Vapor-phase molar Kerr constant values from solution measurements

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ABSTRACT

A method is proposed for determination of molar Kerr constants (mK) by extrapolation of the values measured in a series of selected solvents. The mK values of 19 organic compounds were calculated. Most of the compounds cannot be studied in the vapour phase. The discrete-continuum solvation model was applied to investigate the influence of solvent nature on solubility of the compounds under investigation. It is shown that universal interactions between the solvent and solute molecules, including the dispersive, inductive, and dipole–dipole interactions, dominate the solvation process. The optimum model of internal field was chosen to determine the Kerr constant. **The values of mK_{gas} measured experimentally coincide with the values of $mK'_{\varphi_a=0}$ that were obtained by extrapolation of mK' . Hence, this method can be applied to calculate the values of molar Kerr constants on the basis of measurements in solutions.**

KEYWORDS: molar Kerr constants, polarizability, vapor-phase, intermolecular interactions, London-Debye-Keesom potentials

INTRODUCTION

The most important characteristics of electrical properties of a molecule are its polarizability (α) and the dipole moment (μ) because they directly denote properties of the electron shell of the molecule. The dipole moment (DM) and polarizability determine the interaction forces, the forces that cause absorption, adhesion in case the distance between molecules decreases, transform gases into liquids, stabilize molecular crystals etc.

The determination of DM and average polarizability of molecules (on the basis of molecular refraction) is quite simple nowadays. **The molecular anisotropy and**

polarizability ellipsoids of molecules have been studied to less extent, especially their changes when molecules take part in various intermolecular interactions. It is caused by the fact that determination of such changes implies nontrivial electro-optical methods of investigation (the electro-optic Kerr effect) [1-3]. The double refraction in an electric field, the electro-optic Kerr effect, is connected to the polarizability anisotropy of molecules. If refractive index in the absence of an electric field is equal to n , it becomes equal to n_p for a ray with oscillating electric vector parallel to the field (E), and for perpendicular orientation - n_s . If a ray of light is perpendicular to the field, it creates a path difference, $\Delta_k = nl (n_p - n_s)/\lambda$, where l is the length of the ray of light in the field.

The electro- optic Kerr effect is expressed by the equation:

$$D = 2\pi (n_p - n_s)/\lambda = 2\pi B l E^2, \quad (1)$$

where D stands for birefringence, rad; B is the specific value for each substance, and is called the Kerr constant.

The modern theory of the Kerr effect takes into account the contributions of various physical properties [4,5]. The theory is based on calculations of the interaction energy of a polar or anisotropically polarizable molecule with the electric field:

$$U = -\sum_i \mu_i F_i - \sum_{i,j} a_{ij} F_i F_j, \quad (2)$$

where μ and a_{ij} are the constituents of the DM vector and of the static polarizability tensor; F_i are the constituents of the intensity vector of an electric field acting on the molecule.

G. Briegleb [6] introduced the molar Kerr constant (mK) as the difference in molecular refractions for a ray of light with the orientation of an electric vector parallel (MR_p) and perpendicular (MR_s) to the field, which falls on the distance of 1 cm in a single electric field:

$$MR_p - MR_s = \left[\frac{n_p^2 - 1}{n_p^2 + 2} - \frac{n_s^2 - 1}{n_s^2 + 2} \right] \frac{M}{d} = \frac{n_p - n_s}{n} \frac{6n^2}{(n^2 + 2)^2} \frac{M}{d},$$

where M is the molar weight of a substance, and d – its density.

Taking into consideration the internal field

$$mK = \frac{MR_p - MR_s}{F^2} = \frac{n_p - n_s}{n} \frac{54n^2}{(n^2 + 2)^2 (\varepsilon + 2)^2}.$$

and applying Eq. (1), we obtain

$$mK = \frac{6B\lambda n}{(n^2 + 2)^2} \left(\frac{3}{\varepsilon + 2} \right)^2 \frac{M}{d}. \quad (3)$$

Most data on the values of molar Kerr constant (mK) available in the literature were obtained by measurements in diluted solutions of non-polar solvents; however, some research on mK in crystals [7] has been carried out to show their better practical application [8-10]. The values of mK determined on the basis of measurements in solutions depend on the nature of solvents [11-17], what can be explained by the interaction between the molecules of the solute and the solvent (solvent effect). Since the values of mK , which are based on the analysis of polarizability, in many cases appear most sensitive to the mutual orientation of bonds and the effects of electrons displacement, what makes them indispensable in the conformational analysis, it is very important to possess the experimental values of mK , obtained by measurements in the gas phase. There is very little published data on the measurements of mK in the gas phase [14] because most organic compounds undergo decomposition before the transition into the gas phase [18]. That is why it is essential, taking into consideration the solvent effect, to propose a technique that makes it possible to obtain the values of the molar Kerr constant in the vapour phase on the basis of measurements in solvents.

