

INFLUENCE OF INDUCTIVE EFFECT IN SOME HOMOLOGOUS ORGANIC LIQUIDS ON THE KERR CONSTANT VALUES

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ABSTRACT

We report the values of electro optic Kerr constant of liquids belonging to Carbonyl (Ketone and Aldehyde) and Nitrile series at $\lambda = 632.8\text{nm}$. These investigations have been carried out for the first time in the liquids, Methyl n propyl ketone, Methyl isopropyl ketone, Methyl isobutyl ketone, Propionaldehyde, Butyraldehyde, Propionitrile and Butyronitrile belonging to these homologous series. We have observed a decreasing trend in Kerr constant values with an increasing chain length by a CH_2 intervening group in all these series. The variations in the inductive effect arising from different substituents in the molecular structures of the liquids are used to interpret the decreasing trend in the values of the Kerr constant.

INTRODUCTION

It is well known from the Electro Optic Kerr Effect (EOKE)[1] that a liquid may become birefringent under the application of an electric field, if its molecule possesses an electric dipole moment or a nonspherical shape. It was reported by earlier workers [2-4] that a substituent group in an aromatic compound could change the value of Kerr constant. A change in Kerr constant values was observed in mono and di-substituted benzene derivatives depending upon the nature and position of the substituent[4]. Further a change in Kerr constant was also reported in substituted nitrobenzene with paramethoxy groups[5].

In literature, the relationship between the Electro-optical Kerr constant values of the liquids belonging to a homologous series to their chemical structures is not known though a few reports are available on these aspects with Opto-optical Kerr effects [6-8]. It is the aim of this paper to relate the Electro-optical Kerr constant values of the liquids belonging to three homologous series to their structures in terms of the constants that are characteristic of the substituents.

We know that the magnitude of the Kerr constant of a liquid depends upon a number of macroscopic parameters like dielectric constant, dipole moment etc.[5]. However it is very difficult to account for the variation of Kerr constant of liquids in a homologous series with any one of these parameters, as the relationship between these parameters and the chemical structures of the molecules is not unique in nature.

At this stage, it looks reasonable to compare the decreasing trend observed in the experimentally determined Kerr constant values of the liquids belonging to a homologous series to their Taft sigma (substituent) constants[9]. Taft sigma constant is a measure of the polar nature of the substituent which incorporates the contributions from inductive, mesomeric and steric effects arising from the structures of the molecules. The inductive effect depends upon the intrinsic tendency of a substituent to release or withdraw electrons through the molecular chain or through space. The resonance or mesomeric effect involves delocalization of pi electrons. Steric effect reflects the geometrical restrictions imposed on the molecule as a result of the number and nature of atomic species constituting the substituents [10].

In this paper, we report the influence of the inductive effect arising from the structures of the molecules, on the values of Kerr constant of liquids belonging to three homologous series of Ketone, Aldehyde and Nitriles.

EXPERIMENTAL SETUP

A conventional optical bench has been set up in our laboratory for the static Kerr effect experiments[11]. A Helium-Neon laser with 5 milliwatt power has been used as a probe beam. High voltage pulses up to 20KV DC with pulse width of the order of 100 microseconds are used to generate birefringence. Kerr cells with stainless steel electrodes of length of 8cm and a separation between the electrodes being 4mm have been constructed for our experiments. A PIN Photodiode (S1188-06) is used as light photodetector

and the output has been fed to an Iwatsu oscilloscope (250MHz) fitted with a polaroid camera. The high voltage electric pulses have also been simultaneously recorded using a Tetronix P6015 high voltage probe with 1:1000 attenuation. The crossed polarizer and the analyzer combination has been adjusted to 45 degrees with respect to the electric field direction for maximum intensity output during the application of the electric field. High quality Nicol prisms have been used as polarizers.

