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Probing Intermolecular Interaction through Thermal-Lens Spectroscopy

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Abstract

Binary liquid mixtures are studied using femtosecond pump–probe thermal-lens (TL) spectroscopy. Changes in the measured TL signals as a function of relative concentration of binary mixtures show that these result from a combined effect of physical and molecular properties of the constituent binary liquids. The experimental TL values deviate from the ones calculated from phenomenological equations. These, we argue, are due to an underestimation of the influence of molecular interactions when the TL signals are calculated by using physical parameters only.

Introduction

Thermal-lens (TL) spectroscopy has several potential applications in molecular and solid-state spectroscopy, such as material testing, combustion studies, plasma diagnostics, as well as research in heat diffusion, transport phenomena, and phase transition studies.^{1–6} TL spectroscopy is also widely used in characterizing absorptive materials.⁷ The TL effect⁸ was reported as early as 1965; however, the development of an extra-cavity single-beam thermal-lens spectrometer⁹ came as late as 1973. This single-beam TL technique was improved vastly with the introduction of a dual-beam version.¹⁰ Subsequently, many authors used two-color *Z*-scan techniques and pump–probe experiments to measure TL in different samples.^{11–14} TL spectroscopy is often the preferred analytical tool, particularly for molecular systems with strong absorbance in comparison to fluorescence. The TL studies are also significant in regard to coherent control goals since they have been used as the feedback parameter for nonfluorescing samples.¹⁵ Overall, TL spectroscopy is a highly sensitive, nondestructive, and noninvasive photothermal method.

TL spectroscopy measures the distortion in the probe laser wavefront due to a cumulative heating of the sample induced by the pump laser beam. A pump laser pulse irradiation results in excited molecules. Many such excited molecules undergo relaxation through nonradiative processes, which gives rise to a transient thermal effect in the sample. In the case of high-repetition rate (HRR) lasers, this transient thermal effect from individual pulses adds up cumulatively to result in a spatial distribution of temperature in the sample at longer time scales. Since the refractive index of a sample depends on temperature, a spatial distribution of the index of refraction is generated, which behaves as an ideal thin concave lens and distorts the wavefront of the probe beam. To measure the magnitude of this distortion, we record the probe beam transmittance in the presence of the pump beam through a small aperture located at far field. In fact, for many cases, TL spectroscopy is the most sensitive optical technique for measuring thermal properties of solids and liquids.^{16,17}

Binary liquid mixtures have attracted considerable attention for a long time¹⁸⁻²¹ due to their unusual behavior. The TL signal for a pure sample depends on various physical parameters, such as the refractive index (n), the temperature gradient of the index of refraction or the thermo-optic coefficient (dn/dT), the molar density (ρ), the thermal conductivity (κ), the coefficient of thermal expansion (β), the heat capacity (C_p), and the absorption coefficient (α). Since the change related to every single parameter is different for each solvent, all these parameters change in the binary solution. Until now, TL experiments on different binary liquid mixtures simply attempt to draw a comparison to the TL measurements of their constituent individual components through phenomenological models²²⁻²⁷ involving mutual interaction of physical parameters. On the other hand, for a particular binary liquid mixture, if we gradually change its relative binary composition, molecular interactions also change in addition to the physical properties of the sample. Changes in molecular interactions of the binary liquids originate from variations in the nature and concentration of the liquid components as the sample compositions change. Thus, a combined effect of molecular interactions and physical properties inside the binary liquid samples can also be studied by using TL spectroscopy.

Femtosecond laser pulses offer the advantage of high peak intensity at fairly low average powers that can induce nonlinear thermal effects without any sample damage issues. Thus, HRR femtosecond lasers can generate cumulative heating that can, in turn, be utilized very efficiently to study the TL of highly volatile liquids, such as methanol (CH_3OH). Our experiments use two-color TL Pump-Probe Z-scan technique^{11,28-31} with two femtosecond collinear laser pulses at 1560 nm and 780 nm as the pump and probe beams, respectively. Such experiments measure TL signals for a series of binary liquid mixtures as relative compositions of the binary liquid constituents are varied. We mix methanol with each of dimethyl sulfoxide ($(\text{CH}_3)_2\text{SO}$), dichloromethane (CH_2Cl_2), and carbon tetrachloride (CCl_4), to prepare their respective binary liquid mixtures, ensuring that in each case the TL effect is essentially due to methanol (absorber).

