Importance of Molecular Structure on the Thermophoresis of Binary Mixtures

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ABSTRACT: Using thermal lens spectroscopy, we study the role of molecular structural isomers of butanol on the thermophoresis (or Soret effect) of binary mixtures of methanol in butanol. In this study, we show that the thermal lens signal due to the Soret effect changes its sign for all the different concentrations of binary mixtures of butanol with methanol except for the one containing tertiary-butanol. The magnitude and sign of the Soret coefficients strongly depend on the molecular structure of the isomers of butanol in the binary mixture with methanol. This isomerization dependence is in stark contrast to the expected mass dependence of the Soret effect.

INTRODUCTION
Thermophoresis is a physical phenomenon of concentration gradient arising in a mixture of two or more components when it is exposed to a thermal gradient. This was first observed by Ludwig in 1856. Later in 1879, it was studied in great detail by Charles Soret. So, this phenomenon is also called the Ludwig–Soret effect, though more commonly it is known as the Soret effect. As a result of this phenomenon, under the influence of a thermal gradient, relative thermal diffusion of the components of the mixture occur, resulting in separation of components. However, when this process starts, the Fickian diffusion process starts in the opposite direction to equilibrate the concentration gradient. Then net flux is given as

\[ J = -\rho(DVc + D_r c(1 - c)VT) \]

where, \( \rho \) (kg/m³) is the density of the binary mixture, \( D \) (m²/s) is the molecular diffusion coefficient, \( c \) is the mass fraction of the reference species, \( D_r \) (m²/s K) is the thermal diffusion coefficient, and \( T \) is the temperature in Kelvin. When the net flux is zero, \( V_c = S_r c(1 - c)VT \), where \( S_r = D_r/D \) is the Soret coefficient with unit K⁻¹. It has a positive value when the heavier component migrates to the cold side and a negative value otherwise. Many authors also show that the change of sign of the Soret coefficient takes place with compositions. The Soret effect has a wide range of applications in characterization and separation of polymers and isotopes separation. It is also extensively used for studying various biological processes. A lot of work has been done on the Soret effect for understanding the phenomenon and its applications. Since this concentration gradient (Soret effect) is generated in the millimeter to micrometer range, the thermal lens (TL) spectroscopy becomes a great tool to study this effect.

TL is a result of temperature change arising from the nonradiative relaxation in the system being irradiated by a laser beam. This temperature change results in a refractive index change in the system. This refractive change is in the form of a smooth gradient in the case of the Gaussian laser beam profile. This refractive index gradient makes the system behave as a lens. TL can be either a diverging lens or a converging lens, depending on the thermo-optic coefficient \( (dn/dT) \) of the system under study. The wavelength of the laser beam is chosen in such a manner that couples with either the electronic levels or the vibrational levels of the sample under study. The TL process starts with the absorption of the laser beam and continues until the system reaches thermal equilibrium. The amount of heat deposited in the system depends on the amount of radiationless relaxation. Presently, TL spectroscopy is a well-known, highly sensitive, nondestructive, popular analytical technique for the thermal, optical, and chemical analysis of solids, liquids, and gases.

In 1965, Gordon et al. observed that a laser beam diverges after passing through a nearly transparent solvent. This divergence of the laser beam could only be explained if there is a decrease in the refractive index of the sample due to heat deposition in the system. This observation led to TL spectroscopy using a single laser beam. To enhance the sensitivity of the TL spectroscopy, the dual-beam TL technique has been developed. The dual-beam TL technique is more sensitive compared to the single-beam TL technique, as in the dual-beam case, one beam creates the TL signal while the second beam measures this TL signal. A more accurate signal measurement can be done in this case compared to the single-beam.

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beam TL technique. This dual beam TL technique has two types of experimental setups, namely, the mode-matched and the mode-mismatched, depending on the beam waist parameters of the pump and the probe beams.\(^{48}\) The mode-mismatched TL technique is more sensitive compared to the mode-matched TL technique, and is used widely for photochemical study\(^{50-56}\) and hydrodynamic relaxation to measure the Soret effect.\(^{20-26}\) Continuous wave (cw) lasers are also being used for TL study. Each femtosecond pulse deposits a small amount of energy to the sample and, in the case of the HRR laser, this small amount of energy accumulates to result in a long time TL signal. The HRR laser provides better signal-to-noise ratio compared to the cw laser.\(^{52}\)

The Soret effect depends on the difference in the masses of the components of a mixture. Thus, most of the work on the Soret effect was performed on mixtures containing components of different masses.\(^{6-26}\) Only a very limited study of the effect of molecular structure of the components of a mixture on the Soret effect is available,\(^{53}\) and a systematic study is yet to be done. We explore the molecular structure effect on the Soret phenomenon systematically. For such a study, we used the structural isomers of butanol: normal-butanol (\(n\)-BuOH), secondary-butanol (sec-BuOH), iso-butanol (i-BuOH), and tertiary-butanol (t-BuOH); and prepared their individual binary mixtures with the constant second component as methanol (MeOH).

