Preparation and Characterization of Fe_3O_4 Magnetic Nanofluid in Vegetable Oil

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This paper reports the synthesis of Fe_3O_4 nanoparticles with a hydrophobic surface functionalized with oleic acid through a simple and efficient route in air atmosphere and by co-precipitation. The hydrophobic surfactant agent was added in the magnetic crystal growth stage. Magnetic nanofluid was obtained by ultrasonic dispersion of magnetic nanoparticles in a carrier liquid – vegetable oil. The sample as powder has been characterized by X-Ray Diffraction (XRD), Fourier Transform Infrared (FTIR) spectroscopy, Transmission Electron Microscopy (TEM), and Vibrating Sample Magnetometry (VSM) at room temperature. The magnetic nanofluid in vegetal oil was investigated by determining the stability of the nanoparticles in the vegetable oil through UV-Vis spectrometry method, the magnetic properties through Vibrating Sample Magnetometry (VSM) method at room temperature, and thermal conductivity as function of magnetic nanoparticles volume concentration and of temperature.

Keywords: magnetite nanoparticles, nanofluid magnetic, co-precipitation method, saturation magnetization, hydrophobic surfactant

Ferrofluids (FF) or magnetic nanofluids are stable colloidal systems composed of single domain magnetic nanoparticles dispersed in a liquid carrier [1]. In general, the methods for preparation of magnetic nanofluids are related to the synthetic methods of small sized nanoparticles with a narrow particle size distribution coupled to the liquid phase (the carrier liquid) through the surfactant layer. The surfactant is chosen so that on the one hand it can be adsorbed on the surface of the magnetic nanoparticles and on the other hand at has affinity with the carrier liquid (polar or non-polar). The size of magnetic nanoparticles can generally be controlled by choosing the method and the synthesis parameters. In the literature numerous methods of synthesis of magnetic nanoparticles have been reported, such as the chemical co-precipitation method [2-4], the microemulsion [5], the solvothermal method [6], the hydrolysis [7], the thermal decomposition [8] and sol-gel technique [9]. Nanoparticles of magnetite having a diameter of 3-15 nm acting in a magnetic nanofluid as a magnetic monodomain are in a permanent state of magnetization, i.e. they have a magnetic dipole moment, even in the absence of an applied magnetic field. Therefore, a strong dipole interaction exists between individual particles, resulting in agglomeration and subsequent sedimentation of the particles, which necessitates the long-term colloidal stability of the magnetic nanofluid. The technological applications of magnetic nanofluids are numerous. For example, magnetorheological dampers are constructed as hydraulic dampers, with the difference that magnetic fluid is introduced into the cylinder. Magnetorheological dampers have been studied and developed from the point of view of automotive applications, building control systems and earthquakes mitigation [1, 10-11]. Magnetic nanofluids also have many other industrial applications such as: sealants [12], magneto-optical controlled wavelength filters [13], optical switches and magnetically controlled optical modulators [14], cooling fluids or heat exchangers [15]. In the paper [15] a successful experiment is described in which it has been demonstrated the increase with up to 300% of the heat transfer coefficients by magnetic nanofluids when applying a local magnetic field. The approach of magnetic nanofluids, for coolants, has applications but is not limited to personal computers, servers, lasers, and air conditioning systems. For applications in electrical power (in power and measurement transformers), mineral oils with magnetic nanoparticles have been experimented as electrolytic liquid and cooling agent. The use of mineral oils has the disadvantage that they are easily flammable and non-biodegradable, which can lead to environmental pollution in case of accidental leakage. The main purpose of this article is to prepare and characterize stable suspensions of magnetic nanoparticles (Fe_3O_4) in a carrier liquid (vegetable oil) for applications as a cooling agent in electro energetic equipment.