A range of empirical equations was proposed to evaluate the solvent effect quantitatively, which link mK with the macroscopic characteristics of the medium – the dielectric permittivity (ε) and the refractive index (n).

A critical analysis of these equations can be found in Ref. [11, 12]. None of these equations takes into account all factors that determine the non-specific influence of a solvent on the molecular characteristics. Moreover, these equations cannot be applied to the dependence of different types of intermolecular interactions on the properties of molecules of a solvent and of the structure of solutions [11].

For example, in Ref. [15] the dependence of mK from $\frac{n^2-1}{n^2+2}$ was determined. The extrapolation of this dependence to $n = 1$ fairly presents the values of mK in the gas phase (mK_{gas}); however, from the theoretical point of view such correlation is not totally correct because the parameter of $\frac{n^2-1}{n^2+2}$ (refraction) reflects the trace of polarizability tensor of a molecule, which does not depend on the deviator.

The dependence of mK of anisotropic non-polar molecules dissolved in an isotropic solvent [16] was proposed on the basis of classical static-mechanical theories. A relative decrease of mK in solution compared to mK_{gas} is as following:

$$\frac{mK - mK_{\text{gas}}}{mK_{\text{gas}}} = \frac{\alpha_1}{\alpha_{2zz} - \alpha_{2xx}} \left[2(2\alpha_{2zz} + \alpha_{2xx}) \langle T_{zz}^{(1)} \rangle + 3\nu_1 \langle T_{zz} \rangle \right]$$

The proposed model contains one molecule of non-polar solute with polarizability α surrounded by $N_A - 1$, the molecules of an anisotropic solvent with polarizability α . The anisotropy in distribution of solvent molecules around one molecule of a solute is described by the correlation tensor $\langle T_{\phi} \rangle$. However, as the author states himself, the model is somehow simplified.

The influence of a solvent on the value of the Kerr constant B was studied on the basis of ideas about the non-specific interactions of inductive and dispersive nature [19]. It was shown that, for blends of non-polar substances, the deviations from additivity of the Kerr constants ΔB are proportional to the excessive energies of dispersive interactions.

$$\Delta U_{12} = (U_{11} \cdot U_{22})^{1/2} - 0.5(U_{11} + U_{22}),$$

$$\Delta B_{12} \sim \Delta U_{12} f_1 f_2 = \left[\left(\frac{0.75 I_1 b_1^2}{r_{11}^6} - \frac{0.75 I_2 b_2^2}{r_{22}^6} \right) - 0.5 \left(\frac{0.75 I_1 b_1^2}{r_{11}^6} + \frac{0.75 I_2 b_2^2}{r_{22}^6} \right) \right] f_1 (1 - f_1),$$

where r_i is the distance between molecules calculated from the molecular volumes, b_i – main polarizability axes of molecules, I_i are the ionization potentials of molecules, f_i – mole fractions of the components. If one of the components, for example 2, is polar, we observe the contribution of induction and orientation interaction:

$$\Delta B_{12} \sim \left[\frac{2\mu_2^2 b_1}{r_{12}^6} - 0.5 \left(\frac{2}{3kT} \frac{\mu_2^4}{r_{22}^6} + 0.75 \frac{I_1 b_1^2}{r_{11}^6} \right) \right] f_1 (1 - f_1),$$

$$r_{12} = (r_{11} + r_{22})/2.$$

A very important role in determination of mK plays the mutual orientation between the molecules of the solute and the solvent due to the dispersive, dipole-induced dipole, and dipole-dipole interactions. The influence of intermolecular field interaction on the value of dipole moments (μ) of the molecules was calculated by the authors with the use of London-Debye-Keesom potentials [20]. This allowed us to obtain the correlation between the values of μ and the characteristics of molecular structure of a liquid and, hence, to evaluate the participation of field interactions of different kinds in solutions.

It was of great interest to apply the approach mentioned above and evaluate the influence of universal interactions in solutions on the value of mK . **Hence, the paper aims to establish a correlation between the molar Kerr constants and the parameters that determine universal and specific interactions of molecules in solvents. This gives grounds to determine the values of the molar Kerr constant in the vapour phase and study the space and electron structure of molecules.**

THEORETICAL METHODS

DISCRETE-CONTINUUM MODEL

In dilute solutions, only solvent molecules surround every solute molecule in the first coordination sphere. Therefore, the energy of interaction between the individual solute molecules is very small (Fig. 1).