We calculate the TL signal for every composition of a particular binary mixture by using the above-mentioned physical parameters and compare their trends with experimentally measured values. These studies indicate that the difference between experimentally measured trends in TL signals to those calculated from physical characteristics originates primarily from changes in the intermolecular interaction of binary liquids which in turn is a result of changes in the composition of binary liquid components. In this paper, therefore, we attempt to explain trends in TL signals for binary liquid mixtures that are due to a combined effect of changes in physical parameters as well as molecular properties, such as intermolecular interactions, hydrogen bonding, etc., between the binary liquid components.

Experiment

Our experimental setup (Figure 1) involves a mode-locked femtosecond Er:doped fiber laser (Femtolite, IMRA Inc.), which generates pulses centered at fundamental wavelength 1560 nm and its second harmonic 780 nm, collinearly as a single beam with 50 MHz repetition rate. The 1560 nm pulse has an average power of 25 mW, while the 780 nm pulse is ~100 fs wide and has an average power of 15 mW. The 1560 nm pulse is ~300 fs wide as measured with interferometric intensity crosscorrelation (delay line part of Figure 1 without using any aperture). To measure the thermal-lens signal in the binary liquid samples, we focus these two beams into the sample cell, and the cell is moved across the focal point of the lens along the Z-axis. The 1560 nm, in our case, acts as the thermal pump beam, and we use a silicon-amplified photodetector (Thorlabs: PDA 100A-EC) to detect the transmittance of the 780 nm probe beam through a 60% closed aperture in the far field to measure the thermal-lens signal in our samples. The power of the TL signal is recorded with a 200 MHz oscilloscope

(Tektronix TDS 224) interfaced to a computer with a National Instruments GPIB card. We take the sample in a 1 mm thick quartz cuvette. A motorized translation stage (model ESP-300), which can step with a minimum resolution of 0.000 017 5 mm, moves the sample across the focal point of the first lens, and data acquisition is performed using LabVIEW programming.

Using methanol as the common 1560 nm absorbing component, we prepare three binary liquid mixtures, A, B, and C. The three liquids that we choose to mix with methanol for preparing the binary mixtures A, B, and C do not absorb 1560 nm. Under our experimental conditions, therefore, they do not produce any TL signal of significance as compared to that of methanol. Thus, the common component (CH₃OH) essentially behaves as the solute, which is being diluted with the three different solvents: dimethyl sulfoxide (DMSO) in the case of A, dichloromethane (DCM) in the case of B, and carbon tetrachloride (CCl₄) in the case of C. For any particular binary mixture, A, B, or C, we change the ratio of the two constituent components (solute and solvent) and record their close aperture *Z*-scan data. We use spectral grade samples without further purification after confirming their purity through individual UV-vis spectra. To correlate the spectral data with experimentally measured parameters, we also collected the near-infrared (NIR) spectra for each of the varying ratios of the constituent compositions of the methanol-CCl₄ binary solution (as a representative case) by an UV/vis/NIR spectrometer (Perkin-Elmer Lambda 900) using a 1 mm quartz cuvette. The close aperture *Z*-scan transmittance is plotted against different *z*-positions to generate the closed aperture traces. The TL signal from these traces is calculated and plotted as a function of varying ratio of constituent compositions in the binary liquids, which show how the TL signal varies with the change in their constituent composition across different sets of binary mixtures.

Results and Discussions

As discussed in the Experimental Section, in our binary liquids, methanol is, by design, the only highly absorbing liquid at 1560 nm, and it shows a significant TL signal in the 780 nm probe beam. The vibrational combination states of methanol become coupled with the femtosecond laser pulses at 1560 nm. This coupling results in the nonresonant saturation absorption of 1560 nm, and the excited molecules undergo relaxation through a nonradiative process, which gives rise to a transient thermal effect in the sample. As we use an HRR laser, this transient thermal effect of individual laser pulses accumulates to produce a cumulative thermal effect at longer time scales. We measure the TL signal from this cumulative thermal effect with a mode-mismatched two-color pump-probe *Z*-scan technique. The best approach to probe the TL signal is to measure the probe beam transmittance through a closed aperture in the presence of the pump beam. So we use a 60% closed aperture in the far field to detect the 780 nm probe beam transmittance. From the close aperture *Z*-scan traces of different binary mixtures of methanol at different compositions, we measure the amplitude of thermal-lens signal as

$$S(\lambda_e) = \frac{T_a(\lambda_e) - T_{a0}}{T_{a0}} \quad (1)$$

where $T_a(\lambda_e)$ and T_{a0} are the probe light transmittance through the aperture in the presence of the pump beam and in the absence of the pump beam, respectively.³² We calculate the TL signals using eq 1 for each of the individual pure samples as well as the binary mixtures of methanol, A, B, and C, respectively, at each *Z* position.

