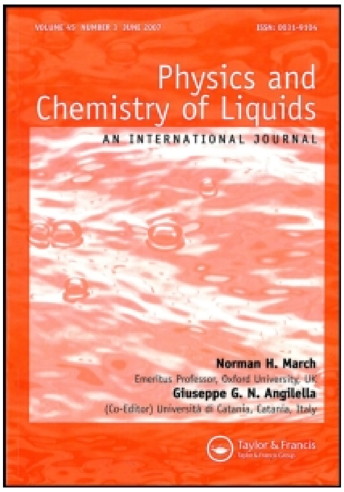

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# Temperature Dependence of Kerr Coefficient of Binary Liquid Mixtures of Aprotic-Aprotic Molecules

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# TEMPERATURE DEPENDENCE OF KERR COEFFICIENT OF BINARY LIQUID MIXTURES OF APROTIC–APROTIC MOLECULES

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The electro optical Kerr coefficients of binary liquid mixtures, comprising of aprotic–aprotic molecules only, are measured over the temperature range of 286 K to 315 K. To with in experimental errors, the logarithm of Kerr coefficient can be expressed as Van't Hoff type expression to the reciprocal of temperature. Information on the interaction energy between the constituents of the binary mixtures is thereby obtained. It is found that the interaction energy in aromatic ketone–aliphatic nitrile binary mixtures is comparatively higher than in the binary mixtures with aliphatic ketone–aliphatic nitriles, aromatic ketone–aromatic nitrile and aromatic ketone–aliphatic ketones components. This is attributed to the dipole–dipole interaction existing between the components of the binary mixtures.

*Keywords:* Electro optical Kerr effect; aprotic–aprotic binary mixtures; interaction energy

## 1. INTRODUCTION

Since the discovery of Electro optical Kerr effect, [EOKE] by John Kerr [1], most of the electro optical Kerr effect studies are performed at room temperature [2–9]. In many instances however it is desirable to acquire data for the temperature dependence of Kerr effect [10–12].

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Further a wide range of temperature is necessary for dynamic Kerr effect studies which when coupled with dielectric measurements can provide valuable information on molecular motions in liquids [13–15]. For simple organic liquids, the experimental evidence [16] and the theoretical investigations [11] indicate that the Kerr coefficient can be expressed as a quadratic function of reciprocal temperature. For a number of nonpolar liquids, the second order hyperpolarizability values are estimated from the temperature dependent studies of Kerr coefficient [17–25]. However only for a few polar liquids [10, 26–30] the temperature variation of Kerr coefficient has been reported.

Experiments on temperature variation of Kerr coefficient of binary mixtures will give information on the interaction energy between the components of the mixtures [31]. Further this study will give an idea regarding the influence of the thermal energy on the dipole–dipole interaction existing between the components of the mixture.

Though there is work available in the literature on the electro-optical Kerr investigation of various isomers of pentanols in *n*-heptane over a wide concentration range (0.3 to 1 mole fraction) from room temperature down to 202 K at $\lambda = 632.8$ nm [32], no report is available on the extraction of information on the interaction energy existing between the components of a binary mixture through temperature variation of EOKE studies on binary mixtures.

Having this in mind, we performed temperature variation of Kerr coefficient of a number of polar–polar binary mixtures, we reported earlier [4], over a wide temperature range of 286 K to 315 K. All the binary mixtures reported in this work consist of only aprotic–aprotic molecules. Liquids drawn from ketone and nitrile series form either one or both participating components of the binary mixtures.

The binary mixtures belonging to ketone series are divided into two categories such as aliphatic–aliphatic and aliphatic–aromatic. In the case of aliphatic–aliphatic binary mixtures, acetone is taken as component A and ethyl methyl ketone and cyclohexanone as component B while acetone (A)–acetophenone (B) mixture is taken as an example for aliphatic–aromatic combination for investigations.