**EXPERIMENT**

The experimental setup used for studying the molecular structure effect on the Soret phenomenon is a two-color pump–probe mode-mismatched TL technique as shown in Figure 1. The experimental setup comprises a mode-locked Er-doped femtosecond fiber laser (Femtolite Mira, Inc.). This laser produces laser pulses of two colors centered at 1560 and 780 nm with a repetition rate of 50 MHz. The laser pulses centered at 1560 nm has the pulse width of \(\sim 300\) fs with an average power of 12 mW at the sample, while the laser beam of pulses centered at 780 nm has the pulse-width of \(\sim 100\) fs with an average power of 6 mW at the sample. The laser beam of pulses centered at 1560 nm acts as the pump pulse and is focused on the sample. The laser beam of pulses centered at 780 nm acts as the probe beam and is collimated through the sample with the telescopic arrangement of two lenses (Figure 1). To measure the position-dependent TL signal, a motorized translational stage (Newport: M-6 UTM150CC.1) is used to scan the sample across the focal point of the pump beam (Figure 2).

The sample cell used has a width of 1 mm. The strength of the TL signal is measured by measuring the transmittance of the probe beam through a 60% closed aperture situated in the far field. The intensity of the probe beam is measured with the help of an amplified silicon photodetector (Thorlabs: PDA 100A-EC) with a 200 MHz oscilloscope (Tektronix TDS 224). A National Instruments GPIB card is used to interface the oscilloscope to the computer. A LabVIEW code is written for data acquisition. An InGaAs photodiode (Acton Research) (Figure 1) is used to measure the absorption of the pump beam by the sample. The same photodiode also used to analyze the fluctuation in the pump beam. The maximum TL signal is found at the focal point of the pump beam. For analysis of hydrodynamics relaxation, a shutter is used in the pump beam, and the sample is placed at the focal point of the pump beam. A telescopic arrangement is used to reduce the activation time of the shutter (Figure 1).

The samples used in this study (\(n\)-BuOH, sec-BuOH, i-BuOH, t-BuOH, and MeOH) are of spectroscopy grade and were purchased from Sigma-Aldrich India. The binary mixtures are prepared by adding MeOH to the respected isomer of butanol (MeOH + \(n\)-BuOH, MeOH + sec-BuOH, MeOH + i-BuOH, MeOH + t-BuOH) volumetrically.

**RESULT AND DISCUSSION**

The alcohols have strong absorption in the communication band due to hydroxyl group (OH). This absorbed energy is transformed to heat via nonradiative relaxation. This heat generated in the sample results in a TL. The strength of the TL signal is measured by observing the change in the probe beam divergence. The change in probe beam intensity through a closed aperture located in the far field is an indirect way of measuring the probe beam divergence. The magnitude of stationary TL signal at different sample positions with respect to the focal point of the pump beam is measured by the relation

![Figure 1. Schematic diagram of experimental setup: (DM) dichroic mirror; (M) mirror; (L) lens; (G) glass plate; (S) sample; (D) detector; (PC) personal computer.]

![Figure 2. TL signals for pure samples, namely, MeOH, \(n\)-BuOH, sec-BuOH, i-BuOH, and t-BuOH, with respect to the Z-position of the sample.](image-url)
Figure 4. Time-resolved signals for the pure samples, namely, MeOH, n-BuOH, s-BuOH, i-BuOH, and t-BuOH fitted to the model described in text. The experimental parameters of the pump and probe beams are shown in the inset.

