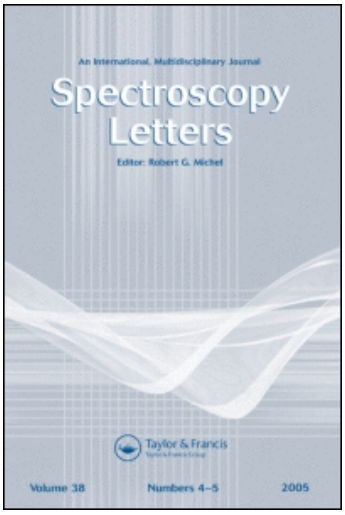

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FIELD EFFECTS IN CONDENSED MEDIA ON POLARIZED ABSORPTION

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The existence of anisotropic local field perturbation on electronic absorption is proved by non-zero linear dichroism of isotropic chromophores ($Mo(CO)_6$) in anisotropic environment. Two sources of such effects are possible: a) perturbation of the electronic energy levels in the chromophore by the static electric solvent field (= Stark effect) or, in case of anisotropic polarizable or dipolar molecules, similar effects involving molecular orientation, and b) dielectric effects on the effective radiation field. The latter effect was considered by various models: The Lorentz field model predicts an effect with wrong sign, it also yields too large a magitude if the anisotropy of the field is considered. If no local field correction is made and the anisotropy only operates in the radiation intensity a result more in agreement with experiment is obtained. By using the Onsager-Böttcher model one may take into account specific properties of the absorbing molecule, like anisotropy in α/r^3 where α is its polarizability and r its Onsager radius.

As a consequence of technical development of photometry it is now possible to study weak polarized absorptions in an in other respects strongly anisotropic system. We now ask to which extent the anisotropic local field perturbs the true absorption intensity differently in different directions. In practice no attempt has yet been made to make a sound analysis of this problem, which is probably just due to the difficulty in experimentally proving the existence of such effects by distinguishing them from dichroism due to orientation of anisotropic chromophores (microscopic dichroism). The fact

that it is common practice to ignore local field problems in other simpler connections (usual absorption) has not directly encouraged people to work on these special problems.

We first suggested the differential solvent effect for circular dichroism in the case of a cubic non-coordinating chromophore in a chiral solvent.[1,2] If the absorption were modulated by the well-known Lorentz factor $(n^2+2)^2/9n$, the absorptions for left and right circularly polarized light should formally differ according to

$$CD = A_l - A_r = \left[\frac{(n_l+2)^2}{9n_l} - \frac{(n_r+2)^2}{9n_r} \right] A_o \qquad (1)$$

in a solution of the inactive chromophore at absorption A_o. The difference between n_l and n_r (circular birefringence) was implied by the optical activity of the solvent ($\alpha = \pi d(n_l-n_r)/\lambda$ radians for a d cm optical path at wavelength λ cm). Even if no Lorentz field was surmized the macroscopic absorption should be modulated by $1/n$, hence yielding an absorption differential, $A_l-A_r = (1/n_l-1/n_r)A_o$. It was quickly realized that the effect had neither theoretical nor practical importance in circular dichroism due to the low magnitude of the circular birefringence (generally less than 10^{-5}- however, in cholesteric solvents birefringences as large as 0.05 are common and such a macroscopic differential field absorption could be important.[3])

If we apply the same reasoning to linearly anisotropic systems (non-cubic crystals, stretched polymers, macroscopically aligned nematic liquid crystals, and so on) we formally expect a corresponding linear dichroism due to linear birefringence,

$$\Delta n = n_{||} - n_{\perp}.$$

Let us use an uni-axial crystal (or oriented nematic liquid crystal) as a model system. The familiar Clausius-Mossotti (or perhaps Poisson-Mossotti-Clausius-Lampa-Lorenz-Lorentz) equation

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi N}{3} \alpha \qquad (2)$$

(where ε is the static electric permittivity, N the number of molecules per unit volume and α an effective molecular polarizability) is by definition (the spherical Lorentz field) only valid for isotropic liquids. A number of more of less sophisticated "adjusted" Clausius-Mossotti equations may be distinguished.

