# Surfactant Effect on the Thermal and Electrical Behaviors of Sonochemically Synthesized Fe and Fe–PVP Nanofluids and Insight into the Magnetism of Their in Situ Oxidized $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> Analogues

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**Supporting Information** 

ABSTRACT: Magnetic nanofluids are dispersions of magnetic nanoparticles in a diamagnetic base liquid, which display distinct physical properties that can be tuned easily by an external magnetic field, electric current, and temperature. Iron nanofluids were synthesized sonochemically in a one-step process and were observed to oxidize in situ over prolonged air exposure, forming  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanofluids. The thermal conductivity measurements on these single-step fabricated magnetic nanofluids were performed for the first time and showed enhanced thermal transport. Hence, we present a new one-pot synthesis approach to improve the heat transfer. The electrical properties of the iron and ferric oxide nanofluids in the presence and absence of a surfactant are also newly



reported in this paper. The different electrical conductivities among the two sets of nanofluids are interpreted, and mechanisms are proposed to account for the observed deviation. The heat transport by Fe<sub>2</sub>O<sub>3</sub> nanofluids with respect to the magnetic flux was investigated by subjecting the samples to an external magnetic field. The presence of a surfactant had a substantial effect on the magnetic field-dependent thermal conductivity. Magnetization data as a function of temperature and magnetic field were obtained using the Mössbauer and superconducting quantum interference device techniques, and the influence of the stabilizer is revealed. The present findings are significant for tailoring the properties of magnetic nanofluids for improved applications.

## INTRODUCTION

Magnetic nanofluids are a distinct class of colloidal liquids comprising magnetic nanoparticles (MNPs) suspended in a nonmagnetic base liquid.<sup>1</sup> The behavior of these nanofluids under the influence of a magnetic field governs their wide range of applications in various fields including catalysis, biomedicine, drug delivery, and heat transfer.<sup>2,3</sup> Physical properties such as thermal and electrical conductivity and magnetic properties play a vital role in controlling the performance of these nanofluids under discrete conditions, which control their ample applications. Iron and iron oxide nanofluids, categorized under magnetic nanofluids, are important classes of nanofluids because of their biocompatibility, ease of synthesis, and cost-effectiveness.<sup>4,5</sup>

Various groups have reported significant studies exploring the thermal conductivity and magnetic properties of Fe<sub>2</sub>O<sub>3</sub>/ Fe<sub>3</sub>O<sub>4</sub> nanofluids.<sup>6,7</sup> Shima et al. measured the temperaturedependent thermal conductivity of Fe<sub>3</sub>O<sub>4</sub> nanofluids loaded with a very low concentration of NPs.<sup>8</sup> The results of this study showed that when NPs are capped with a surfactant in the nanofluid, the increase in thermal conductivity at elevated

temperature due to the aggregation effect is insignificant. Karimi et al. reported the magnetic field-dependent thermal conductivity of hematite and magnetite nanofluids and informed that the magnetic nanofluids in the absence of a magnetic field behave similar to other nanofluids. Also, the effect of a magnetic field is higher for magnetite nanofluids than for hematite.<sup>9</sup> Although much attention has been drawn toward the thermal and magnetic properties, very little is known about their electrical conductivity behavior in the liquid medium. Bai et al. have recently demonstrated the electrical conductivity of Fe<sub>3</sub>O<sub>4</sub>/polyaniline under the magnetic field, which is a function of temperature and concentration of the nanofluid.<sup>10</sup> We are not aware of any report on the electrical conductivity of iron or ferric oxide nanofluids.

To overcome instability issues of the synthesized nanofluids, the use of surfactants has been highly promoted. Angayarkanni et al. and Lenin et al. conducted significant studies on the role

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of stabilizing moieties in the thermal properties of  $Fe_3O_4$ nanofluids.<sup>11,12</sup> These two studies reported contradicting results regarding the effect of the stabilizers on physical properties, in particular, thermal conductivity. Reasonable justification for the role of surfactants in the properties of nanofluids is still lacking. Because of the highly corrosive nature of Fe NPs, the in situ study of the physical properties of iron nanofluids poses a challenge, as it requires to simultaneously maintain the stability of the nanofluid. There were a few attempts to measure the thermal conductivity of iron nanofluids obtained by a two-step method in which the Fe NPs were dispersed in the desired base fluid.<sup>13–15</sup>