Table 1. Sample Parameters Used to Fit the Model Described in Eq 3

<table>
<thead>
<tr>
<th>sample</th>
<th>thermal conductivity (k) (W m⁻¹ K⁻¹)</th>
<th>thermo-optic coefficient (dn/dT) (K⁻¹) x 10⁴</th>
<th>absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-BuOH</td>
<td>0.15(^{a})</td>
<td>-4.11(^{b})</td>
<td>0.194</td>
</tr>
<tr>
<td>s-BuOH</td>
<td>0.13(^{a})</td>
<td>-4.41(^{c})</td>
<td>0.175</td>
</tr>
<tr>
<td>i-BuOH</td>
<td>0.13(^{a})</td>
<td>-3.67(^{d})</td>
<td>0.193</td>
</tr>
<tr>
<td>t-BuOH</td>
<td>0.12(^{a})</td>
<td>-5.63(^{c})</td>
<td>0.153</td>
</tr>
<tr>
<td>MeOH</td>
<td>0.2(^{b})</td>
<td>-3.98(^{b})</td>
<td>0.394</td>
</tr>
</tbody>
</table>

\(^{a}\)From ref 56. \(^{b}\)From ref 57. \(^{c}\)From ref 58. \(^{d}\)From ref 59.

described in eq 3 is fitted with the experimental data measured with the help of shutter by placing the sample at the focal point of the pump beam (Figure 4). The fitted parameters are shown in Table 2, wherefrom it is evident that these samples behave distinctly from each other. For example, methanol has the shortest convective time constant and the largest value of \(h\) in comparison to the rest of the samples. The isomers of butanol also behave differently under the thermal gradient, which is evident from Table 2 as the molecular structure has a strong effect on molecular diffusion.\(^{54}\) It is found that among the isomers, the trans isomer is the most damping and the highest for t-BuOH. The molecular branching makes the system sluggish and corresponding molecular drift becomes progressively difficult as in the case of t-BuOH.
As mentioned previously, the Soret effect mainly depends on the masses of components of a mixture exposed to a thermal gradient. The molecular mass of methanol is different from butanol, while all the isomers of butanol have the same molecular mass. So we prepared the binary mixtures of methanol with each isomer of butanol and successively changed the relative composition of the two components in each binary mixture to study molecular structure effect on the Soret phenomenon. Cabrera et al.\textsuperscript{24,26,42} substantiated the contribution of the TL signal due to Soret effect ($S_\text{s}$) to the total TL signal ($S_{\text{total}}$) measured experimentally as follows:

\begin{equation}
S_{\text{total}}(z, t) = S_{\text{th}}(z, t) - S(z, t)
\tag{4}
\end{equation}

where $S_{\text{th}}$ is the TL generated due to the temperature gradient in the system. In the same spirit, we modify eq 3 after including the Soret contribution in the following manner:

\begin{align}
S_{\text{total}}(z, t) &= 1 - \left(\frac{\theta_1 + \theta_2 - \theta_0}{2}\right) \tan^{-1}\left(\frac{2mv}{\left(\frac{1}{2}\left(\frac{2m+1}{2m+1}\right)\right)}\right) + F \left(\frac{\theta_1 + \theta_2 - \theta_0}{4}\right) \left(\frac{1 + \frac{2m(1-\sin^2\theta)}{2m+1}}{(1+2m)^2 + v^2}\right) \tag{5}
\end{align}

All the parameters are same as previously defined in eq 3, except the parameter $\theta_0$, which is the contribution of the Soret effect to the TL signal as defined by Cabrera et al.\textsuperscript{24,26,42} We modify the form of $\theta_i$ considering conduction and convection as follows:

\begin{align}
\theta_i &= S_T c(1-\epsilon)\frac{dn}{dc} \left(\frac{A}{k} + \frac{(\alpha P_x - A)}{h}\right) \\
&\times \left[1 - \sum_{i=1}^{\infty} \frac{4}{(2i-1)\pi} \sin\left(\frac{(2i-1)\pi}{2}\right) \exp\left[-(2i-1)^2 \frac{t_i(z)}{\lambda_p(z)}\right]\right] \tag{6}
\end{align}

\begin{align}
\theta_i &= \theta_1 \left[1 - \sum_{i=1}^{\infty} \frac{4}{(2i-1)\pi} \sin\left(\frac{(2i-1)\pi}{2}\right) \exp\left[-(2i-1)^2 \frac{t_i(z)}{\lambda_p(z)}\right]\right] \tag{7}
\end{align}

where, $S_T$ is the Soret coefficient and $t_i$ is time constant for the development of concentration gradient, $\epsilon$ is the concentration of the reference compound, $\theta_i$ is the phase change due to the concentration gradient. The rest of the parameters are already defined in eq 3. The total signal for the stationary TL ($t \to \infty$) is given at the focal point of the pump beam as