Experimental part

Materials

Iron (II) chloride tetrahydrate $FeCl_2 \cdot 4H_2O$ ($\geq$ 98%) and iron (III) chloride hexahydrate $FeCl_3 \cdot 6H_2O$ ($\geq$ 98%) were purchased from Fluka and used as reagents. Ammonium hydroxide NH_4OH (25%) puriss p.a and oleic acid $C_{18}H_{34}O_2$ (88%) from SIGMA-ALDRICH, ethylic alcohol C_2H_5OH (> 96%) from Chemical Company and acetone C_3H_6O ($\geq$ 99.5%) was purchased from SIGMA-ALDRICH.

Synthesis of magnetite nanoparticles

The magnetite nanoparticles (Fe_3O_4) were prepared under atmospheric conditions by chemical co-precipitation of solutions of iron (II) and (III) salts in the presence of a strong base (NH_4OH). As the Fe^{2+} ion exhibits oxidative instability in the presence of dissolved or atmospheric oxygen, worked with a non-stoichiometric ratio of the reactants ($Fe^{2+} : Fe^{3+} = 0.65 : 1.15$). The iron salts respecting this molar ratio were dissolved in deionized water to form dilute solutions of 0.05M concentration. The two solutions containing the iron salts were mixed together in another 500 mL Berzelius beaker and heated with magnetic stirring (800 RPM) until the temperature reached

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70°C. Then ammonium hydroxide (25%) was added dropwise until *p*H = 11 was reached. Concomitantly in this step 0.5μL oleic acid surfactant was added to stop the increase in the crystallized size. After reaching *p*H = 11, the temperature of the reaction mixture was increased to 80°C and the formed black precipitate was maintained under magnetic stirring for another 30 min. The magnetite nanoparticles obtained are stabilized by a hydrophobic surfactant oleic acid. The treatment of the magnetite nanoparticles is a very important stage of the magnetic nanofluid preparation. Stabilization of the magnetite nanoparticles was performed in the same step by adding a volume of oleic acid to the reaction mixture and maintained for another 30 min. under magnetic stirring at 80°C. The resulting liquid precipitate was washed three times with deionized water and finally with ethyl alcohol and acetone. The black precipitate separated by magnetic decantation was dried under vacuum at 100°C for 8 h.

Preparation of Fe_3O_4-magnetic nanofluid

As a carrier liquid for the preparation of the magnetic nanofluid was used a vegetable oil - refined high oleic sunflower oil. Prior to use, the vegetable oil was dried over anhydrous calcium chloride ($CaCl_2$) at temperature of 120°C for 24 h. Oleic acid coated Fe_3O_4 nanoparticles were dispersed in the vegetable oil by sonication at room temperature for 45 min.

Characterization

The powder of Fe_3O_4 nanoparticles coated with oleic acid was characterized by XRD for structural determination and estimation of crystallite size. The X-ray powder diffraction pattern of the powder sample was recorded on a Bruker AXS S8 ADVANCE diffractometer with CuKα (1.5406Å) at room temperature in the range of 10 to 100° in the 2θ scale, with a scanning speed of 0.04°/s and a time step of 10s. Fourier Transform Infrared (FT-IR) spectroscope (Perkin Elmer Spectrum 100) was used to characterize the oleic acid coated Fe_3O_4 nanoparticles with KBr method in wavenumber range of 4000-400 cm^{-1} with a resolution of 4 cm^{-1}.

The size and shape of oleic acid coated Fe_3O_4 nanoparticles were determined by a transmission electron microscope (TEM) Zeiss Libra 200FE operated at 200KV. The sample was prepared by applying a drop of suspension containing magnetic nanoparticles dispersed in n-hexane on the surface of a carbon-coated Cu grid and subsequently allowed to dry at room temperature.

The magnetic properties of the nanopowder and nanofluid samples were measured at room temperature with a vibrating - sample magnetometer (VSM) model Lake Shore 7300.

The stability of suspended Fe_3O_4 nanoparticles stabilized with oleic acid in vegetable oil was determined by UV-Vis spectrometry at room temperature and different time interval using the UV-Vis-NIR spectrophotometer of the type V570 (Able/Jasco, Japan).

The thermal conductivity of the magnetic nanofluid sample in vegetal oil was determined based on the specific heat measured by the DSC method with the reference standard of sapphire and of thermal diffusivity with LFA 447 Nano Flash-NETZSCH diffusimeter in the temperature range of 30 to 70°C.