When an electric field is applied to a medium, the difference between the index of refraction for light polarized parallel to the applied field n_{\parallel} and the index n_{\perp} for light polarized perpendicular to the applied field is given by the expression

$$n_{\parallel} - n_{\perp} = \Delta n = B\lambda E^2 \quad (1)$$

where λ is the wavelength of the probe beam, B is the Kerr constant of the medium and E is the electric field strength. From equation (1), it follows that upon propagation of light through the material, the phase shift δ between the components of the light beam polarized parallel and perpendicular to the applied field is given by

$$\delta = 2\pi \int_0^L BE^2 dl \quad (2)$$

where L being the length of the optical path through the electric field. The phase difference δ can be measured using the relation[12].

$$I/I_m = \sin^2 (\delta/2) \quad (3)$$

where I is the instantaneous value of the transmitted light and I_m denotes the maximum intensity of the transmitted light when the polarizer and the analyzer are in perfectly uncrossed position. The layout of the experimental setup has been shown in Figure.1.

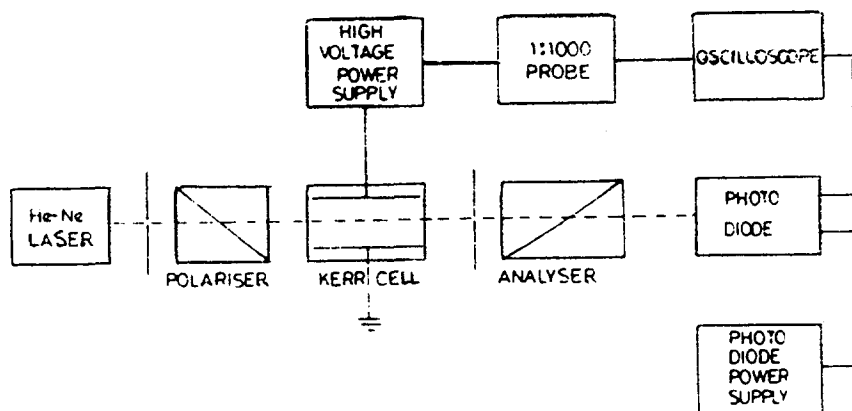


Fig. 1. Diagram of equipment for Kerr effect measurements.

The Kerr cells, after filling with the liquids, are sealed tightly with teflon caps to avoid evaporation and absorption of moisture. The various chemicals that are used in the experiments are of analar grade (E. Merck) and are dried initially with molecular sieves-4A. Care has been taken to avoid all possible impurities in the liquids under consideration by distilling them prior to use. Only middle fractions have been used for the experiments. All the investigations have been carried out at room temperature (299K).

The refractive indices of the liquids are measured using Abbe refractometer (Carl Zeiss) while the dielectric constants have been measured using a Hewlett Packard 4274A multifrequency LCR digital bridge at 100KHz.

3. RESULTS AND DISCUSSION

The instrument has been standardised with a few well known standard Kerr liquids like Nitrobenzene and Acetone. For these liquids, the linear dependence of the birefringence (Δn) up on the square of the electric field strength (E^2) has been verified and the Kerr constant values are evaluated using eqn. (1) and compared with those reported in literature. All these values are given in Table. I.

TABLE I

Experimental Values of Kerr Constant of Nitrobenzene and Acetone from Present Study and due to Literature Values

Liquids	Present work $B \times 10^{15} \text{ mV}^{-2}$ at $\lambda = 632.8\text{nm}$	Literature values $B \times 10^{15} \text{ mV}^{-2}$ at $\lambda = 632.8\text{nm}$
Nitrobenzene	3511	i) 3552[13] ii) 3260($\pm 6\%$)[14] iii) 3690[15] iv) 3515[16]
Acetone	169	i) 172[13] ii) 165[16]

The uncertainty in the measurement of the Kerr constant has been estimated to be less than ± 2 percent by taking average of all the readings after performing the experiment several times in each case.

The Kerr constant values given in the reference [16] were actually determined at $\lambda = 546\text{nm}$. These values are converted to the wavelength $\lambda = 632.8\text{nm}$ in order to compare with the results obtained in the present work using Havelock dispersion law[17] given by

$$h = \frac{B\lambda n}{(n^2 - 1)^2} \quad (4)$$

where h is some constant for all wavelengths. The calculated values are found to be very close to the values experimentally obtained in the present work.

