

Molecular orientation in binary liquid mixtures from excess Cotton-Mouton constant



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ABSTRACT

We show the results of magnetically induced birefringence measurements performed in binary mixtures of simple molecular liquids. New excess function was introduced based on experimentally determined values of Cotton-Mouton constant - a quantity directly related to the induced orientation of anisotropic molecules. Concentration dependencies of excess molar Cotton-Mouton constant were compared with analogous characteristics of excess molar volume. Both excess functions are well reproduced using Redlich-Kister polynomial expansion. The results suggest that in the examined mixtures binary pairs of unlike molecules are formed in which molecular planes are oriented parallel to each other with simultaneous rotation along the axis perpendicular to benzene plane. Such preferred angular arrangement is independent on the average intermolecular distance within a pair-aggregate.

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1. Introduction

In the condensed liquids state direct interactions between closely packed molecules lead to disturbance of the local structure making the physical properties measured to deviate from these expected for non-interacting system. Information on the role of interactions between two unlike molecules is usually provided by studies of binary solutions of two liquids. A convenient way of describing the real solution is to use the so-called excess functions [1]. These are defined as the deviation of the measured physical quantity from the values of hypothetical ideal solution of the same composition, temperature and pressure as the real mixture. Knowledge of the sign and the shape of excess functions provides a way for an analysis of thermodynamics of mixing process and interpretation of interactions responsible for mutual packing of the molecules. The suitability of an excess functions was demonstrated repeatedly in the studies of mixtures of molecular liquids [1–3], ionic liquids [4], mixtures of metals and glasses [5,6] or aqueous protein solutions [7].

Depending on the physical quantity used to be examined in terms of its excess value, different information on the structural or thermodynamic state of the liquid system may be achieved. Often analyzed quantities are volume, entropy, enthalpy, Gibbs free energy [1]. Although each of these excess parameters carry important information on examined system, none of them give direct insight into local orientation of the molecules. The information about angular arrangement of

interacting molecules is essential to explain many interesting physico-chemical effects desirable in bio-medical or industrial applications. In many situations, phenomenon observed is controlled not only by the simple probability that two specifically interacting molecules come into close contact, but also by their relative orientation during this approach. In this respect an electrocatalytic activity, as well as structure and stability of biocatalysts depends on the angular position of reagents [8]. Similarly, efficiency of protein-ligand interaction [9] or Förster resonance energy transfer phenomena (FRET) [10] changes distinctly with molecular orientation. Controlling of optical properties in omnipresent liquid crystalline displays (LCD) or improving the mechanical characteristics of polymers by extrusion [11] are also based on utilization or induction of specific angular correlation of particles.

In the case of the molar volume - the most often examined excess property - change in the average distance between the particles may be inferred. This information can be very important for indication of different structuring effects occurring in the examined system. The question arises if the same interactions that led to change in average molecular separation affect also their mutual orientation. Unfortunately separation of radial from angular arrangements is not possible through examination of the volumetric properties alone. For information about orientational adjustment, it is necessary to use a method sensitive for this particular aspect of molecular arrangement.

A physical phenomenon susceptible to the molecular orientation is an optical birefringence. In liquids, as opposed to solids, the birefringence does not occur naturally. However it can be induced using an external physical fields. Particularly noteworthy are the methods using magnetic fields. The usefulness of magneto-optical method in studies

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of molecular orientation was presented for binary molecular liquid solutions [12], liquid suspensions of magnetic nanoparticles [13,14] or self-organizing micellar forms [15,16].

For the case of liquid solutions of diamagnetic molecules the induced optical birefringence is proportional to the square of the magnetic field intensity where the constant of proportionality is called the Cotton-Mouton constant. This quantity contains information on the anisotropy of magnetic and optical polarizabilities of studied molecules and is a valuable source of information on mutual orientation of molecules of the liquid. With the physical quantity sensitive to changes in molecular angular arrangement, its excess value can be determined in the same way as it is usually made in the case of thermodynamic parameters.

In this paper we study the mixtures of simple anisotropic molecular liquids. We derive the excess molar Cotton-Mouton constant and compare its concentration dependence with analogous characteristic of excess molar volume. We discuss the influence of intermolecular interactions on the shape of the excess functions measured. We demonstrate that examining two physical quantities, each sensitive to different kind of molecular arrangement, it is possible to gain independent information on radial and angular correlations in binary liquid mixtures.