Results and discussions

Characterization of magnetic nanoparticles

Figure 1 shows the X-ray diffraction pattern at room temperature, of the oleic acid coated Fe_3O_4 nanoparticles

All the XRD peaks could be identified with Fe_3O_4 structure using ICDD data base [16]. All the diffraction peaks at (111), (220), (311), (222), (401), (422), (511), (440), (620), (533), (622), (642), (731) were according with indexing code number PDF 01-071-6336, which are indexed to the cubic crystallization system with centered faces, with Fm-3m (227) space group. The lattice constant *a* was found to be 8.3711 Å, which is close to the theoretical value of the lattice parameter for the magnetite of 8.39 Å. The XRD pattern of the powder sample shows broad peaks, which indicates that the sample is nanocrystalline. The crystallite size was obtained using Debye-Scherrer equation (1) with FWHM of (311) peak:

$$D = \frac{0.9\lambda}{B\cos\theta} \qquad (1)$$

where: D is the crystallite mean size, λ =0.154056 nm is the wavelength of the X-rays, B is the full width at half maximum (FWHM) and θ is the Bragg angle. The calculate crystal size were of 9.35 nm. Therefore, the size of the nanoparticles thus obtained corresponds to the recommended range for the preparation of magnetic nanofluids [17].

The FT-IR spectrum of oleic acid coated Fe_3O_4 nanoparticles is shown in figure 2.

In this spectrum, two strong peaks, at 590.92 and 445.27 cm^{-1}, correspond to the vibration of Fe^{2+} - O^{2-} and Fe^{3+} - O^{2-} bonds which confirmed the formation of magnetite crystals in agreement with the results of XRD analysis [18]. Also the FTIR spectrum shows the presence of three peaks at 1619.33 cm^{-1}, 1523.35 cm^{-1} and 1404.70 cm^{-1} that were attributed to the binding mode of the carboxylate ion in oleic acid to the surface of the magnetite nanoparticles. The position and separation of $\nu(COO^-)$ bands, can be used to deduce the carboxylate coordination mode [19]. The carboxylate ion may be coordinated to a metal ion in one of the three structures [19, 20]:

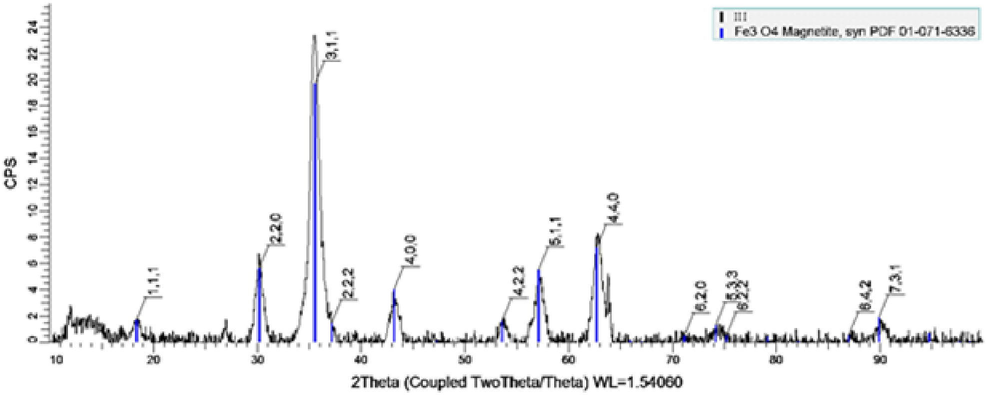

Fig. 1. X-ray power diffraction patterns for oleic acid coated Fe_3O_4 nanoparticles

