140. On Negative Birefringence in Water-in-Oil Microemulsions

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The occurrence of a negative birefringence in water-in-oil (W/O) microemulsions has been substantiated and analyzed. The analysis is based on the well-established aqueous nanodroplet model of W/O microemulsions. In the particularly investigated water/sodium bis(2-ethylhexyl)sulfosuccinate (AOT)/aliphatic oil systems, the AOT monolayer exhibits a negative induced intrinsic birefringence, which is brought about by the pronounced polarizability of the alkyl moiety of the AOT molecule approximately perpendicular to the direction of its permanent dipole moment.

Introduction. – The three-component system H_2O/AOT (= sodium bis(2-ethylhexyl)sulfosuccinate)/oil forms, in a certain range of composition and temperature, thermodynamically stable microemulsions consisting of *nano*meter-sized H_2O *droplets* dispersed in oil and covered by a monomolecular layer of surfactant (= AOT) (for a review, see *e.g.* [1]). The nanodroplet radius, controlled by the ratio $w_0 = [H_2O]/[AOT]$, has values typically between 2 and 10 nm. The nanodroplets are spherically symmetric and rather monodisperse, as has been established both experimentally and theoretically [2] [3]. Furthermore, it has been shown that the nanodroplets have no permanent dipole moment [4]. These systems are good models for so-called one component macrofluids [5].

Occasionally, negative *Kerr* constants for water in oil microemulsions have been observed (see *e.g.* [6]). This behaviour is rather unexpected and can only be explained if the internal structure of the nanodroplets is taken into account. In this communication, we present a thorough investigation of the negative birefringence in the H_2O/AOT/oil system. In contrast to earlier investigations [7] [8], we are concerned with *non*-percolative one-phase microemulsion domains. The *Kerr* effect in the percolation regime is due to an entirely different mechanism, and is larger by several orders of magnitude.

The general formula for induced electric birefringence was derived by *Peterlin* and *Stuart* [9]. If we restrict ourselves to the case that the nanodroplets possess *no permanent dipole moment* and that they are *uniaxial ellipsoids* (or spheroids), we obtain the following formula:

$$\mathrm{K}_{\mathrm{sp}} = \frac{\Delta n}{c_{\mathrm{g}} n E^2} = \frac{2\pi V}{15 n^2 kT} (\mathrm{g}_1 - \mathrm{g}_2)(\mathrm{g}_{1,\mathrm{el}} - \mathrm{g}_{2,\mathrm{el}}) \tag{1}$$

where

$$\mathrm{g}_1 - \mathrm{g}_2 = \frac{4\pi(n_1^2 - n_2^2) - \{(n_1^2 - n_{\mathrm{m}}^2)(n_2^2 - n_{\mathrm{m}}^2)\ (\mathrm{L}_1 - \mathrm{L}_2)/n_{\mathrm{m}}^2\}}{[4\pi + \{(n_1^2 - n_{\mathrm{m}}^2)/n_{\mathrm{m}}^2\} - \mathrm{L}_1][4\pi + \{(n_2^2 - n_{\mathrm{m}}^2)/n_{\mathrm{m}}^2\} - \mathrm{L}_2]} = \frac{\mathrm{R} - \mathrm{S}}{N} \tag{2}$$

An analogous expression for $\mathrm{g}_{1,\mathrm{el}} - \mathrm{g}_{2,\mathrm{el}}$ is obtained by replacing n^2 by ε in *Eqn. 2*. K_{sp} is the specific *Kerr* constant, Δn the birefringence, c_{g} the concentration in mass per volume, E

the electrical field strength, V the volume of the nanodroplet causing the birefringence, n the refractive index of the solution, n_m that of the dispersion medium, n_1 and n_2 are the refractive indices of the particle along and perpendicular to its symmetry axis and L_1, L_2 are the form factors of the uniaxial ellipsoid [10].

