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1996 J. Phys.: Condens. Matter 8 2791

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# The electro-optical Kerr effect in binary mixtures of polar liquids

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Received 6 July 1995, in final form 2 January 1996

**Abstract.** We report in this paper the measurement of the Kerr constant for six mixtures of polar liquids: acetone–quinoline, acetone–isopropyl benzene, acetone–nitromethane, acetone–water, acetone–acetic acid and water–*t*-butyl alcohol. The Kerr constant was measured at the wavelength of 632.8 nm using a pulsed electric field technique. A deviation from the pure additivity of the Kerr constant was observed for all the mixtures. This non-additive behaviour is discussed in terms of the refractive index, dielectric constant and molar volume of the components. We also include the fitting of our data to an equation for mixtures of polar liquids derived from a modified mean field theory, in which the interaction between the permanent dipole moments of the two liquids of the system is included. We also report for the first time the measurement of the constant  $B$ , at 632.8 nm, for four pure liquids: quinoline, *t*-butyl alcohol, isopropyl benzene and nitromethane, using the technique of short-pulse electric field.

## 1. Introduction

The study of the electro-optical Kerr effect in a variety of materials, such as gases, pure liquids and liquid mixtures, allows us to obtain deeper knowledge of the electrical and optical anisotropy of the molecules that constitute those materials, giving us at the same time quite important information about their molecular configuration. The Kerr effect is also largely employed for constructing electro-optical modulators. We should mention that much work is still under progress in order to find new materials with better properties for electro-optic applications than nitrobenzene, which so far is the best material known for electro-optical modulation.

Although the Kerr constant  $B$  has already been measured for a great variety of pure liquids, using dc and ac electric fields and also as a function of the temperature and wavelength [1–11], it is only in the last few years that much effort has been devoted to studying the behaviour of  $B$  for the case of binary mixtures of non-polar liquids and in a few cases also polar ones [12–20]. In the pioneer papers of Patz and Rätzsch [13–15] a theoretical model was developed to explain the behaviour of the constant  $B$  for a mixture, taking into account the effect of the mixture composition on the electrical and optical local fields. They showed experimentally that the constants  $B$  were not additive for many of the non-polar liquid mixtures that they studied. That same effect was also observed later by other authors for some other particular liquid mixtures. We should expect a strict additivity of the Kerr constant only for the case when both liquids have approximately the same value for their refractive index, dielectric constant and molar volume (the molar volume is the

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ratio between the molar weight and the density of the liquid). Differences in their values of  $n$  (refractive index) or  $\varepsilon$  (dielectric constant) would cause a non-additivity, whose sign and amplitude are determined by the concentration and the ratio between the molar volumes ( $V$ ) of the two liquids.

With the purpose of increasing the variety of liquid mixtures investigated so far, extending the study to the lesser known case of mixtures of polar liquids (in particular when one of the components is water, which presents a very high dielectric constant), we carried out measurements of the Kerr constant for six binary systems, where both components were polar liquids. From the analysis of our data it is found necessary to modify the mean field theory, introducing a new parameter that takes into account the interaction between the two components in the mixture. Before measuring the constant  $B$  for the mixtures we did the same for all the pure liquids employed to produce our binary systems, using the technique of short-pulse electric field. As far we know, we are also reporting for the first time measurements of  $B$  for four out of our seven liquids, using this technique: quinoline, *t*-butyl alcohol, isopropyl benzene and nitromethane. The six systems under study were acetone–quinoline (A–Q), acetone–isopropyl benzene (A–Ib), acetone–nitromethane (A–N), acetone–acetic acid (A–Aa), acetone–water (A–W), and water–*t*-butyl alcohol (W–*t*B). For the first five mixtures the acetone was chosen as the solvent because the other liquids were totally miscible with it, whereas for the sixth mixture we used water as the solvent since the *t*-butyl alcohol was only partially miscible with acetone. We measured the Kerr constant for the acetone–water mixture (A–W) for the sake of comparison to the work previously reported by other authors [12, 16]. In those papers, the experimental data for the Kerr constant  $B$  of the acetone–water mixture is shown only as a function of the water concentration, and no fitting to any theoretical expression was intended by the authors. For the four binary mixtures A–Q, A–Ib, A–N and A–W, we found that the Kerr constant  $B$  deviates from additivity in good agreement with the dependence of the parameters  $n$ ,  $\varepsilon$  and  $V$  already described in the above paragraph; i.e., the observed behaviour for  $B$  approaches that expected from the mean field theory of Patz and Rätzsch [13–15]. For the two systems A–Q and A–Ib we have a negative deviation from additivity whereas for the other two, A–N and A–W, the deviation is positive. We shall probe in a later section the fact that the non-additivity of these mixtures cannot be explained only by the non-linear behaviour of the constants  $n$ ,  $\varepsilon$  and  $V$  of the mixture it being necessary to introduce an interaction parameter as well, which will be defined later. As far as we know, no other researchers have yet introduced such a parameter in order to explain their data. The two remaining systems, acetone–acetic acid and water–*t*-butyl alcohol, present a strong anomaly in the variation of the constant  $B$ . This anomaly may be caused by the reaction between the components in each of the systems.