We report the values of Kerr constant in Methyl n propyl ketone, Methyl isopropyl ketone, Methyl isobutyl ketone, Propionaldehyde, Butyraldehyde, Propionitrile and Butyronitrile at $\lambda = 632.8\text{nm}$. A linear dependence of Δn upon E^2 has been verified and shown in figures 2, 3 and 4 for Ketone, Aldehyde and Nitrile series respectively.

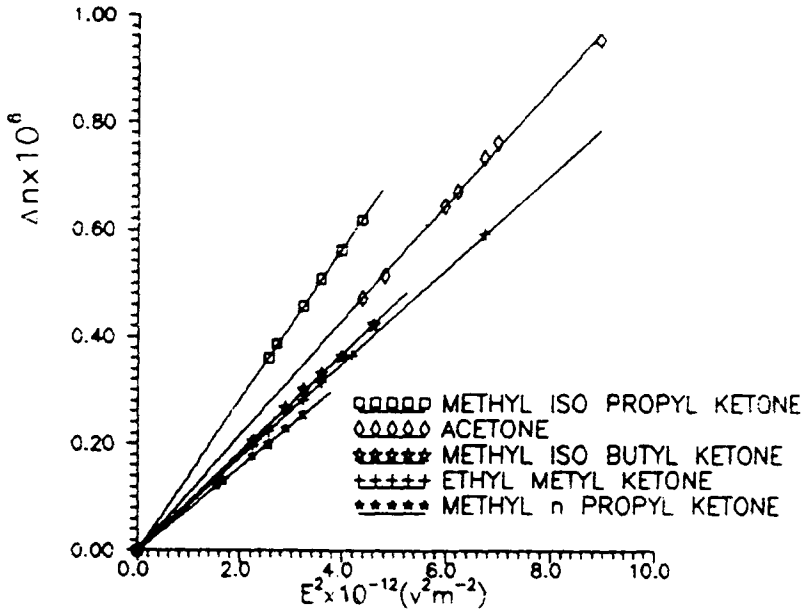


Fig. 2. The variation of the birefringence to the square of the electric field strength (KETONE SERIES).

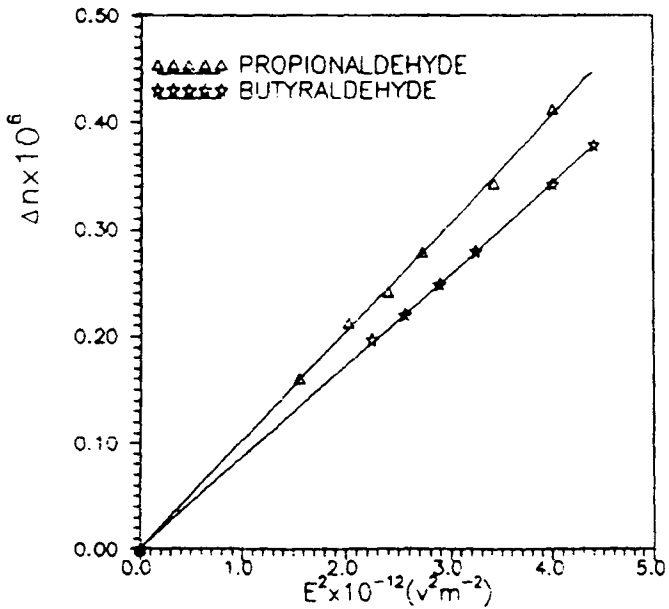


Fig. 3. The variation of the birefringence to the square of the electric field strength (ALDEHYDE SERIES).