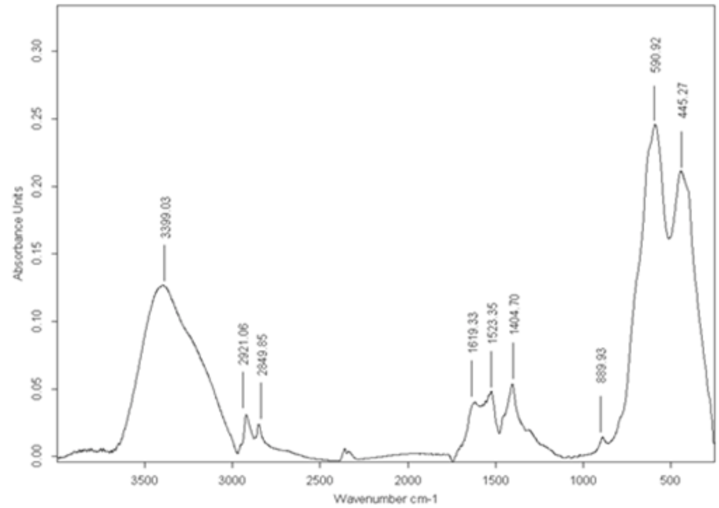

Fig. 2. FT-IR spectra of for oleic acid coated Fe_3O_4 nanoparticles

-unidentate complex where one metal ion is binding with one carboxylic oxygen atom, Δ > 200 cm^{-1};

-bidentate complex where one metal ion is binding with two carboxylic oxygens, Δ < 110 cm^{-1};

-bridging complex where two metal ions are binding with two carboxylic oxygens, Δ is between 140 and 200 cm^{-1}.

The peak at 1619.33 cm^{-1} is the result of band splitting (a doublet at 1619.33 and 1523.35 cm^{-1}) which suggests the coordination of oleic acid in two ways (bidentate and monodentate) on the surface of magnetite nanoparticles.

Absence of the peak to 1710 cm^{-1} characteristic of the C P% O carboxyl group of the carboxylic acid indicates the absence of free oleic acid what confirms that all oleic acid molecules was bond to the surface of the Fe_3O_4 nanoparticles.

The peaks at 2921.05 and 2849.85 cm^{-1} were assigned to the asymmetrical and symmetrical stretching vibration of $-CH_2-$ group from the hydrocarbon chain of the oleic acid structure.

The presence of band at 3399.03 cm^{-1} is because of the O-H surface hydroxyl due to likely ethanol remaining of from washing [21].

The TEM transmission electron microscopy images (fig.3) recorded at different magnification powers show that the nanoparticles thus obtained are spherical in shape with a narrow distribution of particle sizes between 7-9 nm.

In addition, TEM images highlight the formation of a translucent coating around Fe_3O_4 nanoparticles with a thickness of 0.66 nm which confirms the formation the coating with surfactant on their surface. The result is consistent with the result of the FTIR vibration spectrum that supported the binding of oleic acid to the surface of Fe_3O_4 nanoparticles.

The magnetization curve of oleic acid coated magnetite nanoparticles is shown in figure 4. It can be seen from figure 4 that no remanence and no coercivity was observed, suggesting that the synthesized nanoparticles powder exhibits superparamagnetic properties at room temperature. The saturation magnetization (M_s) at 300 K is 19.505 emu/g. The lower saturation magnetization can be due to the smaller size of nanoparticles and the layer of the oleic acid on the surface magnetite nanoparticles.

Characterization of magnetic nanofluid

The clear colloid suspension obtained after 30 min. of sonication of oleic acid coated Fe_3O_4 nanoparticles dispersed in the vegetable oil (0.01%) was used as sample for investigating the stability of suspension at different ranges of the time. Figure5 shows the optical absorbance spectrum of the magnetite nanoparticles as synthesized, at room temperature and under the action of the gravitational field.