## 2. Experimental procedure

Our measurements of the Kerr effect of pure liquids, as well as their mixtures, were carried out by using pulsed electric fields of short duration and high intensity. The field was produced applying a square voltage pulse (up to 4 kV and 1.6  $\mu$ s time duration) across the two parallel stainless steel electrodes of the Kerr cell with an average length of 56.9 mm and a gap of 1.7 mm. The pulse repetition rate for the applied voltage was 10 Hz. The body of the cell was sculpted in Teflon and had a volume of 3 ml for the solution. The optical system was formed by a low-power He–Ne laser operating at 632.8 nm, a polarizer at 45° to the electric field on the Kerr cell, a  $\lambda/4$  achromatic Fresnel romb with its fast axis parallel to the polarizer and an analyser crossed with the polarizer. The angle rotated by the analyser had a

precision of  $0.005^\circ$ . The optical signal was detected by an EMI 6256S photomultiplier and monitored by a Tektronix 2221 digital oscilloscope. A detailed description of the electric pulse generator, liquid cell and detection optical system can be found in our previous work [11]. The Kerr constant  $B$  of the samples was determined through the use of the following relation:

$$\delta = 2\pi BLE^2 \quad (1)$$

where  $\delta$  is the optical phase difference induced into the medium by the applied electric field perpendicular to the light propagation,  $L$  is the optical path length along the sample and  $E$  is the electric field strength. The measurement of  $\delta$  was done by using the null signal technique first introduced by Beevers and Khanarian [10]. The slope of the straight line obtained by plotting  $\delta$  as a function of the squared electric field gave us the value of  $B$  for each sample. All the measurements were carried out at room temperature and at the wavelength of 632.8 nm.

**Table 1.** Refractive index  $n$ , dielectric constant  $\epsilon$ , molar volume  $V$  and Kerr constant  $B$  of the pure liquids used to produce the mixtures. The refractive index  $n$  is given for  $\lambda = 589.3$  nm. All values were measured at room temperature. Units for  $V$  and  $B$  are  $\text{ml mol}^{-1}$  and  $10^{-14} \text{ m V}^{-2}$ , respectively.

Liquids	$n$	$\epsilon$	$V$	$B^a$
Acetone	1.359	20.7	73.52	21.10
Water	1.330	78.5	18.01	2.91
Nitromethane	1.382	36.5	54.01	11.50 <sup>b</sup>
Acetic acid	1.371	6.15	57.19	4.83
Quinoline	1.627	9.00	118.49	16.08 <sup>b</sup>
Isopropyl benzene	1.491	2.38	139.76	0.71 <sup>b</sup>
<i>t</i> -butyl alcohol	1.388	10.9	93.97	5.95 <sup>b</sup>

<sup>a</sup> This work. Values of  $B$  were obtained for  $\lambda = 632.8$  nm.

<sup>b</sup> The measurement of  $B$  for these liquids, using the short-pulse electric field technique, is being reported for the first time in the literature.