\begin{equation}
S_{\text{total}}(z, t_{\infty}) = \left[1 - \left(\frac{\theta_1 + \theta_2 - \theta_0}{2}\right) \tan^{-1}\left(\frac{2mv}{\left(\frac{1}{2}\left(\frac{2m+1}{2m+1}\right)\right)}\right)\right]
+ F \left(\frac{\theta_1 + \theta_2 - \theta_0}{4}\right) \left(\frac{1 + \frac{2m(1-\sin^2\theta)}{2m+1}}{(1+2m)^2 + v^2}\right) \tag{8}
\end{equation}

The stationary TL signal is measured at the focal point of the pump beam by scanning the samples across the focal point while each data point is taken after 5 s, so that a stationary TL formed for every data point. Equation 8 describes the relation between the total stationary TL signal arising from the contribution of the thermal gradient and the concentration gradient (Soret mechanism). The contribution of the Soret effect to the total stationary TL signal is deduced by subtracting the contribution of temperature gradient TL signal from the total stationary TL signal. Equation 8 can be further simplified for deducing the contribution of TL signal for a concentration gradient. Since $\theta_i$ contribution to the TL signal is very small, the second order term in eq 8 can be easily be neglected to arrive at the following form for the TL signal due to Soret effect:

\begin{equation}
S_i(z, t_{\infty}) = S_{\text{total}}(z, t_{\infty}) + \left(\theta_1 + \theta_2\right) X \tag{9}
\end{equation}

where

\begin{align}
X &= \tan^{-1}\left(\frac{2mv}{1+2m}\right) - \left(\theta_1 + \theta_2\right) \\
&\times \left(\frac{1}{4} \tan^{-1}\left(\frac{2mv}{1+2m}\right)^2 + F \left(\frac{1 + \frac{2m(1-\sin^2\theta)}{2m+1}}{(1+2m)^2 + v^2}\right)^2\right) \tag{10}
\end{align}

\begin{align}
\theta_i &= -A(\frac{dn}{dT}/\lambda_p k) \tag{12}
\end{align}

\begin{align}
\theta_{\text{conv}} &= -\left((\alpha P_x - A)(\frac{dn}{dT})/\lambda_p h\right) \tag{13}
\end{align}

All the necessary parameters for the Soret effect (eq 10) can be calculated from the experimental and physical parameters of the binary mixtures in steady state conditions as evident from eqs 11–13. The physical parameters ($k$, $\beta$, $dn/dT$, $c_p$, $h$) for the binary mixture are calculated in the following manner. The molecular interactions between the two components of the binary mixture are taken as ideal since both of the components are organic solvents and they are both alcohols. The refractive index of binary mixtures can be represented using the Lorentz–Lorenz equation as\textsuperscript{28,40}

\begin{equation}
\left(\frac{n^2 - 1}{n^2 + 2}\right) = \left(\frac{x_1}{n_1^2 + 2}\right) + \left(\frac{x_2}{n_2^2 + 2}\right) \tag{14}
\end{equation}
mixtures are calculated in the following equations:

\[ n = \left( \frac{2L + 1}{1 - L} \right)^{1/2} \]  
\[ \text{where} \]
\[ L = \left[ \left( \frac{n_1^2 - 1}{n_1^2 + 2} \right) \rho_1 + \left( \frac{n_2^2 - 1}{n_2^2 + 2} \right) \rho_2 \right] \rho \]  

The parameters \( k, \beta, \rho, A, h, F, \) and \( \text{Abs} \) for binary liquid mixtures are calculated in the following equations:

\[ k = k_1 + (k_2 - k_1)x_2 \]
\[ h = h_1 + (h_2 - h_1)x_2 \]
\[ F = F_1 + (F_2 - F_1)x_2 \]
\[ \rho = \rho_1 + (\rho_2 - \rho_1)x_2 \]
\[ \beta = \beta_1 + (\beta_2 - \beta_1)x_2 \]
\[ A = A_1 + (A_2 - A_1)x_2 \]
\[ \text{Abs} = l \sum_{i=1,2} \epsilon_i \beta_i \]  

