

TEMPERATURE DEPENDENCE OF THE ROTATIONAL RELAXATION TIMES OF ANISOTROPIC MOLECULES IN NEAT AND MIXED BINARY LIQUIDS*

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The relaxation times of the optical Kerr effect of nitrobenzene and *m*-nitrotoluene have been measured as a function of temperature in neat and mixed binary liquids. The activation energy of molecular reorientation motion for various solutions has been determined from Kerr effect and viscosity measurements. A modified Hill theory for the relaxation times provides satisfactory agreement with the experimental measurements for the mixed liquids.

The knowledge of the rotational motion of molecules in liquids is important for a full understanding of the liquid state. Various techniques have been used to probe the rotational kinetics of the molecules in liquids [1–9]. Recently, picosecond laser techniques [10–12] have been used to measure directly the time dependence of the Kerr effect associated with the orientational motion of anisotropic molecules in neat and mixed liquids. For anisotropic molecules, the dominant mechanisms responsible for the Kerr effect are the molecular reorientation motion and electronic cloud distortion [13]. The electronic mechanism is temperature independent and is so fast ($\leq 10^{-14}$ s) that its time dependence cannot be resolved by picosecond techniques. The measurement of the temperature dependence of the Kerr relaxation time will yield information on the kinetics of the *orientational* motion of the molecules. The relaxation time corresponds to an overall rotation of the motion of the molecule ‡‡.

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‡‡ Just like the relaxation time obtained from the depolarized Rayleigh wing linewidth [6], the Kerr rotational relaxation time is a combination of the rotations about the individual axis of the molecules. The relaxation time is more strongly weighted by the orientation about the axis which is associated with the largest polarizability change upon rotation [6].

In this paper, we extend our earlier research [12] by measuring the temperature dependence of the relaxation time (τ) of the optical Kerr effect for nitrobenzene (NB) and *m*-nitrotoluene (mNT) molecules in neat and mixed binary liquids. We confirm within experimental error that the temperature dependence of the relaxation time depends on the measured viscosity in neat liquids as suggested by Debye [1], and on the effective viscosity in mixed liquids as suggested by Hill [14]. These measurements give credence to the use of effective viscosity dependence in the equation for τ for mixed liquids [12]. The form of the effective viscosity was empirically introduced previously [12] from Hill's [14] theory on the mutual viscosity between solute and solvent molecules and arises from the solute–solute and solute–solvent interactions. This is a reasonable model since it only takes into account the solute molecule interaction with its neighbors. The Debye equation for the rotational relaxation time, which depends on the measured viscosity, accounts for an additional interaction between solvent–solvent molecules in mixed liquids.

The single shot picosecond laser technique offers both convenience and accuracy in measuring the kinetics of the optical Kerr effect over the multiple shots technique [10,11]. A schematic of the experimental apparatus used for measuring the Kerr relaxation time is shown in fig. 1. An intense 1.06 μm laser pulse with 8 ps duration induced the Kerr birefringence in the

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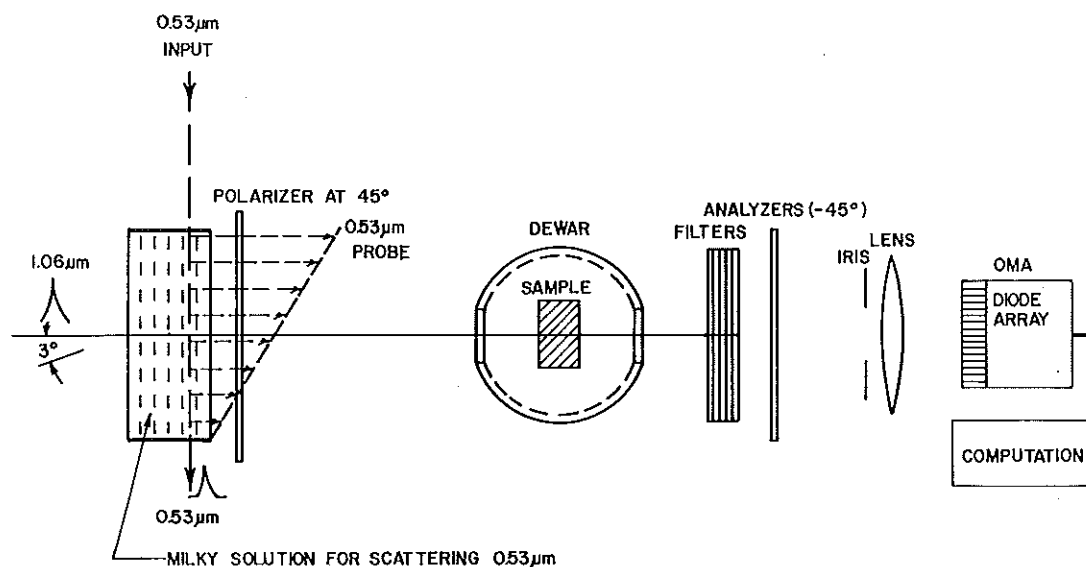