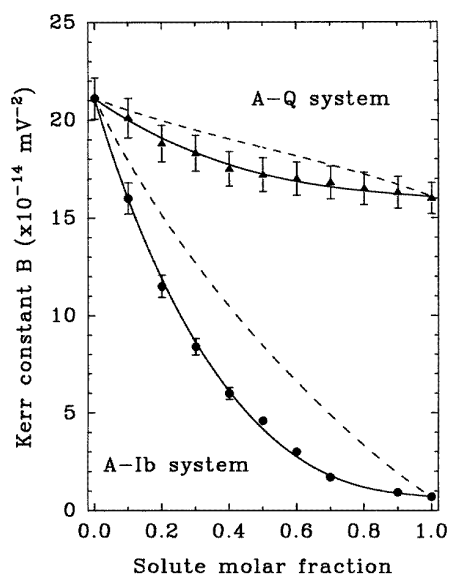
Seven liquids were employed to produce the six mixtures studied in our experiment. In table 1 we list the seven pure liquids, with their corresponding values of refractive index  $n$ , dielectric constant  $\epsilon$  and molar volume  $V$  [21]. These liquids were chosen according to the following criteria: high solubility in acetone or water, a Kerr effect intensity that can be accurately detected by our system and a large span in their values of  $n$  (from 1.33 for water up to 1.6268 for quinoline),  $\epsilon$  (2.38 for quinoline to 78.5 for water) and  $V$  (from 18.01 for water up to 139.76 for isopropyl benzene). Among the liquids that we used only the water was previously distilled and deionized, reducing its electric conductivity to a value of the order of  $10^{-4} \text{ S m}^{-1}$ , whereas the other six liquids were only of spectroscopic grade. This was found to be enough to reduce the liquid conductivity to a convenient level.

We chose acetone as the solvent for preparing the sample mixtures because the other liquids were totally miscible with it, except for the *t*-butyl alcohol, which was only partially miscible. For this last case we used water instead of acetone as the solvent. The Kerr constant as a function of the solute molar fraction was measured for the following six binary mixtures: (i) acetone–quinoline (A–Q), (ii) acetone–isopropyl benzene (A–Ib), (iii) acetone–water (A–W), (iv) acetone–acetic acid (A–Aa), (v) acetone–nitromethane (A–N) and (vi) water–*t*-butyl alcohol (W–*t*B). The mixtures were prepared with their solute molar fractions changing from zero (pure solvent) up to unity (pure solute) in steps of 0.1 or 0.05

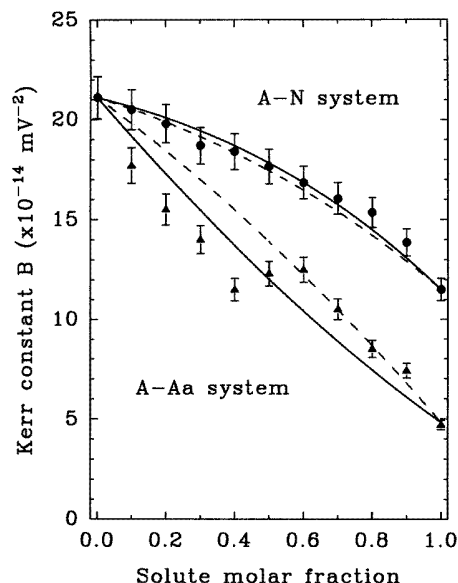
(depending on the need to study the Kerr constant variation with greater detail). We made on average a set of three measurements of the Kerr electric induced birefringence for each sample. We found a maximum deviation between measurements of around  $\pm 5\%$  for all the mixtures.

### 3. Experimental results

First of all, we measured the Kerr constant of all the pure liquids used in our mixtures; the obtained values are displayed in table 1. We are reporting for the first time, as far as we know, the measurement of the Kerr constant using the technique of short-pulse electric fields for the following four liquids: quinoline, *t*-butyl alcohol, isopropyl benzene and nitromethane. Also in table 1 we include information extracted from the literature [21] on the refractive index, dielectric constant and molar volume for the pure liquids.