The absorbance spectrum shows that the absorbance is in the visible range of the wavelength. The absorption

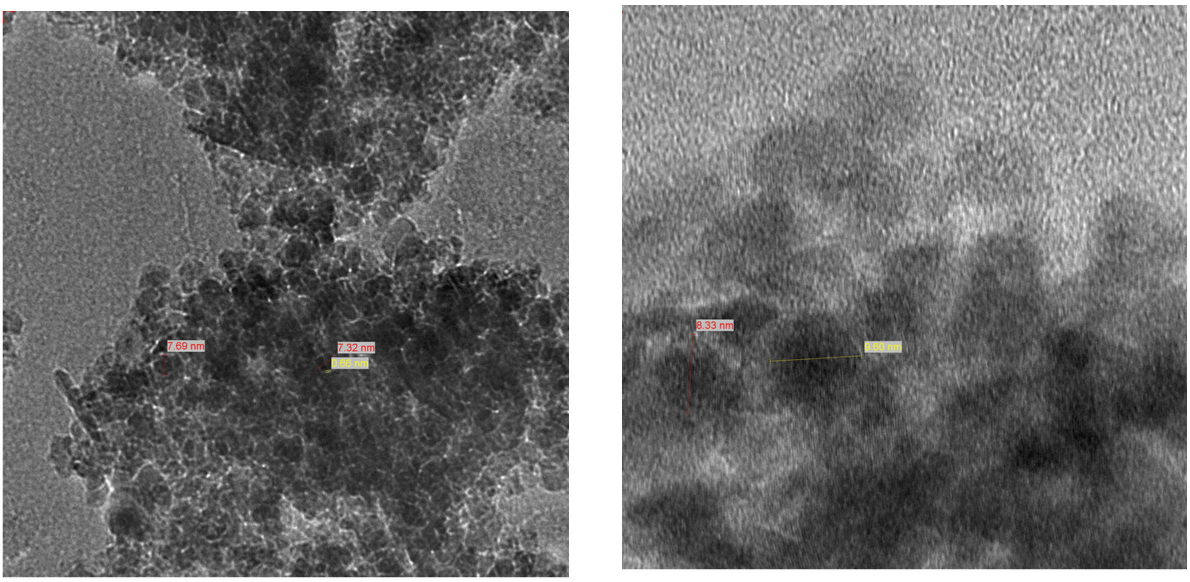

Fig.3. TEM images of oleic acid coated Fe_3O_4 nanoparticles with various magnifications: (a) 125 kX and (b) 500kX.

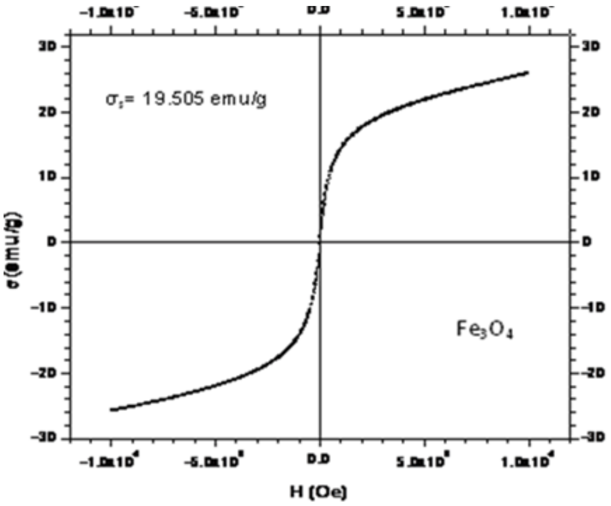

Fig. 4. M *vs.* H hysteresis loop of oleic acid coated Fe_3O_4 nanoparticles.

peak for Fe_3O_4 nanoparticles is at 370 nm and the position and peak intensity do not change between 2 and 6 h, which demonstrates the stability of the suspension. A slight instability occurs after 18 h when the peak is shifted to 374 nm.

Figure 6 shows hysteresis loops at room temperature for the samples Fe_3O_4 magnetic nanofluid in vegetable oil with different volumetric concentration of magnetic nanoparticles. The results for the magnetic properties thus obtained are shown in table 1. The saturated magnetization and susceptibility, which are very important properties for magnetic nanofluid, increase with the concentration of magnetic nanoparticles. For magnetic nanofluid with volumetric concentration of magnetic nanoparticles (Φ= 1.14) the saturated magnetization was 1.85 emu/g and the susceptibility was $3.20x10^{-8}$.