Figure 2 shows the variation of TL signals as a function of sample positions for all pure samples (methanol, DMSO, DCM, and CCl₄). Among all these liquids, methanol shows the

highest TL signal as compared to the others at 780 nm probe, reassuring our approach of considering methanol as the solute. All the other liquids are solvents for diluting methanol in our three binary liquid samples. To study the effect of intermolecular interactions in addition to the changes in physical properties of binary mixtures, we gradually change the composition of the binary sample in each individual mixture and correspondingly measure their TL signals. The variation in the measured TL signals, $S(\lambda_e)$, as a function of sample position (Z) for methanol- CCl_4 binary mixtures across different compositions (as a representative case) is shown in Figure 3, which is generated using eq 1.

As we use mode-mismatched conditions in our experiment, the highest thermal-lens signal appears at $Z = 0$, which is the focal point of the 1560 nm pump beam. The variation in TL signal with different compositions of the binary liquid mixtures is measured from the magnitude of the thermal-lens signal at the focal point ($Z = 0$) of the pump beam for each individual composition of all the binary liquid mixtures (Figures 4-6) by using eq 1. Specifically, eq 1 becomes $|S(\lambda_e, Z = 0)| = (T_a(\lambda_e, Z = 0) - T_{a0}(Z = 0)) / (T_{a0}(Z = 0))$, for probe light transmittance through aperture in the presence of a pump beam, $T_a(\lambda_e, Z = 0)$, as compared to that in the absence of a pump beam, $T_{a0}(Z = 0)$, at the focal point of $\lambda_e = 1560$ nm.

On the other hand, in our particular study of binary mixtures, the experimental conditions are kept constant, which essentially allows us to calculate the magnitude of thermal-lens signals at the focal point for binary liquid mixtures as proposed by Marcano³³ using the time-averaged criteria as

$$S(Z=0) = \frac{\alpha l P_e \left(\frac{dn}{dT} \right)}{\kappa} \quad (2)$$

where $S(Z = 0)$ is the thermal-lens signal at the focal point; α is the absorption coefficient; l is the sample length; P_e is pump laser power; $(dn)/(dT)$ is the thermo-optic coefficient; and κ is the thermal conductivity of the binary liquid samples. Physical parameters, like the refractive index (n) or its temperature gradient $((dn)/(dT))$, the thermal conductivity (κ), and the absorption coefficient (α), as implied in eq 2, change under experimental conditions when we mix two different liquids to prepare the binary solutions. However, by assuming equal interactions between the components of the binary liquids, we can calculate²⁶ all the above-mentioned parameters as a function of their changing compositions in our binary mixtures: A, B, and C, respectively. Thus, in our case, considering that the interactions between the methanol (absorber) and the other solvent (viz. CCl_4 , DCM, DMSO, CD_3OH) are ideal, we can use the Lorentz-Lorentz equation,

$\left[(n^2 - 1) / (n^2 + 2) \right] (1/\rho) = \left[(n_1^2 - 1) / (n_1^2 + 2) \right] (x_1/\rho_1) + \left[(n_2^2 - 1) / (n_2^2 + 2) \right] (x_2/\rho_2)$, which can be rearranged to calculate the refractive index of the sample as

$$n = \left(\frac{2D+1}{1-D} \right)^{1/2} \quad (3)$$

where the parameter “ D ” is given by

$$D = \left[\left(\frac{n_1^2 - 1}{n_1^2 + 2} \right) \frac{x_1}{\rho_1} + \left(\frac{n_2^2 - 1}{n_2^2 + 2} \right) \frac{x_2}{\rho_2} \right] \rho \quad (4)$$

