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Enhanced thermal diffusivity of water in the presence of iron oxide nanoparticles: a laser induced thermal lens measurement

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Abstract

Iron oxide nanoparticles are prepared using co-precipitation method and its thermal diffusivity as a function of concentration in distilled water is measured using laser induced thermal lens technique. The morphology, distribution and particle size are determined using SEM measurements. The elemental composition and optical properties of the sample are obtained from EDAX and UV–visible absorption spectra. It is found that the thermal diffusivity of the nanoparticle solution is larger than that of pure water at low concentrations but it is decreasing with increase in concentration of the nanoparticles. Variation of electrical conductivity and magnetic susceptibility of the same sample are also studied.

Introduction

Several studies have been done on the synthesis and characterizations of metal oxide nanoparticles, especially those exhibiting magnetic behaviour. Among this iron oxide, magnetite ($\text{Fe}_3\text{O}_4$) and maghemite ($\text{Fe}_2\text{O}_3$) have attracted significant attention and are getting the greatest interest of current scientific research due to their important physicochemical properties. These particles find many interesting applications in technological and scientific fields such as materials science, chemistry, biochemistry, environmental remediation, medical imaging etc [1]. It is one of the traditional magnetic materials used in magnetic storage media, catalysis, solar energy transformation, electronics and ferrofluids [2]. However, the thermal diffusivity measurements reported in this paper is first of its kind for iron oxide nanoparticles dispersed in a liquid media.

Thermal lens technique is an established non-contact and non-destructive method for the thermal diffusivity measurements of liquid samples. Absorption of energy from a laser beam by a sample produces local heating inside the medium due to the non-radiative de-excitation of energy which results in thermal blooming or thermal lensing. A radially dependent temperature distribution is created which produces a refractive index variation with temperature [3]. A change in the value of refractive index due to thermo-optic effect generates a virtual optical element (lens) within the sample, thereby changing the propagation properties of the laser beam passing through this element [4–6]. The thermal lens method is employed in a wide variety of measurements such as for the photochemical reaction kinetics, for the determination of the effect of size and concentration of gold nanoparticles on thermal diffusivity of the nanofluids [7, 8].

After the first report of the thermal lens effect with theoretical explanations assuming a parabolic thermal lens approximation by Gordon and his co-workers, an aberrant model of the thermal lens was proposed by Sheldon et al for a single beam or mode-matched double beam thermal lens configurations and later a general aberrant model for all types of thermal lens experimental configurations is proposed by Shen et al [1–5]. In our work, we have used Shen’s aberrant model for our continuous wave single beam thermal lens configuration. The main objective of our work is to study the variation of thermal diffusivity as a function of concentration of iron oxide nanoparticles in distilled water. In addition to this, electrical conductivity and magnetic susceptibility were also measured using standard conductivity meter and Quincke’s apparatus respectively, and the effects of concentration of iron nanoparticles on these parameters are also reported.

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Materials and methods

Materials required: Ammonium ferrous sulphate hexahydrate \((\text{NH}_4)_2\text{Fe(SO}_4\_6\text{H}_2\text{O})\), Ferric chloride anhydrous \((\text{FeCl}_3)\), Sodium lauryl sulphate \((\text{NaC}_12\text{H}_25\text{SO}_4)\), Sodium hydroxide \((\text{NaOH})\), Hydrochloric acid \((\text{HCl})\).

Chemical co-precipitation method is used for the synthesis of iron oxide nanoparticles. Modified Massart’s method is used with a small amount of anionic surfactants \([9]\). Ammonium ferrous sulphate hexahydrate and ferric chloride anhydrous are taken in a stoichiometric proportion of 1:2 and 1mM sodium lauryl sulphate is added to the reacting mixture under magnetic stirring as an anionic surfactant to avoid agglomeration. Initial pH reading is noted as 2 and 2molar NaOH Solution is added drop-wise until the pH meter reads 12, and is stirred using a magnetic stirrer having heating facility. On addition of basic solution, colour of the reacting mixture turns black indicating the formation of iron nanoparticles. 1N HCl solution is prepared and is added drop-wise to neutralise the solution. The chemical reaction is,

\[
\text{Fe}^{2+} + 2\text{Fe}^{3+} + 8\text{OH}^{-} \rightarrow \text{Fe}_3\text{O}_4 + 8\text{H}_2\text{O}
\]