2. Cotton-Mouton effect

The Cotton-Mouton phenomenon is the magnetic equivalent of the Kerr effect [17,18]. It consists of inducing the optical birefringence in macroscopically isotropic medium by the external magnetic field. Emerged birefringence is then attributed to organization of anisotropic particles by magnetic field. In the absence of field particles are randomly distributed, and so are their axes of maximum polarizability. In these conditions the medium is macroscopically optical isotropic. Applying a magnetic field causes the orientation of molecular magnetic dipole moment (permanent or induced) along the direction of the field. As a result, an initial random arrangement of molecules is altered by preferential orientation along the direction of the external field and the medium becomes optically anisotropic.

The molecular orientation process of a single molecule can be analyzed considering magnetic and thermal energies and using classical Maxwell-Boltzmann statistics [19]. For diamagnetic and paramagnetic molecules the magnetic energy is usually lower than thermal energy. In this case the induced birefringence Δn changes with magnetic field of induction B in a simple quadratic way and is often described by

$$\Delta n = C\lambda B^2 \quad (1)$$

where, C is the Cotton-Mouton constant and λ is the wavelength of light used.

It can be shown [19,20] that for the collection of non-interacting particles with number concentration ρ^N , (each described by the optical anisotropy $\Delta\alpha$, permanent magnetic dipole μ_m and anisotropy in the magnetic susceptibility, $\Delta\chi$), the Cotton-Mouton constant may be written as:

$$C = \frac{\rho^N \Delta\alpha}{30n\epsilon_0\lambda} \left[\frac{\Delta\chi}{\mu_0 kT} + \left(\frac{\mu_m}{kT} \right)^2 \right] \quad (2)$$

where n is the refractive index of the solution and ϵ_0 corresponds to permittivity of free space, μ_0 is the permeability of free space, k is the Boltzmann constant and T stands for absolute temperature. As follows from Eq. 2, the value of Cotton-Mouton constant depends on the magnetic and optical properties of particles.

In the condensed phase, particularly in dipolar liquids, significant intermolecular interactions take place. These can lead to the formation of molecular aggregates of particular local structure. External field is responsible for orientation of not only individual molecules, but it influences their aggregates as well, which manifests itself in value of Cotton-Mouton constant observed. The situation complicates even

further when a mixture of two different molecular liquids is examined. Then, the contribution to Cotton-Mouton constant from interactions between each mixture constituent needs to be considered [12,21]. Formation of molecular aggregates influences statistical distribution of particles which is reflected in the value of Cotton-Mouton constant and allows for discussion of structural properties of aggregate [15].

During investigations of liquid mixtures it is convenient to operate on molar properties. The experimental Cotton-Mouton constant may be transformed into the molar Cotton-Mouton constant, C^M , using relation [12,21]:

$$C^M = C \frac{6n^2}{(n^2 + 2)^2} \frac{M}{\rho} \quad (3)$$

where ρ is mass density and M is molar mass of solution.

3. Excess properties

Common method for gaining a knowledge about intramolecular interactions occurring in a liquid mixture is to study behavior of excess values of thermodynamic properties [1]. These are defined as a difference between experimentally measured property (exp) and an ideal state expected for a mixture with no interactions (id). The latter one is usually expressed using an additivity rule.

One of the most commonly examined quantities is an excess molar volume, defined as follows:

$$\Delta V^M = V_{\text{exp}}^M - V_{\text{id}}^M = \frac{M}{\rho} - [x_1 V_1^M + x_2 V_2^M] \quad (4)$$

where $x_{1,2}$ are molar fraction ($x_1 = 1 - x_2$) of both mixture constituents, whereas V_1^M and V_2^M correspond to molar volumes of pure liquids.