The second part of the experiment related to binary mixtures with the participating components pooled from two different series namely ketone and nitriles. They are classified under aliphatic nitrile–

aliphatic ketones, aromatic ketone–aromatic nitrile and aliphatic nitriles–aromatic ketone mixtures.

Acrylonitrile forms the component A and acetone, ethyl methyl ketone and cyclohexanone as B components are investigated under aliphatic nitrile–aliphatic ketone category.

Acetophenone (A)–Benzonitrile (B) has been studied under aromatic ketone–aromatic nitrile category. Whereas acetophenone forms the common component A acetonitrile, propionitrile and acrylonitrile acts as component B under the category of aromatic ketone–aliphatic nitrile binary mixtures.

We performed EOKE experiments in all these binary mixtures at room temperature [4, 9] and established that only in binary mixtures with acetophenone–aliphatic nitriles, an excess values in Kerr coefficients has been observed at a particular molar fraction of the component. In the rest of the binary mixtures only a non additive trend, either positive or negative, in the variation of Kerr coefficient has been observed. These results are substantiated recently by conducting dipole moment measurements and excess parameter studies [9].

Our present study of temperature variation of Kerr coefficient of these binary mixtures revealed the existence of higher values of interaction energy in binary mixtures with aromatic ketone–aliphatic nitrile components. These results validate our recent claim that stronger dipole–dipole interaction exists between the components in aromatic ketone–aliphatic nitrile binary mixtures [9] than in other cases.

## 2. EXPERIMENTAL SECTION

The experimental setup used for the temperature variation of EOKE studies was described elsewhere [5]. The Kerr coefficient values of the binary mixtures are measured using spike type voltage pulses of the order of 100 μsec dination and fields up to $4.5 \times 10^6$ $Vm^{-1}$. A 5 milli Watt helium neon laser has been used as the probe light beam ($\lambda = 632.8$ nm). A PIN photodiode (S1188-06) having a fast response time of the order of 5–10 nsec is used as the light detector and the output of the photodiode is fed to a Iwatsu oscilloscope 250 MHz fitted with a polaroid camera. The high voltage electric pulses have also been simultaneously recorded using a Tektronix P6015 high voltage probe with 1:1000 attenuation. The crossed polarizer and analyzer (high quality nicol prism with high extinction ratio) 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.

The phase difference '$\delta$' between the parallel and the perpendicular components of light after traversing through the liquid is given by

$$\delta = 2\pi l B E^2 \tag{1}$$

where $l$ is the length of the electrode. $B$ is the Kerr coefficient of the medium and $E$ is the electric field strength applied to the electrodes. The phase difference $\delta$ can be measured using the relation [33]

$$I/I_o = \sin^2(\delta/2) \tag{2}$$

where $I$ is the intensity of the light falling on the photodiode when the medium becomes birefringent and $I_o$ is the maximum intensity of the probe beam when the polarizer and analyzer are uncrossed with each other.

A double walled glass Kerr cell containing stainless steel electrode assembly of length 8 cm and with electrode separation 0.4 cm has been used for temperature variation of the Kerr coefficient measurements. Water, from a thermostat controlled temperature bath by a sensitive OMRON (proportional + differential) controller, has been allowed to circulate through the outer chamber of the Kerr cell for temperature variations of the binary mixtures under consideration. Temperature measurements using copper constanton thermocouples revealed no temperature gradient in excess of ±0.2 K between the inner and outer chambers of the Kerr cell. The Kerr coefficients of the binary mixtures have been measured in the temperature range from 286 K to 315 K. The liquids used as a components for making up the binary mixtures are of analar grade (E.Merck). These liquids are initially dued with molecular reives (Type 4A) and distilled prior to use. Only the middle fractions of the samples are considerable for investigations. Generally seven to eight measurements have been made by gradually stepping the applied pulse field both up and down ($0.5 \times 10^6$ to $4.5 \times 10^6\,\mathrm{Vm}^{-1}$) for each molar fraction of binary mixture and at each temperature range. The uncertainly in the measurement of the Kerr coefficient of the binary mixtures at a particular temperature has been estimated to be less than ±2%. Care has been taken to seal the Kerr cells tightly with teflon caps to avoid evaporation of the samples and absorption of moisture.

