while in free space the field is denoted by E_0. The pressure difference is then simplified into

$$p' - p = \tfrac{1}{6} \epsilon_0 (\epsilon - 1)^2 \{2 E_n^2 - E_t^2\} \qquad (3)$$

If the surface $x = a$ is at equilibrium, there must be an equal excess pressure acting on the surface from inside the body of the dielectric.

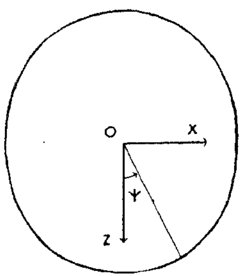

FIG. I

Polar diagram of the distorted particle. ψ is the polar angle.

Taking now a spherical liquid drop in a uniform electric field E_0 along the Z axis in free space, it is easily deduced that the particle will assume greater curvature along the Z-axis than in a perpendicular direction (X), i e., it will become prolate shaped with the major axis along Z Further, the figure must be a surface of revolution about the Z and X axes.

One can easily study the infinitesimal deformation of the spherical particle of radius a. Introducing polar co-ordinates (Fig. 1), the curvature $1/R$ in the plane of the figure is

$$\frac{1}{a}-\frac{1}{a^2}\cdot\frac{d^2r}{d\psi^2}$$

while the curvature $1/R$, in the transverse section is $1/a$. Further,

$$E_n = E\cos\psi\,;\quad E_t = E\,\mathrm{Sin}\,\psi.$$

So the equilibrium of the surface gives the relation

$$\gamma\left\{\frac{2}{a}-\frac{1}{a^2}\frac{d^2r}{d\psi^2}\right\} = p_0 + \tfrac{1}{6}\,\epsilon_0(\epsilon-1)^2E^2\left[2\cos^2\psi - \sin^2\psi\right] \tag{4}$$

where γ is the surface tension of the liquid in contact with the outside medium. Putting

$$\frac{a^2}{\gamma}\left[\frac{2\gamma}{a} - \tfrac{1}{12}\,\epsilon_0(\epsilon-1)^2E^2 - p_0\right] = \alpha\,;\quad \frac{\epsilon_0(\epsilon-1)^2E^2a^2}{4\gamma} = \beta \tag{5}$$

the equation becomes

$$\frac{d^2r}{d\psi^2} = \alpha - \beta\cos 2\psi \tag{6}$$

The solution is

$$r = A + B\psi + \tfrac{1}{2}\alpha\psi^2 + \tfrac{1}{4}\beta\cos 2\psi$$

But one must have (i) $r(+\psi)=r(-\psi)$ and (ii) $r(\pi-\psi)=r(\psi)$ and they give $B=0$ and $\alpha=0$. $\alpha=0$ implies that there is a small change in the mean pressure inside the system. Taking an actual example of a water droplet ($\epsilon=80$; $\gamma=70\times10^{-3}$ newtons/meter; $a=10^{-5}$ meter) in air, the fractional change in the pressure for $E_0=100$ KV/m is $<0.05\%$ and so can be completely neglected. But in emulsions where $\gamma \approx 1\times10^{-3}$ newtons/meter, this is appreciable. The solution of the equation (6) is, then,

$$r = a + \tfrac{1}{4}\beta - \tfrac{1}{2}\beta\sin^2\psi \tag{7}$$

since in the absence of an electric field $A=a$.

Comparing (7) with the equation of an ellipse of small eccentricity, viz. $r=a-\frac{1}{2}ae^2\sin^2\psi$, one sees that the particle, in the first order approximation does become a prolate spheroid, as was assumed by O'Konski and Thacher. The eccentricity is given by

$$e^2 = \frac{\beta}{a} = \frac{\epsilon_0(\epsilon-1)^2aE^2}{4\gamma} \tag{8}$$

Since the particles are nearly spherical $E = 3E_0/(\epsilon + 2)$ and so

$$e^2 = \frac{9\,\epsilon_0\,(\epsilon - 1)^2 a\,E_0^2}{4\,\gamma\,(\epsilon + 2)^2} \tag{9}$$

This is the result for a liquid drop in free space. Using the Wiener proportionality postulate, one can calculate the distortion of a drop of liquid of inductive capacity ϵ_1 in a medium of inductive capacity ϵ_2 as

$$e^2 = \frac{9\,\epsilon_2\,(\epsilon_1 - \epsilon_2)^2 a\,E_0^2}{4\,\gamma\,(\epsilon_1 + 2\epsilon_2)^2} \tag{10}$$

This is exactly the result obtained by O'Konski and Thacher (1953) by a variational procedure of minimising the free energy of the system.