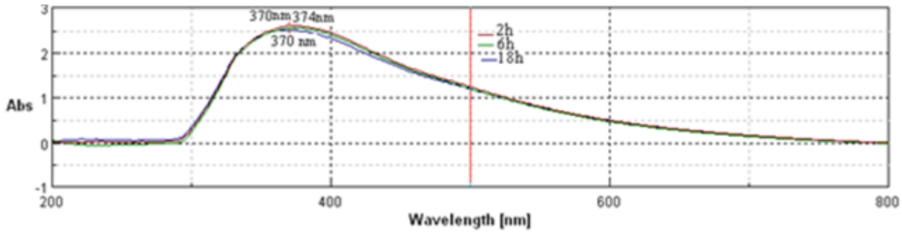

Fig. 5. UV-Vis spectrum of magnetic nanofluid under gravitational field and the different ranges of the time.

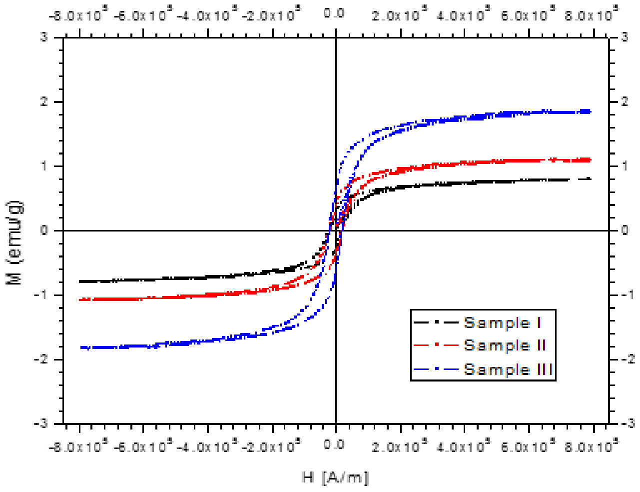

Fig. 6. M vs. H hysteresis loop for the samples magnetic nanofluid in vegetable oil with different volumetric concentration (Φ) of magnetic nanoparticles: (a) sample PI with Φ = 0.66; (b) sample PII withΦ = 0.70; (c) sample PIII with Φ = 1.16.

The thermal conductivity of the magnetic nanofluid samples was calculated based on the experimental data presented in table 2, obtained by measuring the specific heat, diffusivity and density according to equation (2):

$$K = \rho \cdot C_p \cdot a \qquad (2)$$

where:

K -thermal conductivity (W/mK)
ρ -density (g/cm³)
C_p -specific heat (J/g.K)
a -thermal diffusivity (mm²/s)

As can be seen from figure 7, the thermal conductivity of magnetic nanofluid samples increases with the increase in the volume concentration of magnetic nanoparticles dispersed in the base fluid.

Higher values for the thermal conductivity of nanofluid samples compared to those of the base fluid demonstrate their capability of heat nanoconductors to perform the function of cooling agents in power equipment (power transformers).

Conclusions

Table 1
MAGNETIC PROPERTIES OF Fe_3O_4 MAGNETIC NANOFLUID SAMPLES

Sample	Temperature (T) [°C]	Specific heat (C_p) [J/g·K]	Thermal diffusivity (a) [mm²/s]	Density (ρ) [g/cm³]
PI	30	1.2492	0.2969	0.9334
	40	1.2448	0.3200	
	50	1.2318	0.3537	
	60	1.2172	0.3829	
PII	30	1.2637	0.2980	0.9411
	40	1.2613	0.3279	
	50	1.1968	0.3629	
	60	1.1840	0.3959	
PIII	30	1.2797	0.2925	1.14
	40	1.2213	0.3409	
	50	1.1602	0.3719	
	60	1.1455	0.4269	
Vegetable oil of high oleic sunflower	30	1.2908	0.2219	0.9047
	40	1.2723	0.2289	
	50	1.1806	0.2600	
	60	1.1573	0.2729	

Table 2
EXPERIMENTAL VALUES OBTAINED FOR SPECIFIC HEAT, THERMAL DIFFUSIVITY AND DENSITY ON MAGNETIC NANOFLUID SAMPLES AND THE BASIC FLUID