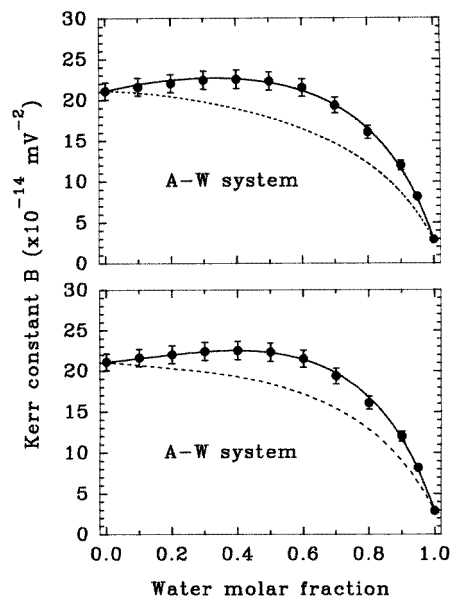


**Figure 1.** The Kerr constant  $B$  as a function of the solute molar fraction for the mixtures acetone–quinoline (A–Q) and acetone–isopropyl benzene (A–Ib). The second liquid is considered to be the solute. The dashed line for each system is calculated according to (10) without the interaction parameter ( $\Lambda_{mAB} = 0$ ). The solid line is the fit to (10) when the interaction is present ( $\Lambda_{mAB} \neq 0$ ).

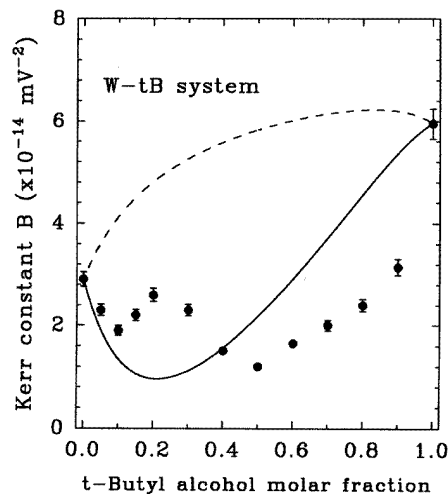


**Figure 2.** The Kerr constant  $B$  as a function of the solute molar fraction for the mixtures acetone–nitromethane (A–N) and acetone–acetic acid (A–Aa). The second liquid is considered to be the solute. The dashed line for each system is calculated according to (10) without the interaction parameter ( $\Lambda_{mAB} = 0$ ). The solid line is the fit to (10) when the interaction is present ( $\Lambda_{mAB} \neq 0$ ).

After measuring the constant  $B$  for the pure liquids we proceeded to do the same for the binary mixtures of liquids, as a function of the solute molar fraction, in the way explained in a previous section. Our results are shown in figures 1–4. In figure 1 we have the corresponding graphs for the two mixtures A–Q and A–Ib, whereas in figure 2 the Kerr constant is plotted for the two mixtures A–Aa and A–N; finally, figures 3 and 4 correspond to the cases of the mixtures A–W and W–*t*B, respectively. The graphs in figure 1 for the systems A–Q and A–Ib show a behaviour that resembles the one observed by other authors in some non-polar liquid mixtures. Both systems are composed of chemically inert liquids,



**Figure 3.** The Kerr constant  $B$  as a function of the water molar fraction for the acetone–water mixture (A–W). Top, a linear relation is assumed for  $n$ ,  $\epsilon$  and  $V$  of the mixture: the dashed line is calculated according to (10) without the interaction parameter ( $\Lambda_{mAB} = 0$ ). The solid line is the fit to (10) when the interaction is present ( $\Lambda_{mAB} \neq 0$ ). Bottom, the same as for the top panel but assuming now a non-linear relation for  $n$  and  $\epsilon$  ((12) and (13)).



**Figure 4.** The Kerr constant  $B$  as a function of the  $t$ -butyl alcohol molar fraction for the water– $t$ -butyl alcohol mixture (W– $t$ B). The dashed line is calculated according to (10) without the interaction parameter ( $\Lambda_{mAB} = 0$ ). The solid line is the fit to (10) when the interaction is present ( $\Lambda_{mAB} \neq 0$ ).

i.e. there is neither dissociation of the components nor hydrogen bond formation. In this case the value of  $B$  decreases monotonically with the solute molar fraction, showing a negative deviation from additivity, the effect being stronger for the A–Ib system for which the ratio between the molar volumes of the two components is  $V_A/V_{Ib} = 0.52$  (the solute predominates over the solvent). Similarly, we have also for the other system, A–Q, a negative deviation, but smaller than that for the mixture A–Ib, corresponding to the fact that in the A–Q case the ratio, although also lower than unity ( $V_A/V_Q = 0.62$ ), is higher than for the other mixture.