Fig. 1. Top view of the single shot picosecond laser optical Kerr gate.

sample solution which was situated between a pair of crossed polarizers. The birefringence was caused by partially orienting the anisotropic molecules in the liquid through the interaction of the optical electric field of the laser pulse with the polarizability of the molecules. Upon passing a second harmonic pulse of 6 ps duration through a dilute milky solution, the 0.53 μm light along the path was uniformly scattered into a continuous series of delayed pulses. The scattered light at 90° forms an oblique wave front in time and was directed into a 1 cm long sample cell. In this manner the scattered light, which was variably delayed with respect to the 1.06 μm exciting pulse, was used to interrogate the time evolution of the induced transitory birefringence of a sample solution in a single laser shot. The 1.06 μm pulse was incident at an angle of approximately 3° to the plane of incidence of the scattered 0.53 μm pulse and was focused to a diameter of about 5 mm into the sample.

The track of the 0.53 μm scattered light from the milky solution was imaged by a camera lens onto the target face of an optical multichannel analyzer (OMA). The time axis was calibrated by moving a prism in the 1.06 μm laser beam path. The induced light intensity profile passing through the Kerr gate was detected by the OMA which has 500 channel detectors over 12.5 mm. The signal was processed in the OMA system and the decay profile stored in the OMA's memory. The

effect of lag of the detector was minimized by scanning most of the charge off the vidicon. In this mode, the system was linear to within 5% over the range used. The length of the track imaged on the detector determined the time span investigated. Typically, a time display of 125 ps was investigated on a single shot with a signal to background ratio ≈ 100 . The intensity profile was then recorded by an *XY*-recorder and replotted on a semi-logarithm graph paper. The relaxation time was extracted from the slope of the measured intensity profile. Deconvolution was not necessary in this study because the Kerr relaxation times of these liquids were longer than the prompted experimental decay of CS₂ Kerr intensity profile (≈ 5 ps).

The chemicals used in the experiments were the highest purity available from Eastman Kodak Company. The sample cell was situated in a dewar with strain free windows. The Kerr effect of the windows, sample cell, and solvents was measured to be less than one hundredth of the solutes. A thermocouple was cleaned and immersed in the samples.

After sealing the cell the temperature was controlled by flowing cooled nitrogen gas into the dewar and surrounding the sample cell holder with heating tape. The sample temperature was controlled to ± 1 K. The temperature variation across the sample region was measured to be less than 1 K. The lowest temperature used

in the experiment was about 20 K below the freezing temperature of the liquid. At this temperature, the liquids were *supercooled*. The highest temperature reached was about 350 K. Above this temperature, the relaxation time was too fast to be deconvoluted reliably from the Kerr decay profile. The viscosity of the samples was measured by an Ostward-type Cannon-Fenske viscometer in a temperature controlled water reservoir. The temperature was controlled to within ± 1 K. The viscosities are measured within a 2% error and are in good agreement with the viscosities listed in the standard tables [15].

A typical single shot Kerr intensity profile versus delayed time for NB at 297 K is displayed in fig. 2. The measured relaxation times and viscosities of NB, mNT, and the mixture of mNT with carbon-tetrachloride (CT) and decyl alcohol (DA) are plotted as a function of temperature in figs. 3, 4, and 5. The relaxation time data presented in these figures are the average of decay times extracted from five to ten different inten-

sity profile curves. The typical error in relaxation time is $\leq 20\%$. The salient feature of the data present in figs. 3, 4 and 5 is that the relaxation times decrease approximately exponentially as $1/T$. The data in fig. 5 shows a curvature at the high temperature end.