In principle, the excess properties of any physical quantity can be obtained [22]. Assuming that only pair interactions between unlike molecules are present, it was shown [23] the molar Cotton-Mouton constant of solution can be written as:

$$C^M = x_1 C_1^M + x_2 C_2^M + 2x_1 x_2 C_{12}^M \quad (5)$$

where C_1^M and C_2^M correspond to molar Cotton-Mouton constants of pure liquids and C_{12}^M represents contribution from pair interaction between unlike molecules in mixture. First two terms in Eq. 5 express the additivity rule as expected for non-interacting (ideal) system. Any interparticle interactions should appear as non-zero value of C_{12}^M . The excess value of Cotton-Mouton constant ΔC^M , can then be written as [23]

$$\Delta C^M = C^M - C_{\text{Add}}^M = 2x_1 x_2 C_{12}^M = 2x_2(1 - x_2) C_{12}^M \quad (6)$$

Observation of how the particular physical quantity differ from ideality, provides an important information on different aspects of interactions between molecules in liquid mixture. In the case of excess molar volume the positive or negative deviation informs about the repulsive or attractive interactions. The excess Cotton-Mouton behavior carries information about the preferential mutual orientation of unlike molecules.

4. Materials and methods

p-Xylene (*p*-X), *o*-Chloroanisole (*o*-CIA) and *p*-Chloroanisole (*p*-CIA) (99%) were purchased from Fluka and used without further purification procedure. The binary mixtures of *o*-CIA in *p*-X and *p*-CIA in *p*-X were prepared by weight to cover whole concentration range from pure Xylene to pure Chloroanisole. The concentrations were expressed in Chloroanisole molar fraction (x).

The refractive index values, n , for each mixture have been measured using a standard Pulfrich refractometer. During the measurement the

587.6 nm helium emission line was used as light source. The relative difference between the refractive index values measured at 587.6 nm and those expected for 632.8 nm used in birefringence measurement is about 0.2%. The concentration dependencies of the density, ρ , were calculated assuming additivity of molar refraction using the refraction index data and the Lorentz-Lorenz relation.

Optical linear birefringence was measured using the laboratory made polarimeter set-up described in details in [20]. The sample was held in a glass cell between 130 mm long poles of iron-core electromagnet ($B \leq 2$ T). In order to maximize sensitivity of birefringence measurement the length of the cell was 130 mm. Magnetic field induction was measured by a teslameter placed in the middle of the optical path. The magnetic field intensity distribution along the optical path was uniform (within 1.5%) except for the very ends of the poles (5 mm from each side). The light from He-Ne laser ($\lambda = 632.8$ nm) was used as a probe. The apparatus allowed measurements of induced birefringence with uncertainty of $2 \cdot 10^{-9}$. Typical plot of induced birefringence as a function of applied magnetic field is shown in Fig. 1.

The Cotton-Mouton constant, C , for each of the mixtures studied was obtained by fitting Eq. 1 to the experimental data. The experimental constants, C , were then recalculated to molar quantities, C^M , using Eq. 3 and the values of refractive index and density.

5. Results and discussion

Concentration dependencies of molar Cotton-Mouton constant obtained for p -X/ o -CIA and p -X/ p -CIA systems are presented in Fig. 2. All of the pure liquids studied are characterized by similar value of measured Cotton-Mouton constant (the maximum difference is 6%). This is not surprising since all these compounds are benzene derivatives of similar molecular structure, thus with similar optical and magnetical properties. The Cotton-Mouton constant obtained for pure p -CIA is higher than this measured for pure o -CIA. According to Eq. 2 this can be justified by the fact that side groups in the *para*-position make the molecule more optically anisotropic than in the *ortho*-position [24,25].

The concentration dependencies of C^M for both of the systems studied, indicate clear negative deviation from simple additive behavior. This observation encourages to calculate the excess value of molar Cotton-Mouton constant, ΔC^M . Composition dependencies of excess molar volume, ΔV^M , and ΔC^M are presented on Fig. 3a and b, respectively.

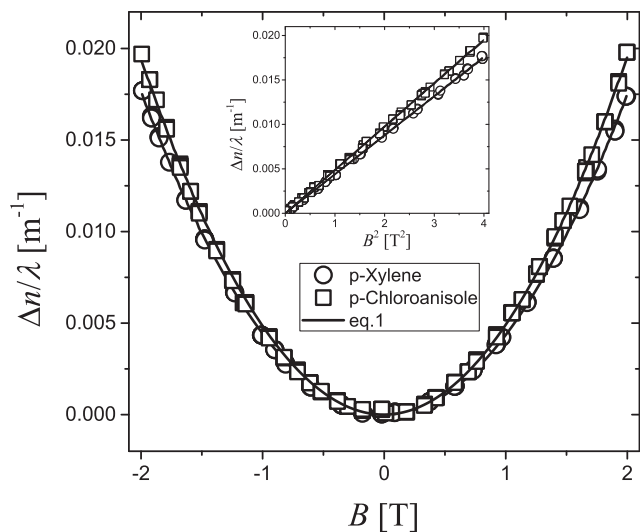


Fig. 1. Magnetically induced linear birefringence in two pure liquids (p -Chloroanisole and p -Xylene). Points show experimental data. Solid lines represent fittings with Eq. 1. Inset shows the same quantity as a function of B^2 indicating parabolic behavior expected for Cotton-Mouton effect.