The birefringence is composed of two contributions: the intrinsic (R) and the form birefringence (S). From inspection of *Eqn. 2*, we come to the following conclusions [11]: *i)* In the optical matching regime [12], where the mean refractive index of the nanodroplet ($(n_1 + 2n_2)/3$) equals the refractive index of the dispersion medium (n_m), the form birefringence is negligible compared to the intrinsic birefringence. *ii)* Pure form birefringence (*i.e.* $n_1 = n_2$) is always positive, (except if prolate/oblate ellipsoids have dipole moments in the direction of the short axis).

Experimental. – The purification of the chemicals and the preparation of the microemulsions were described in [13] and the *Kerr* effect apparatus in [14]. Electric field strengths up to $7 \cdot 10^5$ Vm^{-1} were applied.

Results. – The specific *Kerr* constants of H_2O/AOT/isooctane (2,2,4-trimethylpentane) and H_2O/AOT/hexane microemulsions were determined as a function of w_0 and concentration c_g = mass of (H_2O + AOT) per volume of solution. These systems show a pronounced aggregation tendency; hence, to study the birefringence contribution of single nanodroplets, the concentration dependence of the specific *Kerr* constant was measured and extrapolated to *zero* concentration for each w_0. Also, we normalize the birefringence with respect to the concentration of nanodroplets (*i.e.* $\Delta n/(nE^2c_{nd})$) rather than to the mass per volume concentration c_g of the solute (*i.e.* K_{sp}), which is more meaningful for the following discussion. The conversion of c_g into c_{nd} can easily be carried out. The radius of the aqueous core of the nanodroplets is

$$\mathrm{R} = \frac{3w_0 V_m}{N_A f_{AOT}(w_0)} = 9 \cdot 10^{-29}\,\mathrm{m}^3 \frac{w_0}{f_{AOT}(w_0)} \tag{3}$$

where f_{AOT} (w_0) is the equilibrium area of the H_2O/oil interface covered by one AOT molecule. V_m is the molar volume of H_2O and N_A *Avogadro*'s constant.

The surface of a spherical nanodroplet is $s = 4\pi R^2$ and the number z of AOT molecules in the nanodroplet's monolayer is

$$z = \frac{s}{f_{AOT}(w_0)} = \frac{36\pi^2 V_m^2 w_0^2}{N_A^2 f_{AOT}^3(w_0)} \tag{4}$$

The relation between the AOT concentration, c_{AOT}, and the concentrations c_{nd} of the nanodroplet, or c_g is

$$c_{nd} = \frac{c_{AOT}}{z}, \qquad c_g = c_{AOT}\,(M_{AOT} + w_0\,M_{H_2O}) \tag{5}$$

where M_{AOT} and M_{H_2O} are molar masses. Hence, from *Eqns. 4* and *5* we obtain

$$c_{nd} = c_g \frac{N_A^2 f_{AOT}^3(w_0)}{36\pi^2 V_m^2 w_0^2 (M_{AOT} + w_0 M_{H_2O})} \tag{6}$$

A functional relationship between f_{AOT} and w_0 which simulates the data obtained from the numerical integration of the *Poisson-Boltzmann* equation [3] is

$$f_{AOT}(w_0) = \alpha - \beta \exp(-\gamma \sqrt{w_0}), \tag{7}$$

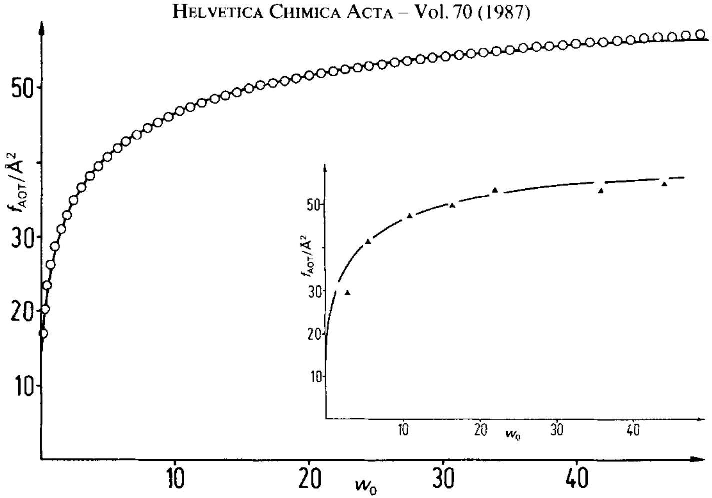

Fig. 1. *Numerical solution of the* Poisson-Boltzmann *equation* (○). Solid line has been calculated due to a further approximation according to *Eqn. 7*. Inset: experimental data (▲) compared with *Eqn. 7*.