Here \(\text{Fe}_3\text{O}_4\) formed is magnetite, which on further oxidation gives maghemite \(\gamma\text{Fe}_2\text{O}_3\).

\[
\text{Fe}_3\text{O}_4 + 2\text{H}^{+} \rightarrow \gamma\text{Fe}_2\text{O}_3 + \text{Fe}^{2+} + \text{H}_2\text{O}
\]

The obtained solution is washed several times, and is filtered and dried to obtain iron oxide nanoparticle powder. Figure 1 explains the experimental procedure for the synthesis of iron oxide nanoparticles.

Confirmation of formed iron oxide nanoparticles is done by various characterization techniques including SEM, EDAX, and UV–visible absorption spectrum.

In order to study the variation of thermal, electrical and magnetic properties with concentrations, the thus obtained dried iron oxide nanoparticle powder is dispersed in distilled water for 10 different concentrations. The SEM image of the synthesised iron oxide nanoparticles is shown in the figure 2. The morphology and arrangement of particles is examined by SEM analysis. It shows uniformly distributed monodisperse particles which are spherical and cubic-spline in shape which confirms the formation of iron oxide nanoparticles. In order to find the average particle size from the SEM image, particle sizes of randomly selected 183 particles are noted from the SEM image and the number of particles for a bin of 3 nm is noted. A Gaussian distribution is fitted to this data plotted with particle size (nm) along the X-axis and number of particles along the Y-axis and is shown in the figure 3. The distribution of particle size is found to be in good agreement with the Gaussian function with peak value at 37.6 nm.

EDAX spectra of the same sample is shown in the figure 4. From the EDAX spectra of iron oxide nanoparticles, no other peaks related to any impurities has been detected in the EDAX, confirms that the grown nanoparticles are composed of iron and oxygen only. Elemental composition of the same sample is also shown in the table 1.

From the table, we can see that the elemental composition of iron and oxygen is found to be 46% and 54% respectively. Thus confirms the formation of iron oxide nanoparticles.

Figure 5 shows the UV-Visible absorption spectrum of iron oxide nanoparticles dispersed in distilled water. In the electronic spectra of iron oxides, three transitions are possible, namely, \(\text{Fe}^{3+}\) ligand field transitions in the spectral regions of 1000-900 and 700-600 nm and the pair excitations or double exciton processes which occurs...
at 550–485 nm due to the simultaneous excitation of the magnetically coupled adjacent Fe$^{3+}$ cations. In addition to that for wavelengths shorter than 400 nm there is a ligand to metal charge transfer transitions (LMCT) [10]. In our measurement two of the above mentioned three transitions are visible. In figure 5 we can see a major peak in between 200 and 300 nm and a broad peak in between 300–400 nm which are due to the Fe$^{3+}$ ligand to metal charge transfer transitions and a very small shoulder peak is obtained in between 500 and 550 nm which is due to the pair excitation by the simultaneous excitation of magnetically coupled adjacent Fe$^{3+}$ cations. Ligand field transitions are not observable in this spectrum because of the low concentration, (0.0528 wt%) of nanoparticles in water.

To determine the thermal diffusivity of iron oxide nanoparticles, laser induced thermal lens technique is used. In our experimental setup (figure 6), we have used a 50 mW, 532 nm DPSS laser having a Gaussian beam intensity distribution to irradiate the sample placed inside a 5 mm cuvette. The laser intensity is appropriately reduced with the help of a neutral density filter to get a good thermal lens signal without overheating the sample. A part of the incident radiation is absorbed by the sample and corresponding non-radiative decay of the excited state population results in local heating of the medium. A homebuilt electromagnetic high speed shutter (response time 0.2 ms) is used to turn on/off the laser beam. A 10 mm focal length plano-convex lens is used to focus the beam on the sample to increase the intensity within the sample. Thermal lens is produced within the sample due to a change in refractive index of the heated sample due to the absorption of the light. On absorption
of light local heating of the sample occurs, temperature distribution in the medium mimics the intensity distribution of the beam. Since liquids expand on heating, density in the central portion where the beam falls decreases and refractive index is also decreased, and hence a refractive index gradient is created in the medium. Hence the sample itself acts as a concave lens and causes the beam to diverge out. A mirror is used to reflect the diverged beam towards the photo-detector. In order to detect the expansion of the probe beam, only a small portion of the beam, the centre, has to be monitored so that the expansion of the beam will result in a decrease in intensity. To achieve this, the beam is made to pass through a pin-hole placed in front of the detector and its

