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ARTICLE

Precise control and measurement of solid-liquid interfacial temperature and viscosity with dual-beam femtosecond optical tweezers in condensed phase

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We present a novel method of microrheology based on femtosecond optical tweezers, which in turn enables us to directly measure and control *in situ* temperature at microscale volumes at solid-liquid interface. A noninvasive pulsed 780 nm trapped bead spontaneously responds to its changes in environment induced by a co-propagating 1560 nm pulsed laser due to mutual energy transfer between solvent molecules and trapped bead. Strong absorption of the hydroxyl group by the 1560 nm laser creates local heating in individual and binary mixtures of water and alcohols. "Hot Brownian motion" of the trapped polystyrene bead gets reflected in the corner frequency deduced from power spectrum. Changes in corner frequency values enable us to calculate the viscosity as well as temperature at the solid-liquid interface. We show that these experimental results can also be theoretically ratified.

1. Introduction

Optical tweezers[1,2] are being used in various fields of research for numerous applications. The principle of optical trapping is based on radiation pressure exerted by light and is mainly used to hold and manipulate various objects with sizes ranging from several nanometers to a few microns. We use 780 nm femtosecond pulsed optical tweezers[3-5] that provide high gradient force from only 7 mW average laser power. Such a high peak-power Gaussian laser beam can easily trap and manipulate small microparticles, nanoparticles or even quantum dots.[6] This trapping wavelength is transparent through water, alcohol, most of the bio-molecule solutions, cells, and is confirmed to be safe and non-invasive due to its very low absorption coefficient.[7] Consequently, temperature rise is negligible for the low laser powers used in such experiments. On the other hand, significant evidence of temperature-rise for 1560 nm pulsed laser occurs because of the strong absorption coefficient at $\upsilon_1 + \upsilon_3$ combination band (*i.e.*, two fundamental vibrational bands are simultaneously excited).[8-10] The vibrational combination band near 1560 nm of hydroxyl, amine and thiol can also be useful for investigating viscosity changes from temperature rise. Earlier, stable 3D trapping of cells, viruses, bacteria, etc. has been demonstrated at 1064 nm continuous wave (cw) laser with low absorption under experimental conditions.[11-14] However, effect on biological systems due to high power 1064 nm absorption arising from vibrational combination band $(2\upsilon_2 + \upsilon_3)$[15,16] of water has also remained a subject of interest. Thus, the possibility to use a single beam laser trap to simultaneously measure thermal effects has its shortcomings.

We have instead devised a two-colour approach, which in contrast, uses one laser at 1560 nm as an independent source of temperature control that is being simultaneously detected by another co-propagating stable laser trap at 780 nm. The co-propagated non-invasive trapping laser at 780 nm probes the effect of pulsed 1560 nm laser. The main uniqueness of this work over already existed methods[17-19] lies in the use of a femtosecond optical trap and a heating laser rather than cw lasers, as well as, in the inclusion of a correction term for the temperature change. Effects of surroundings on bio-systems have often impacted the efficiencies of their physical activities. In this regard, viscosity (η) and temperature (T) are two such physical parameters that have a strong control on the nature of bio-molecular activity.[20-25]

We probe the Brownian motion[26-27] of spherical polystyrene bead suspended in condensed media. Due to Brownian motion, there exists a characteristic frequency of the trapped particle for every trapping laser power, beyond which the particle cannot remain trapped. This characteristic frequency is known as the corner frequency. Our main focus from the newly developed technique is to measure the corner frequency at different heating laser powers, wherein the spherical polystyrene bead spontaneously equilibrates itself to the surrounding temperature. The nature of Brownian motion can be understood by the theory developed by Einstein.[28] The energy transfer occurs between trapped bead and solvents resulting in transformation of thermal energy of solvents into the kinetic energy of the trap bead. Thus the hot solvents molecules resulting from 1560 nm absorption can continuously dissipate heat to the trapped stationary bead which will be reflected on frequency spectrum of Brownian noise exhibited by the bead. Stochastic motion[29] of spherical bead confined in harmonic trapping potential under Gaussian laser pulse having thermal molecular motion will give rise to diffusion, which increases with temperature. Interestingly, the simultaneous increase of diffusion coefficient and corner frequency will keep the net trap stiffness constant. However, the distinct nature of

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individual trapped particles exhibits an independent measure that would elucidate the absolute instantaneous temperature rise at the trapped bead surface-solvent layer. Temperature dependence of viscosity enables us to phenomenologically solve the expression of nonlinear equation for binary liquid mixtures using numerical methods. Our micro-rheological[30-33] investigations on temperature and viscosity of individual and binary solvent media of water and alcohols can be used to map the environmental temperature or viscosity[34] at solid-liquid interface around the confined space of micro to nano size regime.