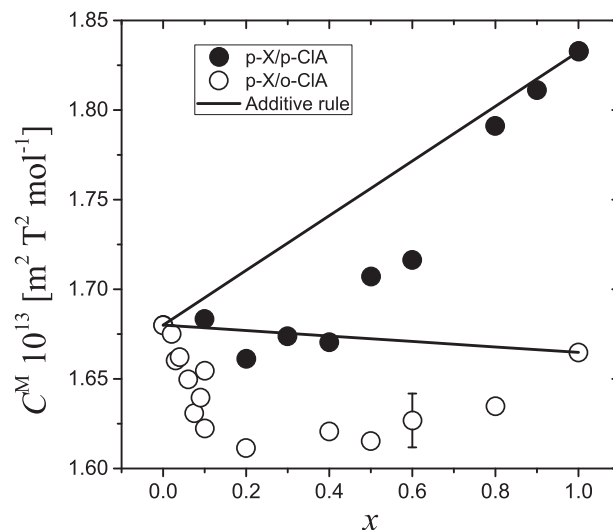


Fig. 2. Concentration dependencies of molar Cotton-Mouton constants obtained for o -Chloroanisole and p -Chloroanisole dissolved in p -Xylene (p -X/ o -CIA and p -X/ p -CIA, respectively). Circles are the experimental data. Lines show concentration dependence under assumption of additive behavior.

An inspection of Fig. 3 allows to indicate three interesting features: 1) for both systems $\Delta V^M < 0$ and $\Delta C^M < 0$ in the whole concentration range; 2) $\Delta C^M(x)$ dependencies seem to overlap (in the range of uncertainty), whereas $\Delta V^M(x)$ are clearly different; 3) $\Delta V^M(x)$ are parabolic in shape, whereas $\Delta C^M(x)$ is not following a simple quadratic form given by Eq. 6.

Observation of non-zero values of excess functions is usually taken as an indication of non-negligible inter-particle interactions leading to formation of molecular complexes [1–3,12,21]. It is reasonable to assume that any interactions present in currently studied mixtures are small and the entropic forces will tend to keep the solution in almost perfect random mixed state. In this case it is justified to consider only pairs of molecules forming short living pair-aggregates.

First insight into the mixing process may be delivered by analyzing the excess molar volume, ΔV^M , calculated according to Eq. 5. Although experimental $\Delta V^M(x)$ seems almost symmetric, small deviation from parabolic dependence can be taken into account with an empirical polynomial expansion - Redlich-Kister polynomials [26]. This widely

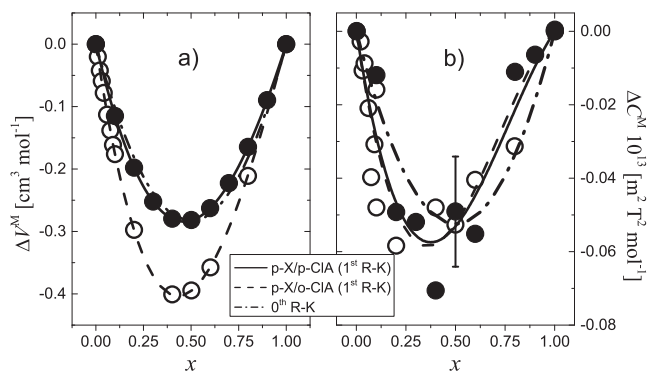


Fig. 3. Excess properties for p -Xylene/Chloroanisole mixtures as a function of Chloroanisole molar fraction a) Excess molar volumes, b) Excess molar Cotton-Mouton constant. The solid and dashed lines on panel b) are the best fits of the 1st order Redlich-Kister (R-K) polynomial. Dash-dotted lines on both panels show the behavior of zero-order Redlich-Kister polynomial.

adopted approach for modeling the excess thermodynamic properties allows to write equation for $\Delta V^M(x)$ in the following form:

$$\Delta V^M = x(1-x) \sum_{i=0}^n v_i (1-2x)^i \quad (7)$$

where v_i are the phenomenological coefficients and n is the order of expansion. The result of the fitting of first-order expansion of Eq. 7 to experimental $\Delta V^M(x)$ is presented on Fig. 3a and the values of coefficients obtained are collected in Table 1.

