ON ELECTRIC ANISOTROPY INDUCED IN DIAMAGNETICS BY A STRONG ALTERNATING MAGNETIC FIELD

S. KIELICH
Department of Molecular Physics,
A. Mickiewicz University, Poznań, Poland

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Electric anisotropy, to an amount measurable by present experimental techniques, is shown to be induced in diamagnetics by a strong magnetic field, thus in quinoline, nitrobenzene or similar liquids. In the case of an oscillating magnetic field the effect is characterized moreover by dispersion and absorption involving a relaxation time τ_2 of the magnetically anisotropic molecules. Simple formulas are proposed and employed for computing numerically the magnetically induced electric anisotropy for several liquids.

Applying a semi-macroscopic theory of nonlinear phenomena in dielectrics [1], a diamagnetic medium can be shown to become nonlinear in the presence of a strong magnetic field H, the variations in

Table 1
Calculated values of magnetically induced electric anisotropy for several liquids *.

Liquid	n λ=5460 Å	$\frac{\delta_m}{\delta_o}\times 10^5$	$K_\lambda\times 10^9$ λ=5460 Å	$B_{em}\times 10^{16}$
Benzene	1.503	2.52	40.3	0.8
Toluene	1.499	2.06	71.4	1.2
p-Xylene	1.499	2.34	75.0	1.4
Mesitylene	1.499	2.67	78.6	1.7
Fluorobenzene	1.465	2.31	678.1	13.1
Chlorobenzene	1.521	1.48	1050.0	12.5
Bromobenzene	1.560	1.28	1029.0	10.7
Iodobenzene	1.621	0.76	1022.4	5.8
Nitrobenzene	1.560	2.66	38600	871.7
Naphtalene	1.589	2.14	257.8	4.8
Pyridine	1.509	2.43	2243.6	44.2
Quinoline	1.623	9.60	1654.3	117.8
Pyrrole	1.500	0.83	42.6	0.3

* Values of n and K_λ for t = 20°C are from ref. 9, whereas those of δ_m/δ_o are calculated from ref. 8.

its electric properties being given by the electric permittivity tensor

$$\epsilon^H_{\sigma\tau} - \epsilon\delta_{\sigma\tau} = F_{em}\,\epsilon_{\sigma\tau\nu}H_\nu + A_{em}\,\delta_{\sigma\tau}H^2 + B_{em}\,(H_\sigma H_\tau - \tfrac{1}{3}\,\delta_{\sigma\tau}H^2), \quad (1)$$

where ϵ is the dielectric constant at $H=0$, and $\epsilon_{\sigma\tau\nu}$ is the Levi-Civitá extensor.

The first term in eq. (1) describes the linear effect, similar to the well-known Faraday effect [2]. Namely, we have from eq. (1) for the difference between the non-diagonal components

$$\epsilon_{xy} - \epsilon_{yx} = 2\,F_{em}\,H_z, \quad (2)$$

if the external magnetic field is applied along the z-axis.

The constant A_{em} in eq. (1) describes variations in $\epsilon_{\sigma\tau}$, isotropic and quadratic in H, related i.a. with magnetostriction (the other effects are not considered here) [3]

$$A_{em} = 2\pi\,\chi_e\,\partial(\chi_m V)/\partial p \quad (3)$$

resulting from changes in volume V of the medium due to the strong magnetic field; χ_e and χ_m are the electric and magnetic susceptibilities, and p the pressure.

Eq. (1) yields the difference in diagonal components $\epsilon_{\sigma\tau}$ measured along the x-and z-axis as

$$\epsilon^H_{zz} - \epsilon^H_{xx} = B_{em}\,(H_z^2 - H_x^2), \quad (4)$$

which defines only the electric anisotropy induced in the isotropic medium by the strong magnetic field (not depending on magnetostriction).

The constant B_{em} is in general of a mathematically complicated form, and for linearly polarizable molecules can be written in molecular statistical form as

$$B_{em} = \frac{2\pi}{15\,V\,kT}\left(\frac{\epsilon+2}{3}\right)^2\left\{\left\langle\sum_{p=1}^{N}\sum_{q=1}^{N}\left(3a^{e(p)}_{\alpha\beta}a^{m(q)}_{\alpha\beta} - a^{e(p)}_{\alpha\alpha}a^{m(q)}_{\beta\beta}\right)\right\rangle + \frac{1}{kT}\left\langle\sum_{p=1}^{N}\sum_{q=1}^{N}\sum_{r=1}^{N}\left(3m^{(p)}_\alpha m^{(q)}_\beta a^{m(r)}_{\alpha\beta} - m^{(p)}_\alpha m^{(q)}_\alpha a^{m(r)}_{\beta\beta}\right)\right\rangle\right\}, \quad (5)$$

where $m^{(p)}_\alpha$ is the electric dipole moment of the p-th molecule immersed in the medium, $a^{e(p)}_{\alpha\beta}$ and $a^{m(p)}_{\alpha\beta}$ are tensors of its electric and magnetic linear polarizabilities, and the symbol $\langle\ \rangle$ denotes classical statistical averageing in the absence of external fields.

It is highly interesting to consider the case when the isotropic medium is acted on by a strong magnetic field $H=H_0\cos\omega t$ oscillating at frequency ω. Here, in calculating the quadratic change in electric permittivity, one can recur to molecular relaxational theory [4,5], obtaining for the electric anisotropy constant

$$B^\omega_{em} = \frac{2\pi\rho}{15\,kT}\left(\frac{\epsilon+2}{3}\right)^2\left(\delta_e\,\delta_m + \frac{\mu^2\,\delta_m}{kT}\right)\left\{1 + \frac{\exp(i\,2\omega t)}{1+i\,2\omega\tau_2}\right\}, \quad (6)$$

with $\delta_e = a^e_{33} - a^e_{11}$ and $\delta_m = a^m_{33} - a^m_{11}$ denoting the electric and magnetic molecular anisotropies.