For all practical purposes, the first order solution given above is sufficient. This has been experimentally verified by O'Konski and Gunther (1955). The exact solution of the problem is slightly complicated and is presented in the appendix. The generating curve becomes a higher transcendental curve which cannot be expressed in terms of the more elementary algebraic and trignometric functions.

3. Application to Polydisperse Emulsions

One can now calculate the effect of this distortion of the particles on the static dielectric constant of the emulsions. For perfectly spherical particles, the dielectric constant is independent of the size of the particle and depends only upon the total volume concentration of the dispersed phase. However, a spheroid of volume $\frac{4}{3}\,\pi\,R^3$ and of small eccentricity e will have an excess polarisation over the same volume of the dispersion medium and this excess is given by Thacher (1952),

$$\Delta\,P = 4\,\pi\,R^3 \cdot \frac{\epsilon_2\,(\epsilon_1 - \epsilon_2)\,E_0}{(\epsilon_1 + 2\,\epsilon_2)} \cdot \left\{1 + \tfrac{2}{5} \cdot \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + 2\,\epsilon_2} \cdot e^2\right\} \tag{11}$$

In the present case, the major axss from (7) is seen to be $a + \frac{1}{4}\beta = a(1 + \frac{1}{4}e^2)$ and so the volume is $4\pi a^3(1 - \frac{1}{4}e^2)$. This volume change has been neglected by Thacher and his expression leads to the result that the polarisation of the system has increased, even though, the particle has done work in the distortion against the surface tension forces. The excess polarisation is seen to be

$$\Delta P = 4\,\pi\,a^3 \cdot \frac{\epsilon_2(\epsilon_1 - \epsilon_2)\,E_0}{\epsilon_1 + 2\epsilon_2} \cdot \left\{1 + \frac{3\,(\epsilon_1 - 6\epsilon_2)}{20(\epsilon_1 + 2\epsilon_2)}\,e^2\right\}$$

or, substituting the value of e^2 from (10)

$$\Delta\,P = 4\,\pi\,a^3 \cdot \frac{\epsilon_2\,(\epsilon_1 - \epsilon_2)\,E_0}{\epsilon_1 + 2\,\epsilon_2} \cdot \left\{1 + \frac{27\,\epsilon_2\,(\epsilon_1 - 6\,\epsilon_2)\,(\epsilon_1 - \epsilon_2)^2}{80\,(\epsilon_1 + 2\,\epsilon_2)^3} \cdot \frac{E_0^2\,a}{\gamma}\right\} \tag{12}$$

In dilute emulsions, one can neglect the interactions among the various particles and the total excess polarisation is the sum of the excess polarisations of the various particles. The excess of the dielectric constant is then

$$\triangle K = \frac{\Sigma \triangle P}{E_0}$$

If all the particles are of the same size

$$\triangle K = 3\, C \cdot \frac{\epsilon_2 (\epsilon_1 - \epsilon_2)}{\epsilon_1 + 2\,\epsilon_2} \cdot \left\{ 1 + \frac{27\,\epsilon_2 (\epsilon_1 - 6\,\epsilon_2)(\epsilon_1 - \epsilon_2)^2}{80\,(\epsilon_1 + 2\,\epsilon_2)^3} \cdot \frac{E_0^2\, a}{\gamma} \right\} \quad (13)$$

where C is the volume concentration of the dispersed particles.