The energy of universal interactions [21,22] of the two molecules i and j in a solution consists of the energies of dispersive interaction [23]

$$E_{disp} = \frac{3I_i I_j}{2(4\pi\epsilon)^2 (I_i + I_j)} \frac{\alpha_i \alpha_j}{R^6} \quad (4)$$

dipole-dipole interaction

$$E_{d-d} = \frac{2}{3} \frac{\mu_i^2 \mu_j^2}{(4\pi\epsilon)^2 kTR^6} \quad (5)$$

and dipole-induced dipole interaction

$$E_{d-id} = \frac{1}{(4\pi\epsilon)^2 R^6} (\alpha_i \mu_j^2 + \alpha_j \mu_i^2). \quad (6)$$

Here, I is the ionization potential, α is polarizability, μ is the molecular dipole moment, ϵ is the dielectric permittivity of the solution, and R is the distance between the interacting molecules.

Thus, the energy of interaction of a solute molecule with solvent molecules may be expressed by Eq. (7)

$$\Delta E = \frac{1}{(4\pi\epsilon)^2} \left(\frac{Z}{R^6} \right)_1 \left[C_{disp} \frac{3}{2} \frac{I_i I_j}{I_i + I_j} \alpha_i \alpha_j + C_{d-d} \frac{2}{3} \frac{\mu_i^2 \mu_j^2}{kT} + C_{d-id} (\mu_i^2 \alpha_j + \mu_j^2 \alpha_i) \right] \quad (7)$$

The number of solvent molecules surrounding a solute molecule in the first coordination sphere (Z) is expressed as $Z = \frac{1}{V_j} \left[\frac{4}{3} \pi R^3 - V_i \right]$, where $\frac{4}{3} \pi R^3$ is the volume of the first coordination sphere, V_i is the volume of one solute molecule, V_j is the volume of one solvent molecule, and R is the radius of the first coordination sphere. The latter may be expressed as a sum of the radii of the solvent and solute molecules, $R = R_i + R_j$. The volumes of the solvent and solute molecules can be obtained by dividing molar volumes V_m by the Avogadro number N_A . For instance, for the solute $V_i = V_{mi}/N_A$.

The coefficients C_i in the above equation are corrections for non-additivity of pairwise interactions. When investigating the same solute in a series of similar solvents, the corrections can be assumed constant [20], leading to

$$\Delta E = \frac{1}{(4\pi\epsilon)^2} \left(\frac{Z}{R^6} \right)_1 \overline{const} \left[\frac{3}{2} \frac{I_i I_j}{I_i + I_j} \alpha_i \alpha_j + \frac{2}{3} \frac{\mu_i^2 \mu_j^2}{kT} + (\mu_i^2 \alpha_j + \mu_j^2 \alpha_i) \right]. \quad (8)$$

Then, a change in property $|\Delta y|$ of the molecules in solution compared to the gas phase is proportional to the energy of the intermolecular interaction:

$$|\Delta y| = y_{gas} - y_{sol} \sim \frac{1}{(4\pi\epsilon)^2} \left(\frac{Z}{R^6} \right)_1 \left[\frac{3}{2} \frac{I_i I_j}{I_i + I_j} \alpha_i \alpha_j + \frac{2}{3} \frac{\mu_i^2 \mu_j^2}{kT} + (\mu_i^2 \alpha_j + \mu_j^2 \alpha_i) \right]. \quad (9)$$

In a series of non-polar solvents ($\mu = 0$) for the same solute ($I_i = \text{const}$, $\mu = \text{const}$, $q = \text{const}$), the energy of interaction can be expressed as

$$|\Delta y| \sim \frac{1}{(4\pi\epsilon)^2} \left(\frac{Z}{R^6} \right) \left[\frac{3}{2} \frac{I_i I_j}{I_i + I_j} \alpha_i \alpha_j + \mu_i^2 \alpha_j \right] \equiv \varphi \quad (10)$$

In a series of non-polar solutes ($\mu = 0$) for the same polar solvent ($I_j = \text{const}$, $\mu = \text{const}$, $q = \text{const}$), Eq. (9) can be expressed as

$$|\Delta y| \sim \frac{1}{(4\pi\epsilon)^2} \left(\frac{Z}{R^6} \right) \left[\frac{3}{2} \frac{I_i I_j}{I_i + I_j} \alpha_i \alpha_j + \mu_j^2 \alpha_i \right] \equiv \varphi_\alpha^*. \quad (11)$$

The connection between the interaction energy of molecules and the changes in properties of a substance is so evident that it is considered a non-alternative hypothesis. It is discussed from historical viewpoint, for example, in a recent book [24]. The dependences (9) – (11) were proved on the spectral characteristics of molecules such as IR-spectra (Δ), NMR-spectra (proton chemical shift, ΔH), and electronic absorption spectra (E_{max} , f) [25].

