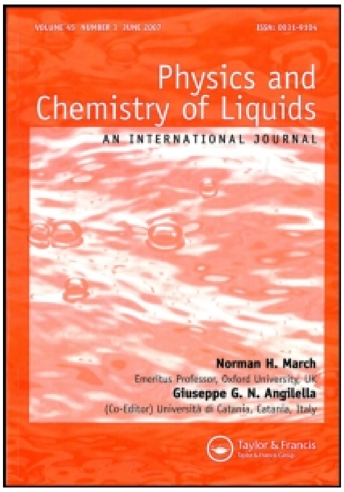

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MOLECULAR COMPLEXES IN DILUTE LIQUID BINARY SOLUTIONS

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Highly diluted solutions of dipolar liquid toluene in nondipolar benzene as well as in nondipolar p-xylene show local extrema of the magnetooptical and light scattering effects. The observed local extremum of the degree of depolarization of unpolarized incident light D_n, the Cotton-Mouton constant C^M and the Verdet constant V (Faraday effect) coincide with the mole concentration $f_2 \sim 0.015$ and $f_2 \sim 0.03$ of toluene in solutions The local extreme of D_n, C^M and V values are interpreted on the grounds of molecular interaction between polar (toluene) and nonpolar (benzene, p-xylene) molecules.

KEY WORDS: Liquid solutions, light scattering, Cotton-Mouton and Faraday effects

1 INTRODUCTION

The magnetooptical Cotton-Mouton[1,2], Faraday[3] effects and light scattering effect are efficient optical methods applied in the studies of molecular interactions in liquids. The choice of these methods follows from correlations in the theoretical description of these effects. The theories of light scattering, Cotton-Mouton and Faraday effects have been exactly formulated for ideal gases. In the real gases, liquids and solutions of liquids theoretical description of the interaction processes between molecules is complicated.

Molecular interaction between molecules are usually studied assuming the model of pair interactions[4] taking into consideration the interaction between two nearest molecules or the interaction of a molecule and its isotropic surrounding[5,6]. Modelling of diffraction data are in progress[7].

For dilute solutions of dipolar liquids in nondipolar solvents[8] we can neglect dipole interactions between dipolar molecules because the latter are effectively isolated by nondipolar molecules of the solvent. For this reason it is interesting to study a dilute solution of a dipolar component surrounded by nondipolar molecules of the solvent. In highly diluted solutions we should be able to observe the coupling effect between a dipolar molecule immersed in the nondipolar solvent because the final statistical ensemble (complex) e.g. a pair must be characterized by effective optical and magnetooptical polarizability of a complex. The anisotropy, if any, of the optical and magnetooptical polarizability of a complex can be easily detected by the Cotton-Mouton, Faraday and light scattering methods[2].

Statistical binary, ternary etc. complexes (dipolar-nondipolar molecules) between a dipolar molecule of the solute and nondipolar molecules of the solvent display different optical, electrooptical and magnetooptical properties than individual molecules of the solvent or the solute in a liquid solution. The coupled statistical molecular ensembles are characterized by specific effective anisotropy of optical, electrooptical and magnetooptical polarizability. Such an ensemble is a dynamic entity and a change in the number of dipolar and nondipolar molecules under a change of the solution mole concentration f_2 effects the effective anisotropy of individual complexes.

The most probable formation of pairs of coupled molecules practically determine the magnetooptical and optical properties of the highly diluted solution. The coupling of the molecules affect the solution concentration dependences of light scattering, Cotton-Mouton and Faraday effect. These dependences, in our case, show local extremes of the degree of depolarization of scattered light (D_n), the molar Cotton-Mouton constant (C^M) and the Verdet constant (V). They are presented in the work.

2 LIGHT SCATTERING EFFECT

The effect of light scattering in a molecular medium is, according to Rayleigh, determined by molecular structure of its molecules. Optical properties of a molecule depend on the kind of bonds between its atoms. For an optically anisotropic molecule of the main optical polarizabilities b_{11}, b_{22} and b_{33} along the three main directions of its symmetry, the square optical anisotropy, δ, is described by the expression:

$$\delta = \frac{(b_{11} - b_{22})^2 + (b_{22} - b_{33})^2 + (b_{33} - b_{11})^2}{(b_{11} + b_{22} + b_{33})^2}. \tag{1}$$

Let's assume that the square optical anisotropy of a coupled binary or ternary ensemble of molecules in solution is given by Eq. 1. However, the binary or ternary ensembles (complex) should be well isolated from each other so that they would not interact with one another and their optical polarizabilities are $b^*_{11}, b^*_{22}, b^*_{33}$. This assumption should be fulfilled for highly diluted solutions in which the number of molecules of the solvent is by a few orders of magnitude higher than the number of the solute molecules. The latter are coupled in binary, ternary etc. complexes with molecules of the solvent. Thus, we assume the occurrence of well isolated ensembles of coupled molecules (mainly pairs of solute-solvent molecules) in a sea of the solvent molecules. Then, an ensemble can be treated as isolated and its optical polarizabilities $b^*_{11}, b^*_{22}, b^*_{33}$ introduced to Eq. 1, instead of b_{11}, b_{22}, b_{33} give the square optical anisotropy, δ^*, of the complex.

For the above formulated model of interaction between polar and nonpolar molecules which are forming complexes we can put forward following remarks:

1. A binary highly diluted solutions contain statistical ensembles of coupled molecules of dipolar solute and nondipolar solvent. The ensembles are isolated from one another by solvent molecules which dominate in the environment.