Indices 1 and 2 refer to the components of the binary mixture. The \( x_2 \) represents the volume fraction of the mixture. "Abs" is the absorption of the sample. The thermo-optic coefficient of the mixture can be obtained by differentiating the refractive index with temperature. The thermo-optic coefficient of the mixture is given by

\[ \frac{dn}{dT} = \frac{3}{2(2L + 1)^{1/2}(1 - L)^{3/2}} \frac{dL}{dT} \]  
\[ \frac{dL}{dT} = \sum_{i=1}^{2} L_i x_i \]  

\[ L_i = \left[ \frac{\rho}{\rho_i} \left( \frac{d}{dT} \left( \frac{n_i^2 - 1}{n_i^2 + 2} \right) \right) + \left( \frac{n_i^2 - 1}{n_i^2 + 2} \right) \left( \frac{d}{dT} \left( \frac{\rho}{\rho_i} \right) \right) \right], \quad i = 1, 2 \]

\[ L_i = \frac{\rho}{\rho_i(n_i^2 + 2)} \left[ 2n_i \frac{dn_i}{dT} \left( 1 - \frac{n_i^2 - 1}{n_i^2 + 2} \right) + \frac{n_i^2 - 1}{n_i^2 + 2}(\beta - \beta_i) \right] \]  

In eq 20, the change in density with temperature at constant pressure has been replaced with the product of the density \( (\rho) \) and the coefficient of thermal expansion \( (\beta) \) of the solution as well as the corresponding \( \beta \rho_i \) of the two components of the binary mixtures. Using this phenomenological model, we calculate the various physical parameters and TL signal for all our binary solutions under ideal theoretical conditions. The variation in refractive index with concentration \( (dn/dc) \) is simply calculated by differentiating the refractive index of the mixture with the mass fraction of butanol isomers obtained from eq 15. The data obtained from TL experiment is corrected with a fourth order polynomial (Figure 5A) for MeOH and n-BuOH binary liquids mixture series as representative case. The corrected data for all four series of binary mixture is shown in Figure 5B.

The absorbance "Abs" calculated from eq 17 is plotted in Figure 6 with the experimentally measured absorbance of MeOH and n-BuOH binary liquid mixture series as a representative case. The experimentally measured absorbance of the series is in good agreement with the theoretically calculated ones. The thermal contribution to the total TL signal is calculated from the described physical parameters. The contribution of the concentration gradient to the total thermal lens is calculated from eq 9, and TL contribution of the concentration gradient is shown in Figure 7. Here, it is
interesting that the contribution of the concentration gradient TL signal to the total TL signal strongly depends on the molecular structure. The concentration TL signal changes its sign from negative to positive with the volume fraction of MeOH for all the isomers of butanol in the binary mixture series except for t-BuOH. In the case of the t-BuOH binary mixture with MeOH, the concentration TL signal has a negative sign across the concentration of MeOH. The Soret coefficients for the four isomers in the binary mixtures is also calculated by calculating the phase change from eq 7 and 10. The trend in the Soret coefficients for all the butanol series is shown in Figure 7B. In this study, we are able to measure Soret coefficients as low as $10^{-4}$ K$^{-1}$. The Soret coefficient has also changed its sign for three isomers of butanol namely, MeOH + n-BuOH, MeOH + s-BuOH, MeOH + t-BuOH. However, the Soret coefficient for MeOH + t-BuOH series remain negative throughout the concentration changes in MeOH. The magnitude and the change of sign for Soret coefficient strongly depends on the molecular structure.

**CONCLUSION**

The Soret effect was assumed to be a mass-driven process that developed when a mixture of two components was subjected to a temperature gradient. Most of the earlier work on the Soret effect was done on mixtures of two components with different masses. We have shown here that even for molecules with the same mass, their structure has a strong effect on the Soret phenomenon. The effect of molecular structure on the Soret phenomenon, possibly due to the diffusion of the molecular isomers, is different under the thermal gradient. The convection time constant ($t_d$) is smaller for n-BuOH and the highest for the t-BuOH. The molecular branching makes the system sluggish, and molecular drift becomes progressively difficult as in case of t-BuOH. This effect of molecular diffusion is reflected in the Soret coefficient. The Soret coefficient changes its sign across the series of MeOH + n-BuOH, MeOH + s-BuOH, MeOH + t-BuOH. The change of sign in this series has also taken place at different compositions of the two components of the binary liquids mixtures, while the Soret coefficient for the series MeOH + t-BuOH does not change its sign and has a negative magnitude. Thus, our systematic study shows that the Soret effect depends on the molecular structure in addition to the dependence on the molecular mass of the two components.

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**Notes**  
The authors declare no competing financial interest.

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