

ELECTRIC POLARIZATION OF ONSAGER FLUIDS. II. BIREFRINGENCE. 2. MOLAR KERR CONSTANTS OF BINARY SOLUTIONS

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On the ground of dielectrometry and electric birefringence data we calculated molar Kerr constants of substances dissolved in organic media of diverse polarity and polarizability under the conditions of infinite dilution. Minimal errors of the calculated constants, in relation to their gaseous phase values, were achieved as a result of the introduction of the local field model, which evolves the concepts of reactive field and local electric induction of a polarized fluid, into the orientational theory of Kerr effect.

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1. Introduction

The estimation of Kerr effect is one of the most precise and highly informative methods of investigation of fundamental properties characteristic of molecular media. In combination with the molecular refraction and light scattering techniques it enables calculation of semi-axes of molecular polarizability ellipsoids. Precise results can be obtained from the gas-phase measurements data which are not inferred with the intermolecular interaction effects. Unfortunately, most of organic compounds are not volatile enough to perform such measurements. For many interesting chemical and biochemical investigations of electro-optical properties they are limited to infinitely diluted binary solution. Now we wish to demonstrate that such studies can provide an exact information on the polarizability of organic molecules.

2. Model description of molar Kerr constant of binary solution

In this paper we present the results of experimental and calculative determination of molar Kerr constants for the substances of diverse polarity and polarizability, dissolved in non-polar and polar media.

From the experimental data on dielectrometry and electric birefringence (EB) original expression for the computation of Kerr constants of pure molecular fluids was deduced in the previous publication [1] (K^1 is Kerr constant of a unit volume containing N molecules):

$$K^1 = \pi N C_L^0 C_{A,B}^e (\Theta_1^g + \Theta_2^l).$$

The above expression was deduced from the Langevin-Born's model with some modifications. Reactive field of an electrically polarized fluid contributes to the potential energy of molecules, hence dipole moments of free molecules μ_0 differ from the corresponding values in liquid state μ_0^l . Consequently, the dipole term Θ_2^l differs from the one Θ_2^g , traditionally used in literature as characteristic of gases. Moreover, the factors C^0 and C^e which establish relationship between high- and low-frequency Maxwell's ($E^{0,e}$) and local ($E_e^{0,e}$) fields ($E_e^{0,e} = C^{0,e} E^{0,e}$) appear in the first and not in the second power. The factor C^e is calculated according to the suggested earlier model of local field, developing the concepts of reactive field and local electric induction of a molecular fluid [2, 3]: $C^e = C_A^e$ and C_B^e while the common pattern of C^e is C_L^e . The factor C^0 is defined according to Lorenz ($C^0 = C_L^0$), since the distribution of the Lorenz internal field of an optical radiation passing through a medium during EB experiments is isotropic as it has been found in [4].

Another important electro-optical characteristic of a substance is molar Kerr constant mK^g which does not contain macroscopic quantities and is connected with the constant K^g of one molecule of a gas by the formula $mK^g = K^g N^{-1} = 3\pi N_A (\Theta_1^g + \Theta_2^g)$. Analogous expression for liquids, as regarded in numerous publications [3], is $mK^l = K^l M n^2 [(C_L^0)^2 (C_L^e)^2 \rho]^{-1}$, where N_A is Avogadro number, M and ρ are molecular weight and density, respectively. In our approach the corresponding equation for molar Kerr constant of liquids has the form

$$\begin{aligned} mK^l &= 3K^l M n^2 [C_L^0 C_{A,B}^e]^{-1} = 3\pi N_A (\Theta_1^g + \Theta_2^l) \\ &= mK^g + 15\pi N_A \alpha t (1 + 0.25\alpha t) (1 - \alpha t)^2 \Theta_2^g, \end{aligned} \quad (1)$$

where α is the average dynamic polarizability of the molecules of a liquid; t is the reactive field factor.