## 3. THEORETICAL BACKGROUND

To extract the information on the interaction energy existing between the components of a binary mixture, the well known Van't Hoff type of expression [34] is considered.

$$\log K = \frac{-\Delta H^0}{2.303\,RT} + \text{constant} \tag{3}$$

where $K$ is the equilibrium constant that depends on the concentration of the participating species, $\Delta H^0$ is the measure of the interaction energy between the components of a binary mixture and $R$ is the universal gas constant (1.987 cal/deg/mol).

As the Kerr coefficient of a Kerr solution depends on the nature and concentration of the interacting components, an assumption is made such that the equilibrium concentration of the interacted species is reflected in the magnitude of the Kerr coefficient values. Using this assumption which is for all practical purposes is logically correct, the following Eq. (4) is considered to estimate the interaction energy between the participating components in a binary mixture from temperature variation of Kerr coefficient measurements,

$$\log B = \frac{-\Delta H^0}{2.303\,RT} + \text{constant} \tag{4}$$

The interaction energy values thus evaluated for various binary mixtures are related to the dipole–dipole interaction existing between the components of the binary mixtures.

## 4. RESULTS AND DISCUSSION

For the liquids used as one component or the other in the binary liquid mixtures reported in this work, the linear dependence of $\Delta n$ with $E^2$ has been verified and reported elsewhere in detail [5, 6]. The Kerr coefficient values of the liquids measured at $\lambda = 632.8$ nm are given in Table I.

The temperature variation of the binary mixtures is carried out with three different concentration of component B in each case, in the temperature range of 286 K to 315 K.

For binary mixtures showing excess values of Kerr coefficient with molar fraction at room temperature measurements [4, 9] namely acetophenone (A)–aliphatic nitrile (B) mixtures, three different molar fractions of the mixtures namely 0.2, 0.3 and 0.4 are considered for temperature variation studies.

Figures 1–3 depict the variation of normalized Kerr coefficient (log scale) with $T^{-1}$ for acetophenone (A)–acetonitrile (B), acetophenone (A)–propionitrile and acetophenone (A)–acrylonitrile binary systems with 0.3 molar fraction of the component B. Similar plots are obtained for the other molar fractions of these binary mixtures.

For calculating the normalized Kerr coefficient value at a particular temperature, the measured Kerr coefficient value of the mixture has been divided by the sum of the Kerr coefficients of the individual components that make up the mixtures.

For the binary mixtures where in only a non additive trend in Kerr coefficients are observed at room temperature EOKE measurements,

TABLE I Experimental values of Kerr coefficient of liquids used as a component in the binary mixtures

| *Liquid* | *Kerr coefficient* $B \times 10^{15} mV^{-2}$ |
|---|---|
| Acetone | 169 |
| Ethylmethyl Ketone | 137 |
| Cyclohexanone | 197 |
| Acetophenone | 695 |
| Acetonitrile | 842 |
| Propionitrile | 526 |
| Acrylonitrile | 1027 |
| Benzonitrile | 2772 |

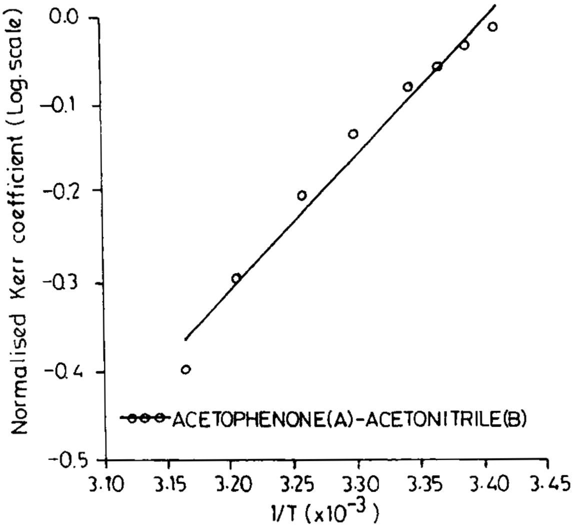

FIGURE 1 The variation of the normalised Kerr coefficient (log-scale) with $1/T$ in acetophenone–acetonitrile mixture (0.3 molar fraction of the component B).