In the theory of dispersive interaction an equation (4) was obtained, which connects E_{disp} with polarizability and the ionization potential of molecules. It was shown that for blends of non-polar compounds the deviations from additivity of the Kerr constants ΔB proportionate to the excessive energies of dispersive interaction [19], and for polar compounds – to the energies of dipole-dipole interaction [26]. Since the Kerr constant (B) and the molar Kerr constant (mK) are connected to the relation used most often [11]:

$$mK = \frac{6B\lambda n}{(n^2 + 2)^2 (\epsilon + 2)^2} \frac{M}{d}, \quad (12)$$

where n is the index of refraction, λ is the wavelength, ϵ - the dielectric permeability, M is molar mass, d - density, and B – the Kerr constant, we can expect that $\Delta B = B_{\text{gas}} - B_{\text{sol}}$, $\Delta mK \sim E$ (the interaction energy between solute and solvent molecules).

To check the trend expressed by Eq. (10), we examined the reference data [14] on mK in a series of non-polar solvents with similar values of the ionization potential (I_j). The solvents included heptane, hexane, cyclohexane, tetrachloromethane, dioxane, benzene, and carbon bisulfide (Table 1). It is evident from Figs. 2 and 3 that the value of $|\Delta mK|$ increases in a series of solvents with similar values of I_j according to Eq. (7) but the value of mK

decreases linearly with the increase in φ value. Further, larger values of mK_{gas} lead to a greater slope of the line. In a series of non-polar substances with close I_i in the same polar solvent C_6H_5Cl , the value of $|\Delta mK|$ linearly increases with rise in the parameter of φ_α^* (Table 2).

The influence of non-polar solvents on the value of mK can be explained by the fact that as a result of solvation there are shells of solvent molecules being formed around the molecules of the solute; these shells of solvent molecules (Fig. 1), which are poorly oriented due to the dispersive and dipole-induced dipole interactions. These interactions contribute to inhibition of free rotation of the solute molecules and, according to the Langevin-Born orientation theory [27, 28], impede the orientation of molecules within the field and, consequently, lead to decrease in the value of mK . The dependence of mK on the parameter of φ which follows from Eq. (10), points at the volume nature of the field interaction of molecules in the solutions [29].

Local complexes are formed in case of a solvent that shows evident anisotropy of polarizability and ability to form the CT complexes such as benzene. The Kerr constant helps to determine the structure of such complexes according to the techniques proposed in Ref. [30].

The values of mK for nitrobenzene, 1,2-dinitrobenzene, and 1,3-dinitrobenzene (Fig. 2), and acetonitrile (Fig. 3) measured in benzene fall out from the general dependence and prove that these compounds with benzene form the complexes of $\pi\pi^*$ type. The substances, which are donors of protons, for example, chloroform, together with dioxane form the complexes with H-bond, what also leads to falling out of the value of mK from the general dependence. In these cases, not single molecules but the whole complexes are oriented to the external field.

MODELS OF INTERNAL FIELD IN ORDER TO DETERMINE THE MOLAR KERR CONSTANT

There are many different equations in the literature on the subject for calculation of the molar Kerr constants in liquids, which give different values of mK . This is connected with modification of the orientation theory of the Kerr effect for condensed media. The theory was improved by the following: 1) modification of an internal field that has an effect on the molecule; 2) taking into account the effect of orientation correlations of molecules on the

measured parameters; 3) determination of influence of the effects of an electric field on birefringence, which were not taken into account by the Langevin-Born theory.

The internal field was modified in the two ways - 1) by the variation in contribution of the internal field to the expression of mK retaining the Lorentz function, 2) by the substitution of this function for a more complex model. Thus, the Onsager theory [31] leads to the expression:

$$mK = \frac{1}{(1-af)(1-bg)} \left(mK^0 - \frac{2\pi N}{9} af\Theta_1 \right), \quad (13)$$

where $f = 2(\epsilon-1)/r^3(2\epsilon+1)$; $g = 2(n^2-1)/r^3(2n^2+1)$; r is an average radius of a molecule; mK^0 – a “true” molar Kerr constant; a and b are constants.