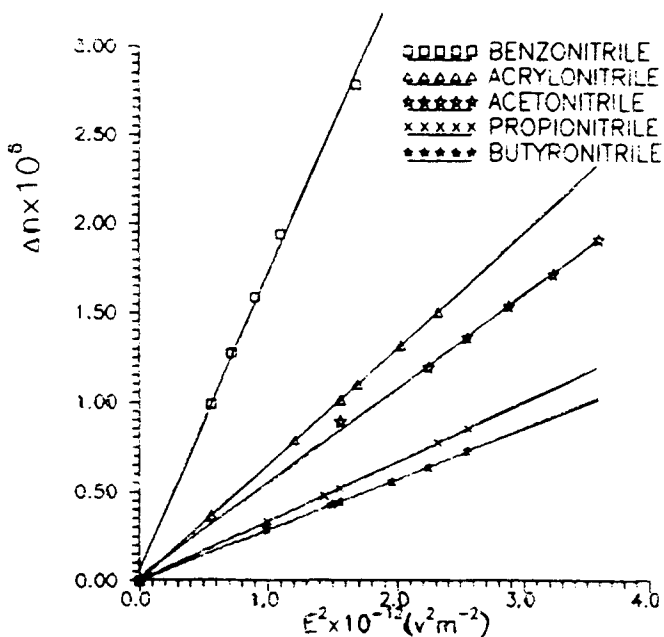


Fig. 4. The variation of the birefringence to the square of the electric field strength (NITRILE SERIES).

The Kerr constant values of these liquids belonging to the three homologous series can be obtained by measuring the slopes of the graphs in figures 2-4 using equation (1). The evaluated Kerr constant values of the liquids with other physical parameters measured experimentally are given in Table II along with the chemical structures of the liquids in all these series. On inspection of Table II, one observes a common interesting feature in all the three homologous series that as the chain length increases between any two adjacent molecules by a CH_2 intervening group the Kerr constant value decreases.

TABLE II
 Experimental values of Kerr constant (B), refractive index (n), dielectric constant (ϵ), dipole moment (μ), molar volume (V_m), Taft sigma (substituent) constant (σ^*) and third order non-linear susceptibility $\chi^{(3)}$ of the liquids

Liquid	Chemical Structure	Kerr Constant ($B \times 10^{15} \text{ m}^3 \text{ v}^{-2}$)	Refractive Index (n)	Dielectric constant (ϵ)	Dipole moment (μ) Debye	Molar volume (V_m)	Taft Sigma substituent constant [σ^*]	$\chi^{(3)}$ ($\sigma^2, \sigma, 0, 0$) $\times 10^{-22} \text{ m}^3 \text{ v}^{-2}$
KETONES:								
1. Acetone	$\text{CH}_3\text{C}(=\text{O})\text{CH}_3$	169	1.3561	20.3244	2.77[9]	73.4446	0.0	9.617
2. Ethyl methyl ketone	$\text{CH}_3\text{CH}_2\text{C}(=\text{O})\text{CH}_3$	137	1.3762	18.7873	2.76[9]	89.6208	-0.10	7.911
3. Methyl n Propylketone	$\text{CH}_3(\text{CH}_2)_2\text{C}(=\text{O})\text{CH}_3$	123	1.3853	15.4613	2.72[9]	106.3990	-0.12	7.150
4. Methyl iso propyl ketone	$(\text{CH}_3)_2\text{CHC}(=\text{O})\text{CH}_3$	221	1.3823	16.4644	2.80[18]	107.3940	-0.19	12.819
5. Methyl iso butyl ketone	$(\text{CH}_3)_2\text{CH}_2\text{CHC}(=\text{O})\text{CH}_3$	142	1.3903	12.9060	2.80[18]	125.106	-0.13	8.284
ALDEHYDES:								
1. Propional/ dehyde	$\text{CH}_3\text{CH}_2\text{C}(=\text{O})\text{H}$	162	1.3591	18.6342	2.57[9]	71.9613	-0.10	9.239
2. Butyral/ dehyde	$\text{CH}_3(\text{CH}_2)_2\text{C}(=\text{O})\text{H}$	136	1.3772	13.7610	2.45[9]	89.9451	-0.12	7.859
NITRILES:								
1. Acetonitrile	$\text{CH}_3\text{C}\equiv\text{N}$	842	1.3445	36.7524	3.47[9]	52.2464	0.0	45.505
2. Propionitrile	$\text{CH}_3\text{CH}_2\text{C}\equiv\text{N}$	526	1.3601	24.7049	3.60[9]	70.4528	-0.10	30.021
3. Butyronitrile	$\text{CH}_3(\text{CH}_2)_2\text{C}\equiv\text{N}$	451	1.3782	24.3315	3.60[9]	86.8745	-0.12	26.083
4. Acrylonitrile	$\text{H}_2\text{C}=\text{CHC}\equiv\text{N}$	1027	1.3883	33.0904	3.54[9]	65.8312	0.56	59.831
5. Benzonitrile	$\text{C}_6\text{H}_5\text{C}\equiv\text{N}$	2772	1.5229	25.2860	3.90[9]	103.0581	0.60	177.149