2. It should be expected that in certain molar concentration range of the solution all dipolar molecules are coupled with solvent molecules forming complexes.
3. With increasing molar concentration of dipolar molecules, the interactions among them play a dominant role in molecular effects in the liquid state[1].

In a highly diluted solutions the molecules forming a complex interact and the effective result of the coupling (dipol-nondipol configuration) changes significantly with the concentration f_2 of the dipolar component in the solution. The change in configuration of the molecules in complex causes changes in the main optical polarizabilities $b^*_{11}, b^*_{22}, b^*_{33}$ of the complex and thus in the square optical anisotropy δ^* whose value is found from measurements of the degree of light depolarization D_n, in Rayleigh scattering. The measured values of D_n are presented in Figure 1.

A complex (dipolar–nondipolar coupled molecules) in the case of a binary solution is described by δ^*_{CM} as follows[9]:

$$\delta^*_{CM} = \frac{10 D_n \gamma_R}{(6 - 7D_n)(1 + J^*_{12})} \tag{2}$$

where γ_R is the factor of intermolecular radial correlation[2]. The value of γ_R is obtained from measurements of β_τ which is isothermal compressibility of the medium: $\gamma_R = \varrho_0 kT\beta_\tau$ and ϱ_0 is the number of molecules in the unit volume, k–Boltzmann constant, T–temperature in K. The factor of angular correlations, J^*_{12}, appears also in description of the Cotton-Mouton effect[2].

3 MAGNETOOPTICAL COTTON-MOUTON EFFECT

(An external magnetic field of $\underline{H}$ perpendicular to the light beam in a medium induces its birefrignence)

From the measurements of the Cotton-Mouton effect and from the molar Cotton-Mouton constant C^M of the studied toluene-benzene, toluene-p-xylene binary solutions the value of J^*_{12}, the factor of angular correlations, has been calculated. We assume that for a binary highly diluted solution the following relations[2,9] gives a good description of J^*_{12}:

$$J^*_{12} = \Delta C^M / \{2f_2(1-f_2)[(1-f_2)C^M_1(g) + f_2 C^M_2(g)]\} \tag{3}$$

where $\Delta C^M = 2f_2(1-f_2)C^M_g$ is the difference between C^M_{12}, the measured value of the molar Cotton-Mouton constant of the solution influenced by the interaction of molecules in complexes, and the additivity relation $C^M_{f_2} = [(1-f_2)C^M_1 + f_2 C^M_2]$. The quantities $C^M_1(g)$ and $C^M_2(g)$ stand for molar Cotton-Mouton constant of the solvent, $C^M_1(g)$, and the solute, $C^M_2(g)$, in gas state whereas C^M_1 and C^M_1 are the molar constant of the solvent and solute in liquid state. From the measured C^M_{12} (Fig. 2), C^M_1 and C^M_2, the values of ΔC^M are:

