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ON NONLINEAR CHANGES IN REFRACTIVE INDEX OF LIQUIDS DUE TO ELECTROSTRICTION AND ELECTROCALORIC EFFECT

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Recent papers note the rôle of electrostriction in the various nonlinear optical effects induced in isotropic bodies by an intense laser beam [1]-[3]. Here, the problem will be considered quantitatively from thermodynamical relationships and the experimental data available for liquids.

When an isotropic medium of volume V is acted on by a high electric field E_0, electrostriction in a first approximation induces a quadratic change in volume [4]:

$$\Delta V = -\frac{V}{8\pi}\left\{\left(\frac{\partial\varepsilon}{\partial p}\right)_T - (\varepsilon-1)\,\beta_T\right\} E_0^2 \tag{1}$$

(ε is the dielectric permittivity, p the pressure and β_T the isothermal compressibility coefficient).

In the same approximation, the electrostrictive change in pressure in a liquid of number density ϱ is [4]:

$$\Delta p = \frac{\varrho}{8\pi}\left(\frac{\partial\varepsilon}{\partial\varrho}\right)_T E_0^2. \tag{2}$$

It is our aim to calculate the change in refractive index n due to light of high intensity I_0 propagating and oscillating along the y- and z- axes, respectively. In general we have:

$$\Delta n(V, T, E) = \Delta n_V + \Delta n_T + \Delta n_E, \tag{3}$$

wherein by (2)

$$\Delta n_V = \frac{1}{8\pi\beta_T}\left(\frac{\partial n}{\partial p}\right)_T\left\{2n\left(\frac{\partial n}{\partial p}\right)_T - (n^2-1)\,\beta_T\right\}\left(\frac{n^2+2}{3}\right)^2 I \tag{4}$$

is the change in refractive index due to electrostriction, and

$$\Delta n_T = -\frac{TV}{8\pi C_p}\left(\frac{\partial n}{\partial T}\right)_p\left\{2n\left(\frac{\partial n}{\partial T}\right)_p + (n^2-1)\,\alpha_p\right\}\left(\frac{n^2+2}{3}\right)^2 I \tag{5}$$

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that due to the rise in temperature. α_p and C_p are the thermal expansion coefficient and specific heat at $p = \text{const}$; $I = \left(\frac{3}{n^2+2}\right)^2 I_0$ is the light intensity within the medium of refractive index n.

Provided there is no change in shape of V, the variations (4) and (5) are of an isotropic nature, whereas the increment Δn_E due to nonlinear polarisation of the medium by the field E of the light wave depends on the direction (with regard to E) in which n is measured. We have [5]:

$$\Delta n_{zz} = \frac{2}{3}\lambda B_\lambda I \quad \text{and} \quad \Delta n_{xx} = -\frac{1}{3}\lambda B_\lambda I, \tag{6}$$

B_λ being a constant defining the birefringence induced in the medium by the strong beam of intensity I and wavelength λ:

$$\Delta n_B = \Delta n_{zz} - \Delta n_{xx} = \lambda B_\lambda I. \tag{7}$$

On calculating instead of (1) the change in n due to electrostrictive pressure, we get by (2) in the optical case:

$$\Delta n_p = \frac{n}{4\pi\beta_T}\left(\frac{\partial n}{\partial p}\right)_T^2 \left(\frac{n^2+2}{3}\right)^2 I. \tag{8}$$

TABLE I

Calculated values of variations in refractive index due to pressure (Δn_p), opticostriction (Δn_V) and birefringence (Δn_B)[1]

Liquid	n $\lambda = 5460$Å	$\beta_T \times 10^{12}$ (cm²/dyn)	$\left(\frac{\partial n}{\partial p}\right)_T \times 10^{12}$ (cm²/dyn)	$B_\lambda \times 10^9$ $\lambda = 4880$Å	$\frac{\Delta n_p}{I} \times 10^{12}$	$\frac{\Delta n_V}{I} \times 10^{12}$	$\frac{\Delta n_B}{I} \times 10^{12}$
Benzene	1.503	95	52.3	40	6.95	1.67	1.95
Toluene	1.499	92	48.6	93	6.11	1.31	4.54
Cyclohexane	1.426	112	50.8	4.1	4.72	0.95	0.20
Isooctane	1.391	152	62.9		4.97	0.90	
n-Hexane	1.374	170	66.5		4.75	0.80	
n-Octane	1.398	125	52.8		4.31	0.84	
n-Decane	1.413	105	46.9		4.17	0.89	
n-Hexadecane	1.435	83	39.1		3.86	0.85	
Carbon tetrachloride	1.460	106	52.8	5.1	5.82	1.30	0.25
Carbon disulphide	1.634	94	68.2	418	15.68	4.70	20.40
Methyl ethyl ketone	1.379	108	44.2		3.36	0.66	
Water	1.334	46	15.2	2.9	0.84	0.10	0.14
Nitrobenzene	1.560	49	33.3	290	6.14	1.98	14.15
Chloroform	1.446	87	37.7	16.5	3.49	0.45	0.81
Acetone	1.359	125	43.6	7.3	2.70	0.27	0.37