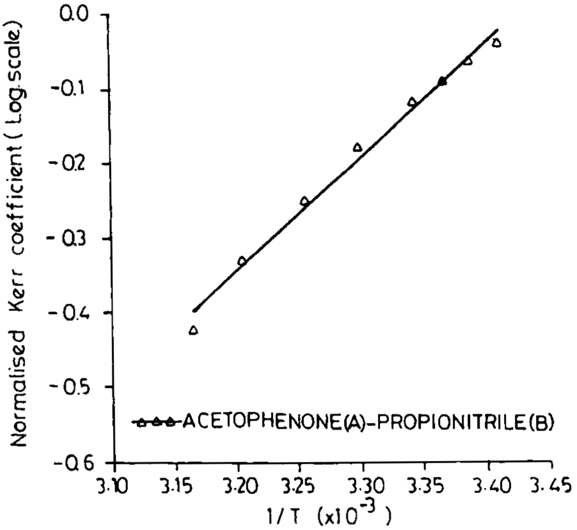

FIGURE 2 The variation of the normalised Kerr coefficient (log-scale) with $1/T$ in acetophenone–propionitrile mixture (0.3 molar fraction of the component B).

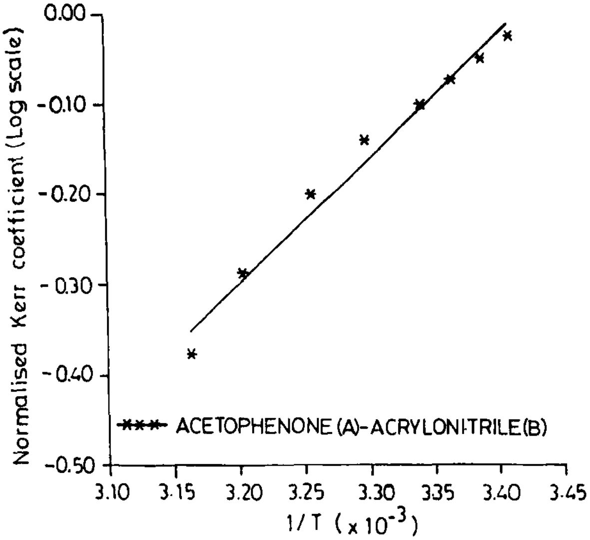

FIGURE 3 The variation of the normalised Kerr coefficient (log-scale) with $1/T$ in acetophenone–acryloritrile mixture (0.3 molar fraction of the component B).

[4] three different molar fractions of the solutes namely 0.25, 0.50 and 0.75 of component-B are considered for the temperature variation studies. Figures 4–7 depict the variation of the normalized Kerr coefficient (log-scale) with $T^{-1}$ for acetone (A)–ethyl methyl ketone (B), acetone (A)–acetophenone (B), acrylonitrile (A)–ethyl methyl ketone (B) and acetophenone (A)–benzonitrile (B) binary mixtures with 0.50 molar fraction of component B. Similar curves are obtained for the other molar fraction of these mixtures.

Temperature variation of Kerr coefficient has also been performed in acetone (A)–cyclohexanone (B), acrylonitine (A)–acetone (B) and acrylonitine (A)–cyclohexanone (B) binary mixtures.