This contactless temperature measurement in sub-microscale volume also leads to the inception of a new micro-viscometer, which can be used to probe the physical property of a confined system and the effect of surrounding on their behaviour.[35] Furthermore, we can apply our method to elucidate the trapped protein macromolecule[36] structural responses at different solvent and at different temperatures.

Here we demonstrate the measure of local temperature as well as viscosity in water-methanol and water-ethanol binary mixtures both theoretically and experimentally. Our initial model was based only on conduction,[9,37] thereafter, we observed a deviation between the calculated and experimental data towards higher temperatures.[38,39] We show here that it is possible to match experimental results better with a modified model for such liquid mixtures, when we take advantage of our pure sample data. The observed deviation in water has helped to introduce new correction term in the theoretical model. With this approach, our method can be extended to any complex fluid media of solvent mixtures having N-H, S–H, O=C-O–H, P–H groups.

2. Methods and Materials

In our optical tweezers setup (Fig. 1), the laser source used is an Er-doped fibre laser (Femtolite C-20-SP, IMRA Inc. USA), which generates femtosecond laser pulses centred at fundamental 1560 nm wavelength and at its second harmonic 780 nm with pulse-widths 300 fs and 100 fs, respectively. The two laser pulse outputs are collinear at a repetition rate of 50 MHz. A commercial
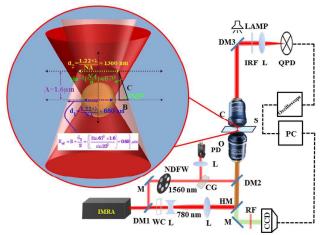

Figure 1. Optical setup with labels: DM (1-3): Dichoric mirror; M: Mirror; CG: Cover glass; NDFW: Neutral Density Filter Wheels; L: Lens; PD: Photodiode; WC: Water cuvette; HM: Hot mirror; O: Objective lens; S: Sample chamber; C: Condenser lens; IRF: Infrared filter; RF: Red filter; QPD: Quadrant photodiode; CCD: Camera (Charge coupled device). Ray – Optics diagram (inset) **(see S1)**

oil immersion objective (UPlanSApo, 100X, 1.4 NA, OLYMPUS Inc. Japan) was used to achieve tight focusing; simultaneously the forward scattered light was collected with another oil immersion objective (60x, PlanAapo N, 1.42 NA, OLYMPUS Inc. Japan) and focused onto a quadrant photodiode (QPD) (2901, Newport Co. USA). The QPD output was connected to a digital oscilloscope (Waverunner 64Xi, LeCroy USA) interfaced with a personal computer through a GPIB card (National Instruments, USA). Data was acquired using LabVIEW program. Spectroscopic grade methanol (MeOH) and ethanol (EtOH) was purchased from Merck, India and were used without any further purification. We used 500 nm mean radius (T8883, Life technology, USA) fluorophore coated polystyrene sphere suspended in H_2O-MeOH and H_2O-EtOH mixtures. The commercially available polystyrene nanosphere solution (T8883: concentration 3.6×10^{10} particles/ml) was diluted to nano-molar concentration and well sonicated for immediate use in trapping experiments. The video of the trapping events was monitored using CCD camera (350 K pixel, e-Marks Inc. USA). White light is used for bright field illumination. Trapping laser power was measured with a power meter (FieldMate, Coherent USA) as well as a silicon amplified photodiode (PDA100A-EC, Thorlabs USA) and 1560 nm power was measured with a calibrated biased InGaAs detector (DET10C/M, Thorlabs USA). All laser power measurements with power-meter were made just before the sample chamber. The absorption spectrum was collected by the absorption spectrometer (Lambda 900, PerkinElmer USA). A linear motorized stage (UE1724SR driven by ESP300, Newport Co. USA) was used, which was interfaced with a personal computer through the GPIB card. We used a mechanical shutter (SR475), controlled through LABVIEW programing, operating at the maximum rate of 100 kHz to result in an opening time that is shorter than or comparable to the thermal relaxation time. Thermal relaxation time is defined as the average time required to achieve maximum temperature at the surface of the bead.[40] The entire experiment has been done twice to ensure that at least 10 data points are averaged for each time point.