More general theories take into account the non-sphericity of molecules. According to the Scholte's theory [11]

$$mK = \frac{2\pi N}{9} \left[\frac{1}{45kT} \frac{1}{(1-af)(1-bg)} \sum (b_{ii}m_{ii} - b_{jj}m_{jj}) (a_{ii}k_{ii}^2 - a_{jj}k_{jj}^2) + \frac{1}{45k^2T^2} \frac{1}{(1-af)(1-bg)} \times \right. \\ \left. \times \sum (b_{ii}m_{ii} - b_{jj}m_{jj}) (\mu_i^2 k_{ii}^2 - \mu_j^2 k_{jj}^2) \right]. \quad (14)$$

Here, $m_{ii} = (2n^2 + 1)/[3n^2 + 3(1 - n^2)O_i]$; $k_{ii} = (2\epsilon + 1)/[3\epsilon + 3(1 - \epsilon)O_i]$; O_i is the ellipticity factor [32].

The equations of this type have some parameters that are difficult to determine. The theories, in which the type of function of Lorentz internal field varies as $(n^2 + 2)/3$ or $(\epsilon+2)/3$, were not related.

The eq. (15) – (17) are widely used. In Ref. [32] the molar Kerr constant was introduced, which takes into account the internal field according to Lorenz:

$$mK = \frac{6\lambda nB}{(n^2 + 2)} \cdot \left(\frac{3}{\epsilon + 2} \right)^2 \cdot \frac{M}{d}. \quad (15)$$

The phenomenological theory of the Kerr effect leads to the expression for mK [33]:

$$mK' = \frac{6\lambda nB'M}{3(n^2 + 2)^2(\epsilon + 2)d}. \quad (16)$$

In Ref. [34] the equation was obtained on the basis of analysis of the relationship between the refraction and polarizability in anisotropic media:

$$mK'' = \frac{2\lambda n B'' M}{3(n^2 + 2)(\varepsilon + 2)d}. \quad (17)$$

Here n stands for the refractive index, λ is the wave length, ε - dielectric permeability, M is the molar mass, d - density, B - the Kerr constant. The classical approach to the Kerr theory implies

$$B = \frac{3\pi N_1}{n\lambda} \left(\frac{n^2 + 2}{3} \right)^2 \left(\frac{\varepsilon + 2}{3} \right)^2 (\theta_1 + \theta_2),$$

where N_1 is the number of molecules in a unit of volume, θ - the anisotropic constituent of the Kerr constant, θ - the dipole constituent of the Kerr constant:

$$B' = \frac{3B}{\varepsilon + 2}; \quad B'' = B \left(\frac{\varepsilon + 2}{3} \right) \left(\frac{n^2 + 2}{3} \right)$$

RESULTS AND DISCUSSION

It is easy to show [14] that mK (the experimental molar Kerr constant) obtained on the basis of the diluted solutions in non-polar isotropic solvents according to Eq. (15) and mK' determined according to Eq.(16) correlate:

$$mK' = \frac{mK}{3(\varepsilon_1 + 2)}, \quad (18)$$

mK and mK'' determined on the basis of Eq. (14) are brought into correlation:

$$mK'' = mK \left(\frac{\varepsilon_1 + 2}{3} \right) \left(\frac{n_1^2 + 2}{3} \right) \quad (19)$$

Here ε and n_1 stand for the dielectric permeability and refractive index correspondingly. The key choice criterion for the equation to calculate mK was the coincidence of the values of mK , mK' and mK'' with the gas values of mK_{gas} presented in Ref. [11]. However, as it was shown in several papers [12, 35-38], the value of mK depends on the nature of a solvent. The authors have presented above that the influence of intermolecular field interaction on mK can be determined by the London-Debye-Keesom potentials for pairwise interactions in condensed media. It was also shown that $\Delta mK = mK_{\text{gas}} - mK \sim \varphi$ for

one and the same substance in a series of non-polar solvents with close first potentials of ionization and polarizability of molecules.

The authors of this paper suggest that the reproducibility of the value of mK_{gas} using extrapolation of mK as the function from φ to $\varphi = 0$ should be considered as the choice criterion for the equation to determine mK . Table 3 shows the values of mK obtained according to the classical formula (12) in a series of non-polar solvents and the experimental data of mK_{gas} . The values of mK' and mK'' calculated according to Eq.(16) and (17) are shown in Tables 4 and 5. The dependences of mK on φ were suggested along with the extrapolation of mK to $\varphi = 0$ on the basis of the data in Tables 3-5. It is evident from the examples in Figs. 4-6 that in all cases, except CCl_4 , the extrapolation of mK' leads to mK_{gas} measured experimentally. The above deviation is obviously connected with the deviation of mK' can be attributed to a greater error in determination of mK_{gas} CCl_4 due to the small absolute value of mK_{gas} ($mK_{\text{gas}}(\text{CCl}_4) = 0.933$). The extrapolation of the values of mK and mK'' does not give the values of mK_{gas} .