The slopes from the linear graphs (Figs. 1–7) will give a measure of the interaction energy between the participating molecules of the mixtures. Table II gives the average values of the interaction energies of the aprotic–aprotic binary mixtures.

It is clear from Table II that in binary mixtures such as acetophenone (A)–aliphatic nitriles (B) of aprotic–aprotic category,

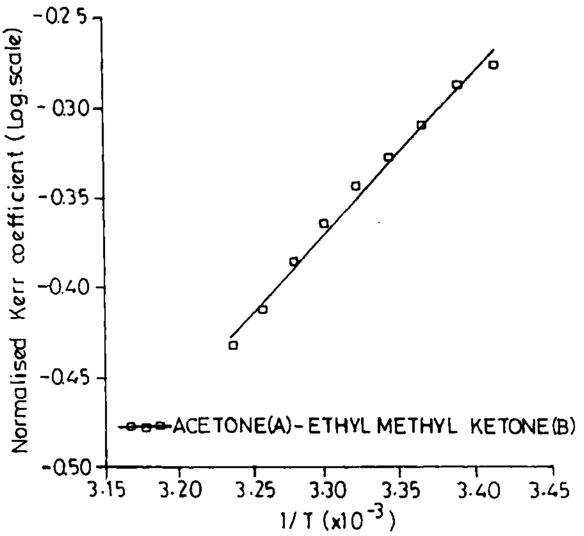

FIGURE 4 The variation of the normalised Kerr coefficient (log-scale) with $1/T$ in acetone (A)-ethyl methyl ketone mixture (0.5 molar fraction of the component B).

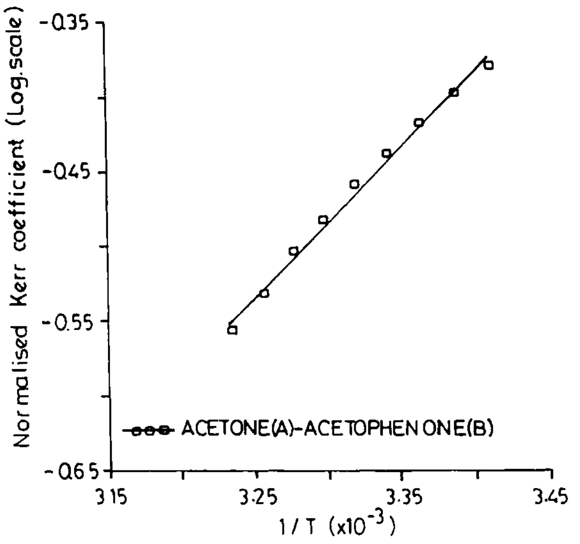

FIGURE 5 The variation of the normalised Kerr coefficient (log-scale) with $1/T$ in acetone-acetophenone mixture (0.5 molar fraction of the component B).

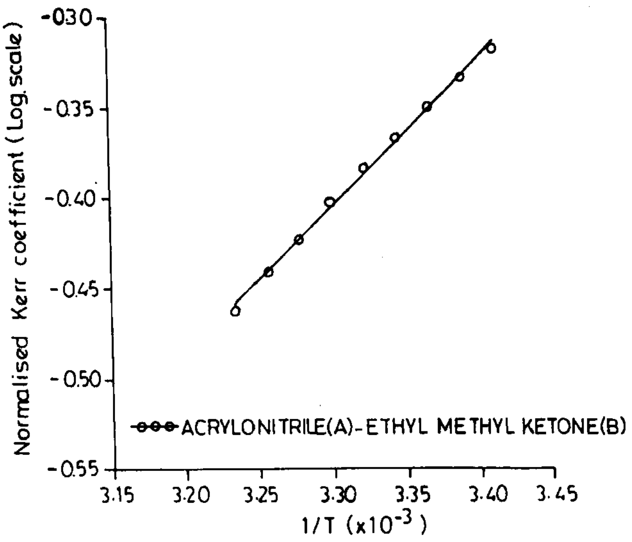

FIGURE 6 The variation of the normalised Kerr coefficient (log-scale) with $1/T$ in acrylonitrile–ethyl methyl ketone mixture (0.5 molar fraction of the component B).