To extend the formula (1) to binary solutions let us assume that under the experimental conditions molar Kerr constant is additive over the weight factors X_i ; $sK_0^l = X_i sK_i^l$; $sK_i^l = mK_i^l M_i^{-1} = 3\pi N_A M_i^{-1} [\Theta_{1,i}^g + (1 + 1.5\alpha_i t_i)^2 \Theta_{2,i}^g \times (1 - \alpha_i t_i)^{-2}]$, and the following parameters of the solution are linear in X_2 ($X_2 < 0.02$):

$$\begin{aligned} K_0^l &= K_1^l (1 + \xi X_2), & \rho_0 &= \rho_1 (1 + \beta X_2), \\ n_0 &= n_1 (1 + \gamma X_2), & \varepsilon_{C_0} &= \varepsilon_{C_1} (1 + \delta X_2), \end{aligned} \quad (2)$$

n , ϵ_C — refraction index and statistic permittivity of the medium; the indices i, j denote: $i = j = 0$ — solution, $i = 1$ — solvent, $i = 2$ — solute. Denoting $s\tilde{K}_i^1 = sK_i^1(1 - \alpha_i t_0)^{-1}$, $i = 1, 2$, we can restate the assumption of additivity as follows:

$$3K_0^1 n_0^2 [g_0(n_0^2 + 2)\rho_0^{-1}] = X_2 s\tilde{K}_2^1 + (1 - X_2) s\tilde{K}_1^1, \quad (3)$$

where g_0 is the cavity field factor. Employing independent extrapolations (2) and differentiating Eq. (3) with respect to X_2 (when $X_2 \rightarrow 0$) we achieve the expression (Eq. (4)) which makes possible to determine molar Kerr constants $m\tilde{K}_2^1|_{X_2=0} \equiv \infty(mK_2^1)$ of solutes from experiments on dielectrometry and EB of infinitely diluted solutions

$$\begin{aligned} \infty(mK_2^1) = & \frac{3M_2(1 - \alpha_2 t_1)n_1^2}{\rho_1 g_1(n_1^2 + 2)} K_1^1 \left\{ 1 + \xi - \beta - \left[\frac{\partial}{\partial X_2} \ln g_0 \right]_{X_2=0} \right. \\ & \left. - \frac{1}{1 - \alpha_1 t_1} \left[\frac{\partial}{\partial X_2} \alpha_1 t_0 \right]_{X_2=0} + \frac{4\gamma}{n_1^2 + 2} \right\} - F = \infty(mK_2^g). \end{aligned} \quad (4)$$

For non-polar ($\mu_1 = 0$) solvents $F = 0$; if $\mu_1 \neq 0$,

$$F = 15\pi N_A(1 + 1.5\alpha_1 t_1)(1 - \alpha_2 t_1)(1 - 4\alpha_1 t_1)^{-1} M_2 M_1^{-1} (\partial \alpha_1 t_0 / \partial X_2)_{X_2=0}$$

with accuracy of $(\alpha t)^2$.

A lack of reliable data on the components of A_{ij}^0 and μ_{0i} of the majority of polar compounds inevitably compels us to restrict our studies to the molecules with the symmetry C_2 , C_{2v} , and higher, because dipole direction in these molecules is parallel to one of the axes of the A_{ij}^0 tensor. In that case the dipole term in (1) takes the form: $\Theta_2 = (\mu_{02}^l) (2\alpha_l^0 - \alpha_m^0 - \alpha_n^0)$, $l \neq m \neq n = 1, 2, 3$; where α_{pr}^0 are calculated from $\bar{\alpha}_0$ and γ^2 by application of valency schemes ($\gamma^2 = 2 \sum_{i,j} \alpha_i^0 \alpha_j^0 - 6 \sum_{i,j} \alpha_i^0 \alpha_j^0$ is optical anisotropy).

3. Experimental test of the model

To experimentally test the expression (4) and to compare it with the results of other EB theories of liquids and known values of mK^g we measured Kerr constants $B^1 = nK^1 \lambda^{-1}$ (λ is the wavelength of an analyzing beam of light) of a series of binary extremely diluted solutions, showing weak intermolecular interaction with components which have widely varying polarities and polarizabilities. The equipment and the procedure of compensational measurements are described in [5].

The outcomes of juxtaposition of gaseous phase Kerr constants mK_2^g with the calculated ones $\infty(mK_2^1)_i$ of substances dissolved in non-polar and polar solvents are compared in Tables I and II: $\Delta mK_2^g = |mK_2^g - \infty(mK_2^1)_i| (mK_2^g)^{-1}$.