3. Results and discussion

1.1 Theoretical Section

When two different colours light beams are focused by the same objective they do not focus at the same plane. Our proposed model (**see S1**) is able to calculate the effective fluence of 1560 nm pulse laser at the focus of 780 nm laser, where the polystyrene particle is trapped. This new approach overcomes the difficulty of two different colour pulsed laser fluence calculation of any desired plane though they focus at different positions with 1.6 µm separation when focused by the same objective as shown in the experimental section (Fig 1). We measured this distance between two colour focal points by placing a thin cover slip sample chamber containing 10^{-4} M Rhodamine-6G in water. The maximum two photon fluorescence (TPF) is emitted from the focal plane of 780 nm laser. This epifluorescence is measured on CCD at the back focal place (Fig. 1). When the illuminated sample is moved with respect to the 780 nm focal plane with a linear motorized stage (of minimum resolution 0.00001 mm), the minimum transmittance signal occurs on the InGaAs 1560 nm detector at a position 1.6 µm further, which is the focal plane of 1560 nm. For this calibration measurement, we placed an aperture just before the InGaAs detector, which replaces DM3 in Figure 1. Using "Law of sines",[41] the fluence of 1560 nm pulsed laser at the focus of 780 nm trapping laser focus can be calculated by the following equation (**see S1**)

$$F_0 = \frac{PulseEnergy}{\pi[\{(\frac{\sin 67^0}{\sin 23^0}\times 1.6)+.68\}\times 10^{-6}]^2} \qquad (1)$$

The half angle of the objective does not change since focal length of the 100X objective is higher (above 100 times) than the separation between the two focal points of two colours (Fig 1). We have thus effectively used the geometric model as a reasonable approximation. The half angle of the cone formed by the focusing laser beam is ~67° calculated from the relation: $NA = n\sin\alpha$, using 1.4 Numerical Aperture (*NA*) of objective lens and refractive index (*n*) of 1.52 for the immersion oil. Using the formula[42]: *focal spot* = (1.22×*λ*)/*NA*, where *λ* is laser wavelength, we calculate the beam waist of 780 nm and 1560 nm laser at focus as 680 nm and 1360 nm respectively. Temperature rise with respect to room temperature (T_0) due to absorption of 1560 nm Gaussian beam by solvent media can be evaluated using the following equation[43]

$$T_{max} - T_0 = 0.783\frac{F}{\tau_p}\frac{2\sqrt{\tau_p}}{\sqrt{\pi K \rho C}} \qquad (2)$$

The total fluence (F) absorbed by solvents used are calculated from: $F = A\times(1-|r_f|^2)F_0$, where F_0 is the laser fluence before the sample chamber and r_f is the reflection coefficient, which is calculated from the cover glass refractive index, n, using the relation: $r_f = \left|\frac{n-1}{n+1}\right|$.

"*A*" is the measured absorbance of binary mixtures in thin sample chamber. The other parameters used in eq 2 (**see S2**) are density (ρ), thermal conductivity (κ), and heat capacity (C) for binary mixtures that can be calculated from the following set of equations, using pure component physical parameters (Table 1)[44-48]:

$$\left.\begin{array}{l} \rho_{mix} = \sum_{i=1}^{j} X_i\rho_i \\[2mm] \kappa_{mix} = \sum_{i=1}^{j} X_i\kappa_i \\[2mm] C_{mix} = \sum_{i=1}^{j} X_iC_i \end{array}\right\} \qquad (3)$$

In eq 3 the index j is 2 for binary mixtures whereas the index i represents the pure component of binary mixtures. Mole fraction (X) is calculated from volume fraction (φ) and molecular weight (M) and density (ρ). We note that use of such an ideal behaviour is impractical for viscosity, which is dependent on intermolecular interaction. The viscosity of binary mixtures is calculated as a result