One of the first attempts to derive a generalized Clausius-Mossotti equation was made by Neugebauer [4] (the first attempts in this direction can probably be assigned to van Santen [5] and Slater [6]) who obtained for the permittivity, ε_X, along the principal dielectric Cartesian crystal axis X

$$\frac{\varepsilon_X - 1}{\varepsilon_X + 2} = \frac{4\pi N\beta_X}{3} \qquad (3)$$

where an "apparent polarizability"

$$\beta_X = [A_X + (\alpha_{YY}\alpha_{ZZ} - \alpha_{YZ}^2)/|\alpha_{IK}|]^{-1},$$

contained the effect of the crystal structure (represented by A_X) as well as the effect of the anisotropy of the molecules (by elements of the molecular polarizability tensor). Neugebauer assumed that the principal axes, XYZ, of the crystal coincided with the molecular axes, xyz.

Some years later Vuks (obviously unaware of Neugebauer) [7] made another correction of the isotropic CM equation:

$$\frac{\varepsilon_i - 1}{\bar{\varepsilon} + 2} = \frac{4}{3}\pi N\alpha_i \qquad i = X,Y,Z \qquad (4)$$

α_i may represent the polarizability of an individual molecule (or rather its component along the principal polarization direction, i, of the crystal). Note that the permittivity in the denominator is the average $\bar{\varepsilon} = (\varepsilon_X + \varepsilon_Y + \varepsilon_Z)/3$, which makes the form of the equation different from that of Neugebauer. Vuks further showed (for optical frequencies $n_i^2 = \varepsilon_i$) that his equation gives more reasonable molecular polarizabilities α_{xx}, α_{yy}, α_{zz} on naphtalene and anthracene from measured crystal refractive indices n_X, n_Y, n_Z, than did the isotropic CM equation. Though the Vuks equation was rather tentatively derived, as compared to the Neugebauer equation, it is "the right one" in our opinion.

A number of departures from the rule that nematic liquid crystals with positive dielectric anisotropy are expected to be oriented by electric fields with the long molecular axes parallel to the field, and vice versa, encouraged Dunmur [8] to use a simple tetragonal lattice to descirbe the anisotropic local field in such systems. He obtained the following generalized CM equation (cf. Ewald [9])

$$\frac{\varepsilon_{ii} - 1}{1 + L_{ii}(\varepsilon_{ii} - 1)} = 4\pi N\alpha_{ii} \qquad (5)$$

when α_{ii} is the effective polarizability per molecule in the $\underline{i}$ direction. L_{ii} is the Lorentz factor tensor which is diagonal with respect to the principal axes, its trace is unity. For uniaxial crystals two elements are equal, so $L_{XX} = 1/2(1 - L_{ZZ})$. In the case of isotropy $L_{XX} = L_{YY} = L_{ZZ} = 1/3$, and we have the usual CM equation. The L_{ii} values have been tabulated for different unit cell dimensions [10] (by Dunmur for the different cell dimension ratios $l_Z/l_Y = l_Z/l_X$)[8]. As a possible explanation for the experimental observations Dunmur claimed the trivial fact that adopting fixed molecular polarizabilities and cell dimensions the dielectric anisotropy $\varepsilon_{ZZ} - \varepsilon_{YY} = n_{ZZ}^2 - n_{YY}^2 = \Delta n(n_{ZZ} + n_{YY})$ as calculated from the CM equation, changed sign at a certain mean permittivity $\varepsilon = (\varepsilon_{ZZ} + 2\varepsilon_{XX})/3$. It may be observed that the equations of Neugebauer and Dunmur are equivalent and can be written

$$\frac{\varepsilon_i - 1}{(\varepsilon_i + 2) + (3L_i - 1)(\varepsilon_i - 1)} = 4\pi N\alpha_i/3 \qquad (6)$$

In the Neugebauer version $3L_Z - 1 = 2 - 6L_X = -3A_1/4\ N = 6A_2/4\ N$, $(L_Z + 2L_Y = 1)$.