Acetone, Ethyl methyl ketone and Methyl n propyl ketone are compared one with the other to observe this feature in Ketone series. In the same series, Methyl isopropyl ketone and Methyl isobutyl ketone are compared with each other as both of them belonging to the iso group of ketones. In both these categories of Ketones, the decrease in the values of Kerr constant with increasing chain length by CH_2 intervening group is very conspicuous.

A similar trend in the decrease of Kerr constant values has been observed in the Aldehyde series by comparing Propionaldehyde with Butyraldehyde and in the Nitrile series by comparing Acetonitrile with Propionitrile and Propionitrile with Butyronitrile.

From Table II, it is also clear that the dielectric constant values show a decreasing trend similar to Kerr constant variation with increasing CH_2 intervening group in all the series while the variation of refractive index shows an increasing trend. The variation in the dipolemoment values has not shown any regular trend in Nitrile series. It is difficult to account for the decreasing trend in the Kerr constant values of liquids of these homologous series with increasing chain length to the physical parameters mentioned above, as the relation between these parameters to the chemical structure of the molecules is not unique in nature.

Thus it is more realistic to relate the decreasing trend of the Kerr constant values of these series of liquids to the Taft sigma (substituent) constants. The Taft sigma constant is a measure of the polar nature of the substituent and incorporates the contribution from inductive, mesomeric and steric effects arising from the structures of the molecules. The Taft sigma constants for the different substituents are also given in Table II. For the organic liquids considered in our electro optic Kerr investigations, the contributions due to the mesomeric effect is considerably small and hence can be neglected. The contribution due to the steric effects can be minimized by the way of evaluating the normalized Kerr constant values of the liquids. Thus any change in the values of the Kerr constant of liquids belonging to a homologous series can be attributed to the predominant nature of the inductive effect that arises due to the structural changes of the molecules in that series.

Figure 5, shows the variation of the normalized Kerr constant values (in log. scale) to the Taft sigma constants of different substituents of the liquids belonging to the Ketone and Nitrile series.

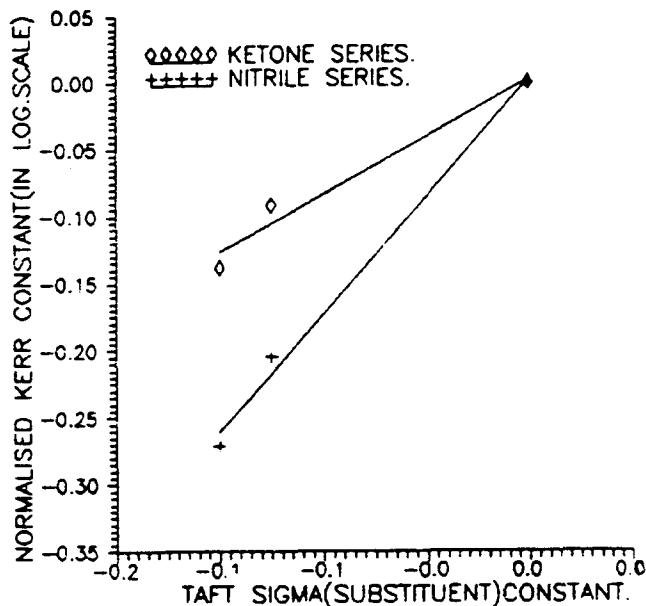


Fig. 5. The variation of the normalised Kerr constant values (in Log. scale) of Ketone and Nitrile series with Taft sigma (Substituent) constant.