$$\Delta C^M = C^M_{12} - C^M_{f_2}, \tag{4}$$

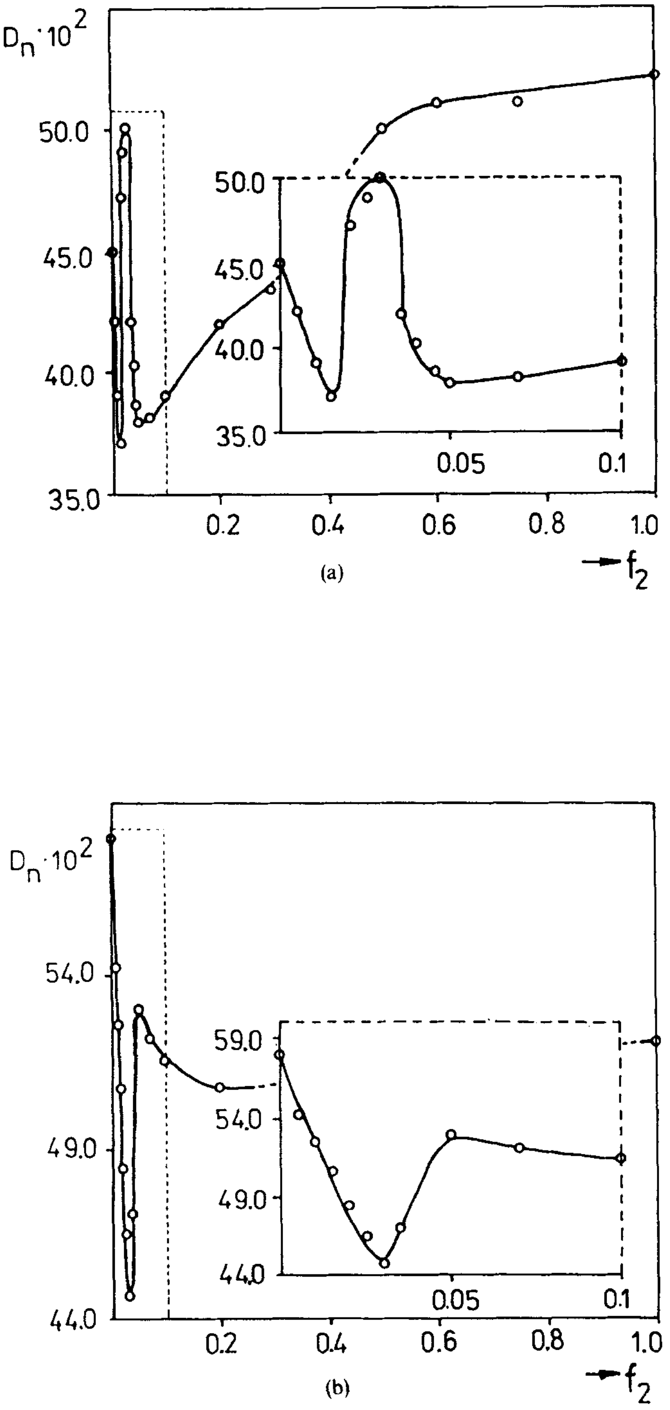
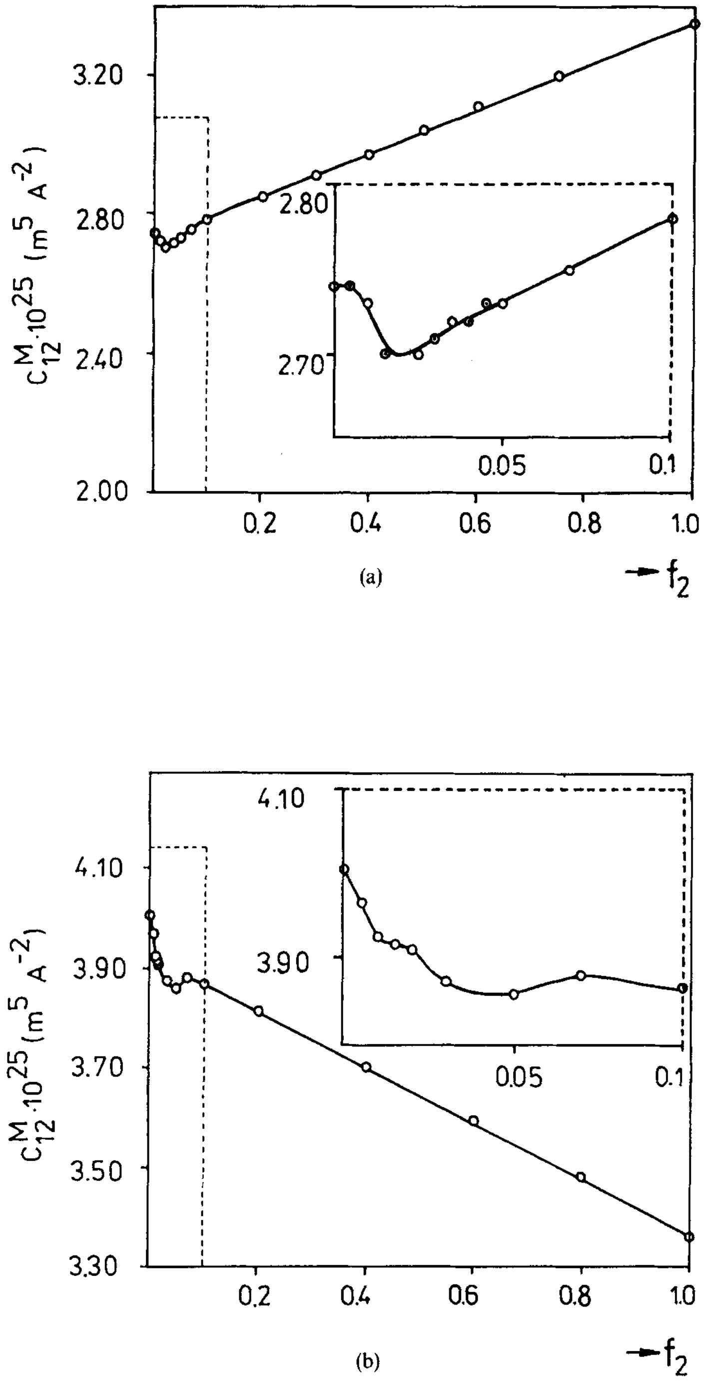


Figure 1 Light depolarization factor D_n of the solutions: toluene in benzene (a), toluene in p-xylene (b).



(a)

(b)

Figure 2 Molar Cotton-Mouton constant C^M_{12} of the solutions: toluene in benzene (a), toluene in p-xylene (b).

and the values of J^*_{12} with respect to the mole concentration f_2 of the solutions are determined (Eq. 3).

The values of D_n (Fig. 1) and C^M_{12} (Fig. 2) found from measurements of light scattering (D_n) and Cotton-Mouton effect (C^M_{12}) permit determination of δ^*_{CM} from Eq. 2 which is valid for molecule interaction in the complex.

The γ_R value for solution is calculated from the additivity rule and the known γ_R values[9,13] for toluene: $2.15 \times 10^{-2}\,\mathrm{mol}^{-1}$, benzene: $2.65 \times 10^{-2}\,\mathrm{mol}^{-1}$, p-xylene: $1.35 \times 10^{-2}\,\mathrm{mol}^{-1}$. In this way we get the information about the effective optical anisotropy of the coupled statistical complex in the solutions and about the dependence of δ^*_{CM} on the mole concentration f_2 of the solutions. The calculated values of J^*_{12}, the angular correlation factor, are presented in Figure 3 and the square optical anisotropy δ^*_{CM} in Figure 4.