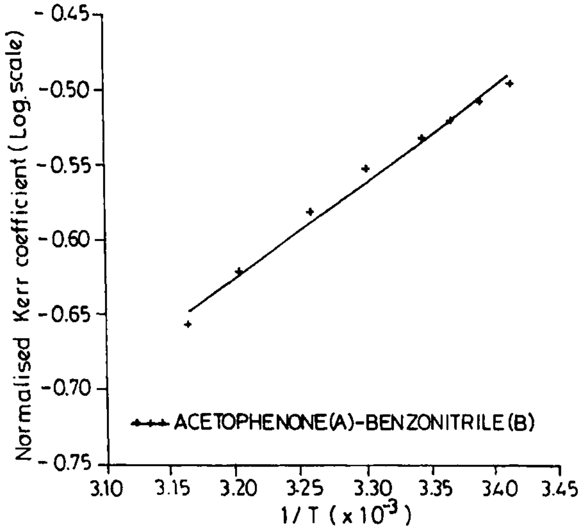

FIGURE 7 The variation of the normalised Kerr coefficient (log-scale) with $1/T$ in acetophenone–benzonitrile (0.5 molar fraction of the component B).

TABLE II Average values of the interaction energy in aprotic–aprotic binary mixture

| *Sl. no.* | *Name of the mixture* | *Average of value of interaction energy (K cal)* | *Remarks* |
|---|---|---|---|
| 1 | Acetophenone (A)–Acetonitrile (B) | −6.9 | Excess Kerr coefficient value observed at room temperature EOKE measurements [4] |
| 2 | Acetophenone (A)–Propionitrile (B) | −6.9 | |
| 3 | Acetophenone (A)–Acrylonitrile (B) | −6.7 | |
| 4 | Acetone (A)–Ethyl methyl ketone (B) | −3.5 | No excess Kerr coefficient observe room temperature EOKE measurements [4] |
| 5 | Acetone (A)–cyclohexanone (B) | −3.3 | |
| 6 | Acetone (A)–Acetophenone (B) | −3.8 | |
| 7 | Acrylonitrile (A)–Acetone (B) | −3.4 | |
| 8 | Acrylonitrile (A)–Ethyl methyl ketone (B) | −3.6 | |
| 9 | Acrylonitrile (A)–Cyclohexanone (B) | −3.5 | |
| 10 | Acetophenone (A)–Benzonitrile (B) | −2.9 | |

the average values of the interaction energy estimated are found to be higher, than in the case of other binary mixtures. This may be attributed to the formation of some well structured complexes due to strong interactions between the participating components on account of dipole–dipole interaction. This configuration may yield high polarizability values in the presence of the field. The effect of solvation between the solute and solvent molecules of these binary mixtures will be more predominant due to dipole–dipole interaction than in the other binary mixtures.

These experiment also establishes the fact that the complexes so formed between the participating components of a mixture due to dipole–dipole interactions at room temperature are not affected by increase in thermal energy.

The decrease in the values of the Kerr coefficient of these mixtures with increase in temperature only shows that the alignment of the resultant dipole moments of the participating molecules of the mixture with respect to the field direction is getting disturbed. However, the complexes so formed are not getting dissociated as the interaction energy is always greater than the thermal energy in all these cases.

## 5. CONCLUSIONS

The temperature variation of Kett coefficient of many binary mixtures consisting of aprotic–aprotic molecules is used to evaluate the interaction energy between the components of the mixtures. It is established that the interaction energy is more in aromatic ketone–aliphatic nitrile binary mixture than in other mixtures. This may be attributed to the strong dipole–dipole interaction present between the components of Acetophenone (A) – aliphatic nitrile (B) mixtures which validates a similar earlier experimental prediction of the same mixtures.

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