Therewith, according to (4), $\infty(mK_2^g)_i = \infty(mK_2^1)_i + F_i$ and the index i denotes the explicit form of the local field either employed within the limits of Langevin-Born's theory: $i = 1$ — the Lorenz model, $i = 2$ — Onsager's one, $i = 3$ — Block-Walker's [6]; or used in the expression (4): $i = 4$ [2], $i = 5$ [3].

The data presented in Tables I and II demonstrate the following regularities: in accordance with the conclusions of the orientational theory and Eq. (1)

TABLE I
 Molar Kerr constants in gas phase (mK^g) and solvent effect ($\Delta mK_{2,i}^g$) in non-polar media.

<i>N</i>	Substance	mK^g [10 ¹² CGSE]	$\Delta mK_{2,1}^g$	$\Delta mK_{2,2}^g$	$\Delta mK_{2,3}^g$	$\Delta mK_{2,4}^g$	$\Delta mK_{2,5}^g$
1	1,4-dichlorbenzene*	36.74	0.614	0.457	0.206	0.126	0.098
2	<i>p</i> -xylene	31.10	0.559	0.429	0.194	0.093	0.084
3	mesitylene	30.19	0.546	0.404	0.187	0.083	0.073
4	benzene	17.16	0.534	0.392	0.167	0.076	0.061
5	<i>n</i> -octane	9.64	0.532	0.387	0.155	0.071	0.061
6	<i>n</i> -heptane	6.51	0.528	0.383	0.149	0.070	0.058
7	nitrobenzene**	1332.0	1.909	0.998	0.672	0.364	0.253
8	nitromethane*	53.62	1.857	0.754	0.551	0.319	0.188
9	chlorobenzene*	191.2	1.772	0.613	0.468	0.267	0.163
10	<i>o</i> -xylene*	47.0	1.593	0.487	0.372	0.225	0.119
11	toluene	39.8	1.456	0.482	0.349	0.183	0.098
12	<i>m</i> -xylene	33.5	1.434	0.474	0.223	0.179	0.087

Solvents: cyclohexane, * tetrachloromethane, ** benzene.

 TABLE II
 Molar Kerr constants of polar compounds dissolved in non-polar media (mK^l) and solvent effect ($\Delta mK_{2,i}$) in polar media (water).

<i>N</i>	Substance	∞mK_2^l [10 ¹² CGSE]	$\Delta mK_{2,1}$	$\Delta mK_{2,2}$	$\Delta mK_{2,3}$	$\Delta mK_{2,4}$	$\Delta mK_{2,5}$
1	dimethylsulphoxide	143.4	2.249	1.286	0.945	0.320	0.304
2	formaldoxim	290.9*	2.241	1.294	0.939	0.317	0.281
3	nitromethane	89.0**	2.037	1.260	0.988	0.323	0.272
4	acetoamide	261.3	2.185	1.237	0.947	0.298	0.226
5	aceton	102.0	2.206	1.191	0.894	0.286	0.213
6	pyridine	142.6*	2.091	1.174	0.873	0.286	0.209

Non-polar solvents: tetrachloromethan, * dioxan, ** benzen.

the magnitudes of electro-optical constants of both pure and dissolved non-polar compounds are proportional to the optical anisotropies of molecules. Thus, for instance, the largest mK_2 pertains to $C_6H_4Cl_2$ ($\gamma^2 = 106 \text{ \AA}^6$) for all studied non-polar solutions, while the smallest one — to *n*-heptane ($\gamma^2 = 5.13 \text{ \AA}^6$). Polar substances (numbers 7...12 in Table I) manifest complex dependence of mK_2 on molecular properties. Nevertheless, they confirm constant's additivity with respect to anisotropic ($\Theta_1 > 0$) and dipole ($\Theta > 0$ or $\Theta_2 < 0$) terms. As there exists the general tendency toward the increase in electro-optical effect with the growth of μ_0 and γ^2 of molecules of a dissolved compound: molar Kerr constant (mK_2) of nitrobenzene ($\mu_0 = 4.17 \text{ D}$, $\gamma^2 = 75 \text{ \AA}^6$) exceeds that mK_2 of methylbenzene ($\mu_0 = 0.37 \text{ D}$, $\gamma^2 = 37 \text{ \AA}^6$). The data in Table II confirm this conclusion as well.