with $\alpha = 5.96 \cdot 10^{-19}$ m², $\beta = 4.68 \cdot 10^{-19}$ m², and $\gamma = 0.401$, it fits the original plot for $0 < w_0 < 50$ rather well within 0.5% error (see *Fig. 1*). *Eqn. 7* is nicely confirmed by experimental results [15], as seen from the insert of *Fig. 1*.

With the help of *Eqn. 7*, we arrive at a simple relation between $\Delta n/(nE^2c_{nd})$ and the specific *Kerr* constant K_{sp}.

$$\left(\frac{\Delta n}{nE^2 c_{nd}}\right)_{c_{nd} \to 0} = (K_{sp})_{c_{nd} \to 0}\, \xi\,(w_0) \tag{8}$$

where function $\xi\,(w_0)$ is completely known. *Eqn. 8* permits us, to calculate $\{\Delta n/(nE^2c_{nd})\}_{c_{nd} \to 0}$ *via* an extrapolation of the experimental values of K_{sp} towards $(K_{sp})_{c_{nd} \to 0}$, *i.e.* the birefringence contribution due to individual nanodroplets.

Fig. 2 displays the experimental data (processed in this way) as a function of w_0 for microemulsions with isooctane and hexane as dispersion media, respectively. The most

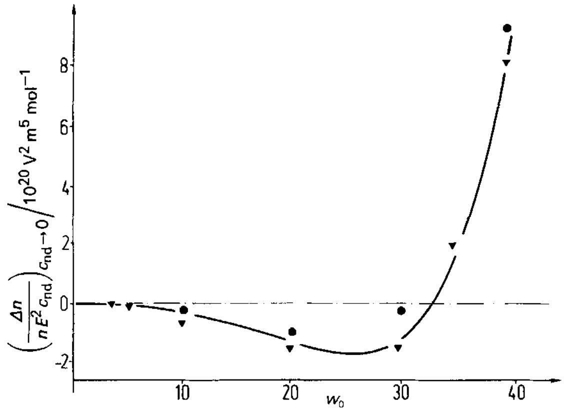

Fig. 2. *Specific* Kerr *constant per nanodroplet* (see text) *against* $w_0 = [H_2O]/[AOT]$; $H_2O/AOT/$*aliphatic oil*; (▼): *isooctane*; (●): *hexane*. Solide curve has been calculated for the isooctane system according to *Eqn. 12*.

obvious finding concerns the index of refraction of the dispersion medium which does not seem to affect the plot, *i.e.* the change of sign of the birefringence occurs at practically the same w_0 for both dispersion media.

To prove unambiguously that the observed birefringence is not due to form birefringence, one may suitably discuss the dependence of the refractive-index increment (dn/dc) of the microemulsions on w_0, or $\Phi^*_{H_2O}$. $\Phi^*_{H_2O}$ is the volume fraction of H_2O in the nanodroplet phase with composition $\Phi^*_{AOT} + \Phi^*_{H_2O} = 1$. This implies that the total amount of H_2O added to the system is assumed to be confined in the nanodroplets, which are covered by a monomolecular layer of AOT molecules. Likewise, all of the AOT molecules are thought to be accumulated in the H_2O/oil interface. These assumptions are sufficiently supported by experiments (see *e.g.* [1] for an overview). $\Phi^*_{H_2O}$ and w_0 are related by $\Phi^*_{H_2O} = M_{H_2O}w_0/(M_{H_2O}w_0 + M_{AOT})$, where M_{H_2O} and M_{AOT} are the molar masses of H_2O and AOT (the densities of these components are taken to have approximately the same value (difference about 10%)), respectively. The refractive-index increment is proportional to the difference of the refractive indices of the nanodroplets and the dispersion medium.