The modified Debye model for molecular rotation relaxation time which is generally applicable to single particles rotational motion in pure polar liquid is [1,16]

$$\tau = \frac{4}{3} \pi a^3 \xi \eta_m(T) / kT, \quad (1)$$

where τ is the relaxation time; k , the Boltzmann constant; T , the absolute temperature; $a = (M/\rho N)^{1/3}$, the radius of the molecules; ξ is a dimensionless parameter which is proportional to the ratio of the mean square intermolecular torques to the mean square intermolecular force [16]; and $\eta_m(T)$ is the measured viscosity. In mixed liquids, it has been observed [12,17] that the measured viscosity dependence given in eq. (1) is not followed by the measured relaxation time. Apply-

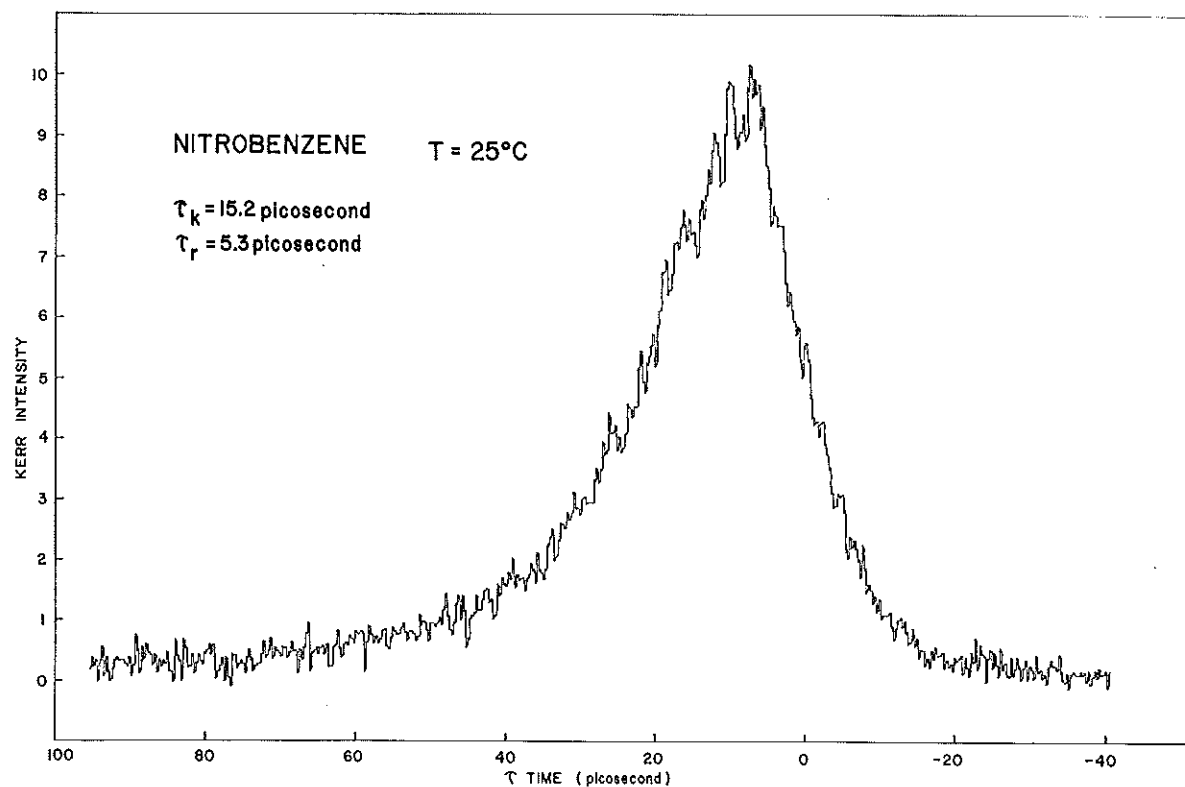


Fig. 2. Intensity profile of optical Kerr effect of NB at 25°C versus time. The zero time is arbitrary and the peak transmission of the Kerr effect is about 10%. The rise time is 5.3 ps and the decay time is 15.2 ps. This decay time corresponds to a molecular orientation time of 30.4 ps.