For molecular complexes of axial symmetry we have equal values of optical polarizabilities $b^*_{22} = b^*_{33}$ and we assume the magnetooptical polarizabilities a^*_{22}, a^*_{33} are also equal.

For the axial symmetry of a molecule or a complex the molar Cotton-Mouton constant, C^M, is determined[1,2,9,10] by:

$$C^M = B(a^*_{11} - a^*_{33})(\delta^*_{CM}/2)^{1/2} \tag{5}$$

where $B = (n^2 - 1)M/(n^2 + 2)\rho kT$ is a parameter dependent on the density, ϱ, molar mass, M, light refraction index, n, and temperature, T, of the solution, $(a^*_{11} - a^*_{33})$ is the anisotropy of magnetooptical polarizabilities of the complex.

The values of $(a^*_{11} - a^*_{33})$ can be calculated from (Eq. 5) provided that from the experiment C^M and δ^*_{CM} are known. Results of the $(a^*_{11} - a^*_{33})$ calculation for toluene-benzene and toluene-p-xylene solutions are presented in Figure 5.

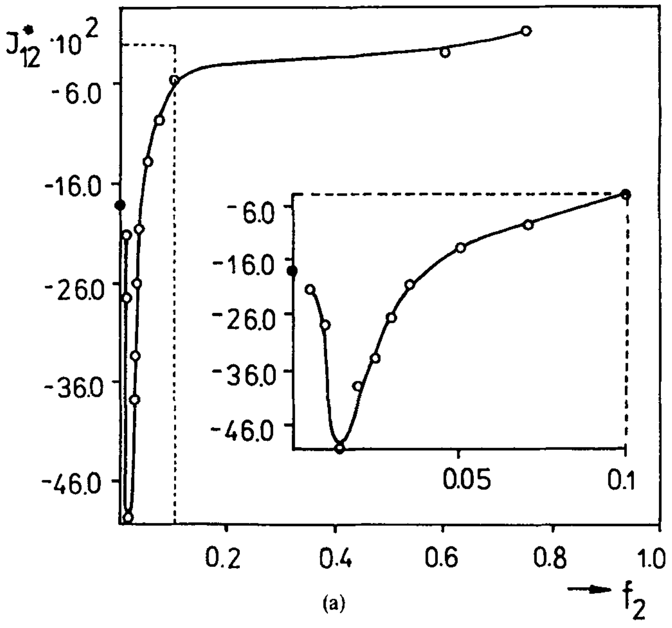
4 MAGNETOOPTICAL FARADAY EFFECT

(An external magnetic field of $\underline{H}$ parallel to the light beam induces the rotation of the light polarization plane in a medium)

The square optical anisotropy denoted now as δ^*_V can be determined from the magnetooptical Faraday effect[10]. In the classical description, the Faraday effect in molecular systems is in the first approximation described by the Verdet constant, V, given as:

$$V = A\frac{(n^2 - 1)^2}{n\lambda^2}(1 - \delta^*_V/2) \tag{6}$$

where, $A = \pi/2N_L ep$, is a coefficient characterizing electron structure of an atom or molecule, n is the refraction index, λ is the wavelength of the light propagating in the medium, N_L-Loschmidt number, e-electron charge, p-number of dispersion electrons of a molecule and δ^*_V is the square optical anisotropy of the same physical meaning as



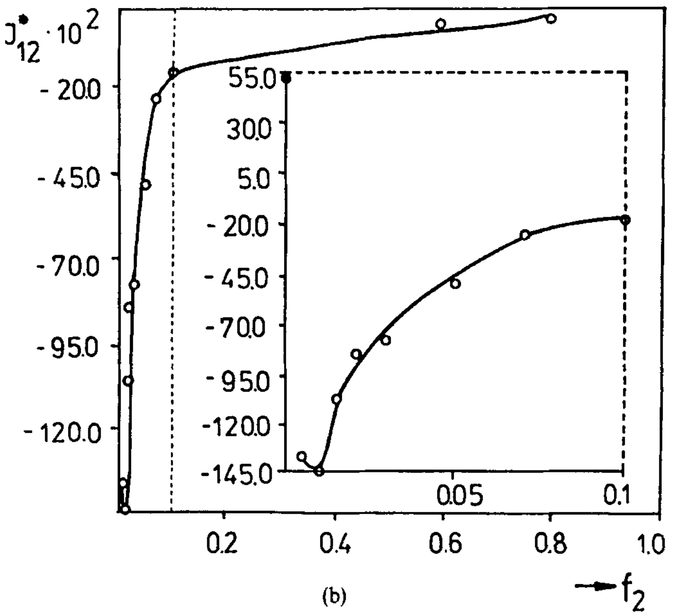


Figure 3 Angular correlation factor J^*_{12} and its dependence on the mole concentration f_2 of the solutions: toluene in benzene (a), toluene in p-xylene (b).