Table 1. The used physical parameter of the trapping solvent

Sample	Density (ρ) (kg.m^{-3})	Heat Capacity (C) (J.kg^{-1}.K^{-1})	Thermal Conductivity (κ) (W.K^{-1}.m^{-1})	Absorbance ($\mathcal{A}$)
H_2O	997[a]	4180[c]	0.600[e]	
MeOH	786[b]	2250[d]	0.206[e]	
EtOH	785[b]	2440[c]	0.178[e]	
H_2O-EtOH mixture	990	4120	0.586	0.113
H_2O-MeOH mixture	987	4090	0.581	0.117

[a]From ref 44; [b]From ref 45; [c]From ref 46; [d]From ref 47; [e]From ref 48

of temperature rise (Tables 2 and 3) from following equations[49-51]

$$\ln \eta_{binary\ mix} = \varphi_1 \ln \eta_1 + \varphi_2 \ln \eta_2 + \Delta\ln\eta^{excess} \qquad (4)$$

$$\eta_{binary\ mix} = \exp\left\{(0.9\times\ln(2.414\times10^{-2}\times10^{\frac{247.8}{140-T}}))+(0.1\times(A_i+\frac{B_i}{C_i+T}))+\Delta\ln\eta^{excess}\right\} \qquad (5)$$

Here $\Delta\ln(\eta^{excess})$ is the excess viscosity due to mixing, which is calculated by using the method developed by Wolf et. al.[52,53] For each individual alcohol, A, B and C are the Vogel's equation parameters (**see S3**).

2.1 Experimental Section

We have used pulsed laser at 780 nm with 7 mW of average power to trap the polystyrene bead of 500 nm mean radius. The solvent media used are: H_2O-EtOH mixture and H_2O-MeOH mixture. In both the cases, a volume ratio of 90:10 is used. The trapping laser can be considered non-invasive due to very low absorption coefficients of the solvents used.[54] Simultaneously, we also irradiated our trapped volume by 1560 nm IR laser where binary solvents have high absorption coefficients resulting in local heating around the trapped particle. The beam waist spot size of trapping laser is 680 nm and heating laser is 1360 nm whereas the effective heating beam radius at the trapping plane is out of the Rayleigh range ($\pi\omega_0^2/\lambda$=931 nm) as the separation is 1.6 µm (see theoretical section for details). Due to temperature rise, the trapped 500 nm mean radius particle will show a different behaviour, which is reflected in its "Hot Brownian motion".[55-57] We measure the temperature change between polystyrene bead surface and surrounding liquid layer (through the corner frequency shift) to indicate that thermal flow exists, and the bead displacement due to this flow is coupled with that of a regular confined Brownian motion. We only correlate the measured displacement of the confined Brownian motion as long as our temperature change is not very large according to our model. We have thus probed the confined Brownian motion of the polystyrene bead trapped in a harmonic potential[58] generated by a Gaussian laser pulse, which can be described by the Langevin equation[59]

$$m\ddot{x}(t) + \gamma\dot{x}(t) + \kappa_{TS}x(t) = \zeta_{therm}(t) \qquad (6)$$

where m denotes particle mass, x signifies time dependent position, γ is the viscous drag coefficient as per Stokes' Law, κ_{TS} is the spring constant (or Trap Stiffness) and ζ_{therm} is the time dependent random force. By solving the above equation, we can fit our experimental one-sided power spectrum. Typically, in power spectrum, power is measured in the interval f and f+df, which does not distinguish between +f and –f. In such cases, it is possible to define one-sided power spectral density[60] (PSD) (**see S4**) by the following Lorenzian[61]

$$p_x(f) = \langle p_x(f)^{(exp)}\rangle = \frac{A}{(f_c^2 + f^2)} = \frac{D}{\pi^2(f_c^2 + f^2)} \qquad (7)$$

Here A is a fitting parameter which has information about D, the diffusion coefficient. "A" has a unit V^2/sec. Diffusion coefficient can be evaluated from A using voltage to position calibration[62,63] factor. We have analysed the forward scattered data of trapped bead that has been collected with QPD at 20 kHz sampling rate for the first 2.5 seconds of trapping. This is to minimize convection effects. The acquired data of channel X and Y is de-correlated by removing the cross-talk[61,64] between them. The processed data is then fitted with eq 7 to obtain the respective corner frequency within different solvents and at different 1560 nm laser heating powers.