![Figure 4. EDAX spectrum of iron oxide nanoparticles.](image)

**Table 1. Elemental composition of iron oxide nanoparticles.**

| Element     | Weight% | Atomic% |
|-------------|---------|---------|
| Oxygen (O)  | 25.17%  | 54%     |
| Iron (Fe)   | 74.83%  | 46%     |

![Figure 5. UV–Vis absorption spectra of iron oxide nanoparticles in water (0.0528 wt%).](image)
position is adjusted such that only a small portion at the center of the beam reaches the detector. The photodiode output is amplified and fed to a digital storage oscilloscope and to the computer where it is processed.

The growth (divergence) rate of the beam depends on the thermal properties of the sample used, primarily the thermal diffusivity, where thermal diffusivity is defined as

\[ D = \frac{k}{\rho C_p} \]  

where \( k \) is the thermal conductivity, \( \rho \) is the density, and \( C_p \) is the specific heat capacity.

The observed temporal variation of the thermal lens signal is fitted with the aberrant model developed Shen et al as given by [5]

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

where the variable \( t_c \) is related to thermal diffusivity of the sample through the relation

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

where \( \omega \) is the laser beam spot size inside the sample. The experimental setup is calibrated using distilled water as sample, whose thermal diffusivity is measured as \( 1.45 \times 10^{-7} \text{ m}^2 \text{ s}^{-1} \). The fit parameters used are \( m = 1, \ V = 0.3, \) and \( \omega = 92 \mu \text{m} \).

For the measurements of electrical conductivity and magnetic susceptibility of the same sample standard conductivity meter and Quincke’s apparatus were used. It can be used to analyse the variation of these parameters with concentrations.

**Results and discussion**

Iron oxide nanoparticle are prepared at different concentrations in distilled water and thermal lens measurements are carried out in each of these samples. Temporal development of the thermal lens signal from 0.0528 weight percentage of \( \gamma \)-Fe\(_2\)O\(_3\) in water is given in figure 7. The variation of thermal diffusivity as a function of concentration is plotted in the figure 8. The absorption coefficient of the lowest concentration sample is 0.065 cm\(^{-1}\) and that of highest concentration sample is 0.602 cm\(^{-1}\) at 532 nm.

It can be seen that the thermal diffusivity is decreasing with increase in concentration. The behaviour of decrease in thermal diffusivity with concentration is already reported for a ferronematic fluid, measured using different method. [11]. Although it is not clear to us why the thermal diffusivity decreases with increase in concentration range we measured, it is reasonable to assume that the rate increase of specific heat capacity might be greater than the rate of increase of thermal conductivity, which results in the decrease of thermal diffusivity with increase in concentration. It should be noted that the lowest value of the thermal diffusivity for the highest iron oxide nanoparticle concentration we studied is of the order of the thermal diffusivity of pure water, meaning the addition of iron oxide nanoparticles enhances the thermal diffusivity of water. We could not increase the nanoparticle concentration further as the particles are found to aggregate and sediment at higher concentrations.
Still it is very interesting to see that the small concentration of iron oxide nanoparticles in water gives higher thermal diffusivity than high concentration of nanoparticles. Magnetic susceptibility of the same samples are also determined and its variation with concentration is studied. Mass Magnetic susceptibility $\chi_{\text{mass}}$, measured in $m^3/kg$ indicates the degree of magnetization of a material in response to an applied magnetic field. Quincke’s method is a simple method to determine the magnetic susceptibility of paramagnetic or diamagnetic substance in liquid form. Figure 9 gives the variation of magnetic susceptibility of water with the concentration of the nanoparticles. For all the 10 samples we measured, mass magnetic susceptibility is found to be within the range of $-11.72 \times 10^{-9} m^3 kg^{-1}$ and $-9.097 \times 10^{-9} m^3 kg^{-1}$, with an average value of $-9.88 \times 10^{-9} m^3 kg^{-1}$ which is nearly close to the measured magnetic susceptibility value of pure distilled water $-9.83 \times 10^{-9} m^3 kg^{-1}$ using the same experimental setup (literature value of water is $-9.051 \times 10^{-9} m^3 kg^{-1}$). Also we have not observed any measureable systematic increase or decrease in the susceptibility values within the iron nanoparticle concentration we used for the investigations. This indicates that the concentration of iron nanoparticles we used is so small to alter the magnetic susceptibility of water.