[1] Values of n, β_T and $(\partial n/\partial p)_T$ are from refs [6] and [8], whereas those of B_λ are from ref. [7].

All quantities appearing to the right of Eqs (4—8) are available from experiment [6—8]. Table I contains the various contributions of Eq. (3) computed numerically from the thermodynamical formulas (4), (7) and (8) and the experimental results of Coumou et al [6] and Paillette [7]. One sees that the increments Δn_B due to optical birefringence exceed those due to pressure Δn_p in the case of carbon disulphide and nitrobenzene only. In the other, weakly birefringent liquids the variations from opticostrictive pressure generally predominate, Δn_V being in all cases smaller than or comparable to Δn_B and markedly smaller than Δn_p.

Quite recently, Shen [2] calculated Δn_p for some liquids from a formula derived from Eq. (8) on the approximate assumption $2n(\partial_n/\partial p)_T = (n^2-1)\beta_T$ (the values of Δn_p in ref. [2] are twice larger) and Δn_B from a formula containing the anisotropic part of Kerr's constant (*cf.* ref. [9]).

Table II gives the calculated changes Δn_T in refractive index due to the electrocaloric effect. In all cases, Δn_T is negative. On referring to Table I, $|\Delta n_T|$ is in general seen to be smaller than the variation Δn_V from opticostriction. Hence, the sum $\Delta n_V + \Delta n_T$ is slightly lowered and in strongly birefringent liquids $\Delta n_V + \Delta n_T < \Delta n_B$ whereas in liquids with small optical birefringence constants $\Delta n_V + \Delta n_T > \Delta n_B$. The latter conclusion was reached earlier by Shen [2]. The thermodynamical and molecular effects have already been discussed in part elsewhere [5] and will be dealt with in detail in a subsequent paper [10].

TABLE II

Calculated values of variations in refractive index due to opticocaloric effect (Δn_T)[2]

Liquid	V_M $\left(\frac{\text{cm}^3}{\text{mol}}\right)$	$C_p^M \times 10^{-7}$ $\left(\frac{\text{erg}}{^\circ\text{C mol}}\right)$	$\alpha_p \times 10^3$ $(^\circ\text{C})^{-1}$	$-\left(\frac{\partial n}{\partial T}\right)_p \times 10^5$ $(^\circ\text{C})^{-1}$	$-\frac{\Delta n_T}{I} \times 10^{12}$	$\frac{\Delta n_V + \Delta n_T}{I} \times 10^{12}$	$\frac{\Delta n_B}{I} \times 10^{12}$
Benzene	89.4	136.1	1.21	63.8	0.39	1.28	1.95
Toluene	106.6	162	1.08	56.2	0.30	1.01	4.54
Cyclohexane	108.5	156.5	1.21	53.8	0.23	0.72	0.20
n-Hexane	131.2	195.0	1.38	52.8	0.16	0.64	0.36
n-Octane	163.2	254.1	1.15	47.6	0.16	0.68	0.47
n-Decane	195.5	314.5	1.04	44.8	0.13	0.76	0.56
Carbon disulphide	60.2	75.6	1.19	81.6	1.26	3.44	20.40
Water	18.0	75.2	0.18	11	0.01	0.09	0.14
Nitrobenzene	102.3	187.3	0.83	46	0.19	1.79	14.15
Chloroform	80.2	77.3	1.28	61	0.51	−0.06	0.81
Acetone	73.4	125	1.43	50	0.08	0.19	0.37
Carbon tetrachloride	96.9	131.7	1.21	58.6	0.33	0.97	0.25

[2] Values of V_M, C_p^M, α_p and $(\partial n/\partial T)_p$ are from refs [6] and [8].

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