According to classical dispersion theory we have

$$\hat{n}^2 - 1 = \frac{e^2 N}{\pi m} \Sigma \frac{f_j}{\nu_j^2 - \nu^2 + i\Gamma_j\nu} \qquad (7)$$

$$\hat{n} = n - i\kappa \ (= \text{the complex refractive index}) \qquad (8)$$

$\kappa = \varepsilon C \log_e 10/4\pi\nu$, ε = decadic extinction coefficient, C concentration of the absorbing solute (M), $N = 6.02 \cdot 10^{20} \cdot C$

molecules per cm^3, ν = wavenumber (cm^{-1}). We may apprehend e and m for charge and mass of electron, f_j the strength of the absorbing transition j, ν_j the resonance frequency of this transition and Γ_j the damping factor of the corresponding absorption band. Obviously $\hat{n}$ becomes complex when ν_j approaches ν, and we get absorption κ.

We introduce the Lorentz field by replacing $\hat{n}^2 - 1$ by $3(\hat{n}^2 - 1)/(\hat{n}^2 + 2)$ or rather by the left member in one of our sophisticated CM equations (Dunmur-Evald).

$$\frac{\hat{n}_i^2-1}{(\hat{n}_i^2+2) + (3L_i-1)(\varepsilon_i-1)} = \frac{e^2\cdot 6.02\cdot 10^{20}}{3\pi m}\left[\frac{Cf_{ji}}{\nu_{ji}^2-\nu^2+i\Gamma_j\nu} + \right.$$

$$\left. + C\,\Sigma' \frac{f_{ki}}{\nu_{ki}^2-\nu^2+i\Gamma_j\nu} + C_o\Sigma^o\right]$$

$$i = \parallel,\perp \qquad (9)$$

The first term represents the isolated solute absorption band we are interested in, the second and third sums are contributions from transitions in solute and solvent, respectively (C_o = solvent concentration). It is easy to realize by excluding the transition j, that the remainder can be contained in an "anchor term"

$$\frac{\hat{n}_{oi}-1}{(\hat{n}_{oi}^2+2) + (3L_i-1)(\hat{n}_{oi}^2-1)} = \frac{e^2}{3\pi m}\,6.02\cdot 10^{20}(C\Sigma' + C_o\Sigma^o) \qquad (10)$$

which is real (provided the j-band is sufficiently removed from all other transitions). In this view $\hat{n}_{oi}$, $i = \parallel,\perp$, is not simply the refractive index of the transparent solvent (= for instance a liquid crystal) but it is the refractive index at the absorption frequency ν_o of the solution but without this absorption.

Introduction practical simplifications ($\Gamma << 2\nu_o$, assuming n_{oi} independent of wavelength under the absorption band)[11] one may identify the $f_{obs,\,i}$ to be observed in the condensed medium

(= $\int \kappa_i \, d\nu$) with the theoretical f_i times a field factor:

$$f_{obs,\,i} = \frac{1}{n_i}[1 + L_i(n_i^2-1)]^2 \cdot f_i \qquad i = ||,\perp \qquad (11)$$

A shift is also to be observed in the position of the absorption maximum: [12]

$$\nu_{max,\,i} = \sqrt{\nu_o^2 - \frac{L_i n_{oi}}{[1+L_i(n_{oi}^2-1)]} \cdot \frac{2.303C\nu_o}{\pi^2} \int \frac{\varepsilon(\nu)}{\nu} d\nu} \qquad (12)$$

In a lattice of molecules for which the average repeat distance in the direction of largest molecular polarizability (generally the long-axis) is greater than that in the transverse direction (i.e. l_Z/l_Y is greater than 1) $L_Z < L_X$. With usual values of n_i (say $n_{||} = 1.52$, $n_\perp = 1.50$, which corresponds to polyethylene in the visible, or $n_\perp = 1.50$ and $n_{||} = 1.52$) the frequency shift according to eq. (12) generally implies the peak to be observed at the lower frequency. In other words LD spectrum should be superimposed by an S-shaped curve centered around the absorption maximum, and with a negative extremum at the lower frequency side. Even if the frequency shift has negligible effect there will be a finite LD due to eq. (11):