Sample	Temperature (T) [°C]	Specific heat (C_p) [J/g·K]	Thermal diffusivity (a) [mm^2/s]	Density (ρ) [g/cm^3]
PI	30	1.2492	0.2969	0.9334
	40	1.2448	0.3200	
	50	1.2318	0.3537	
	60	1.2172	0.3829	
PII	30	1.2637	0.2980	0.9411
	40	1.2613	0.3279	
	50	1.1968	0.3629	
	60	1.1840	0.3959	
PIII	30	1.2797	0.2925	1.14
	40	1.2213	0.3409	
	50	1.1602	0.3719	
	60	1.1455	0.4269	
Vegetable oil of high oleic sunflower	30	1.2908	0.2219	0.9047
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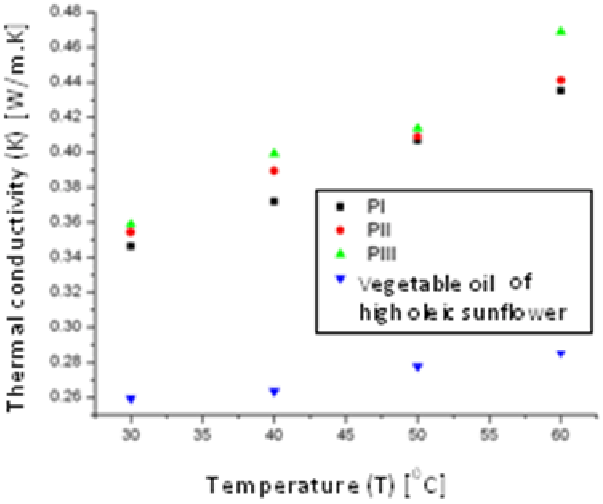

Fig.7 Thermal conductivity depending on temperature for the samples of magnetic nanofluid

Were been prepared Fe_3O_4 nanoparticles functionalized with oleic acid, in a single step by co-precipitation method under atmospheric conditions, worked with a non-stoichiometric ratio of the reactants ($Fe^{2+} : Fe^{3+} = 0.65 : 1.15$). The peaks of at 1619.33 cm^{-1}, 1523.35 cm^{-1}, and 1404.70 cm^{-1} in FTIR spectrum supports bidentate and monodentate binding group (-COO) of oleic acid to group (-OH) on the surface Fe_3O_4 nanoparticles; TEM micrographs have revealed the formation of spherical nanoparticles of approximately 7 - 9 nm. The result is also supported by their superparamagnetic behavior according to magnetic measurements (VSM); UV-Vis absorption spectra showed good stability over time (>18h) of the Fe_3O_4 coated with oleic acid nanoparticles suspension in sunflower vegetable oil. The magnetic nanofluid in sunflower vegetable oil showed a ferromagnetic behavior. The Ms and ÷m increases with the volume concentration magnetic nanoparticles of at Ms = 0.79 emu/g and $\chi m = 1.45x10^{-8}$ for $\Phi = 0.60$ at Ms = 1.85 emu/g and $\chi m = 3.20 x10^{-8}$ for $\Phi = 1.14$. The thermal conductivity of magnetic nanofluid samples increases with the increase in the volume concentration of magnetic nanoparticles dispersed in the base fluid and with increase the temperature so the thermal conductivity increases of at 0.2925 mm^2/s at 0.4269 mm^2/s for $\Phi = 1.14$ and the temperature of 60°C. The results obtained for the magnetic and thermal properties support the properties of the magnetic nanofluid obtained for applications as a cooling agent in electro-energetic equipment.

Acknowledgement: This work was supported by Romanian Ministry of Research and Innovation (MCI), projects PN 16110208/2016 and 30PFE/2018 and by Romanian National Authority for Scientific Research and Innovation, CNCS/CCCDI-UEFISCDI, project PN-III-P2.-2.1-PED-2016-0451, within PNCDI III.

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Manuscript received: 17.11.2018