Similarly, under these conditions, the density, thermal conductivity, and thermal expansion coefficient are given by the following equations

$$\begin{aligned}\rho &= \rho_1 + (\rho_2 - \rho_1) x_2 \\ \kappa &= \kappa_1 + (\kappa_2 - \kappa_1) x_2 \\ \beta &= \beta_1 + (\beta_2 - \beta_1) x_2\end{aligned}\quad (5)$$

where n , x , ρ , κ , and β refer to the refractive index, mole fraction, density, thermal conductivity, and thermal expansion coefficient, respectively. Indices 1 and 2 refer to the components of the mixture. The thermo-optic coefficient of the mixture can be calculated by differentiating the refractive index with temperature. The thermo-optic coefficient of the mixture is given by

$$\begin{aligned}\frac{dn}{dT} &= \frac{3}{2(2D+1)^{1/2}(1-D)^{3/2}} \left(\frac{dD}{dT} \right) \\ \left(\frac{dD}{dT} \right) &= \sum_{i=1}^2 D_i x_i\end{aligned}\quad (6)$$

$$D_i = \left(\frac{\rho}{\rho_i} \left(\frac{d}{dT} \left(\frac{n_i^2 - 1}{n_i^2 + 2} \right) \right) + \left(\frac{n_i^2 - 1}{n_i^2 + 2} \right) \left(\frac{d}{dT} \left(\frac{\rho}{\rho_i} \right) \right) \right), \quad i=1, 2 \quad (7)$$

$$D_i = \frac{\rho}{\rho_i (n_i^2 + 2)} \left(2n_i \left(\frac{dn_i}{dT} \right) \left(1 - \frac{n_i^2 - 1}{n_i^2 + 2} \right) + (n_i^2 - 1) (\beta - \beta_i) \right), \quad i=1, 2 \quad (8)$$

In eq 8, the variation of the density with temperature at constant pressure has been replaced by the product of the density (ρ) and the coefficient of thermal expansion (β) of the solution as well as the corresponding $\beta_i \rho_i$ of two components of the solution. Using these phenomenological models, we calculate the various physical parameters and TL signal for all our binary solutions under ideal theoretical conditions providing us an opportunity to correlate the deviations of these calculated values as compared to our experimental TL signals generated from eq 1. We base our correlations on contributions arising from the intermolecular interaction part and the change in bonding situations, which mostly originate at the molecular level when the compositions of the binary mixtures change along a particular series.

Specifically, our experimental results from eq 1, when compared with the calculated trends from eq 2 (Figures 4-6), suggest that the TL signal in the binary liquid samples depends on two factors: one being the concentration of the absorbing sample (in our case, methanol) and the other being the intermolecular interactions between the solvent and solute molecules. The concentration dependence of methanol is a direct consequence of the fact that the absorbance of the pump beam (1560 nm) depends on the concentration of methanol, which is the absorber of the pump beam in the binary solution. Upon absorption of the pump beam, though various mechanisms of de-excitation are possible, the dominant one in the case of methanol is through the nonradiative channel.³¹ Hence, the higher the concentration of methanol, the higher the absorbance of the pump beam is, resulting in a higher nonradiative deexcitation, which, in turn, generates a larger thermal-lens signal. On the other hand, the intermolecular interactions contribute differently in different binary samples in the measurement of the TL signal. Intermolecular interactions and the change in bonding situations that result from the molecular properties generally depend on various parameters like the inter- and intramolecular bonding nature of individual binary components, molecular diffusion under steady state condition (Sorret effect)^{26,34} of the binary solutions,

critical time constants of the solutions, etc. Thus, the contribution originating from the change in the molecular properties of the binary mixture results in the observed difference between experimental and calculated trends of the thermal-lens signal across the change of the composition of the binary solutions under the experimental conditions. We show the experimental and calculated thermal-lens signal trends for all the binary liquid solutions at different compositions in Figures 4, 5, and 6. We also plot the variation of the reciprocal of thermal conductivity ($1/\kappa$) and the thermo-optic coefficient $(dn)/(dT)$ (in their functional form as they appear in eq 2) and the experimentally measured absorption of the solutions at 1560 nm at each of the compositions of the binary mixtures. The NIR spectra for methanol- CCl_4 binary mixtures as a representative case for these nonabsorbing solvents are also shown which support the observed trends. In all our experiments with binary solutions, A, B, and C, we ensured that the solvent used (either DMSO, DCM, or CCl_4) does not absorb 1560 nm and hence does not have any significant TL contribution at the 780 nm probe beam in comparison to methanol.

In the case of methanol-DMSO binary mixtures (Figure 4), DMSO is a highly polar aprotic solvent, which does not absorb 1560 nm under the experimental conditions. Here the absorption at 1560 nm and the calculated thermo-optic coefficient $(dn)/(dT)$ almost linearly increases when the volume fraction of methanol changes from 0 to 1. As both the pure methanol and DMSO have the same thermal conductivity (κ) values, the reciprocal of the calculated values of the thermal conductivity ($1/\kappa$) does not change with the change in composition. The experimentally measured TL signal trend differs from that of the calculated trend, and this deviation results from the change of the molecular properties of the solutions due to the variation of the compositions.