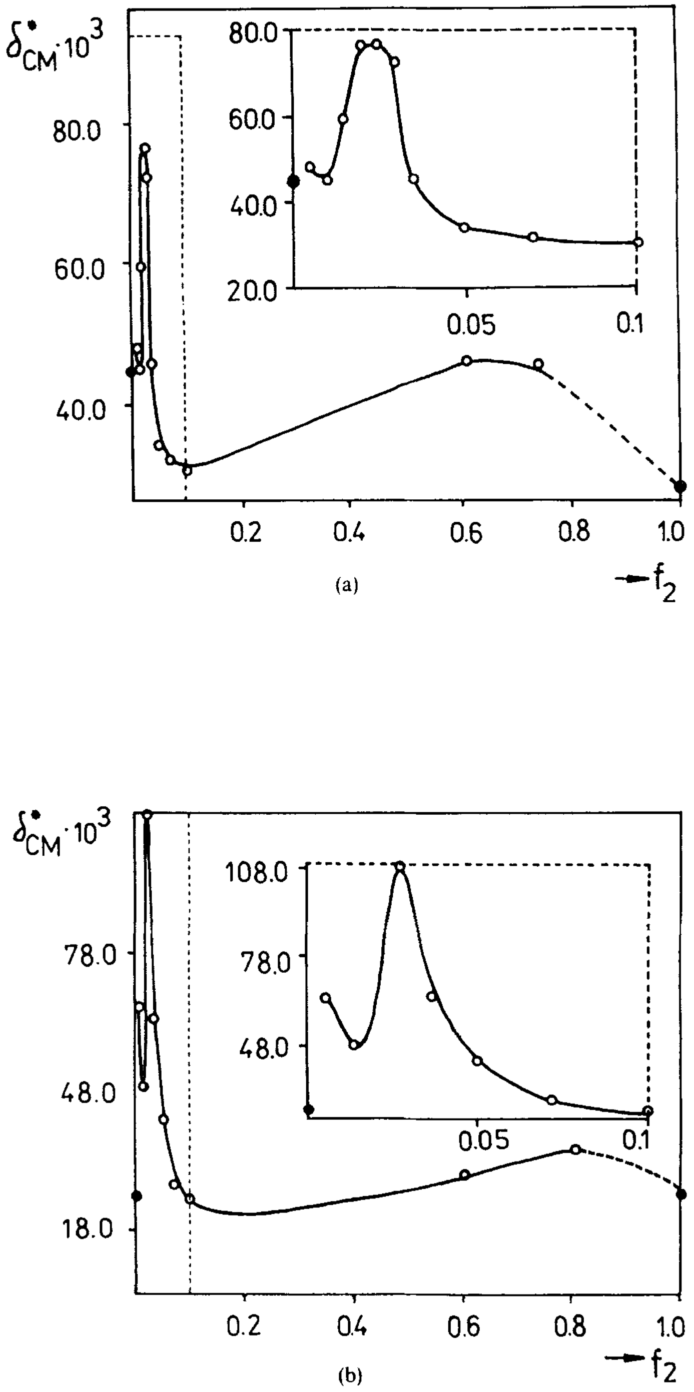


Figure 4 Optical anisotropy δ^*_{CM}: (a) – solutions of toluene in benzene, (b) – solutions of toluene in p-xylene.

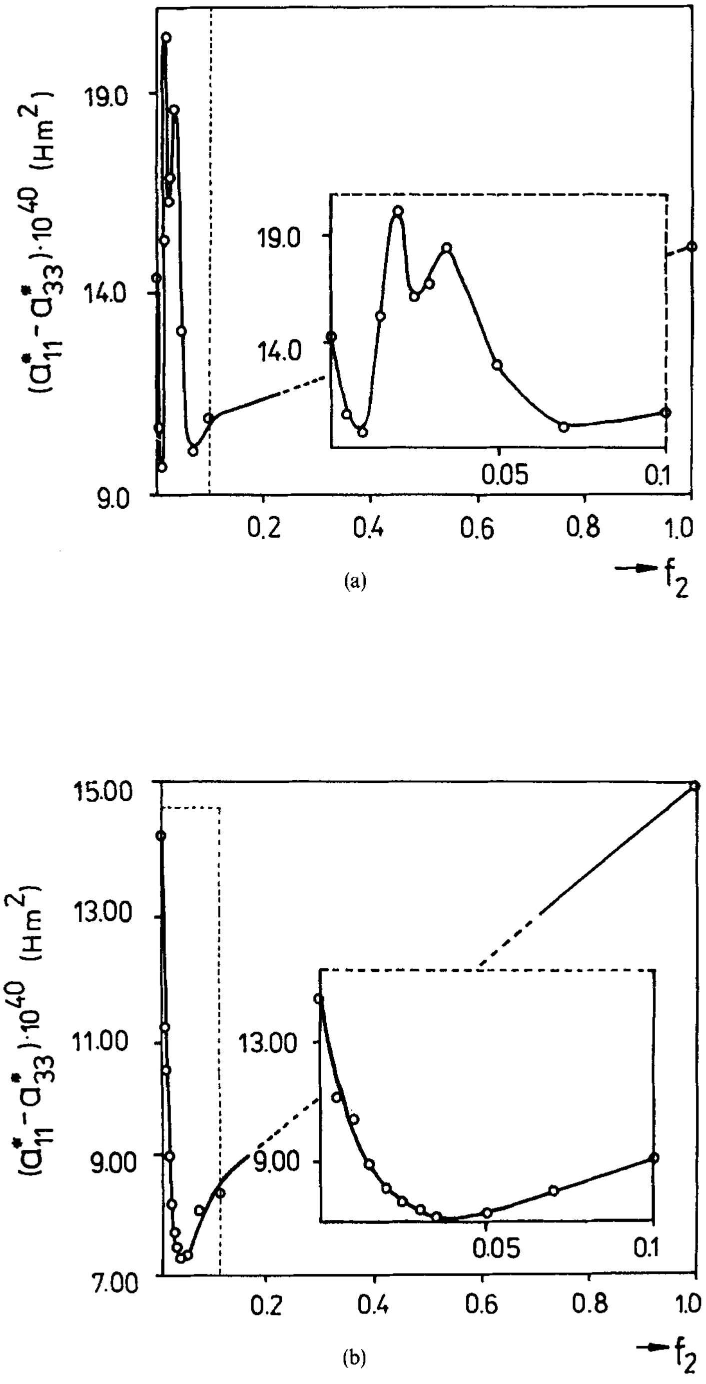


Figure 5 Anisotropy of magnetooptic polarizability $(a^*_{11}-a^*_{33})$: (a) – solutions of toluene in benzene, (b) – solutions of toluene in p-xylene.