In case of the solvents with evident anisotropy of polarizability and the ability to form CT complexes or H-bond, the values of mK fall out sharply from the linear dependence, which describes the volume non-specific interaction of molecules in solvents; this points at the local interaction with formation of the complexes oriented in the electric field as a whole. This takes place, for example, in case of carbon disulphide in dioxane (Fig. 5), chloroform in dioxane, nitrobenzene in benzene etc.

CONCLUSIONS

The evaluation of the effect of the solute-solvent interaction on mK of dissolved molecules using the London-Debye-Keesom potential allowed us to establish the correlations of mK measured in a series of non-polar solvents, similar ionization potentials, and molecular size with the interaction parameter φ . The established dependence is relevant to the compounds which do not form H-bonds and other specific interactions because the parameter φ relates to the universal intermolecular interactions only.

Good coincidence between the values of mK_{gas} measured experimentally and the values of $mK'_{\varphi=0}$ obtained by the extrapolation of mK' , which were determined according to the formula (16) gives us a good reason to believe that it should be preferably used to calculate the values of molar Kerr constants on the basis of solutions. Moreover, the values of

$mK'_{\varphi=0}$, the changes of which have not been made or just are impossible in the gaseous state (Table 4), were obtained by the extrapolation of the values of mK' to the zero value of φ . Thus, the method proposed by the authors can be applied to determine the gas values of molar Kerr constants on the basis of changes in a series of non-polar solvents with volume nature of interaction between the molecules of a solute and a solvent.

Determination of the values of molar Kerr constant in the vapour phase on the basis of solution measurements as it was presented allows us to apply the molar Kerr constants in various fields of chemistry. Especially it is important during the study of intramolecular effects, for which the theory of changes in internal field only was developed along with empirical studies on the polarizability anisotropy and conjugation. The qualitative studies on the polarizability as one of the main factors that determine the chemical behavior of molecules give grounds for modern electron theory [39].

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Figure captions

Figure 1. Discrete-continuum model of interaction of a solute molecule (i) with solvent molecules (j) in a medium with dielectric permittivity ϵ .

Figure 2. Dependence $mK - \varphi$ for methanedithione (the — line), benzene (the --- line), and $\Delta mK - \varphi$ for methanedithione (theline), benzene (the ... line) in non-polar solvents, namely heptane (◐), hexane (●), cyclohexane (□), tetrachloromethane (■), dioxane (Δ), benzene (▲), carbon bisulfide (○).

Figure 3. Dependence $mK - \varphi$ for nitrobenzene (the — line), 1,2-dinitrobenzene (the line), 1,3-dinitrobenzene (the ... line), and $\Delta mK - \varphi$ for nitrobenzene (the --- line) in non-polar solvents, namely heptane (◐), hexane (●), cyclohexane (□), tetrachloromethane (■), dioxane (Δ), benzene (▲).

Figure 4. Dependence $mK - \varphi$ for benzene: mK (the — line), mK' (the --- line), and mK'' (the ... line) in non-polar solvents, namely heptane (◐), hexane (●), cyclohexane (□), tetrachloromethane (■), dioxane (Δ), benzene (▲), carbon bisulfide (○).

Figure 5. Dependence $mK - \varphi$ for methanedithione: mK (the — line), mK' (the --- line), and mK'' (the ... line), and tetrachloromethane: mK (the -- line), mK' (the --- line), and mK'' (the line) in non-polar solvents, namely heptane (◐), hexane (●), cyclohexane (□), tetrachloromethane (■), dioxane (Δ), benzene (▲), carbon bisulfide (○). For methanedithione the mK scale is given in brackets.

Figure 6. Dependence $mK - \varphi$ for acetonitrile: mK (the — line), mK' (the --- line); for propanone: mK (the line), mK' (the ... line); and mK'' (the -. line) in non-polar solvents, namely heptane (◐), hexane (●), cyclohexane (□), tetrachloromethane (■), benzene (▲). For propanone the mK scale is given in brackets.