4. Discussion

The technique of infinite dilution enables us to minimize the impact of intermolecular interactions between solute molecules on their properties. However, solvent effect remains quite noticeable. Thus, in our experiments the influence of intermolecular (dispersive) reciprocity on the computed values of mK_2 of non-polar substances dissolved in C_6H_{12} (numbers 2...6 in Table I) reveals itself in the linear correlation between the relative errors ΔmK_2^g and polarizational characteristics of molecules: α and γ^2 of C_8H_{10} equal 16.6 \AA^3 and 78.6 \AA^6 , and those of *n*-heptane — 1.63 \AA^3 and 5.12 \AA^6 , respectively. For the solutions of polar compounds in tetrachloromethane (numbers 8...11), which exhibit coupling of dipole-induced dipole nature, the errors ΔmK_2^g augment with the enlargement of molecular moments: μ_{O_2} of CH_3NO_2 and C_8H_{10} amount to 3.5 D and 0.47 D, respectively. The same tendency is detected for polar solvents ($\mu_{O_1}, \mu_{O_2} \neq 0$, Table II) with conspicuous dipole-dipole reciprocity. As it has already been intimated, the assortment of polar compounds with known mK^g is sharply limited. This is the reason which forces us to comparison of the calculated values ${}_{\infty}(mK_2^g)_i$ of substances dissolved in water (Table II) with relevant characteristics ${}_{\infty}(mK_2^l)_i$ of solutions with non-polar solvents. The latter have been determined by the classical orientational theory with the Lorenz local field. It is seen from Table II that the magnitudes of relative errors ΔmK_2^g for polar solutes in polar solvents are systematically greater than the errors for substances dissolved in non-polar solvents (Table I), cf. for example, the solutions of nitromethane. An obvious explanation of this fact is dissimilarity of intermolecular interactions solute-solvent.

The discrepancy between the gaseous phase values of molar EB constants and those computed from the information on binary solutions within the limits of Langevin-Born's theory of Kerr effect is mainly conditioned by the types of model descriptions of both interrelations between Maxwell's and local fields and anisotropy of molecular polarizabilities. Introduction of Onsager's internal field, which implicitly (via the reactive field) accounts for the intermolecular coupling solute-solvent, instead of the Lorenz one into the theory of birefringence of condensed media somewhat corrects the figures (mK_2) for all binary solutions examined: $\Delta mK_{2,1}^g > \Delta mK_{2,2}^g$. Subsequent evolution of this idea needs the explicit representation of the dielectric permittivity function at the boundary Onsager cavity-continuum [5]: $\Delta mK_{2,2}^g > \Delta mK_{2,3}^g$. Considering inductive-orientational contributions of reactive field to the potential energies of molecules in a solution under the conditions of EB experiments, we obtain: $\Delta mK_{2,3}^g > \Delta mK_{2,4}^g \geq \Delta mK_{2,5}^g$, because local distribution and dielectric induction enhances dipole moments in condensed phase. According, for instance, to the data in Table I, for the model $i = 5$ relative errors in molar constants of polar substances dissolved in non-polar media are associated with the corresponding values of mK_2^g by the expression: ${}_{\infty}(mK_2^g)_5 \approx (1 + \overline{\Delta mK_{2,5}^g})mK_2^g \approx (1 + 0.151) mK_2^g$, while the same correlation in the case of the Lorenz local field ($i = 2$) has the form ${}_{\infty}(mK_2^g)_2 \approx (1 \pm 0.742)mK_2^g$, with the inaccuracy five times larger.

The data presented above indicate that the theory of EB must be completed with the theory of local fields which can account for the local electric induction.

The outcomes of known approaches to the calculations of molar Kerr constants (mK_2) of a great number of binary solutions display the following tendency:

$$\Delta mK_{2_1}^g > \Delta mK_{2_2}^g > \Delta mK_{2_3}^g.$$

Our results confirm this sequence and supplement it enhancing previous developments

$$\Delta mK_{2_3}^g > \Delta mK_{2_4}^g \geq \Delta mK_{2_5}^g.$$

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