δ^* and δ^*_{CM}. From this point of view, Eq. 5 is the relation between the Verdet constant, V, and the square optical anisotropy δ^*_V. Thus, the latter can be determined from the measurements of Faraday effect. The results of Verdet constant measurements for diluted solutions of toluene in benzene and in p-xylene are shown in Figure 6. From Eq. 5 and the measured V the δ^*_V values have been calculated. This means we have at our disposal two independent experimental methods of δ^* determination. In the first one δ^*_{CM} is found from the light scattering (D_n) data and magnetooptical Cotton-Mouton effect (J^*_{12}) measurements and in the second one δ^*_V (Eq. 6) is obtained from Faraday effect measurements.

If the independent relations (Eqs. 2, 3 and 6) are valid for the liquids investigated, the numerical values of δ^*_{CM} (Eq. 2) and δ^*_V (Eq. 6) have to be identical for the analysed solutions and moreover identical to the value of δ^* (Eq. 1) for the individual molecules of toluene, benzene and p-xylene within an experimental error. The data collected in Table I prove the validity of the above remark. However, the δ^*_{CM} results are in a better agreement with the literature data for benzene, p-xylene and toluene molecules in liquid state while the δ^*_V data are in a better agreement with the literature data for these molecules in the gas state.

The complexes, as was assumed, do not interact in dilute solution with one another. Their formation in dilute solutions of toluene in benzene or p-xylene as well as in other binary solutions in these solvents is beyond doubt[2,3]. In this paper it is proved by the presence of local extremes in the concentration dependences of D_n (Fig. 1), C^M_{12} (Fig. 2), V (Fig. 6), J^*_{12} (Fig. 3) and δ^*_{CM} (Fig. 4).

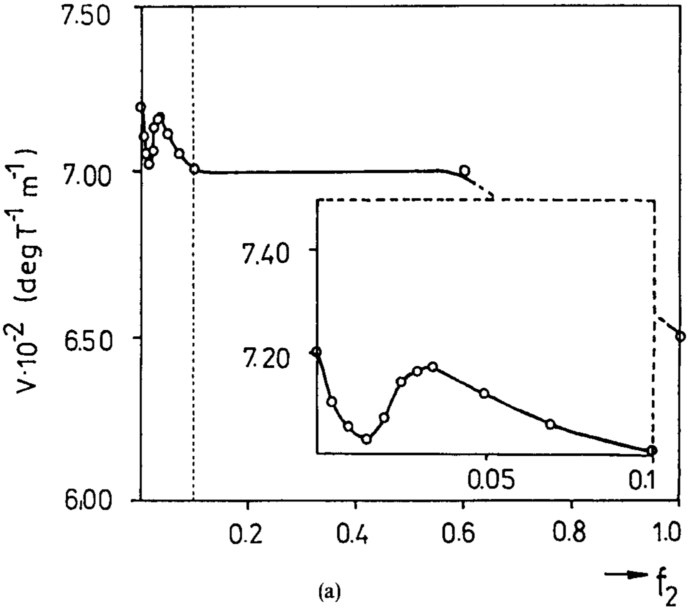
From the experimental results of δ^*_{CM} the optical anisotropy $(b^*_{11} - b^*_{33})$ of the complex toluene-benzene and toluene-p-xylene have been calculated. The values of $(b^*_{11} - b^*_{33})$ are obtained from Eq. 2 if we introduce $b^*_{22} = b^*_{11}$ and $\delta^*_{CM} = 2(b^*_{11} - b^*_{33})^2/(b^*_{11} + b^*_{33})^2$. Thus, we have:

$$(b^*_{11} - b^*_{33}) = 3\bar{b}^*(\delta^*_{CM}/2)^{1/2} \tag{7}$$

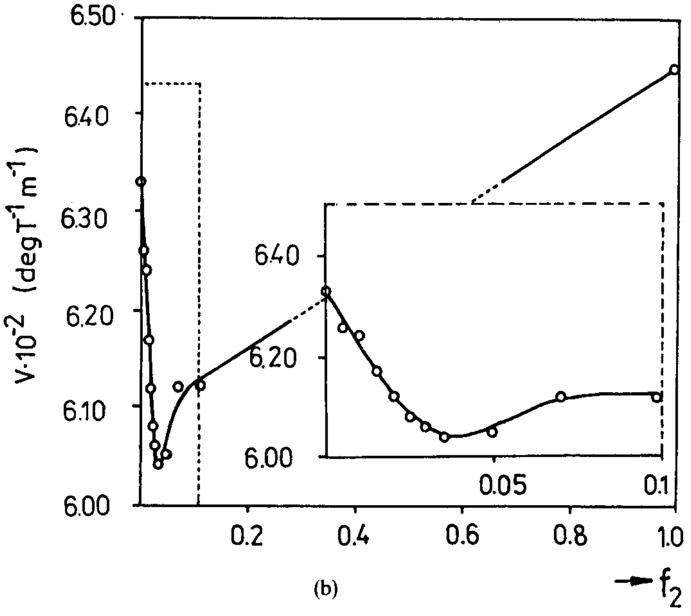
where $\bar{b}^*$ is the mean optical polarizability of the complex: $\bar{b}^* = (b^*_{33} + 2b^*_{11})/3$.