Table 1. The values of molar Kerr constants ($mK \times 10^{12}$) and ρ_K parameter ($\rho_K \times 10^{18}$) in non-polar solvents

Compound	$mK_g \times 10^{12}$	Heptane		Hexane		Cyclohexane		Tetrachloromethane		Dioxane		Benzene		Methanedithione	
		mK	ρ_K	mK	ρ_K	mK	ρ_K	mK	ρ_K	mK	ρ_K	mK	ρ_K	mK	ρ_K
Chloroform	-29.41	-25.2	6.20	-	-	-27	7.90	-24.1	9.23	-34.39	8.36	-31	1.002	-	-
Tetrachloromethane	0.933	-	-	1.3	5.80	-	-	1.5	8.21	-	-	1.6	9.21	1.12	1.518
Methanedithione	47.4	30	6.80	30	7.01	31.9	8.90	27.8	1.05	33.2	1.070	27.1	1.171	24.9	1.914
Acetonitrile	363	-	-	25.9	5.05	219	9.35	217	1.060	-	-	244	1.390	-	-
Methoxymethane	-8.7	-	-	-	-	-8.1	1.170	-5.5	1.324	-	-	-6.6	1.514	-	-
Propanone	99	66	6.25	-	-	-	-	93	9.23	-	-	51	1.038	-	-
Ethoxyethane	-11.4	-8.94	5.59	-	-	-	-	-7.5	7.92	-	-	-8.5	1.13	-	-

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Pyridine	-	120	6 0 5	-	-	119.2	7 8 4	128	8 9 2	11 1.5	9 0 8	-	-	-	-
Nitrobenzene	11 32	888	5 4 9	-	-	920	6 4 4	880	8 0 8	88 0	8 1 4	980	8 9 7	-	-
Benzene	12 .8	8.3	5 8 0	8.5 8	5 9 8	8.14	7 5 4	7	8 5 0	6.5 7	8 6 9	8.1	9 5 5	6.3	1 5 8 6
Methylbenzene	33	18. 5	5 4 1	-	-	-	-	13.7	7 8 0	13	8 0 1	13.	9 5 0	-	-
Phenylamine	-	-	-	-	-	22.2	7 4 5	12.5	8 4 1	51. 2	8 6 9	17. 2	9 4 0	-	-
1,4-Dimethylbenzene	21 .3	15. 6	5 0 8	-	-	13.7	6 5 5	10.6	7 3 0	-	-	14. 93	8 2 7	-	-
N,N-Dimethylaniline	-	-	-	-	-	177	6 4 2	158	7 2 2	19 5	7 7 4	134 .2	8 0 7	-	-
1,2-Dinitrobenzene	-	-	-	15 10	5 4 9	-	-	1300	7 4 5	11 60	7 9 0	187 0	8 7 5	-	-
1,3-Dinitrobenzene	-	-	-	55 0	5 5 3	-	-	580	6 7 7	46 0	7 9 5	685	8 8 5	-	-
Octane	8. 4	-	-	3.3 4	4 0 7	2.16	5 6 6	3.06	6 3 4	-	-	-	-	-	-
Bicyclo[4.4.0]decane - 1,3,5,7,9-pentene	-	40	5 3 1	49. 4	6 0 2	42.3	6 7 8	40.9	7 6 2	-	-	45. 5	8 2 4	45	1 4 1 3

Phenanthrene	-	114	465	-	-	114.1	596	97.6	660	-	-	78.8	735	-	-
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Table 2. The molar Kerr constants of non-polar compounds (mK) and the values of parameter ϕ in polar solvent (chlorobenzene)

Compound	$mK_{\text{gas}} \times 10^{12}$	$mK \times 10^{12}$	$\Delta mK = mK_{\text{gas}} - mK$	$\phi \times 10^{18}$
Tetrachloromethane	2.0	44.3	-42.3	726
Benzene	15.6	53.3	-27.7	755
Methanedithione	52.3	49.3	3.2	814

Table 3. The values of molar Kerr constant ($mK \times 10^{12}$) calculated according to Eq. (15) and the values of gas molar Kerr constants ($mK_{\text{gas}} \times 10^{12}$).

No.	Compound	Heptane	Hexane	Cyclohexane	Tetrachloro-methane	Dioxane	Benzene	Methanedithione	$mK_{\text{gas}} \times 10^{12}$
1	Chloroform	-25.2	-	-27	-24.12	-34.29	-31	-	-29.41
2	Tetrachloromethane	-	1.3	-	1.15	-	1.6	1.12	0.933
3	Methanedithione	30	30	31.9	27.8	38.2	27.1	24.8	47.4
4	Acetonitrile	-	259	219	217	-	244	-	363
5	Methoxymethane	-	-	-8.1	-5.5	-	-6.6	-	-8.7
6	Propanone	66	65	-	93	-	51	-	99