$$\frac{LD}{A} = \frac{\frac{1}{n_{||}}[1 + L_{||}(n_{||}^2-1)]^2 - \frac{1}{n_\perp}[1 + L_\perp(n_\perp^2-1)]^2}{\frac{1}{n}(\frac{n^2+2}{3})^2} \qquad (13)$$

where $n = (n_{||} + 2n_\perp)/3$

This LD should have the same shape as the absorption curve with maximum at the same frequency. Even with modestly elongated unit cells strongly negative effects are obtained irrespective of variations (within reasonable limits) of the optical anisotropy: With $L_{||} = 0$, $L_\perp = 0.5$ (corresponds to $l_Z/l_X = 1.4$) and $n = 1.51$ and $n_{||} - n_\perp = + 0.02$ and -0.02, $LD/A = -0.82$ and -0.85, respectively. With further lower lattice anisodimensionality the LD is still of an unreasonably large magnitude ($L_{||} = 0.239$, $L_\perp = 0.380$ i.e. $l_Z/l_X = 1.1$ yields $LD/A = -0.23$ and -0.35 for $\Delta n = +$ and -0.02, respec-

tively, n = 1.51). For $L_{||} = L_{\perp}$ (a cubic crystal) we get the result which should have been obtained from the usual CM equation:

$$\frac{LD}{A} = [(n_{||}^2+2)^2/9n_{||} - (n_{\perp}^2+2)^2/9n_{\perp}]/(n^2+2)^2/9n \qquad (14)$$

Now the LD sign is due to the sign of Δn: LD/A = + 0.015 and - 0.015 as Δn = + and - 0.02, respectively (n = 1.51 as before). The magnitudes of these effects are reasonable but the spherical degeneracy is not physically relevant. Nor are the signs compatible with experimental observations.

We finally apply the model of Vuks [7] to the present dichroism problem. Since the average $\bar{n}$ in the denominator of the CM equation according to Vuks will appear by the factor $(1/\bar{n}+2)$ in the field adjusted dispersion formula for || as well as for $\perp$ polarization this factor will vanish and the result be the same as without any field correction:

$$LD/A = (1/n_{||} - 1/n_{\perp})/1/n \approx (n_{\perp} - n_{||})/n \qquad (15)$$

Again we have direct sign dependence on Δn, but this time a reversed one as compared to the spherical Lorentz field, LD/A = -0.013 and +0.013 as Δn = +0.02 and -0.02, respectively (n = 1.51).

In FIG 1 LD and A spectra are shown of $Mo(CO)_6$ in anisotropic environment. The molecule is octahedral so no LD can arise by its orientation. The resulting negative LD/A (of the order of -0.01) is only consistent with one of the here derived relations for solvent field LD, namely eq. (15), which assumed the averaged field according to Vuks.

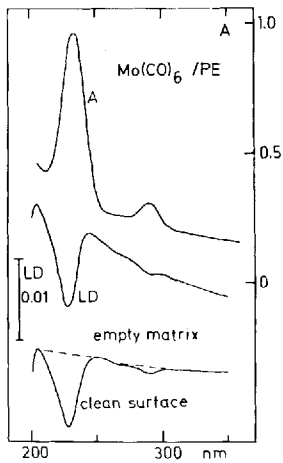


FIG 1

$Mo(CO)_6$ in stretched polyethylene (20μm) sheet. Surface scattering was minimized by removing crystallites by washing with ethanol.

In crystals numerous discrepancies have been found between the numerical values of the observed dichroic ratio ($A_{||}/A_{\perp}$) and that calculated according to the generally accepted relation

$$\frac{A_{||}}{A_{\perp}} = (\Sigma\vec{\mu}_i \cdot \vec{E}_{||})^2 / (\Sigma\vec{\mu}_i \cdot \vec{E}_{\perp})^2 \qquad (16)$$

containing the dot products between molecular transition moments, $\vec{\mu}_i$ (of transition i) and the electric field vectors of the radiation. Ward [16] and Rohleder and Luty [17] tried with little success to focus attention to this fact some time ago, and suggested from theoretical and experimental considerations that the observed dichroic ratio should be multiplied by the ratio $n_{||}/n_{\perp}$ before it gets the theoretical significance according to eq. (16). We note that this correction is in agreement with eq. (15). Eq. (15) is also in agreement with the observation by Blinov et al of a finite negative dichroism of $[P\,Mo_{12}O_{40}]^{3-}$ in a nematic optically positive liquid crystal [18] (LD/A = -0.25, $n_{||}$ = 1.9, $n_{\perp}$ = 1.5).

