

148. The Distortion of Electrically Conducting, Thermodynamically Stable Microphases by an Electric Field

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Summary

O'Konski's considerations regarding the distortion of spherical droplets by electric fields in binary two-phase systems has been extended to three-component water/surfactant/oil systems with so-called ultra-low interfacial tensions, *i.e.* spherically aqueous microphases. It is shown that the deformation is almost negligible for fields up to about $5 \cdot 10^5 \text{ Vm}^{-1}$ such as those applied in electro-optical *Kerr*-effect measurements with microemulsions if only perturbations of the mean orientation of the surfactants in the interface are considered.

Introduction. – In the last few years electro-optical *Kerr*-effect measurements were increasingly used [1] [2] [3] to supplement quasi-elastic light-scattering and rheological investigations on concentrated dispersions of thermodynamically stable aqueous microphases to obtain information on hydrodynamic properties of these particles. Various observations and suppositions were contradictory regarding the possible deformation of spherical microphases by electric fields. It appeared worthwhile, therefore, to study the question whether relatively weak electric fields could deform these spherical aqueous microphases and thus produce an additional intrinsic anisotropy of the sample.

Since a thermodynamically stable microphase ensemble, *i.e.* a so-called microemulsion, is characterized by rather low interfacial tensions, typically 10^{-3} to $10^{-2} \text{ mN m}^{-1}$ [4] [5] which are also attributed to single microphases (see below), one might believe that electric fields should considerably distort such entities.

The general problem regarding deformation of droplets by external forces operating against the effect of interfacial tension has been considered by *C. T. O'Konski* and coworkers [6] [7] with respect to binary, two-phase systems. These systems are characterized by interfaces with well-defined, finite, interfacial tensions. In particular, these authors could demonstrate that a droplet is elongated in the direction of the electric field whether its dielectric constant is greater or less than that of the surrounding medium if the latter can be considered a perfect dielectric.

Contrary to the above-mentioned systems, thermodynamically stable microemulsions are made of, at least, three components, *i.e.* oil (O), water (W) and

surfactant. These particular dispersions are characterized by an almost complete accumulation of the surfactant molecules in the O/W-interface. The monolayer of these amphiphilic molecules is responsible for the depression of the interfacial tension. The maintenance of this, sometimes called ‘ultra-low’ interfacial tension, is (in the presence of ionic surfactants) due to a sensitive balance [8] [9] between two interfacial free energy contributions, *i.e.* $\gamma_{\text{uncharged}}$ which corresponds to the surfactant if no electrical double layer has been formed under otherwise constant composition and $\gamma_{\text{electrostatic}}$ which comprises the long-range *Coulombic* contributions. Moreover, experimental evidence has been presented [10] [11] that steric accommodation of the surfactants, particularly with respect to the aqueous phase, is essential to achieve the lowest possible free interfacial energy of the system. Since all surfactant molecules possess more or less pronounced dipole moments it is to be expected that an electric field will affect this balance and accordingly increase the interfacial tension by changing the optimum orientation of the surfactants towards the interface. The following considerations are, therefore, believed to be generally valid with respect to so-called microemulsions.

The present paper is concerned explicitly with the field-dependent perturbation of this optimum mean orientation of the surfactant molecules in the O/W-interface, *i.e.* exclusively with orientational motions of the molecules at fixed positions. This effect will precede a real change of the interfacial surfactant concentration. The latter would give rise to the *Gibbs-Marangoni* effect [12], *i.e.* an interfacial mass flow counteracting the surface free energy gradient. The just mentioned change of the average orientation of the surfactants with respect to the O/W-interface by the electric field will prove to be sufficient to produce a relatively large effect if the above-mentioned very low interfacial tensions are considered.

Hence, the final goal will be to calculate an ‘effective’ interfacial surfactant concentration which depends on the (directing) field at the interface and to introduce the corresponding field dependent interfacial tension into *O’Konski’s* equations which relate the eccentricity with field strength, droplet radius, and interfacial tension.

Theoretical Considerations. – At any point on the spherical W/O-interface covered with an (equilibrium) surfactant concentration $\bar{\Gamma}$ the electric (directing) field E produces an angular flux of dipole axes (which are thought to be fixed within the surfactant molecules), *i.e.*

$$j_E = -\Gamma(\theta) \frac{D_r}{kT} \mu E \sin \theta \quad (1)$$

where θ denotes the angle between E and the average equilibrium orientation of a surfactant dipole (μ), D_r the rotational diffusion coefficient, D_r/kT the angular mobility due to the momentum of force, $\mu E \sin \theta$.