We observed an increasing trend in the corner frequency (f_C), which is deduced from the power spectrum (Fig. 2a, b) with an increase in 1560 nm laser power. From our theoretical model (see eq 2), we notice that there is a linear relationship between 1560 nm
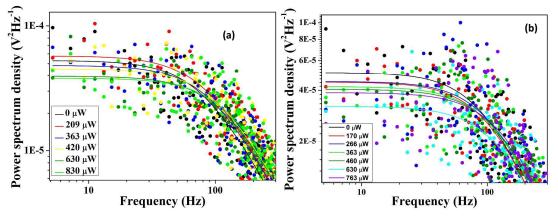

Figure 2. Experimentally measured power spectrum (Scatter points) and respective Lorenzian fitted data (Solid line) for 500 nm radius fluorophore coated polystyrene bead in (a) water-ethanol mixture (b) water-methanol mixture

Table. 2 Theoretical and experimental data for 90:10 (volume-wise) a H_2O-EtOH mixture

1560 nm Power (μW)	Corner Frequency (Hz)	Fluence (J/m^2)	Theoretical data				Experimental data	
			T_{max}–T_0 (K)	Viscosity (Pa.s)X10^{-3}	Corrected ΔT_{theo}	Corrected Viscosity (Pa.s)X10^{-3}	Temperature rise (K)	Viscosity (Pa.s)X10^{-3}
0	83	0	0	1.60	0	1.60	0	1.60
209	88	0.0672	7.6	1.32	5.5	1.35	2.2	1.51
363	96	0.1167	13.2	1.23	9.6	1.29	6.1	1.38
420	110	0.1351	15.3	1.19	11.1	1.25	12.5	1.20
630	119	0.2026	22.9	1.10	16.6	1.18	16.2	1.11
830	133	0.2669	30.2	1.02	21.9	1.10	21.5	0.99

Table. 3 Theoretical and experimental data for 90:10 (volume-wise) a H_2O-MeOH mixture

1560 nm Power (μW)	Corner Frequency (Hz)	Fluence (J/m^2)	Theoretical data				Experimental data	
			T_{max}–T_0 (K)	Viscosity (Pa.s)X10^{-3}	Corrected ΔT_{theo}	Corrected Viscosity (Pa.s)X10^{-3}	Temperature rise (K)	Viscosity (Pa.s)X10^{-3}
0	106	0	0	1.30	0	1.30	0	1.30
170	116	0.0547	6.5	1.14	4.8	1.18	3.9	1.19
266	122	0.0855	10.1	1.10	7.4	1.14	6.2	1.13
363	129	0.1167	13.8	1.05	10.2	1.10	8.8	1.07
460	137	0.1479	17.5	1.00	12.9	1.06	11.5	1.01
630	143	0.2026	23.9	0.93	17.6	1.00	14.0	0.96
763	150	0.2454	29.0	0.88	21.4	0.96	16.1	0.92

laser power and the corresponding temperature rise. Simultaneously, from eqs 4 and 5, we note that viscosity decreases with increase in 1560 nm power. Within our experimental range, when the viscosity change with respect to temperature change lies in the linear regime, we have considered the trap stiffness (κ = 2πf_Cγ) as a constant parameter. This statement is correct as long as there is a continuous change in viscosity with the heating laser source for a constant-sized trapped particle in the same solvent medium (**see S5**). This has enabled us to measure (Tables 2 and 3) the viscosity change and temperature rise around the interface of trapped bead and surroundings solvent molecules from the formula η.f_C = constant.[19,65] All our experimental measurements are performed with respect to the room temperature viscosity at the corresponding corner frequency in individual binary solvents when 1560 nm laser is absent.

