Thermal conductivity measurement of organic solvents incorporated with silver nanoparticle using photothermal techniques

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Abstract: The present paper summarizes our recent work on heat transfer of nanofluid in different organic solvents determined using photothermal techniques. UV-Visible absorption spectrum shows an intense surface plasmon absorption peak at 427 nm. TEM indicates the presence of well dispersed silver nanoparticles having spherical morphology with particle size ranging from 10 to 13 nm. The experimental results show that thermal conductivity of organic solvents increases with the incorporation of silver nanoparticles.

1. Introduction.
The Heat transfer fluids such as water, ethylene glycol and mineral oils etc have immense applications in the field of power generation, chemical production, automobiles, computing processes and refrigeration. Nanofluids are colloidal suspensions engineered from conventional base fluids by dispersing solid nanoparticles (less than 100 nm). Metallic nanoparticles, particularly silver nanoparticles have strong absorption in the visible range due to surface plasmon resonance and have got much attention from chemical industry and medicine due to unique properties such as high thermal conductivity, high resistance of oxidation, and antibacterial activity. Nowadays, highly sensitive photothermal techniques such as thermal lens and photoacoustic techniques are utilized to investigate thermal parameters (thermal diffusivity and effusivity) of nanofluids. The thermal diffusivity is the quantity which measures the rate of heat diffusion through the sample and thermal effusivity is a measure of its ability to exchange heat with its surroundings. The thermal diffusivity $\alpha$ and thermal effusivity $e$ can be related to thermal conductivity by $e = \frac{k}{\sqrt{\alpha}}$. 
2. Experimental
In order to synthesize silver nanoparticles numerous methods have been adopted including chemical reduction method, polyol method and radiolytic process. For the present study citrate reduction method is used for the preparation of silver nanofluid. The silver nanofluid is then diluted to 0.16mM in ethylene glycol and ethanol respectively. The absorption spectrum recorded exhibits an intense absorption peak at 427 nm due to surface plasmon absorption and TEM indicates spherical silver nanoparticles of size ranging from 10-13 nm, which is shown in figure 1 (a and b).

![Absorption spectrum of Ag nanofluid](image)

**Figure 1** (a) Absorption spectrum of Ag nanofluid (b) TEM image of silver nanoparticle

3. Result and Discussions
3.1. Thermal lens measurement
Thermal lens technique is highly sensitive and powerful technique enough to measure very small refractive changes due to the temperature variations in the medium. Such refractive changes can be thermally induced by the gaussian laser beam which is the fundamental principle of thermal blooming technique. Due to this modification in refractive index, the medium mimics a lens, called thermal lens (TL). The experimental setup for the thermal diffusivity measurement is shown elsewhere[1]. Gordon et al. [2] reported a detailed theoretical analysis of the formation of thermal lens. The expression for the time dependent probe beam intensity is given by

\[ I(t) = I(0) \left[ 1 - \theta (1 + t_c / 2t)^{-1} + \frac{1}{2} \theta^2 (1 + t_c / 2t)^{-2} \right]^{-1} \]

(1)

The parameter \( \theta \) and \( t_c \) can be generated by fitting equation (1). The characteristic time constant \( t_c \) is related to the thermal diffusivity \( D \) and beam radius \( \omega \) through the relation

\[ t_c = \frac{\omega^2}{4D} \]

(2)

To eliminate the uncertainty in the determination of beam radius, a reference sample with known thermal diffusivity is used to determine the thermal diffusivity of unknown sample. From this we can calculate the thermal diffusivity \( D \) as

\[ D = D_{\text{reference}} \frac{t_{\text{reference}}}{t_c} \]

(3)

Here water is used as the reference sample with known thermal diffusivity \( 14.3 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \). Thermal diffusivity of ethanol /ethylene glycol nano mixtures shows an enhancement with respect to pure solvents [3] and solvent –water mixtures as given in table 1. The thermal lens decay curve of Ethylene glycol/nano mixture is given in figure 2 and the variation of the intensity of the TL signal with time was studied.
3.2. Photoacoustic measurement