This force is counterbalanced by a rotational diffusion flux according to *Fick’s* law. Hence, the equilibrium condition reads

$$D_r \nabla^2 \Gamma(\theta) - \text{div } j_E = 0 \quad (2)$$

which (in spherical coordinates) can be rewritten in a second-order homogeneous differential equation

$$\frac{d^2\Gamma}{d\theta^2} + \frac{\mu E}{kT} \operatorname{tg} \theta \frac{d\Gamma}{d\theta} + 2 \frac{\mu E}{kT} \Gamma = 0. \quad (3)$$

With the help of the relations

$$\Gamma(\theta) = y(x) \quad \text{and} \quad \sin \theta = 2x - 1$$

Equation 3 can be transformed into a *Gaussian* or hypergeometric differential equation [13], i.e.

$$x(1-x) \cdot y'' + \left\{ \frac{1-A}{2} - (1-A)x \right\} \cdot y' + 2A y = 0 \quad (4)$$

with $A = \mu E/kT$ and y', y'' the first and second derivatives of y with respect to x .

One particular integral of *Equation 4* is the hypergeometric series

$$y = 1 + \frac{ab}{1!c} x + \frac{a(a+1)b(b+1)}{2!c(c+1)} x^2 + \dots \quad (5)$$

which is convergent for $x < 1$ if c is no negative integer or zero. It will be seen that the series (*Eqn. 5*) converges even for $x = 1$ in the present case since $a + b < c$. The values of the parameters a , b and c can be obtained by comparing *Equation 4* with the normal form of the hypergeometric differential equation (see, e.g. [14]).

Hence,

$$a + b = -A, \quad ab = -2A, \quad c = \frac{1-A}{2}. \quad (6)$$

Since $A \ll 1$ under the prevailing physical situation, a is taken approximately to be $\sqrt{2A} - A/2$, $b \approx \sqrt{2A} - A/2$ and $c = (1-A)/2$. These values fulfil simultaneously the above-mentioned condition, $a + b < c$.

Inserting the relations (*Eqn. 6*) into *Equation 5* and re-transformation of y and x into the original variables, yields

$$\frac{\Gamma(\theta, E)}{\bar{\Gamma}} = 1 - 2 \frac{\mu E}{kT} (1 + \sin \theta) - \frac{1}{3} \frac{\mu E}{kT} (1 - 2 \frac{\mu E}{kT}) (1 + \sin \theta)^2 - \dots \quad (7)$$

Equation 7 suggests to interpret the right hand side as an activity coefficient of the interfacial surfactant concentration which is dependent upon the electric field and the angle between the mean equilibrium position of a surfactant molecule in the interface and the direction of the field.

The series converges relatively rapidly, thus the fourth term contributes only a small correction. Averaging the effect of the electric field over the whole spherical droplet yields the ‘effective’ interfacial concentration in the presence of a field, *i.e.*

$$\langle \Gamma \rangle \approx \bar{\Gamma} \left\{ 1 - 5 \frac{\mu E}{kT} \right\} \quad (8)$$

This may be introduced into *Gibbs’* adsorption isotherm relation which yields the ‘effective’ interfacial tension $\langle \gamma \rangle$, *i.e.*

$$\langle \gamma \rangle - \gamma_0 = -RT \cdot \bar{\Gamma} \cdot \left\{ 1 - 5 \frac{\mu E}{kT} \right\} \ln \frac{c}{c_0} \quad (9)$$

where it is assumed that the ratio c/c_0 is not changed (c_0 being the bulk concentration of solute corresponding to γ_0). Considering this assumption it is easily possible to obtain an upper limit of the expected increase of the interfacial tension. Hence, taking as an example the well-known AOT molecule (sodium di(2-ethylhexyl)-sulfosuccinate) which has a dipole moment of about 6 D [15] and $E \approx 4 \cdot 10^5 \text{ V m}^{-1}$, the value within the braces in *Equation 9* amounts to about 0.99. Thus the interfacial tension might increase (with varying field strengths) between about 0.1–0.5 mN m^{-1} .

Adopting now *O’Konski’s* approximation [6] to calculate the electric field-produced eccentricity (e) of a spherical conducting microphase with radius (R) dispersed in a medium with dielectric constant (ϵ_{medium}), one obtains

$$e_{\text{microphase}} \approx \frac{3}{2} E (\epsilon_{\text{medium}} R / \langle \gamma \rangle)^{1/2} \quad (10)$$

and considering the above $\langle \gamma \rangle$ -values, the eccentricity is expected to be in the range between 0.035 and 0.077 which corresponds to the ratios of the semi-axes, *i.e.* 1.0006 and 1.0030, respectively. Thus the deviation from a spherical shape are quite small for the field strengths applied.

Discussion. – From the above considerations it appears that the large deformation predicted from the low interfacial tensions of the thermodynamically stable microphases by formal application of *O’Konski’s* results does not lead to the correct answer regarding the distortion of the spherical droplets. This conclusion is in agreement with experimental findings by *Rouvier et al.* [1]. Accordingly, the strong increase in the relaxation time with temperature in electro-optical *Kerr-effect* measurements cannot be attributed to a particle deformation.

A strong hint as to the essential contribution of the dipolar interfacial surfactant layer to the over-all polarization is seen in the observation of *Kerr*-effects with non-ionic surfactants [16].

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