The Kerr constant of the A–N system, displayed in figure 2, shows a small positive deviation from additivity, which can be also explained by the ratio between the molar volumes of the two liquids, that for this case is slightly higher than one ( $V_A/V_N = 1.28$ ). In a similar way, the A–W system displayed in figure 3 shows a strong positive deviation from the straight additivity. This fact can be attributed not only to the high ratio between the molar volumes of the two liquids involved ( $V_A/V_W = 4.08$ ) but also to the large difference between their dielectric constants ( $\Delta\epsilon = 57.8$ ). The Kerr constant of the mixture between the solute molar fractions of 0 and 0.6 is higher than the one corresponding to the solvent alone. We should remark at this point that there is a difference between this last system and the three other mentioned before: the two components in the A–W system are not chemically inert. The ketone group tends to be partly hydrated in aqueous solution, meaning that for the acetone–water system the dihydroxy structure  $(\text{CH}_3)_2\text{C}(\text{OH})_2$  is favoured [12].

Finally, an anomalous behaviour for the two remaining systems, A–Aa and W–*t*B, as compared to the other mixtures already discussed, is observed. The curve for the A–Aa mixture (figure 2) presents a negative deviation between zero and 0.5 solute molar fraction, which is inverted to a positive value from the solute concentration of 0.5 up to 1.0. On the other hand, the second mixture, W–*t*B (figure 4) shows an unexpected and strong bump in the solute molar fraction range of 0.1–0.4. This different behaviour for these two mixtures may be due to the strong interaction between their components. For instance, we have for the A–Aa system a partial ionic dissociation of the acetic acid in acetone, forming a weak electrolytic solution. In fact, it is the high conductivity of this electrolytic solution that constitutes the main source of error in the measurement of the constant  $B$  of the A–Aa system.

In order to explain the behaviour of the W–*t*B system (figure 4) it will be useful to refer to the work of Bradley *et al* [22] on the non-linear electric field effect on the relative permittivity of aqueous systems. This work shows how the Piekara factor changes as a function of the solute molar fraction for some binary mixtures, one of them being the system under study by us. The Piekara factor,  $P$ , is defined by the relation

$$P = \Delta\varepsilon/E^2 \quad (2)$$

where  $\Delta\varepsilon$  is the difference between the dielectric constant of the system when an electric field of strength  $E$  is applied and without it. Bradley observed that ‘small additions of this alcohol (*t*-butyl alcohol) to water lead to a marked increase in the “structure” of the water medium, as is shown by a variety of physical properties’. We should also mention at this point that the W–*t*B mixture tends to present associations of the hydrogen bond type [23], which are believed to have a strong influence on the behaviour of the Piekara factor of the system [22]. Bradley found the interesting result that the Piekara factor for the W–*t*B mixture, which initially (pure water) has a negative value of  $-10.8 \times 10^{-16} \text{ m}^2 \text{ V}^{-2}$ , becomes more negative with increasing molar fraction of *t*-butyl alcohol, reaching a negative peak of  $-14 \times 10^{-16} \text{ m}^2 \text{ V}^{-2}$  at the molar fraction of approximately 0.04. After that negative peak, the Piekara factor increases fast towards positive values, switching sign around the solute concentration of 0.25. Between the molar fractions of 0.5 and 1.0 it becomes almost constant, at the value of approximately  $0.5 \times 10^{-16} \text{ m}^2 \text{ V}^{-2}$ . If we compare Bradley’s results with ours for the W–*t*B system (the plot shown in figure 4) we find that the constant  $B$  of the mixture has a relative maximum at the same point in which its Piekara factor switches sign, i.e. between the molar fractions of 0.2 and 0.25, showing a slow increase of  $B$  after the 0.5 molar fraction of *t*-butyl alcohol. From this similar anomalous behaviour observed for the Piekara factor and the Kerr constant  $B$ , as a function of the solute concentration, we can infer that the anomaly in both may have the same origin, for instance the formation of hydrogen bonds in the mixture.