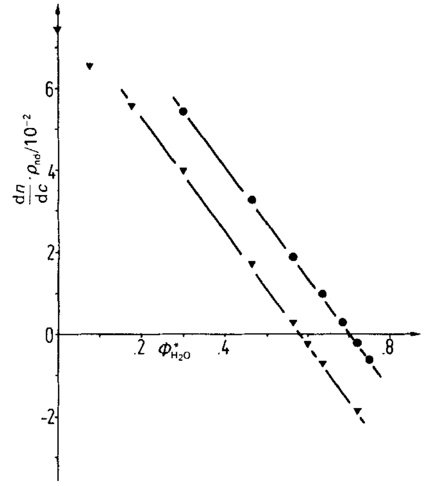

Fig. 3. *Refractive-index increment* ($\rho_{nd} \approx 1$ gcm^{-3}) *against H_2O content of nanodroplets* ($\Phi^*_{H_2O}$). H_2O/AOT/aliphatic oil, (▼): isooctane; (●): hexane; $T = 298$ K.

In *Fig. 3*, the refractive-index increment is plotted against $\Phi^*_{H_2O}$. The plot displays two parallel straight lines, one for isooctane, the other for hexane as dispersion media. (At small amounts of H_2O (*i.e.* $w_0 = [H_2O]/[AOT] < 6$, corresponding to $\Phi^*_{H_2O} < 0.25$), deviations from straight lines are observed.) An interpretation of the slopes (above $w_0 = 6$) of these lines and of their intercepts can be given if the formula of *Arago-Biot* [16] is adopted, *i.e.*

$$n = \sum_i \Phi_i n_i \qquad (9)$$

This relationship assumes that the total refractive index (n) of the mixture is the sum of the refractive indices of its components weighted by their respective volume fractions (Φ_i). This ansatz is strictly valid for a gas mixture, however, it is also useful as a first-order approximation in the present case. By taking *Eqn. 9* and introducing $\Phi^*_{H_2O}$, one obtains *Eqn. 10*, after having converted Φ into volume concentration c ($\Phi = c/\rho, \rho$ = density).

$$(\mathrm{d}n/\mathrm{d}c)\rho_{nd} = (n_{H_2O} - n_{AOT})\Phi^*_{H_2O} + n_{AOT} - n_{Oil} \qquad (10)$$

The observation of constant slopes, independent of the dispersion medium is reflected by *Eqn. 10*. Hence, one has to conclude that the refractive-index difference of $n_{H_2O} - n_{AOT}$ is independent of the dispersion medium, *i.e.* the structure of the AOT monolayer stays the same. The deviations from constant slopes at low amounts of H_2O indicate a violation of the additivity rule for the refractive indices of H_2O and AOT. This is to be expected since for low amounts of solubilized H_2O the strong hydration effects between Na^+ ions and H_2O control the refractive-index increment (hydration number of Na^+ is 5 ± 1 [17]).

The most important finding in relation to *Fig. 3* is the observation of a pronounced (positive) electrical birefringence (Δn) in the H_2O/AOT/hexane system at the particular composition (and temperature), where $(dn/dc) = 0$, *i.e.* where the refractive index of the particle equals that of the dispersion medium. (Incidentally, in the H_2O/AOT/isooctane mixture (dn/dc) and Δn vanish simultaneously). This situation is represented in *Fig. 2*, where data points of the H_2O/AOT/hexane and H_2O/AOT/isooctane systems are plotted in a $\{\Delta n/(nE^2c_{nd})\}_{c_{nd}\to 0}$ *vs.* w_0 diagram. As has been pointed out in the introduction, the occurrence of induced birefringence in the optical matching regime proves unambiguously that the observed birefringence is entirely intrinsic. This refers to the positive birefringence at $w_0 = 55$.