For the evaluation of the normalized Kerr constant values, the Kerr constant value of the first liquids of each series namely Acetone in Ketone series and Acetonitrile in Nitrile series have been considered as standard references. We observe a linear relationship between the normalized Kerr constant values with Taft sigma constants in these series. The presence of the positive slopes in both cases is an indication of predominance of the inductive effect arising from the different structures of the molecules. Further the decreasing trend in the Kerr constant values of a series with increasing chain length is clearly reflected in the decreasing trend of the inductive effect arising from the structures of the molecules.

The electron charge density at the functional group of a molecule is responsible for the inductive effect. Thus any decrease in the inductive effect contribution due to an increase in the chain length of molecules belonging to a homologous series is to be related to the decrease in the electron charge density at the functional group of the molecules in the following way.

Organic systems that are rich in π electrons show strong nonlinear optical effects and fast response times[19]. Thus the π electron charge density

of a molecule is responsible for the nonlinear electro optical Kerr constant value of a liquid via the third order nonlinear susceptibility value $\chi^{(3)}$ by the relation[13],

$$\chi_{1212}^{(3)}(\omega; -\omega, 0, 0) = \frac{Bn\lambda}{48\pi} m^2 v^{-2} \quad (5)$$

where B is the Kerr constant, n is refractive index and λ is the wavelength of the probe light.

For a homologous series of liquids, as the number of π bonds is fixed because of a common functional group, namely C = O in Ketone and Aldehyde series and C \equiv N in Nitrile series, any decrease in the nonlinear parameter values may be influenced by the decrease in the electron charge densities at the functional groups due to different substituents.

It is of interest to add that the decreasing trend in the values of Kerr constant may also be attributed to the increase in the values of the molar volumes of the liquids with increasing chain length in a homologous series using the relation[20]

$$B = \frac{K_m (n^2 + 2)^2 (\epsilon + 2)^2}{\lambda n V_{mole}} \quad (6)$$

where B is the volume Kerr constant, K_m is the molar Kerr constant and V_{mole} is the molar volume of the liquid. The values of the density and molecular weights of the liquids are taken from reference[9] for the evaluation of molar volumes. It is clear from Table II that as CH_2 intervening group increases in a homologous series, the molar volume increases and hence the values of the Kerr constant decreases.

One can further substantiate the observed decrease in the experimental Kerr constant values with the increasing CH_2 intervening group in a homologous series through NMR electric field studies. The dipolar orientational alignment with the electric field direction is the common feature in both the Kerr studies and in NMR electric field studies. It was reported[21] that the magnitude of the term representing the alignment of dipoles is comparatively less in Propionitrile than in Acetonitrile eventhough the dipolemoment value of the former is larger than the later. This may be attributed to the heaviness of Propionitrile molecule because of the additional CH_2 intervening group.

In order to further establish the intimate relationship between $\chi^{(3)}$ values with π bond electrons, we have also chosen two liquids belonging to Nitrile series namely, Acrylonitrile which is aliphatic in nature having three π bonds and Benzonitrile which is aromatic in nature for our EOKE studies. The Kerr constant values of these two liquids are also given in Table II. It is quite clear from Table II, that the increase in the values of Kerr constant and hence in $\chi^{(3)}$ of Benzonitrile and Acrylonitrile are attributed to the increase in electron charge density values at the functional groups. This is clearly reflected in the higher values of Taft sigma (substituent) constant of these liquids compared to other liquids in the Nitrile series. Further the enormous increase in the $\chi^{(3)}$ value of Benzonitrile compared to any other liquid of Nitrile series can be related to the more number of π bonds available in this aromatic compound establishing that the fact the degree of delocalization is increasing with increasing number of π bonds.

CONCLUSIONS

We report the electro optic Kerr constant of liquids belonging to the three homologous series of Ketone, Aldehyde and Nitrile series. The experimentally observed decreasing trend in the Kerr constant values due to increase in the chain length by CH_2 intervening groups in these series are attributed to the decreasing trend in the inductive effect arising from the structure of the molecules.

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