Experimentally, we first observe the corner frequency change, which allows us to calculate viscosity around the trapped bead. From our experimentally measured viscosity, we calculate the temperature rise of the respective binary mixtures (Tables 2 and 3) by rearranging the variables in eq 5 and solving with MATLAB®. The particle experiencing viscous drag, $\gamma = 6\pi\eta r$ (r = 500 nm) has trap stiffness, κ_{TS} for H_2O-EtOH, H_2O-MeOH binary mixtures as 0.0078±0.0002 pN/nm and 0.0081±0.0002 pN/nm respectively. The confidence range of our trap stiffness (**see S5**) results are obtained by the standard deviation of all stiffness measurements at different temperatures. As expected, viscosity changes around the trapped bead with respect to temperature changes are linear (Fig. 3a). Our experimental data in Tables 2 and 3 show that the temperature rise between theoretical calculation and experimental measurement deviates with increase in temperature, which is also true for viscosity. This is due to the fact that besides conduction, convection also plays an important role in heat transfer towards high temperature, since with temperature rise, the focal plane separation changes. Refractive index changes as a result of diverging optical lens[66] formed in solvent media with temperature increase at focal volume. Additionally, due to the high NA objective, there could be critical angle effect, which could consistently result in overestimating our theoretically estimated temperature change.

Consequently, the separation of focal points for the two laser wavelengths becomes slightly more, which reduces the temperature at focal volume around optical trap and this is reflected in our experimental results. To account for this, we add a correction term to eq 2 from our earlier study (**see S6**) and generalize it for use in binary mixtures:

$$T_{max} - T_0 = 0.783\frac{F}{\tau_p}\frac{2\sqrt{\tau_p}}{\sqrt{\pi K\rho C}} - \left\{ x_1[(\frac{dT}{dP})_{Theo} - (\frac{dT}{dP})_{Exp}]C_1 \right. \\ \left. + (1-x_1)[(\frac{dT}{dP})_{Theo} - (\frac{dT}{dP})_{Exp}]C_2 \right\} \times P_{avg} \quad (8)$$

Since water is the dominant species in our particular experiments, we can simplify eq 8 further as follows:

$$T_{max} - T_0 = 0.783\frac{F}{\tau_p}\frac{2\sqrt{\tau_p}}{\sqrt{\pi K\rho C}} - [(\frac{dT}{dP})_{Theo} - (\frac{dT}{dP})_{Exp}]C_1 \times P_{avg} \quad (8a)$$

Here C1 represents pure water while the other parameters are the same as explained in the theoretical section. In pure water, the
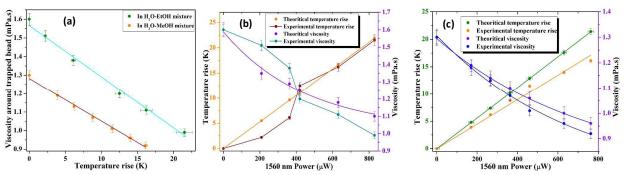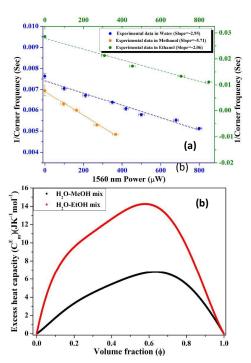

Figure 3. (a) Experimental data for viscosity versus temperature rise (scatter plot) around trapped bead and corresponding linear fitting (solid line). The comparison of our theoretically corrected data for temperature rise (Left side Y axis) and viscosity (Right side Y axis) with experimental data in the respective (b) water-ethanol mixture and (c) water-methanol mixture.

theoretical gradient of temperature rise, calculated from eq 2, is: $(dT/dP)_{Theo}$=0.034 K/µW, while the measured experimental gradient of temperature rise is: $(dT/dP)_{Exp}$=0.024 K/µW. The correction term introduced is the difference of these two values for binary solvent mixtures in eq 8a. We plot the corrected theoretical temperature rise and the corresponding viscosity in Figures 3b and 3c for H_2O-EtOH and H_2O-MeOH respectively and compare them to the corresponding experimental data (also presented in Tables 2 and 3). For theoretical calculations, we first estimated the temperature rise $(T_{max}-T_0 (K))$ from applied 1560 nm pulse laser fluence using eq 2, which is converted via eq 5 to measure the surroundings viscosity. The corrected ΔT_{theo} is evaluated from eq 8a, which is again transformed to measure the corrected viscosity using eq 5.