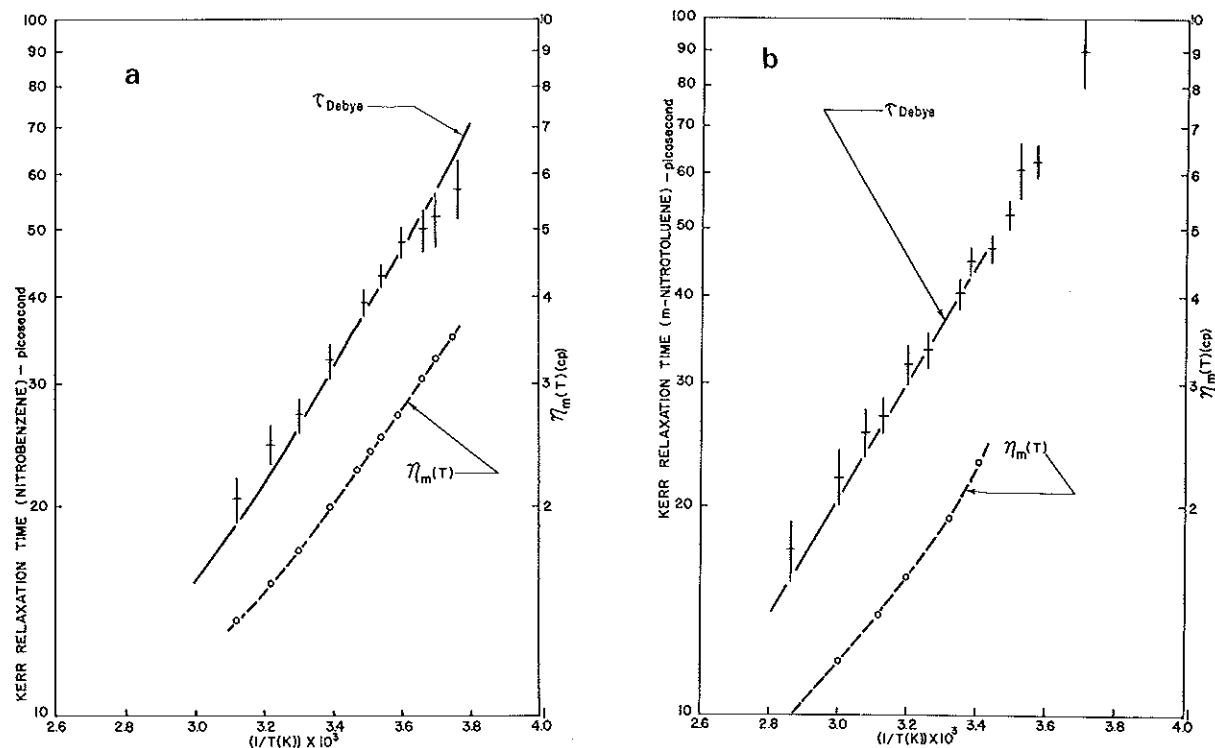


Fig. 3. (a) Kerr relaxation time versus $1/T$ of pure NB. The data \bullet are the measured viscosities in cP and the data \dagger are the measured Kerr relaxation times (ps) $\times 2$. The solid line is the theoretical fit to Debye's model $\tau = \frac{4}{3}\pi a^3 \xi \eta_m(T)/T = 5.2 \times 10^{-9}$ (K s/cP) $\eta_m(T)/T$. (b) Kerr relaxation time versus $1/T$ of pure mNT. The data \bullet are measured viscosities in cP and the data \dagger is theoretically fitted to Debye's model $\tau = \frac{4}{3}\pi a^3 \xi \eta_m(T)/T = 5.7 \times 10^{-9}$ (K s/cP) $\eta_m(T)/T$.