To make the picture more complete we also consider the case of an alternative field model to Lorentz, namely the one according to Onsager [19] and Böttcher. [20] A simpler way of introducing the field correction than passing over the CM equation is to realize that the extinction coefficient at linear optical absorption is given by the ratio between, w, the average energy absorbed per molecule per second and, I, the intensity of the radiation in ergs cm^{-2} sec^{-1} (famous review by Schellman [21])

$$\varepsilon = \frac{6.02 \cdot 10^{20}}{2.303} \cdot \frac{W}{I} \qquad (17)$$

I is given by the Poynting vector, $I = (c/4\pi)|\vec{E}x\vec{H}| = cnE_o^2/8\pi$ (E_o is the amplitude of $\vec{E}$). For electric dipol absorption, time-dependent perturbation theory yields [21]

$$w_i(\nu) = \pi\nu|\vec{v}_i \cdot \vec{\mu}_j|^2 \rho_j(\nu) E_o^2 / 2\hbar \qquad (18)$$

$i = ||, \perp$

($\vec{v}_i$ is the direction unit vector of the electric field, $\rho_j(\nu)$ is a normalized, $\int\rho_j(\nu)d\nu = 1$, line shape function, $\vec{\mu}_j$ is the transition dipole moment for the transition j). If the field on the chromophore, E_{eff}, is related to the applied average field, E_{av}, by $E_{eff} = \hat{q}E_{av} = (q - iq')E_{av}$ the factor $(q-iq')(q+iq')E_{av}^2$ is introduced instead of E_o^2 in eq (18) and so follows

$$\varepsilon_i(\nu) = \frac{q^2+q'^2}{n} \cdot \frac{4\pi^2\nu\rho(\nu)\cdot 6.02\cdot 10^{20}}{2.303\hbar c} <\mu_i>^2$$

$$i = ||,\perp \qquad (19)$$

(the transition dipole moment is averaged for orientation parallel to the electric field direction i over the appropriate molecular distribution function).

In the Onsager-Böttcher approach the microscopic properties of the molecules are introduced by the idea of a reactive field due to the influece of molecules upon each other through the surrounding medium. According to OB

$$\hat{q} = \frac{3\hat{n}^2}{2\hat{n}^2+1} \cdot \frac{1}{1-\hat{f}\hat{\alpha}} = \underline{\text{complex field factor}}$$

$$\hat{\alpha}(\nu) = \alpha(\nu) - i\alpha'(\nu) = \underline{\text{complex polarizability of the molecule}}$$

$$\hat{f} = \frac{1}{r^3} \cdot \frac{2(\hat{n}^2-1)}{(2\hat{n}^2+1)} = \underline{\text{complex reactive field}} \text{ (r is the Onsager radius)}$$

From to the above said follows that the effect to be expected in LD for a cubic chromophore is

$$\frac{LD}{A} = \left(\frac{q_{||}^2+q_{||}'^2}{s^n{}_{||}} - \frac{q_\perp^2+q'^2}{s^n{}_\perp}\right) / \left(\frac{q^2+q'^2}{n}\right) \qquad (20)$$

which is essentially the field contribution term for which ordinary LD has to be corrected (with s we have here given a separate indication of the refractive index introduced via the Poynting vector in eq. (17) which we below distinguish from the

n introduced via q). The separation of real and imaginary parts of $\hat{n}$, $\hat{f}$ and $\hat{\alpha}$ leads to a cumbersome complete LD/A expression. Seeking small departures from the Lorentz models we find a differential approximation justified:

$$\frac{LD}{A} \approx \frac{n}{q^2+q'^2}\{(n_{||}-n_{\perp})[\frac{\partial}{\partial n}+\frac{\partial}{\partial_s n}]+(r_{||}-r_{\perp})\frac{\partial}{\partial r}+$$