The change in anisotropy of optical polarizability $(b^*_{11} - b^*_{33})$, (Fig. 7), and of magnetooptical polarizability $(a^*_{11} - b^*_{33})$, (Fig. 5), with the mole concentration f_2 of the solutions is the effect of changes in the configuration of molecules in the complex for different f_2. The same conclusion follows from the mole concentration f_2 dependence of the parameter of angular correlations J^*_{12} (Fig. 3). It is very interesting to observe an extraordinary increase of the J^*_{12} value for highly diluted solutions of toluene in p-xylene (Fig. 3b). The solution of mole concentration $f_2 = 0.005$ gives $J^*_{12} = -1.36$ while for pure p-xylene in liquid state ($f_2 = 0$) $J^*_{22} = 0.54$. According to the general theoretical result[11,12] the p-xylene molecules in liquid state are coupled mainly to form statistical pairs of perpendicular orientation ($J^*_{22} > 0$) of their main symmetry axes. The complex toluene—p-xylene ($f_2 = 0.005$) represents interaction with parallel ($J^*_{12} < 0$) orientation of the main symmetry axes of these molecules.

For the parallel orientation of molecules in a complex its optical anisotropy $(b^*_{11} - b^*_{33})$ tends to reach a minimum[11,12]. The result in Figure 7b is a good verification of the theoretical prediction. From this point of view, we can argue that magnetooptical Cotton-Mouton effect and Rayleigh scattering of light are powerful



(a)



(b)

Figure 6 Verdet constant of diluted solutions: (a) – toluene in benzene, (b) – toluene in p-xylene.

Table 1 Optical, Magneto-Optical Polarizabilities and Anisotropy Parameters of Benzene, p-Xylene, Toluene

	References Data									*Present Results*			
		13			14								
Liquids	b_{11}	b_{22} $(10^{-40}\mathrm{Fm}^2)$	b_{33}	$\bar{b}$	δ^*	δ^*_{CM} (10^{-3})	δ^*_V	J^*_{22} (10^{-2})	D_n	C^M $(10^{-25}\mathrm{m/A}^2)$ $\lambda = 546\,\mathrm{nm}$	V (deg/Tm) $\lambda = 488\,\mathrm{nm}$	$(b^*_{11} - b^*_{33})$ $(10^{-42}\mathrm{Fm}^2)$	$(a^*_{11} - a^*_{33})$ $(10^{-42}\mathrm{Hm}^2)$
Benzene	1.09	1.09	0.60	0.92	73 (gas)							49 (gas)[13]	
C_6H_6					38 (liq)	52	62	−18	45	2.74	720	48 (extrap)	14.24
p-Xylene	1.38	1.61	0.78	1.26	77 (gas)							83⁺ (gas)[13]	
$C_6H_4(CH_3)_2$					35 (liq)	26	75	54	58	4.00	630	80 (extrap)	14.14
Toluene	1.21	1.38	0.66	1.08	79 (gas)							55 (gas)[13]	
$C_6H_5CH_3$					37 (liq)	28	63	72	52	3.35	649	54 (extrap)	14.99

⁺ data for $(b^*_{22}) - b^*_{33})$; b^*_{33} axis is perpendicular to the plane of the molecule