ing the concept of the mutual viscosity introduced by Hill [14], an expression for the temperature and concentration dependence for the molecular rotational relaxation time of solute molecules in a binary liquids is obtained [12]:

$$\tau(T) = (C/T) [(1 + \lambda\chi)\chi\eta_B(T) + (1 - \chi)\eta_{BA}(T)], \quad (2)$$

where χ is the mole fraction of solute molecules B which has a much larger Kerr effect than the solvent molecules A in this experiment; η_B , is the pure solute viscosity; η_{BA} , is the mutual viscosity between solute B and solvent A molecules; C , is a constant parameter related to the molecular sizes in solutions; and λ , is a constant parameter to account for the pair correlation effect among the solute molecules at different concentrations. Values for C and λ were numerically determined from our early experiments [12] on the concentration dependence of τ at room temperature 296 ± 2 K. The parameters are $C_{mNT+CT} = 7.3 \times 296$ K

s/cP*, $\lambda_{mNT+CT} = 2.0$ (slightly changed due to the correction of mNT viscosity measurement), $C_{mNT+DA} = 5.5 \times 296$ K s/cP, and $\lambda_{mNT+DA} = 2.56$. A similar formula to eq. (2) was used by Kivelson and Tsay [18].

Using Hill's [14] model for mixed liquids, the temperature dependence equation for the measured viscosity is given by

$$\eta_m(T) = (\chi^2/a_m)a_B\eta_B(T) + [2\chi(1-\chi)/a_m]a_{BA}\eta_{BA}(T) + [(1-\chi)^2/a_m]a_A\eta_A(T), \quad (3)$$

where $\eta_m(T)$, $\eta_B(T)$, $\eta_A(T)$ are the measured viscosities of the mixture, solute and solvent liquids; $\eta_{BA}(T)$ is the mutual viscosity between the solute and the solvent molecules; a_B , a_A , a_{BA} , a_m are the average values of intermolecular distance [14]; and χ is the mole frac-

* From ref. [12], we determined $C/T = 7.3$ ps/cP at 296 K, this implies $C = 7.3 \times 296$ K ps/cP.

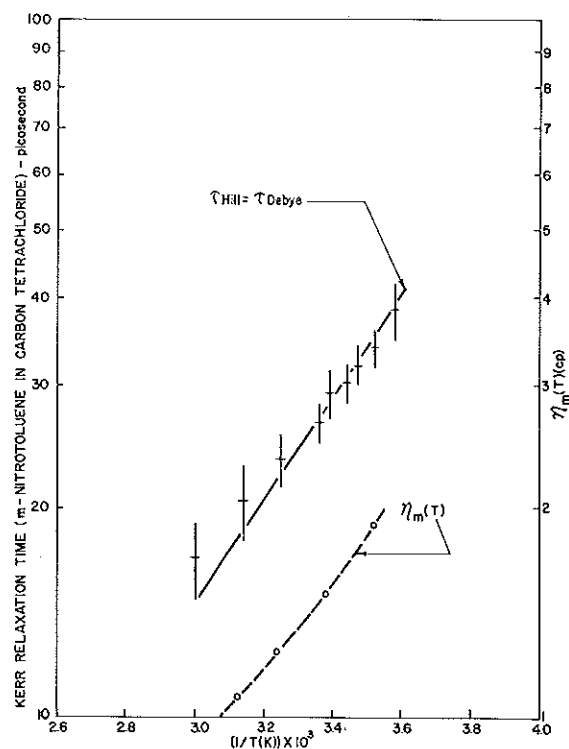
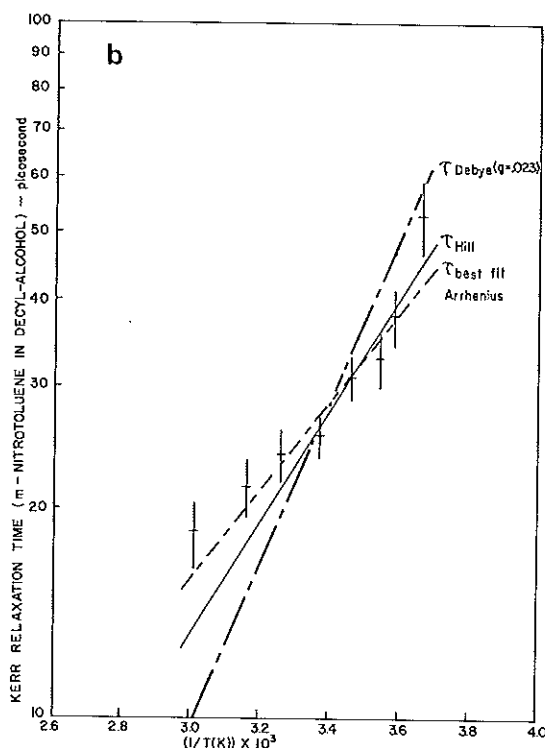
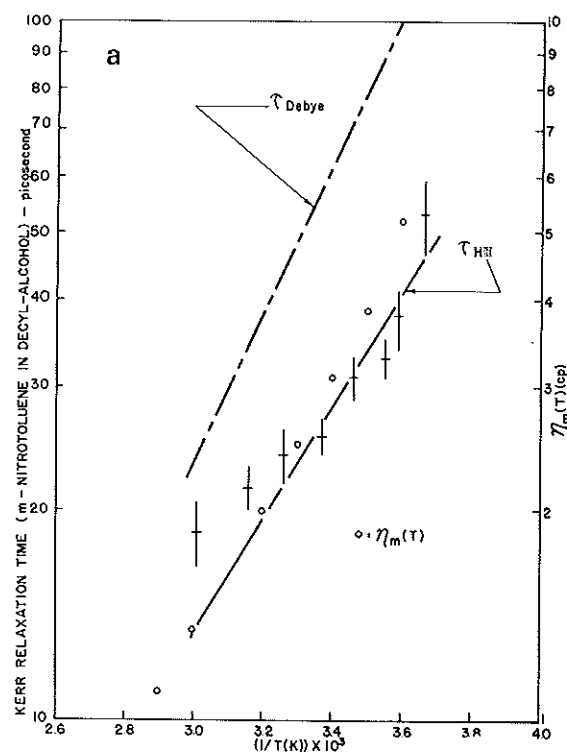