Again, in the case of methanol-DCM binary mixtures (Figure 5), DCM is also an aprotic solvent and shows no absorption at 1560 nm. So, for methanol-DCM mixtures, the trend of absorption and $(dn)/(dT)$ with respect to the change of the composition of the binary mixture is similar to methanol-DMSO mixtures. Since the thermal conductivities (κ) of pure methanol and pure DCM are different, the plot of $1/\kappa$ vs the composition of the mixture (Figure 5) looks different compared to that of the methanol-DMSO case. On the other hand, DCM is less polar than DMSO. This polarity difference between DMSO and DCM affects the change of the molecular properties of the methanol-DMSO and methanol-DCM binary liquid solutions at different compositions, which in turn results in the difference in the TL signal trends when measured with these solutions experimentally. The experimental TL signal trend deviates from that of the calculated trend in the case of methanol-DMSO mixtures, while in the case of methanol-DCM binary mixtures the experimentally measured trend almost follows the calculated TL signal trend.

Surprisingly, methanol- CCl_4 binary solutions (Figure 6a) show a huge deviation between the experimentally measured and calculated TL signal trends as compared to that in the methanol-DMSO and methanol-DCM case. CCl_4 is also an aprotic solvent, which shows no absorption at 1560 nm. In this case, the trends in absorption, $(dn)/(dT)$ and $1/\kappa$, with respect to the change in composition of the binary mixture are almost as similar as the methanol-DCM solutions. On the other hand, CCl_4 is a completely nonpolar solvent, and this fact results in a significant molecular property mismatch between the solute (methanol) and solvent (CCl_4) molecules. Thus, the deviation between the experimentally measured and calculated TL signals is the highest in the case of methanol- CCl_4 binary mixtures as compared to the methanol-DMSO and methanol-DCM binary solutions. The variation of the NIR spectra at different compositions of the methanol- CCl_4 binary solutions is shown in Figure 6b. We also plot from these spectral traces the absorption of methanol- CCl_4 solutions at 1572 nm as a function of methanol concentration (Figure 6c), which essentially

supports the absorption trend (Figure 6a) measured using 1560 nm pulses from the IMRA laser.

The TL experiments with binary liquid mixtures discussed here predict that the higher the mismatch between the molecular properties of the solute and solvent molecules, the higher the deviation between the trends will be in experimentally measured and calculated TL signals. Thus, the molecular property information plays a very important role when the TL signals are studied for binary liquid solutions by changing their compositions.

We explore the prospect of explaining the trends in TL signals with changes in the composition of binary mixtures based on the pure molecular properties of individual binary mixture constituents. The equation we use for calculating the magnitude of the thermal-lens signal (eq 2) contains only the physical parameters of the binary liquid samples since all the experiments were done with identical laser conditions. However, it does not contain any parameter that originates from their pure molecular properties, such as intermolecular interactions or changes in bond characteristics, etc. Thus, changes in the trends of the TL signal with changing molecular properties of binary liquid composition are absent from those calculated by using eq 2. Consequently, the experimentally measured TL trends deviate from the calculated ones (Figures 4-6). To realistically quantify trends in the observed modulation of the experimental TL signal in binary samples, therefore, in addition to the changes in the physical parameters as in eq 2, it is necessary to incorporate the changes in the molecular properties arising from varying binary mixture compositions. From our analysis, we propose that the total TL signal for the binary liquid mixtures originates from two sources: one is from the change of physical parameters, while the other is from purely molecular properties. Considering these two TL parameters as mutually exclusive, eq 2 can be modified to a more complete expression to include the molecular property variation as

$$S_{\text{Total}}(z, m) = S(z) \times S(m) \quad (9)$$

where $S_{\text{Total}}(z, m)$ is the total TL signal of the binary liquid sample, comprised of TL signals $S(z)$ and $S(m)$. The $S(z)$ part is calculated from the physical parameters like the absorption coefficient (α), the thermo-optic coefficient $[(dn)/(dT)]$, and the thermal conductivity (κ) as in eq 2. The $S(m)$ part can be attributed to the molecular contribution of TL resulting from the change of the composition of the binary liquid solutions. So, to extract the molecular property information responsible for the modulation of the TL signal trends, we take the ratio between the TL trends obtained from the experiment and calculated by using the physical parameters only as