The above result is for a diamagnetic of density ρ, with axially-symmetric molecules presenting a permanent dipole μ and relaxation time τ_2 related with that of Debye as $\tau_D = 3\tau_2$. If in particular $\omega = 0$, eq. (6) yields the well known result [2,6,7].

Eq. (6) shows that in the case of an oscillating magnetic field the constant B_{em} is a complex quantity and can be resolved into real and imaginary parts

$$B_{em}^{\omega} = B'_{em} - i B''_{em},$$

wherein the constants, defining dispersion and absorption, are

$$B'_{em} = \tfrac{1}{2} B^{0}_{em} \left\{ 1 + \frac{\cos 2\omega t + 2\omega\tau_2 \sin 2\omega t}{1 + 4\omega^2\tau_2^2} \right\}, \qquad B''_{em} = B^{0}_{em} \frac{2\omega\tau_2 \cos 2\omega t - \sin 2\omega t}{1 + 4\omega^2\tau_2^2}, \tag{7}$$

with B^{0}_{em} given by eq. (6) for $\omega = 0$.

In the case of nondipolar substances the magnetically induced electric anisotropy constant B_{em} is related with the measured Cotton-Mouton constant C_λ as follows:

$$B_{em} = 2n\lambda \left(\frac{\epsilon + 2}{n^2 + 2}\right)^2 \frac{\delta_e}{\delta_o} C_\lambda, \tag{8}$$

where n is the refractive index, λ the light wavelength, and $\delta_o = a^{o}_{33} - a^{o}_{11}$ the optical molecular anisotropy.

For the general case of dipolar substances we have instead of eq. (8)

$$B_{em} = 2n\lambda \left(\frac{3}{n^2 + 2}\right)^2 \frac{\delta_m}{\delta_o} K_\lambda, \tag{9}$$

where K_λ is the measured Kerr constant.

For benzene at $t = 20^{o}$C we have $n = 1.503$, $\epsilon = 2.28$ and [8] $C_\lambda = 56.7 \times 10^{-14}$, and eq. (8) on assuming $\delta_e \approx \delta_o$ leads to an electric anisotropy of $B_{em} = 0.94 \times 10^{-16}$. On the other hand, we have [8] $\delta_o = - 3.84 \times 10^{-24}$, $\delta_m = -9.7 \times 10^{-29}$ and [9] $K_\lambda = 40.3 \times 10^{-9}$, whence eq. (9) yields $B_{em} = 0.8 \times 10^{-16}$. Thus, eqs. (8) and (9) are found to yield values of B_{em} for benzene that are in sufficiently good agreement.

Owing to the fact that, quite recently, Le Fêvre and Murthy [8] by Cotton-Mouton constant measurements in infinitely dilute solutions succeeded in determining the magnetic polarizabilities a^{m}_{33} and a^{m}_{11} for a large variety of molecules, all quantities appearing in the right hand term of eq. (9) are now available and we are in a position immediately to calculate the value of the constant B_{em}. The values thus computed are given in table 1.

Applying a pulse magnetic field of 10^5 Oe (as done by Surma [10] when measuring the Cotton-Mouton constant in solutions) for the measurent of electric anisotropy, one sees that for benzene $\epsilon_{zz} - \epsilon_{xx} = 0.8 \times 10^{-16} H^2 \approx 10^{-6}$ whereas for nitrobenzene $\epsilon_{zz} - \epsilon_{xx} = 8.6 \times 10^{-14} H^2 \approx 10^{-3}$. Hence, in nitrobenzene and some other substances (see table 1), existing experimental techniques [10] are adequate for the detection of the electric anisotropy induced by strong magnetic fields.

Doubtless still more considerable effects are to be expected in paramagnetics [6], where even nonlinear changes in magnetic permeability [11] have to be envisaged.

It would be highly worth while to carry out dispersion and absorption measurements of the electric anisotropy in the context of eqs. (7). This would provide information regarding the relaxation time τ_2, as can be obtained from the Kerr effect [4] and optical birefringence [5,12]. Experimental attempts in this direction are being made in the High Magnetic Fields Laboratory of this Department.

References

1. S.Kielich, Acta Phys. Polonica 17 (1958) 239.
2. M.Born, Optik (J.Springer, Berlin 1933).
3. S.Kielich, Acta Phys. Polonica 22 (1962) 299.
4. A.Peterlin and H.Stuart, Doppelbrechung insbesondere künstliche Doppelbrechung (J.W.Edwards, Ann Arbor, Michigan 1948).
5. S.Kielich, Acta Phys. Polonica 30 (1966) 638.

6. J.H. Van Vleck, The theory of electric and magnetic susceptibilities (Oxford University Press, London 1932).
7. S.Kielich and A.Piekara, Acta Phys. Polonica 18 (1959) 439.
8. R.J.W. Le Fèvre and D.S.N.Murthy, Australian J. Chem. 19 (1966) 179, 1321.
9. Landolt-Börnstein Tables (Springer-Verlag, Berlin).
10. M.Surma, Acta Phys. Polonica 25 (1964) 485.
11. S.Kielich, Physica 32 (1966) 385.
12. N.Bloembergen and P.Lallemand, Phys. Rev. Letters 16 (1966) 81.

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