Fig. 4. Kerr relaxation time versus $1/T$ for 75% mole fraction of mNT and 25% mole fraction of CT. The solid line is the theoretical fit of Hill's model $\tau_{\text{Hill}} = (6.9 \times 296/T) \times [(1 + 2\chi)\eta_{\text{mNT}}(T) + (1 - \chi)\eta_{\text{mNT}+\text{CT}}(T)]$, where $\chi = 0.75$. Debye's model of τ is almost identical to $\tau_{\text{Hill}}(T)$.

tion of the solute. The temperature dependence is assumed to arise from the viscosities $\eta_B(T)$, $\eta_A(T)$, and $\eta_{\text{BA}}(T)$. All other terms are assumed to be constant with respect to the temperature variation. The temperature dependence of the viscosity in pure liquid can be expressed [19,20] by

Fig. 5. (a) Kerr relaxation time versus $1/T$ for 72% mole fraction of mNT and 28% mole fraction of DA. The solid line is $\tau_{\text{Hill}} = (5.5 \times 296/T)[(1 + 2.56\chi)\eta_{\text{mNT}}(T) + (1 - \chi)\eta_{\text{mNT}+\text{DA}}(T)]$, and the dashed line is $\tau_{\text{Debye}} = 5.7 \times 10^{-9} (\text{K s/cP}) \eta_{\text{m}}(T)/T$. (b) Comparison of modified Hill, Debye and Arrhenius forms for the relaxation time of mNT in Da. The solid line is $\tau_{\text{Hill}} = (5.5 \times 296/T)[(1 + 2.56\chi)\eta_{\text{mNT}}(T) + (1 - \chi)\eta_{\text{mNT}+\text{DA}}(T)]$, and the dashed line is $\tau_{\text{Debye}} = 1.2 \times 10^{-9} (\text{K s/cP}) \eta_{\text{m}}(T)/T$, where the value 1.2×10^{-9} is chosen to force the curve to lie on the data point of 296 K. The dotted line is the best fit by assuming an Arrhenius behaviour: $\tau_{\text{Arrh.}} = 9.1 \times 10^{-14} (\text{s}) \exp(1500/T)$.



$$\eta_m(T) = (RT/E)^{1/2} [(2mkT)^{1/2}/v^{2/3}p_v] e^{E/RT}, \quad (4)$$

where E is the potential barrier or activation energy; R , the gas constant; m , the molecular mass; v , volume of a molecule; and p_v , the probability that there is a sufficient local free volume for transition to occur. When the temperature is changed, the viscosity of the pure liquids of the solute and the solvent will be varied as $T \exp(E_i/RT)$. The mutual viscosity [21] between the solute and the solvent molecules is assumed to vary similarly:

$$\eta_{BA}(T) \propto T \exp(E_{BA}/RT), \quad (5)$$

where E_{BA} is the potential energy barrier between the positions of the solute and solvent molecules. From the measurements of the viscosities $\eta_B(T)$, $\eta_A(T)$ and $\eta_m(T)$, the mutual viscosity $\eta_{BA}(T)$ can be calculated from eq. (3).