But in practical cases of emulsions, the particles are of various sizes. Experimental and theoretical studies (Rajagopal, to be published) show that these variations are well represented by the logarithmiconormal distribution

$$d n = \frac{n_0\, d x}{x \sigma \sqrt{(2\,\pi)}} \cdot \exp \left\{ - \frac{(\ln x - \ln \xi)^2}{2\,\sigma^2} \right\}$$

Here σ^2 is the variance of the distribution and $\ln \xi$ is the mean of the distribution of $\ln x$. One seas that the average value of x^n is $\langle x^n \rangle_{Av} = \xi^n \exp\,(n^2\sigma^2/2)$. In such an emulsion, on averaging the two terms of (11) one gets

$$\triangle K = 3\, C \cdot \frac{\epsilon_2 (\epsilon_1 - \epsilon_2)}{\epsilon_1 + 2\,\epsilon_2} \cdot \left\{ 1 + \frac{27\,\epsilon_2 (\epsilon_1 - 6\,\epsilon_2)\,\epsilon_1 - \epsilon_2)^2}{80\,(\epsilon_1 + 2\,\epsilon_2)^3} \cdot \frac{E_0^2}{\gamma} \cdot \xi \exp\left(\tfrac{7}{2}\,\sigma^2\right) \right\} \quad (14)$$

If we denote the mean size of the particle $\langle x \rangle_{Av}$ by $\langle a \rangle$ the term $\xi \exp\left(\tfrac{7}{2}\,\sigma^2\right)$ is $\langle a \rangle \exp\,(3\sigma^2)$.

The relation (14) shows that larger particles have geater effect on the dielectric constant of the system. This is quite natural since the distortion of the drop is increased, if the sizes of the particles are increased. The experimental evidence (O'Konski and Gunther, 1955; Pearce, 1955) agrees with these conclusions.

The particle size distribution will also affect the other phenomena where the distortion of the spherical drop by the electric field is significant.

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APPENDIX

The exact shape of the liquid particle in the electric field can be solved in a formal way. This is of interest in itself, since no exact solution of a three dimensional capillarity problem is known. The matter is treated at length by Bakker

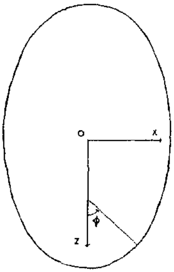

FIG. II
X-ϕ co-ordinate of the distorted particle. ϕ is the angle made by the normal with the Z axis.

(1928). Following Bakker, one uses x and ϕ as the co-ordinates of any point on the surface of revolution, (Fig. II) where ϕ is the angle made by the normal with the z axis. The

$$\frac{1}{R} = \frac{1}{\sin\phi} \cdot \frac{d\phi}{dx} \quad \text{and} \quad \frac{1}{R'} = \frac{\sin\phi}{x}$$

So the equilibrium of the surface gives the equation

$$\frac{1}{x} \cdot \frac{d(x\sin\phi)}{dx} = \lambda - \mu \sin^2\phi \tag{15}$$

where λ and μ are related to α and β of (6).

The substitution $x\sin\phi = y$ immediately shows that the equation is of the Riccati's form and that it cannot be solved fully in terms of the elementary (algebraic and trignometric) functions (Forsyth, 1948). Putting

$$\sin\phi = \frac{1}{\mu}\cdot\frac{1}{u}\cdot\frac{du}{dx}$$

the differential equation becomes

$$\frac{d^2u}{dx^2} + \frac{1}{x}\frac{du}{dx} - p^2 u = 0, \qquad (p^2 = \lambda\mu) \tag{16}$$

which is simply the Bessel equation of order zero in the argument ipx. The solution is, therefore

$$\sin\phi = \frac{1}{\mu}\cdot\frac{A_1 p I_1(px) - B_1 p K_1(px)}{A_1 I_0(px) + B_1 K_0(px)} \tag{17}$$

with the usual notation of the modified Bessel function of the first and the second kind (Menzel, 1955). Both K_1 and $K_0 \to \infty$ as $x \to 0$ while $I_1 \to 0$ and $I_0 \to 1$ in the same limit. From the nature of the problem $\sin\phi \to 0$ as $x \to 0$ and so $B_1 = 0$. The solution is thus

$$\sin\phi = \left(\frac{\lambda}{\mu}\right)^{\frac{1}{2}}\cdot\frac{I_1[x(\lambda\mu)^{\frac{1}{2}}]}{I_0[x(\lambda\mu)^{\frac{1}{2}}]} \tag{18}$$

The solution automatically satisfies the conditions of the problem that it must be symmetric about the X and Z axes. Sin ϕ increases from 0 to 1 as x increases from 0 to l (a particular constant depending upon λ and μ) after which ϕ is undefined. The curve is a higher transcendental curve and cannot be described in terms of the ordinary algebraic or trignometric functions.