$$+(\alpha_{||}-\alpha_{\perp})\frac{\partial}{\partial\alpha}+(\alpha'_{||}-\alpha'_{\perp})\frac{\partial}{\partial\alpha'}\}\frac{q^2+q'^2}{s^n}\equiv$$

$$\equiv (n_{||}-n_{\perp})[A+B]+(r_{||}-r_{\perp})C+(\alpha_{||}-\alpha_{\perp})D+$$

$$+(\alpha'_{||}-\alpha'_{\perp})E \qquad (21a)$$

We now assume that $\kappa<<n$ which holds for all practical cases. The essentially new is our idea of different effective Onsager "radii" parallel and perpendicular to the orientation direction of the solvent. It is our belief that the different fields experienced by a solute molecule in the neighborhood of a hydrocarbon chain in a polymer matrix of polyethylene in these two directions may be accounted for by $r_{||}/r_{\perp}\neq 0$. We further put $\hat{\alpha}=\alpha$ in the terms which not concern α or α' differentials, and get:

$$A = \frac{4[1-(\alpha/r^3)6n^2/P(2n^2+1)]}{n(2n^2+1)}$$

$$B = -1/n$$

$$C = -\frac{6P(2n^2-2)(\alpha/r^4)}{(2n^2+1)}$$

$$D = \frac{2(2n^2-2)(1/r^3)P}{(2n^2+1)[P^2+(\alpha'/r^3)^2(2n^2-2)^2/(2n^2+1)^2]}$$

$$E = -\frac{2(2n^2-2)^2(\alpha'/r^6)}{(2n+1)^2[P^2+(\alpha'/r^3)^2(2n^2-2)^2/(2n^2+1)^2]}$$

where $P = 1-(\alpha/r^3)(2n^2-2)/(2n^2+1)$ (21b)

The following extreme alternatives may be noted:

i) Anisotropy of the system only reflected in the real refractive index, n, and its birefringence $n_{||}-n_{\perp}$:

$$\frac{LD}{A} = (n_{||}-n_{\perp})\cdot(A + B) \qquad (22)$$

ii) A CM equation according to Vuks is assumed. This can be shown equivalent to averaging $\hat{q}$ but not $\hat{n}_s$ over space, so $A\Delta n = 0$:

$$\frac{LD}{A} = -\ (n_{||}-n_{\perp})/n \qquad (23)$$

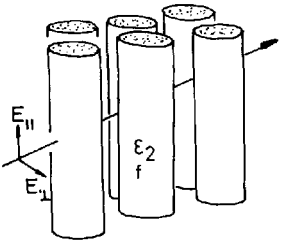
iii) If the deformed Onsager sphere is the main contribution

$$\frac{LD}{A} = -\ \frac{r_{||}-r_{\perp}}{r}\ .\ (-Cr) + \ldots\ \mathcal{O}(\delta n,\ \delta\alpha,\ \delta\alpha') \qquad (24)$$

iv) The case of important molecular alignment and intrinsical molecular anisotropy

$$\frac{LD}{A} = (D\ \underline{Re} + E\ \underline{Im})(\hat{\alpha}_{||}-\hat{\alpha}_{\perp}) + \ldots \qquad (25)$$

We finally consider so called Wiener dichroism of mixed bodies, a phenomenon which is simply the complex manifestation of the form- (or Wiener-) birefringence well-known in the real refractive index. However, though it was predicted already in the beginning of this century [22] its existence [23] as a measurable effect was first recently proved.[24] Consider a system of well aligned rods, with refractive index $n_2 = \sqrt{\varepsilon_2}$, occupying the volume fraction f, dispersed in a different dielectric ($n_1 = \sqrt{\varepsilon_1}$, volume fraction 1-f). Without needing the passage via microscopic phenomenological properties it is easy to derive a mixing formula for how the dielectric permittivity, ε, of the mixture depends on the permittivities,