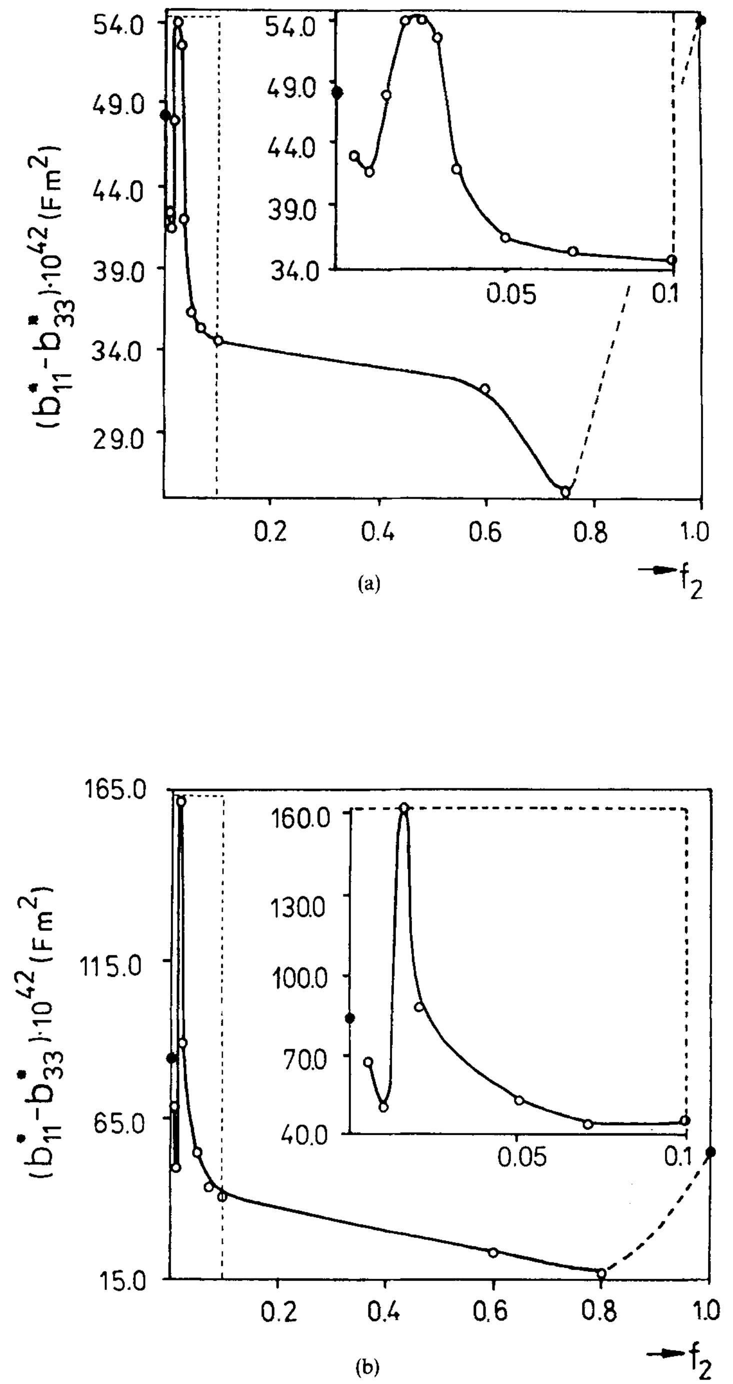


Figure 7 Anisotropy of optical polarizability $(b_{11}^{*}-b_{33}^{*})$: (a) – solutions of toluene in benzene, (b) – solutions of toluene in p-xylene.

methods of analysis of molecular interactions in liquids. We can also point out that for a diluted binary solutions of liquids the main mechanism of molecular interactions between polar and nonpolar molecules involves creation of complexes formed by pairs of polar-nonpolar molecules. Assuming this kind of interaction a coherent analysis of the experimental data obtained in this paper can be provided. For example the extrapolation to $f_2 = 0$ of the curve in Figure 3a gives $J^*_{22} = -0.18$ (dot) which is the value of J^*_{22} for liquid benzene[1] (Table I). Similarly, from Fig. 3b (dot) we have for p-xylene $J^*_{22} = 0.54$ which is the value for liquid state of p-xylene[3] (Table I). Also, the extrapolated value for $f_2 = 0$ of the $(b^*_{11} - b^*_{33})$ dependence of f_2 gives (dots, Fig. 7) a very good agreement between the literature data[13] and the present results (Table I) for toluene, benzene (Fig. 7a) and p-xylene (Fig. 7b).

An independent confirmation of this conclusion is provided by the Faraday effect measurements and δ^*_V results. The values of δ^*_V (Table I) are correlated with the data presented in literature for gaseous state instead of liquid state. It means that Faraday effect is less sensitive to the molecular interaction in liquids and depends mainly on the structure of the individual molecule. However, the existence of complexes in diluted solution of investigated liquids is clearly indicated from the local extreme value (minimum and maximum) of the Verdet constant (Fig. 6).

CONCLUSION

The results of the performed investigations bring a coherent information about molecular structure of the medium—(liquid solutions) obtained from the measurements of light scattering, Cotton-Mouton and Faraday effects. This coherence proves the validity of the model based on the assumption of complexes between toluene and benzene or toluene and p-xylene molecules in their binary diluted solutions.

The changes of the anisotropy of the optical and magnetooptical polarizabilities of the complexes with respect to the mole concentration f_2 of the solutions is a direct indication of the molecular interaction in diluted solutions of liquids. It may be used for analysis of the geometric configuration of molecules in a complex. The concentration dependences of $(b^*_{11} - b^*_{33})$ and $(a^*_{11} - a^*_{33})$ reveal local extremes e.g. for toluene solution in benzene and in p-xylene: a minimum at $f_2 \sim 0.015$ and a maximum at $f_2 \sim 0.03$. This means that the toluene dipolar molecule is coupled to the solvent nondipolar molecule benzene or p-xylene with a tendency to perpendicular configuration of their longer symmetry axes for $f_2 \sim 0.015$ and the molecules in the complex change the orientation into a parallel configuration for increasing f_2. This interaction gives an increase of the $(b^*_{11} - b^*_{33})$ values (Fig. 7) and the local maximum of δ^*_{CM} value at $f_2 \sim 0.03$ (Fig. 4).

A quantitive analysis of the changes of the optical and magnetooptical effective polarizabilities in connections with the conformation of molecules in a molecular complex is in progress.

The experimental results of the paper permit concluding that investigation of light scattering, Cotton-Mouton and Faraday effects provides the information about the value of square optical anisotropy δ^* of the molecular complexes in liquid medium and thus about the anisotropy of the optical and magnetooptical polarizabilities of a molecule or, in the case of complexes, about the anisotropy of the complex. The experimental results presented in the paper contribute to the discussion on the interaction between molecules in solution[7,15,16,17] aiming at a better insight into the mechanism of interactions among molecules in the liquid environment.

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