It is important to note from figure 3b that we observed a very unusual experimental behaviour of temperature rise (ΔT) and viscosity (η) in the H_2O-EtOH binary mixture. This is in spite of the fact that the theoretical temperature rise (ΔT) followed a linear increase with 1560 nm laser power, and the viscosity (η) followed the Vogel equation. This unusual behaviour is due to the loss of individual property of the constituent liquids in the binary mixtures, which is better explained in terms of non-ideal behaviour of the

binary mixture as presented in figure 4. Figure 4a shows the comparative plot of the slope of $1/f_C$ with 1560 nm laser power for water with methanol as well as ethanol. The distinct behaviour of the nature of trap is evident from the distinct slopes in figure 4a for the three pure liquids, i.e., water (-2.95), methanol (-5.71) and ethanol (2.06), which also conform to the trend in the respective viscosities (η) of these pure liquids ($\eta_{EtOH}>\eta_{H2O}>\eta_{MeOH}$). These numbers are indicative of the fact that the intermolecular forces in pure water and in pure ethanol are more similar as compared to the intermolecular forces in pure methanol. This would mean that in case of binary mixtures of water with ethanol or methanol, the water-ethanol mixture would overall have more intermolecular force as compared to that of water-methanol. To further ratify our conjecture obtained from figure 4a, we plotted the comparative excess heat capacity in figure 4b, which shows that for 10% volume mixture of H_2O-MeOH and H_2O-EtOH, the excess heat capacity, $C_{p,mix}^E$, of water-ethanol mixture (6.69 $JK^{-1}mol^{-1}$) is higher than that of water-methanol mixture (1.74 $JK^{-1}mol^{-1}$).

ARTICLE

Journal Name

Figure 4. (a) Comparative plot of Inverse corner frequency versus power of 1560 nm femtosecond laser with linear fitting (Solid line) of water with pure MeOH and pure EtOH (b) The comparison between excess heat capacity of H_2O-MeOH (black line) and H_2O-EtOH (red line) binary mixture at 25^OC.

Since excess heat capacity is the measure of deviation from ideal nature of mixtures, water-ethanol shows higher deviation from ideal behaviour as compared to water-methanol. This corresponds to our figure 3 observation that water-methanol mixture follows the expected trend of 1560 nm laser heating while water-ethanol mixture shows deviation.

The isobaric molar heat capacity of the binary mixture can be expressed by eqs 9 and 10. Thus, the excess heat capacity can be calculated by using eq 11[67]:

$$\left(\frac{\partial H_{m,mix}}{\partial T}\right)_p = X_{C1}\left(\frac{\partial H_{m,C1}}{\partial T}\right)_p + X_{C2}\left(\frac{\partial H_{m,C2}}{\partial T}\right)_p + \left(\frac{\partial H_m^E}{\partial T}\right)_p \quad (9)$$

$$C_{p,m,mix} = X_{C1}C_{p,C1} + X_{C2}C_{p,C2} + C_{p,mix}^E \quad (10)$$

$$C_{p,mix}^E = \phi(1-\phi)\sum_{i=1}^{n}a(1-2\phi)^{i-1} \quad (11)$$

where C2 represents the second component of the binary mixture with water, H is enthalpy, φ is volume fraction of water and "a" value is used from the reference [67].

Thus, our experimental results follow our theoretical framework that we have developed for measurement of sub-micron volume temperatures as well as viscosity. For trapping polystyrene beads, individual solvents like H_2O, MeOH and EtOH are good solvents and they are also miscible among each other.[68] We report our findings for 90:10 volume mixture of H_2O-EtOH and H_2O-MeOH. After 10% volume mixture the viscosity of water-alcohol mixture increases expeditiously.[69] Higher viscosity results in lower corner frequency. Thus, the corner frequency shift due to temperature rise will be small, which will decrease experimental signal to noise ratio.

4. Conclusions

In this work, based on a non-invasive 780 nm femtosecond optical trap, we have demonstrated control and measurement of direct *in situ* temperature at solid-liquid interface, induced by a co-propagating 1560 nm pulsed laser. The viscosity as well as temperature around the trapped bead has been measured from changes in corner frequency values. These measurements represent that the thermal energy of solvents is transformed into the kinetic energy of the trapped bead. Correspondingly, we have developed a theoretical model that can explain these experimental results. Last but not the least, we were also able to probe the intermolecular interaction between two closely behaving solvent molecules.

Acknowledgements

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