To measure the electrical conductivity of the prepared iron oxide nanoparticles, we have used standard conductivity meter, which is calibrated using distilled water, and electrical conductivity of all these 10 different

Figure 7. Thermal lens signal from 0.0528 weight percentage of $\gamma$-Fe$_2$O$_3$ in water.

Figure 8. Variation of thermal diffusivity for different weight percentage of iron oxide nanoparticles in water.
samples are determined. The variation of electrical conductivity with concentrations is evaluated and is plotted graphically in the figure 10. It is found that the electrical conductivity is increasing with increase in concentration as we expected. When the concentration of iron oxide nanoparticles increases, the number of metallic nanoparticles for conduction increases and hence the electrical conductivity also increases.

Conclusion

In summary, Thermal, magnetic and electrical properties of iron oxide nanoparticles dispersed in water were studied by laser induced thermal lens set up, Quincke’s apparatus and standard conductivity meter. The synthesis and characterizations of maghemite nanoparticles were confirmed by SEM, DLS, EDAX and UV-Visible absorption spectrum. Thermal diffusivity of iron oxide nanoparticles were calculated, is found to be decreasing with increase in concentrations, although the overall thermal diffusivity of iron nanoparticle in water is greater than that of pure water. The magnetic susceptibility was measured using Quincke’s apparatus, but magnetic susceptibility is found to be constant in a range of \(-11.72 \times 10^{-9} \text{ m}^3 \text{ kg}^{-1}\) and \(-9.097 \times 10^{-9} \text{ m}^3 \text{ kg}^{-1}\), with an average value of \(-9.88 \times 10^{-9} \text{ m}^3 \text{ kg}^{-1}\) which is nearly close to the measured magnetic susceptibility value of pure distilled, which is due to the very low concentration of iron nanoparticles. The electrical conductivity was also measured and it is found that the electrical conductivity is increasing with
increase in concentration. Thus we conclude that iron nanoparticles exhibits interesting thermal and electrical behaviour.

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**References**

1. Lu A H, Salabas E L and Schuth F 2007 Magnetic nanoparticles: synthesis, protection, functionalization, and application Angew. Chem. Int. Ed. 46 1222–44
2. Wu S et al 2011 Fe3O4 nanoparticles synthesis from iron tailings by ultrasonic chemical co-precipitation Mater. Lett. 65 1882–4
3. Gordon J P, Leite R C C, Moore R S et al 1965 Long transient effects in lasers with inserted liquid samples J. Appl. Phys. 36 3–8
4. Sheldon S J, Knight L V and Thorne J M 1982 Laser-induced thermal lens effect: a new theoretical model Appl. Opt. 21 1663–9
5. Shen J, Lowe R D and Snook R D 1992 A model for cw laser induced mode-mismatched dual-beam thermal lens spectrometry Chem. Phys. 165 385–96
6. Franko M and Tran C D 1996 Analytical thermal lens instrumentation Rev. Sci. Instrum. 67 1–18
7. Astrath N G C et al 2009 Thermal-lens study of photochemical reaction kinetics Opt. Lett. 34 3460–2
8. Lopez-Munoz G A et al 2012 Thermal diffusivity measurement of spherical gold nanofluids of different sizes/concentrations Nanoscale Res. Lett. 2012 7 423
9. Massart R 1981 Preparation of aqueous magnetic liquids in alkaline and acidic media IEEE Trans. Magn. 17 1247
10. Chatzikyriakos G, Iliopoulos K, Bakandritsos A and Couris S 2010 Nonlinear optical properties of aqueous dispersions of ferromagnetic γ-Fe2O3 nanoparticles Chem. Phys. Lett. 493 314–8
11. Shibili S M, Dantas A L L and Walton D 1998 Collinear mirage effect measurement of the thermal diffusivity in Ferronematica Appl. Phys. Lett. 72 674