7	Ethoxyethane	-8.94	-	-	-7.5	-	-8.5	-	- 11.4
8	Pyridine	120	-	119.2	128	111.5	-	-	-
9	Nitrobenzene	888	-	920	880	880	980	-	133 2
10	Benzene	8.3	8.58	8.14	7	6.57	8.1	6.3	12.8
11	Phenylamine	-	-	22.2	12.5	51.2	17.2	-	-
12	Methylbenzene	18.5	-	-	13.7	13	13.8	-	33
13	1,4-Dimethylbenzene	15.6	-	13.7	10.6	-	14.93	-	21.3
14	N,N-Dimethylaniline	-	-	177	158	195	134.2	-	-
15	Octane	-	3.34	2.16	3.06	-	-	-	8.4
16	Bicyclo[4.4.0]deca-1,3,5,7,9-pentene	40	49.4	42.3	40.9	-	45.5	45	-
17	Triphenylmethane	-	-	18.2	13.7	-	12.5	-	-
18	Phenanthrene	114	-	114.1	97.6	-	78.5	-	-
19	Pirene	-	-	173	161	-	160	-	-

Table 4. The values of molar Kerr constant ($mK' \times 10^{12}$) calculated according to Eq. (16) for compounds 1-19 (see Table 3) and the molar Kerr constants ($mK'_{\varphi_\alpha=0} \times 10^{12}$) calculated by extrapolation.

Compound	$mK'_{\varphi_\alpha=0}$	Heptane	Hexane	Cyclohexane	Tetrachloromethane	Dioxane	Benzene	Methanethione
1	-30	-33	-	-36.1	-34	-48	-44.1	-
2	1.9	-	1.67	-	1.62	-	2.27	1.59
3	47	38.8	38.8	42.7	39.2	53.5	38.6	35.3
4	362	-	335	293	306	-	348	-
5	-9	-	-	-10.8	-7.8	-	-9.4	-
6	100	86.4	84	-	131	-	72.6	-
7	-11	-11.7	-	-	-10.6	-	-12.1	-

8	170	157	-	160	180	156	-	-
9	1330	1168	-	1231	1240	1233	1390	-
10	13	10.9	11.1	10.9	9.9	9.3	11.5	9
11	45	-	-	29.7	17.6	72	24.5	-
12	31	24.2	-	-	19.3	18.2	19.7	-
13	22	20.4	-	18.3	14.9	-	-	-
14	350	-	-	237	223	213	191	-
15	8.5	-	4.4	2.9	4.3	-	-	-
16	65	52.4	63.8	56.6	57.8	-	64.8	64
17	50	-	-	24.4	19.3	-	17.8	-
18	230	149	-	153	138	-	112	-
19	234	-	-	232	227	-	228	-

Table 5. The values of molar Kerr constant ($mK'' \times 10^{12}$) calculated according to Eq. (17) for compounds 1-19 (see Table 3) and the molar Kerr constants ($mK''_{\varphi_\alpha=0} \times 10^{12}$) calculated by extrapolation

Com- pound	$mK''_{\varphi_\alpha=0}$	Heptane	Hexane	Cyclo- hexane	Tetrachloro- methane	Dioxane	Benzene	Methane- dithione
1	-14	-43.2	-	-50.4	-46.8	-64.4	-62.6	-
2	2.2	-	2.17	-	2.23	-	3.23	2.47
3	54	51.4	50.3	59.5	53.9	71.8	54.7	54.6
4	*	-	434	408	421	-	492	-
5	-	-	-	-15.1	-10.7	-	-13.3	-
6	125	113	109	-	180	-	103	-
7	-	-15.3	-	-	-14.6	-	-17.2	-
8	-	206	-	222	248	209	-	-
9	-	1521	-	1717	1708	1653	1979	-
10	15.8	14.2	14.4	15.2	15.3	12.3	16.4	13.9
11	-	-	-	41.4	24.3	96.2	34.7	-
12	33	31.7	-	-	26.6	24.2	27.9	-
13	-	36.7	-	25.6	20.6	-	-	-
14	-	-	-	330	307	286	270	-
15	-	-	5.6	4.03	5.94	-	-	-
16	-	68.5	82.8	78.9	79.4	-	91.9	99.2
17	-	-	-	34	26.6	-	25.2	-
18	-	195	-	213	189	-	158	-
19	-	-	-	323	312	-	323	-

*Missing $mK''_{\varphi_\alpha=0}$ values mean that the spread and the small number of experimental points do not provide $mK''_{\varphi_\alpha=0}$ values according to the extrapolation formula (17)

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Graphical abstract