$\varepsilon_1, \varepsilon_2$, of the pure components. This is simply done by signing the average polarization $(\varepsilon - 1)E = 4\pi P$ in two ways $(\varepsilon - 1) \cdot [fE_i + (1-f)E_o] = (\varepsilon_2 - 1)fE_i + (\varepsilon_1 - 1)(1 - f)E_o$ where $E_i = E_o/\{1 + L(\varepsilon_2 - \varepsilon_1)/\varepsilon_1\}$ is the field inside an ellipsoid with permittivity ε_2 and depolarizing coefficient L immersed in an infinite medium of permittivity ε_2 if the field E_o is applied.[25] One then obtains

$$\varepsilon_i = \varepsilon_1 + f(\varepsilon_2 - \varepsilon_1)/[1 + (1-f)L_i(\varepsilon_2 - \varepsilon_1)/\varepsilon_1]$$

$$i = \|, \perp \qquad (26)$$

By inserting the refractive indices, n_1, n_2, for the two "phases", this eq. yields the form-birefringence. If we instead insert $\hat{n} = n + iA_i \log_e 10/4\pi\bar{\nu}d$, $\hat{n}_1 + iA_1 \log_e 10/4\pi\bar{\nu}d$ and $\hat{n}_2 = n_2 + iA_2 \log_e 10/4\pi\bar{\nu}d$ and identify imaginary parts in both membra we get

$$A_i = \frac{(1-f)A_1\{n_1^4 + L_i(n_2^2 - n_1^2)[2n_1^2 + f \cdot (n_2^2 - n_1^2)] + L_i^2(1-f)(n_2^2 - n_1^2)^2\} + fn_1^3 n_2 A_2}{\{n_1^2 + [f + (1-f)L_i](n_2^2 - n_1^2)\}^{1/2} \; [n_1^2 + (1-f)L_i(n_2^2 - n_1^2)]^{3/2}}$$

$$i = \|, \perp \qquad (27)$$

This equation gives the Wiener dichroism due to isotropic absorption inside (A_2, cm^{-1}) and outside (A_1, cm^{-1}) ellipsoidal particles. If the particles are infinite cylinders ($L_{\|} = 0$, $L_{\perp} = 0.5$) and the absorption is only in phase 1 the following approximation holds

$$\frac{LD}{A} \approx -2f(1-f)[(n_t/n_a) - 1] \qquad (28)$$

where n_t is the refractive index of the transparent phase and n_a of the absorbing phase.

We propose Wiener LD be contributing in any system of regularly arranged inhomogenities with extensions approaching the order of radiation wavelength. Maximum effect is expected at f = 0.5. Conditions for Wiener LD are optimized in a sheared solution of 20 % by weight cetyltrimethylammoniumbromide

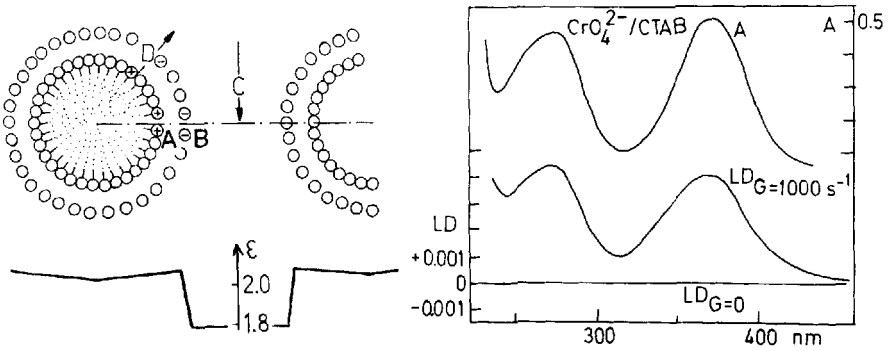


FIG. 2

Crossection through CTAB micelle solution (A inside, B outside the bromide ion layer) an the corresponding permittivity profile. K_2CrO_4 (0.025 %) in CTAB (20 %)/H_2O in a Couette flow cell with and without hydrodynamical gradient. Cell lengths in A and LD, 0.10 cm.