#### 4. Theoretical approach

Let us investigate whether the non-additive behaviour of the Kerr constant of our binary mixtures as a function of the solute concentration can be explained using the mean field theory of Patz and Rätzsch [13–15]. The Kerr constant  $B$  for a pure liquid can be expressed by

$$B = [9(n^2 + 2)^4 \varepsilon^2 / \lambda V n (2\varepsilon + n^2)^2] K_m \quad (3)$$

where  $\lambda$  is the wavelength of the incident light and  $n$ ,  $\varepsilon$  and  $V$  are the refractive index (at the wavelength  $\lambda$ ), the dielectric constant and the molar volume, respectively. The constant

$K_m$ , called the molar Kerr constant, is given in terms of the molecular parameters of the liquid by the relation

$$K_m = (N_A/108\varepsilon_0)\{[3(2\varepsilon + n^2)/(2\varepsilon + 1)(n^2 + 2)]\theta_1 + \theta_2\} \quad (4)$$

$$\theta_1 = [1/(15kT)] \sum_{\sigma,\tau=1}^3 \alpha_\sigma^w \alpha_\tau^s (\delta_{\sigma\tau} - 1/3) \quad (5)$$

$$\theta_2 = \{1/[15(kT)^2]\} \sum_{\sigma,\tau=1}^3 \alpha_\sigma^w \mu_\tau^2 (\delta_{\sigma\tau} - 1/3) \quad (6)$$

where  $N_A$  is the Avogadro constant,  $\varepsilon_0$  is the vacuum susceptibility,  $k$  is the Boltzmann constant,  $T$  is the absolute temperature,  $\sigma$  and  $\tau$  are the molecular coordinates,  $\alpha^w$  is the molecular polarizability at optical frequencies whereas  $\alpha^s$  stands for the same molecular parameter but at low frequency (static),  $\mu$  is the permanent molecular dipole moment and  $\delta_{\sigma\tau}$  is the Kronecker delta symbol. The parameters  $\theta_1$  and  $\theta_2$  are the molecular anisotropy and permanent dipole moment contributions to the Kerr constant, respectively. For a molecule with azimuthal symmetry we have that  $\alpha_x = \alpha_y = \alpha_1$  and  $\alpha_z = \alpha_3$ , and using the symbols  $\delta$  for the difference  $\delta = \alpha_3 - \alpha_1$  and  $\mu$  for the permanent dipole moment along the symmetry axis  $\mu = \mu_z$ , we obtain the following new expression for the parameters  $\theta_1$  and  $\theta_2$ :

$$\theta_1 = [2/(45kT)]\delta^w \delta^s g^{(2)} \quad \theta_2 = \{2/[45(kT)^2]\}\delta^w \mu^2 g^{(3)} \quad (7)$$

where  $g^{(2)}$  and  $g^{(3)}$  are molecular orientation parameters, whose respective expressions are given in [15]. We are neglecting the hyperpolarizability and the permanent dipole moment linear contributions to the molar Kerr constant (first and second terms in (2) of [15]). We have for polar liquids  $\theta_1 \ll \theta_2$  and the molar Kerr constant is then reduced to the expression

$$K_m = (N_A/54\varepsilon_0)\theta_2. \quad (8)$$

Let us consider now a mixture of two polar liquids A and B. We will assume that the following relation holds between the molar Kerr constants of the mixture  $K_m$  and its corresponding value for the pure components A and B,  $K_{mA}$  and  $K_{mB}$ , respectively:

$$K_m = K_{mA}X_A + K_{mB}X_B + K_{mAB}X_AX_B. \quad (9)$$

$X_A$  and  $X_B$  are the molar fractions of the two components in the mixture, and  $K_{mAB}$  is a parameter that takes into account the contribution to  $K_m$  due to the electric dipole interaction between the permanent dipole moments of liquids A and B. This interaction term should be proportional to the product of the molar fractions of the two liquids. The calculation to obtain an expression for  $K_{mAB}$  should use some kind of averaging process over all the possible relative orientations between the permanent dipole moments of molecules A and B. The last term in (9),  $K_{mAB}X_AX_B$ , is known as the excess molar Kerr constant, i.e. the difference between the actual value of  $K_m$  for the mixture and the one corresponding to a linear relation. We should remark at this point that  $K_{mA}$  and  $K_{mB}$  depend for polar liquids only on the intrinsic molecular parameters of each liquid, (8) and (7), and, therefore, they are independent of the presence of the other liquid in the mixture.