We also mentioned in the *Introduction* that induced negative birefringence is always intrinsic. This case is encountered in the w_0 range from 0 to 32. Thus, we can safely assume that the observed induced birefringence is of intrinsic nature within the whole range from $w_0 = 0$ to 55.

Discussion. – Finally, we propose a physical model which predicts a functional relationship between $\{\Delta n/(nE^2c_{nd})\}_{c_{nd}\to 0}$ and w_0 (or R, the radius of the nanodroplet), as shown in *Fig. 2*. The birefringence is proportional to the optical and electrical polarizabilities, and hence to α^2, since both polarizabilities are, in general, mutually proportional; also, α is proportional to the respective volume. In view of the structure of the nanodroplet, two contributions to the birefringence are to be anticipated: *i)* from the aqueous core and *ii)* from the surfactant monolayer of the droplet. Accordingly, we put

$$V_{H_2O} = \frac{4\pi}{3}R^3$$

$$V_{AOT} = \frac{4\pi}{3}\{(R+d)^3 - R^3\} \tag{11}$$

where d is the thickness of the AOT layer. Hence, we make the ansatz

$$\left(\frac{\Delta n}{nE^2c_{nd}}\right)_{c_{nd}\to 0} = a\{4\pi R^3/3\}^2 + b\{4\pi[(R+d)^3 - R^3]/3\}^2 \tag{12}$$

a and b of *Eqn. 12* are adjustable parameters describing the response of the aqueous core and the surfactant monolayer to an electric field. The plot in *Fig. 2* has been calculated according to *Eqn. 12* with $a = 1.9\ 10^{29}\ V^{-2}\cdot m^5\cdot mol^{-1}$ and $b = -1.6\ 10^{29}\ V^{-2}\cdot m^5\cdot mol^{-1}$. The values of a and b suggest that the electric field induces positive birefringence in the aqueous core and negative birefringence within the surfactant layer. The particles become optically anisotropic due to partial orientation of the surfactant and H_2O molecules by the electric field. The occurrence of a negative birefringence is indeed unusual and caused by the permanent dipole moment of the AOT molecule [18]. In particular, it has to be

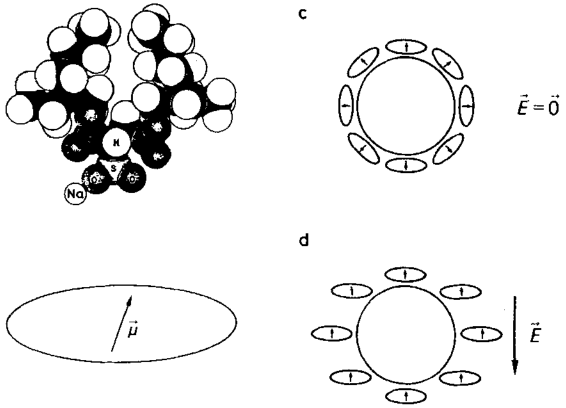

Fig. 4. a) *AOT-molecule;* b) *schematic representation of the dipole moment and the ellipsoid of polarizabilities of the AOT molecule; configuration of the nanodroplet without* c) *and with* d) *electric field*

assumed that the polarizability of the ellipsoidally shaped apolar moiety is approximately perpendicular to the symmetry axis of the AOT molecule (which is thought to have the shape of a truncated cone, see *Fig. 4*) and thus contributes the largest instantaneous moment. The permanent dipole moment of the AOT molecule coincides to a reasonable approximation with its symmetry axis. *Fig. 4* illustrates rather schematically the proposed mechanism.

The relaxation time for the buildup and decay of the induced birefringence is shorter than the resolution time of the apparatus, which is 50 ns. This time is much longer than the rotational diffusion times of molecules, but much shorter than the rotational diffusion time of the nanophases. Our view of molecular orientations in the core and surfactant monolayer is, thus, further supported.

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