(CTAB) in water where practically infinite micellar cylinders (length 10^5 Å, diameter 50 Å) are known to be formed and well aligned. In FIG. 2 a possible permittivity profile is sketched through a plane perpendicular to the || direction in such a solution. The drop from n = 1.40 in CTAB to 1.33 in water does probably not occur until outside the polarizable bromide counterion layer. Thus while the Wiener LD is negative for isotropic cationic chromophores (these are preferentially located outside the bromide layer) a positive LD is observed when adding the isotropic tetrahedral CrO_4^{2-}. Inserting f = 0.20, n_a = 1.33 and n_t = 1.40 we obtain LD/A = -0.017 which with sign and magnitude agrees well with the LD observed for a series of in practice cubic cations.[24] In neither the cationic nor the anionic case there is any significant variation in LD/A with wavelength. The monotonic dependences observed (in general larger values at shorter wavelength) are accounted for by the dispersions in n_t/n_a.

In FIG. 3 we report the interesting LD spectrum of the inert but non-spherical complex $Co(EDTA)^-$. The unequal signs of the two bands can not be explained by the n_t/n_a dispersion (LD/A is practically constant under each band) so none of

the macroscopic field mechanisms suggested above applies here. Nor is the Onsager differential r a plausible LD source. The chromophore is anisotropic and in our opinion two explanations are possible both of which are due to the strong electric field (probably of the order 10^6 V cm^{-1}) outside the positively charged alkylammonium cylinder mantle

i) Perturbation of the electronic states involved in the absorption (anisotropic electrochromism [26])

ii) Orientation of the transition dipole by the permanent molecular dipole moment (a possible polarisation anisotropy is shetched in FIG. 3 due to different electric dipole allowance of the T_{1g} and T_{2g} transitions after the symmetry descendence to C_2).

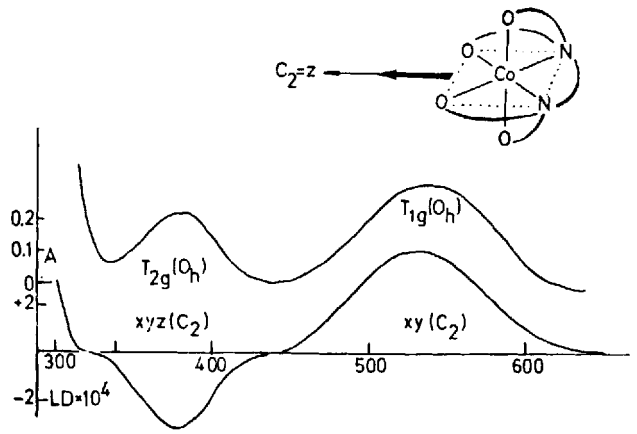


FIG. 3

The anisotropic $Co(EDTA)^-$ (0.5 % KCo(EDTA) in CTAB (20 %) in H_2O. Above, absorption, below LD in Couette cell with and without gradient (cell lengths in A and LD 0.10 cm).

Recent studies in our laboratory on electric linear dichroism indicate that the first effect can often be of a magnitude comparable with that of the second. In any case the result is interesting since electric studies of high field have by obvious reasons not before been applicable to electrolytes in solution.

Though one might get the impression that we have theory to account for anisotropic solvent phenomena in LD, I would like to close this section by leaving the question of recommendable solvent corrections open. Thus we have exceptions from the rule by eq. (23) of negative LD for an isotropic chromophore in optically positive matrices: Positive essentially constant LD/A was observed for CBr_4 (+0.04 at 225 nm) and $Sn(C_6H_5)_4$ (+0.04 at 250 nm) in stretched polyethylene film. We can therefore not eliminate that microscopic perturbation plays an important role, which question is to be studied by artificial field dichroism.

It should be observed that the refractive index of the solution does not differ significantly from that of the solvent in any of the presented experiments (the refractive index of a mixture of volume fractions f_1 and f_2 of components n_1 an n_2 is given by $n^2 = f_1 n_1^2 + f_1 n_2^2 + \delta(n_1 - n_2)$, but can also be separately measured). The insensitivity to modest changes in the refractive index of the solvent was confirmed by changing H_2O (n = 1.332) against D_2O (n = 1.338) in the CrO_4^{2-}/CTAB experiment: no significant difference could be detected in LD/A.

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