Finally, using (3) and (9) we can express the Kerr constant of the mixture  $B$  as a function of the value for each pure liquid,  $B_A$  and  $B_B$ , the molar fractions of both liquids,  $X_A$  and  $X_B$ , and the interaction parameter  $\Lambda_{mAB}$ . This last parameter can be determined by the fitting of the experimental data to the following relation:

$$B = [(n^2 + 2)^4 \varepsilon^2 / Vn(2\varepsilon + n^2)^2] \{ [V_A n_A (2\varepsilon_A + n_A^2)^2 / (n_A^2 + 2)^4 \varepsilon_A^2] B_A X_A \\ + [V_B n_B (2\varepsilon_B + n_B^2)^2 / (n_B^2 + 2)^4 \varepsilon_B^2] B_B X_B + \Lambda_{mAB} X_A X_B \} \quad (10)$$



where the new interaction parameter  $\Lambda_{mAB}$  is defined in terms of the old one by  $\Lambda_{mAB} = (9/\lambda)K_{mAB}$ . The values of the constants  $n$ ,  $V$  and  $\varepsilon$  in (10) are now those for the mixture.

For our calculations we will consider in a first approximation that  $n$ ,  $V$  and  $\varepsilon$ , are linear functions of the solute molar fraction, i.e.

$$n = (1 - X_B)n_A + X_B n_B \quad (11)$$

since we have that  $X_A + X_B = 1$ , with similar relations for the other two constants  $V$  and  $\varepsilon$ . We used for our calculus the data on the refractive index for  $\lambda = 589.3$  nm, instead of  $\lambda = 632.8$  nm. In any case, the difference introduced in the calculation of  $B$  due to the dispersion of  $n$  with the wavelength can be neglected when compared with our experimental error. For instance, we have for acetone that the difference in the value of  $n$  is as small as  $\Delta n = 0.02\%$  [20, 21].

The dashed curve for each mixture displayed in figure 1–4 was obtained using (10) considering first that there was no interaction between the permanent dipole moments of the two liquids, i.e. assuming that  $\Lambda_{mAB} = 0$ , whereas the solid lines in the same plots correspond also to the fitting of the data to (10) but using now the whole expression which includes the interaction parameter  $\Lambda_{mAB}$ .

We can observe that an excellent fit is obtained for four out of the six mixtures when we include the interaction parameter: A–Q, A–Ib, A–W and A–N. For these systems the concentration curves are smooth. For the other two samples, A–Aa and W–tB, for which some compound formation is expected, the fit gives us only some information about the average behaviour of the mixture as a function of the solute concentration.

Let us now try to estimate the error introduced in our calculations due to our initial supposition of a linear relation for the constants  $\varepsilon$  and  $n$  of the mixture. We will concentrate our discussions on the A–W mixture, since both liquids are strongly polar and a bigger deviation from linearity is therefore expected for  $\varepsilon$  and  $n$  than for any other of the mixtures. Data on  $\varepsilon$  (at  $4 \times 10^8$  Hz and  $19^\circ\text{C}$ ) and  $n$  (at 589.3 nm) for the A–W mixture were extracted from the literature [24]. These data were fitted to a general non-linear relation, including a cross term:

$$\varepsilon = (1 - X_W)^{\alpha_1} \varepsilon_A + X_W^{\beta_1} \varepsilon_W + \lambda_1 (1 - X_W) X_W \varepsilon_A \varepsilon_W \quad (12)$$

$$n = (1 - X_W)^{\alpha_2} n_A + X_W^{\beta_2} n_W + \lambda_2 (1 - X_W) X_W n_A n_W \quad (13)$$

where  $X_W$  is the water molar fraction,  $\varepsilon_A$  and  $\varepsilon_W$  are the dielectric constants of pure acetone and water, respectively, and  $\alpha_1$ ,  $\beta_1$  and  $\lambda_1$  are fitting parameters. In the equation for  $n$  we have similar meaning for the symbols. We obtained the following values for the fitting parameters:

$$\begin{aligned} \alpha_1 &= 1.34 & \beta_1 &= 1.58 & \lambda_1 &= 0.00 \\ \alpha_2 &= 0.938 & \beta_2 &= 0.994 & \lambda_2 &= -0.028. \end{aligned}$$