As follows from Fig. 3a and Table 1, the shape of $\Delta V^M(x)$ for *p*-X/*p*-CIA mixture is almost perfectly described by zero-order Redlich-Kister equation (dot-dashed line in Fig. 3b). This is what should be expected for solution of molecules with the similar molar volumes ($V^M_{p-X} \approx V^M_{p-CIA} = 123 \text{ cm}^3/\text{mol}$). A bit higher deviation from symmetric behavior found for *p*-X/*o*-CIA mixture can be justified by the slightly higher molar volume of *o*-CIA (127 cm^3/mol). The negative sign of $\Delta V^M(x)$ informs that formation of a complex is related with decrease in distance between molecules in a pair-complex. This indicates the existence of attractive interactions between *p*-X and CIA molecules, most probably of dipole/induced-dipole nature. This kind of interaction may be also inferred from higher absolute values of ΔV^M obtained for *p*-X/*o*-CIA system. Higher permanent electric dipole moment of *o*-CIA molecule ($\mu = 2.77\text{D}$ compared to $\mu = 1.28\text{D}$ for *p*-CIA [27]) interacts stronger with induced dipole moment of non-polar *p*-Xylene, which eventually results in larger reduction in mixture molar volume.

In contrast to $\Delta V^M(x)$, the shape of $\Delta C^M(x)$ is clearly non-parabolic and for this reason Eq. 6 cannot be a proper description of a real situation (see Fig. 3 dash-dotted line). We described experimental $\Delta C^M(x)$ using Redlich-Kister expansion in analogous manner to that used in calculation of ΔV^M :

$$\Delta C^M = x(1-x) \sum_{i=0}^n c_i (1-2x)^i \quad (8)$$

It is clear that zero-order Redlich-Kister expansion is equivalent to Eq. 6 and appropriate expansion coefficient corresponds to Cotton-Mouton contribution from pair-complexes, $c_0 = 2C^M_{12}$. In order to obtain good description of experimental $\Delta C^M(x)$ dependencies, the first-order expansion ($n = 1$) of Eq. 8 was used (Fig. 3b; solid and dashed lines). The values of coefficients obtained from fitting procedure are collected in Table 1. The negative deviation from additivity rule ($\Delta C^M < 0$) informs that molecules in pair-complex are oriented in such a way, that their resultant optical anisotropy (and/or anisotropy in the magnetic susceptibility) is lower than this expected for unassociated state.

Before suggesting any possible configuration of molecules in a binary mixture, we first need to consider local orientation of molecules in pure liquids studied. Structural studies performed using wide-angle X-ray scattering method [27,28] showed that dipolar molecules of pure liquid benzene derivatives tend to orient their dipole moments in anti-parallel fashion due to dipole-dipole interactions. At the same time the benzene rings forms plane-parallel molecular arrangement. Similar parallel arrangement of phenyl rings was also found for non-polar *p*-Xylene molecules [29]. In this case, however, the lack of direct dipolar interactions makes the liquids local structure weaker. When CIA and *p*-X molecules are mixed together, the binary pair of unlike

molecules is stabilized by the dipole-induced dipole interactions. The negative value of ΔC^M indicates that during mixing process orientation of molecules in a pair-complex reduces its average optical anisotropy. Transition from plane-parallel to perpendicular orientation of benzene rings would strongly decreases pair's net anisotropy. However, such a transformation would be accompanied by decrease in molecular packing, which contradicts observation of $\Delta V^M < 0$. Moreover, the results presented in Fig. 3 clearly indicate how the orientational correlations between molecules in pair-complex are decoupled from their radial correlations. Changing the position of side groups in Chloroanisole molecule (from *orto*- to *para*-) changes the strength of dipolar interaction with *p*-Xylene molecule. This is reflected in the change in average molecular separation within *p*-X/CIA pair. Surprisingly, such distinct change in radial distance is not accompanied by relevant change in the relative molecular orientation. This suggests that plane-parallel molecular arrangement of benzene rings, observed in pure liquids, is also preserved in *p*-X/CIA complex. This suggestion is consistent with the results of the structural analysis of 10% solution of *p*-CIA in *p*-X [27]. Small decrease in pair anisotropy can be justified by the local structure where benzene rings of *p*-X and CIA molecules stays parallel, but the molecules are rotated (along the axis perpendicular to the benzene plane) in such a way that directions indicating positions of side groups are perpendicular. This configuration meet the requirement of local structure which is more compact and less anisotropic than this expected for ideal (additive) mixture.