$$S(m) = \frac{S(z, m)}{S(z)} \quad (10)$$

The results are shown in the Figure 7, which indicates that the trends in the modulation of the TL signal mostly originate from changes in the molecular properties of the binary liquid mixtures as their relative composition changes. A closer inspection of Figure 7 also indicates that the signature of the molecular properties of the individual binary liquid components is effectively reflected and is dominant at the two end points of the x -axis, when the volume fraction of the solute (in our case methanol) is approaching 0 or 1. The individual characteristics of the binary liquid components are suppressed, and the mixture properties become important and show almost the same trend when the volume fraction of methanol varies from 0.3 to 0.7 in the binary samples.

The above binary mixture studies reveal that the consideration of molecular properties is very critical when thermal-lens properties of binary liquid samples are studied by varying the composition of the liquid samples. Intermolecular interactions and changes in the bond characteristics play a significant role in addition to the already well-accepted role of the changes in physical properties of the sample, and thus both have to be considered carefully for analyzing the experimental results. We have, therefore, established that the molecular and physical properties are equally important when the binary liquid samples are studied at various compositions by thermal-lens spectroscopic techniques. Further investigations are currently being pursued in our laboratory to identify the specific molecular parameters that are important and the level of their contribution in the trends of the thermal-lens signal for varying compositions of binary liquid mixtures.

Conclusion

In this paper, we have shown how the molecular and physical properties become critically important when we study binary liquid mixtures at varying compositions by the TL spectroscopic technique. We use a two-color thermal-lens pump–probe *Z*-scan technique to measure the relative magnitude of the thermallens signal in our binary liquid samples, where 1560 nm is the thermal pump and 780 nm is the probe. The TL trends in the binary liquid samples are calculated from the physical parameters responsible for the TL signal. We compare the experimentally measured and theoretically calculated TL trends for each of the binary samples. We explain the deviations of the experimentally measured trends from that of the calculated ones mostly on the basis of the change of the intermolecular interactions that originate from the variation in the compositions of binary liquid samples. Thus, our binary liquid studies show how molecular properties are significant in addition to the physical parameters when TL signals are measured by varying the compositions of any binary liquid mixture.

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Figure 1. Schematic of the experimental setup. BS1 and BS2, dichroic beam splitter; M1, M2, and M3, mirrors; L1 and L2, lenses; A, removable aperture; PD, silicon photodiode.

Figure 2. Thermal-lens signal for different Z -positions in the case of pure methanol, DMSO, DCM, and carbon tetrachloride.

Figure 3.

(a) Variation of TL signal as a function of the sample position for methanol-CCl₄ binary mixtures where the volume fraction of methanol changes from 0 to 1. (b) Representative (0.5 volume fraction methanol-CCl₄) raw z-scan data collected from the experiments are shown with error bars. These data are used in eq 1 to result in TL signals.

Figure 4.

Variation of TL signal, measured absorption at 1560 nm, reciprocal of thermal conductivity ($1/\kappa$), and the thermo-optic coefficient (dn/dT) at different compositions of methanol–DMSO binary mixtures, where the volume fraction of methanol changes from 0 to 1 and the volume fraction of DMSO changes from 1 to 0.

Figure 5.

Variation of TL signal, measured absorption at 1560 nm, reciprocal of thermal conductivity ($1/\kappa$), and the thermo-optic coefficient (dn/dT) at different compositions of methanol–DCM binary mixtures, where the volume fraction of methanol changes from 0 to 1 and the volume fraction of DCM changes from 1 to 0.

Figure 6.

(a) Variation of TL signal, measured absorption at 1560 nm, reciprocal of thermal conductivity ($1/\kappa$), and the thermo-optic coefficient (dn/dT) at different compositions of methanol- CCl_4 binary mixtures, where the volume fraction of methanol changes from 0 to 1 and the volume fraction of CCl_4 changes from 1 to 0. (b) The spectra for methanol- CCl_4 binary solutions at each of the compositions using a 1 mm cuvette. (c) The absorption of methanol- CCl_4 solutions at 1572 nm from the spectral traces and its linear fit.

Figure 7. Ratio between the experimental and calculated TL signal trends for different binary mixtures in comparison to their individual characteristics: volume fraction 1 corresponds to pure methanol, while that of zero corresponds to 100% of either CCl_4 , DMSO, or DCM.