From these data we can see that  $n$  deviates only slightly from the linear relation ( $\alpha_2$  and  $\beta_2$  are very close to one, and  $\lambda_2 \approx 0$ ). For  $\varepsilon$  the non-linearity is higher, approaching a three-halves law. We will assume for future calculations that the molar volume  $V$  is still linear, since  $V$  contributes to (10) only to the inverse of the first power, so any possible deviation of  $V$  from linearity will be of lesser importance to  $B$ . This same approximation is routinely used by other authors [16–20]. Using the expressions (12) and (13) for  $\varepsilon$  and  $n$  of the mixture we recalculate the Kerr constant  $B$  of the mixture as given by the (10). These new plots for  $B$ , corrected for non-linearity of  $n$  and  $\varepsilon$ , are given in figure 3 (lower panel): the dashed line for the case  $\Lambda_{mAB} = 0$  and the solid line when it is assumed that an interaction exists, i.e.  $\Lambda_{mAB} \neq 0$ . We can conclude by observing figure 3 that the

behaviour of the Kerr constant of the mixture cannot be explained, by any means, only by the non-linearity of  $n$  and  $\varepsilon$ , it being necessary to introduce a new parameter that takes into account the interaction between the permanent dipole moments of the two liquids of the system. From the curves shown in figure 3 we can see that the effect of correcting  $\varepsilon$  and  $n$  is smaller than the corresponding experimental error, even for the A–W mixture for which is expected the maximum correction. Based on this fact we did not try to make any correction because of the non-linearity of  $\varepsilon$  and  $n$  for the other five mixtures. The values of  $\Lambda_{mAB}$  for the six binary liquid mixtures, obtained by fitting the data to (10), are displayed in table 2. We can see that the interaction parameter is very small for the A–Q system and that it can be positive as well as negative. For the two last mixtures shown in table 2 (A–Aa and W–*t*B), presenting an anomalous behaviour, the value of  $\Lambda_{mAB}$  gives us only an order of magnitude of the interaction, since we do not have any good fitting.

**Table 2.** Values of the interaction parameter  $\Lambda_{mAB}$  obtained by fitting the data to (10).

Binary liquid system	Interaction parameter $\Lambda_{mAB}$ ( $\times 10^{-20} \text{ m}^4 \text{ mol}^{-1} \text{ V}^{-2}$ )
Acetone–nitromethane	0.29
Acetone–water	1.82
Acetone–quinoline	1.24
Acetone–isopropyl benzene	–5.17
Acetone–acetic acid	–1.52
Water– <i>t</i> -butyl alcohol	–2.35

## 5. Conclusions

We report in this work the measurements of the Kerr constant  $B$  for six binary systems of polar liquids, studying the variation of the electro-optical Kerr constant as a function of the solute molar fraction. For four of these systems, we observe a non-additivity of the constant  $B$  that follows only qualitatively the trend predicted by the mean field theory of Patz and Rätzsch [13–15]. The sign and the magnitude of the deviation from additivity depend on the ratio between the molar volumes of the solvent and solute. The deviation will be positive or negative if this ratio is higher or lower than 1.0, respectively, and its magnitude will be higher for increasing values of this ratio (absolute value). It was proved necessary to modify the theory, introducing an extra term that takes into account the interaction between the molecular permanent dipole moments of the two liquids of the system. We obtain a very good fitting of our data using this new interaction parameter.

In the other two systems the behaviour of  $B$  with the solute fraction is more complex and the mean field theory gives us only the average behaviour of the system. We found that a possible explanation for this anomalous dependence is the fact that in both systems there is some kind of chemical interaction, such as the ionic dissociation of acetic acid in acetone that produces a weak electrolytic solution or the formation of hydrogen bonds as in the case of water–*t*-butyl alcohol. The behaviour of the Piekara factor for the W–*t*B system shows the importance of such an interaction in the dielectric properties of the mixture and we believe that the same should be the case for the electro-optical Kerr effect.

## Acknowledgments

We are glad to acknowledge the financial support of the Fundo de Apoio a Pesquisa da Universidade Estadual de Campinas, Financiadora de Estudos e Projetos do Brazil and Conselho Nacional de Desenvolvimento Científico e Tecnológico do Brazil, which made possible this work. We also thank Professor Francisco B N Pessine for his helpful comments.

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