As a final point we would like to refer to non-parabolic dependence of $\Delta C^M(x)$. Although there is no straightforward explanation for observed deviation from symmetric behavior of $\Delta C^M(x)$, expected for randomly mixed system, we can still point few possible factors influencing orientational behavior of molecules in solution. 1) The difference in molecular shapes can play similar role in orientational process as mismatch in diameters in volumetric properties; 2) Permanent electric dipole moment of CIA molecules favor their anti-parallel orientation. This anti-parallel "self-orientation" of alike molecules competes with perpendicular orientation within pair-complex of unlike molecules, which should have similar effect on Cotton-Mouton constant as self-association have for compressibility [30]; 3) Domination of simple binary interactions could be too simple approximation. In this case deviation from Eq. 6 could indicate that much more complex (ternary) interactions should be considered.

6. Conclusions

The linear optical birefringence was magnetically induced in binary solutions of simple organic liquids composed of anisotropic molecules with different dipolar properties. From magnetic field dependence of induced birefringence, the value of Cotton-Mouton constant (C^M) was derived. This quantity is sensitive to the anisotropy in magnetic and dielectric properties of molecules. Concentration dependencies of C^M constant was found to deviate from additivity rule. This observation was attributed to the existence of binary pairs formed inside mixtures by un-like molecules, stabilized by dipole-induced dipole interactions. We proposed to calculate and discuss the concentration dependence of the "excess" value of C^M (ΔC^M) defined customary as a difference between experimental and additive behavior. This excess quantity, in contrast to thermodynamic excess parameters, provides direct insight into mutual orientation of molecules in the interacting molecular pair. We found that the ΔC^M was negative in whole concentration range, which indicates that orientation of molecules within complex formed makes it less anisotropic than expected for unassociated (additive) mixture. Also the excess molar volume (ΔV^M) was found negative, which suggest that interactions between molecules leads to more compact local structure. The shape of the concentration dependence of ΔC^M , together with analogous characteristic of excess molar volume, were reproduced by the Redlich-Kister polynomial expansion. Plots of excess volumes were symmetric (characterized by low value of first-order polynomial

Table 1

Phenomenological expansion coefficients of Redlich-Kister Eqs. 7 and 8 used to describe concentration dependencies of the excess molar volume and the excess molar Cotton-Mouton constant.

	v_0 [$\text{cm}^3 \text{ mol}^{-1}$]	v_1 [$\text{cm}^3 \text{ mol}^{-1}$]	$c_0 \cdot 10^{13}$ [$\text{m}^2 \text{ T}^{-2} \text{ mol}^{-1}$]	$c_1 \cdot 10^{13}$ [$\text{m}^2 \text{ T}^{-2} \text{ mol}^{-1}$]
<i>p</i> -X/ <i>p</i> -CIA	−1.130	−0.174	−0.210	−0.157
<i>p</i> -X/ <i>o</i> -CIA	−1.582	−0.460	−0.212	−0.131

coefficient) but differed in magnitude when mixtures of *o*-CIA or *p*-CIA molecules were considered. On the contrary, concentration characteristics of ΔC^M , were clearly asymmetric with their shape and magnitude almost indistinguishable. These observations demonstrate that the change in the molecular structure of one of the mixture component leads to the change in the radial correlation between interacting particles, while their relative orientation is preserved. These results suggest that planes of phenyl rings of *p*-X and CIA molecules, within binary pair, stays parallel. The molecules are however rotated in such a way that the positions of side groups are not pointing in the same direction. This configuration of pair-complex meets the conditions of simultaneous reduction in molecular separation with decrease in optical anisotropy.

In conclusion, presented results indicate how excess Cotton-Mouton constant can provide important information on angular correlations between molecules. Studies of this parameter, in combination with usual thermodynamic excess properties, provide broader picture of the local structure of liquid mixtures.

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