The microphone based open cell photoacoustic (PA) technique depends upon the detection of pressure fluctuations in a closed cavity created by the periodic thermal waves from the sample. The experimental arrangement and detailed theory for the thermal effusivity measurement is shown elsewhere [4]. The thermal effusivity of organic solvents incorporated with silver nanofluid can be calculated according to Rosencwaig-Gersho theory of PA effect [5]. Sikorska et.al. [6] modified the expression for thermal effusivity $e$ by including the thermal effusivity value of known sample. The expression for thermal effusivity value is rewritten as

$$e_s = \frac{\sqrt{(e_d \sqrt{d} + 1)^2 + 1 - R^2}}{R} - 1$$

(4)

where, $d = (e_s l_s)^2 \frac{\alpha_s}{\pi f}$, $\alpha$ represents thermal diffusivity and $l$ denotes the thickness of aluminium foil, subscripts $s$ and $x$ refer to the metal foil and liquid respectively. By measuring the ratio of PA amplitudes as a function of modulation frequency $f$, one can evaluate the thermal effusivity value. Compared to pure solvents [7], solvent-nano mixtures showed an enhancement in thermal effusivity.

The thermal conductivity of organic solvents can be calculated using the relation $e = \frac{k}{\sqrt{\alpha}}$ by putting the corresponding values of thermal diffusivity and thermal effusivity and is shown in table1. There are several mechanisms proposed for the experimentally observed enhancement in thermal properties of the nanofluids. In the present study when silver nanofluid is added to organic solvents an enhancement in thermal conductivity was observed. Since water has a higher thermal conductivity than organic solvents, any presence of water in organic solvents would lead to an increase in the effective thermal conductivity. The prepared silver nanofluid is water based and therefore the presence of water in solvent-nanofluid mixture could lead one to erroneously conclude that the measured enhancement is due to the presence of nanoparticles. In order to ensure that whether the enhancement is due to the presence of water or nanoparticles, we measured the thermal conductivities of both the solvent-water mixture and solvent-nano mixture. From the result it is clear that thermal conductivity of solvent nano mixture is greater than that of solvent-water mixture. The increase in thermal diffusivity.
of binary (solvent-water) solution with respect to pure organic solvents may be explained on the basis of cohesive interactions due to hydrogen bonding within the solutions.

Table 1. Thermal parameters of organic solvent-nanofluid mixtures.

| Sample                | Thermal diffusivity $\alpha$ ($10^{-8}$ m$^2$/s) | Thermal effusivity $e$ ($10^{-4}$ W$^{1/2}$/m K$^{-1}$m$^2$) | Thermal conductivity ($W/mK$) |
|-----------------------|---------------------------------------------------|---------------------------------------------------------------|-------------------------------|
| Solvent-water mixture | 10.5 ± 0.1                                        | 0.108 ± 0.001                                                 | 0.3669                        |
| Solvent-nano mixture  | 13.2 ± 0.1                                        | 0.101 ± 0.001                                                 |                               |
| Solvent-water mixture | 0.072 ± 0.001                                     | 0.067 ± 0.001                                                 |                               |
| Solvent-nano mixture  | 0.2387                                            |                                                               |                               |

Influence of nanoparticles on the thermal diffusivity of organic solvents can be explained on the basis of nanolayers. Liquid molecules close to a solid surface are known to form layered structures. The layered molecules are in an intermediate physical state or acts as a thermal bridge between a bulk liquid and a solid nanoparticle [8]. This solid-like nanolayer of liquid molecules would be expected to be the reason for thermal conductivity enhancement in organic solvent-nano mixtures.

4. Conclusions

Photothermal techniques have been successfully utilized for the evaluation of thermal conductivity of organic solvent-nanofluid mixtures. Enhancement in thermal conductivity was observed with the incorporation of silver nanoparticles.

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