A list of activation energies calculated from different measurements is displayed in table 1 for various solutions. The first column shows the activation energies obtained from measuring the viscosity as a function of temperature. Using eqs. (3) and (4), the activation energies E_{BA} between solute and solvent molecules are calculated; E_{mNT+CT} ($\chi = 0.75$) = 2.2 kcal/mole and E_{mNT+DA} ($\chi = 0.72$) = 3.8 kcal/mole. These are listed in column 2. The third column in the table is obtained by fitting the measured Kerr relaxation times displayed in figs. 3, 4 and 5 to a simple Arrhenius behaviour of the form:

$$\tau = A \exp(E/RT). \quad (6)$$

The energies listed in columns 1 and 2 of the table are used for curve fitting the relaxation time data displayed in figs. 3–5. The Hill relaxation times data are calculated from eq. (2) using the *previously measured* [12] parameters C and λ , the measured $\eta_B(T)$, and the calculated $\eta_{BA}(T)$ ($E_{BA}(T)$). The Debye relaxation times are calculated from eq. (1) by using $\eta_m(T)$, $\xi_{NB} = 0.1$ and $\xi_{mNT} = 0.1$. These values are plotted in figs. 3–5. As shown in figs. 3a and 3b the calculated curve from Debye's and Hill's models give excellent fits to the τ data for the neat liquids. Also, these models agree well with the temperature dependence of τ for the mixture of mNT and CT (fig. 4). This is reasonable since the effective and the measured viscosities are about the same at different temperatures. This is not so for the mixture of mNT and DA. The dashed curve in fig. 5a is a plot of the relaxation time calculated from eq. (1) of Debye's model using the measured value of $\eta_m(T)$ and the calculated values α^3 and ξ_{mNT} from the neat liquids. Using $\xi_{mNT} = 0.1$, this curve does not agree with the data. Even if we force fit Debye's equation for τ to the data point of fig. 5a at $T = 296$ K by changing $\xi = 0.023$, the slope of the curve from the Debye equation is still off by 40% with the slope of the data (see fig. 5b). On the other hand, Hill's model provides a better fit to the experimental data which is only about 20% off at the higher temperature end. The deviation of the data at high temperatures from a linear dependence in fig. 5 may arise from a low intensity slow relaxation component which merges with the main fast component as the temperature is increased. A possible mechanism

Table 1
Activation energy E (kcal/mole \pm 10%)

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	E_{Debye} (viscosity measurement)		E_{Hill} solute-solute solute-solvent		E_{Kerr} (measured) (Arrhenius form)
NB	3.0	3.0	—	—	3.0
mNT	3.6	3.6	—	—	3.6
mNT + CT ($\chi = 0.75$)	2.9	3.6	2.2	—	3.2
mNT + DA ($\chi = 0.72$)	4.2	3.6	3.8	—	3.0
CT	2.5	—	—	—	—
DA	6.2	—	—	—	—

which may cause such a component is the reorientation of a solvent molecule by the field of the neighboring solute molecules. At this time, from the concentration and temperature dependence Kerr relaxation experiments, Hill's theory seems to be an appropriate model to explain the molecular orientational time in mixed liquids.

In conclusion, the relaxation time of the optical Kerr effect and the viscosity of the neat and the mixed liquids as a function of temperature were measured. The activation energies were calculated from the measurements of the temperature dependence of the Kerr relaxation time and viscosity. The Debye equation gives excellent agreement with the Kerr relaxation time measurements in pure liquids. To describe the relaxation time in mixed liquids, an effective viscosity is introduced to interpret the measured values of τ . This is a simple physical model for a complex situation which provides reasonable agreement with the experimental data. What is needed is a microscopic theory for the Kerr rotational relaxation time of molecules in *neat* and *mixed* liquids to account for both the *concentration* and *temperature* dependence.

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