Considering the aspects mentioned above, a clear understanding of the properties of Fe and Fe<sub>2</sub>O<sub>3</sub> in their colloidal form demands a consistency in their commonly varying parameters, such as synthesis procedures, surfactant, and particle size. Therefore, the current study is focused on the above-mentioned factors: iron nanofluids were synthesized using a single-step process in the absence and presence of poly(vinylpyrrolidone) (PVP). By virtue of their lower stability, the suspended Fe NPs undergo native oxidation over a prolonged exposure to air, leading to an in situ conversion to the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanofluid. The results reported in the current study are believed to clear the previously reported discrepancies on the effect of the synthesis methods and the surfactant on the physical properties of the magnetic nanofluids. Moreover, this paper unveils for the first time the electrical conductivities of metallic nanofluids and their oxidized form, with and without stabilizers, under identical conditions and also contemplates the effect of the surfactant on the magnetically influenced thermal conduction.

## RESULTS AND DISCUSSION

The synthesis of ferromagnetic nanofluids of iron was achieved by decomposition of the organometallic compound iron pentacarbonyl ( $Fe(CO)_5$ ) in an organic solvent (1-decanol) under an inert argon atmosphere. This sound-driven (sonolytic) method for the formation of metallic NPs is highly susceptible to coalescence of the synthesized NPs.<sup>16</sup> The current methodology corroborates the reported procedure for the synthesis of monodispersed and highly stable nonagglomerated Fe nanocolloids.<sup>17,18</sup> The carbonyl complex is decomposed under strong acoustic cavitation, and the resultant Fe(0) NPs are nucleated. The Fe NPs formed with and without the presence of the surfactant (PVP) are designated as Fe-PVP and Fe, respectively, and the morphology of the products is demonstrated in Figure 1. The absence of PVP resulted in agglomeration, as depicted in Figure 1a, whereas the formation of a highly dispersed (nonagglomerated) nanofluid (Figure 1b) in the polymer matrix evidenced the role of the surfactant in sterically screening the strong interparticle attraction.<sup>18</sup> The high-resolution transmission electron microscopy (HR-TEM) image of the synthesized MNPs indicates a layer surrounding the core particle (Figure 1c). The appearance of this encapsulated layer surrounding the core in both types of MNPs (with and without PVP) excludes the possibility of capping by PVP. The existence of this amorphous coating is thus attributed to the decomposition of the organometallic precursor  $(Fe(CO)_5)$  to form the carbon, which deposits on the nucleated MNPs enwrapping the iron core.<sup>19</sup> The amorphous nature of the fabricated MNPs is confirmed by the X-ray diffraction (XRD) pattern (Figure S2). The selected area electron diffraction (SAED) pattern in

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**Figure 1.** HR-TEM micrographs of (a) Fe NPs and (b) Fe-PVP NPs. (c) Magnified image of a single MNP showing the carbon layer and (d) SAED pattern of the Fe NP.

Figure 1d also shows the absence of diffraction spots or rings, characteristic of a crystalline material. The average particle size of the NPs with and without the surfactant is observed to be about 10 and 15 nm, respectively.

The formation of the Fe NPs was confirmed by UV-vis and Raman spectroscopy. Absorbance peaks for Fe and Fe-PVP NPs were observed at 235 and 232 nm, respectively, as presented in Figure 2, which are in accord with previous



Figure 2. UV-vis spectra of (a) Fe NPs and (b) Fe-PVP nanofluids.

reports by Singh et al.<sup>20</sup> and Morgada et al.<sup>21</sup> These studies identified the UV absorbance maxima at 235 and 238 nm, as arising from Fe(0) NPs. The Raman spectra (Figure S3) indicated the absence of any significant scattering peaks, as expected for pure metals which are an assembly of single atoms with no interatomic vibrations and therefore no change in polarization.<sup>22</sup> However, some metals display a few Raman shifts assigned to the optical phonon scattering arising from their ordered unit cell.<sup>23</sup> These phonons are detected at low

frequencies below those of the molecular vibrations. This also affirms the findings that the synthesized Fe(0) MNPs are amorphous, lacking order in their structure.

The Fe-PVP nanofluid showed superior colloidal stability of over 4 months (Figure S4). Owing to the high chemical instability of Fe NPs, the storage of the Fe nanofluids plays a crucial role in maintaining the chemical nature of Fe(0). The synthesized Fe nanofluids were observed to oxidize after 2 days of exposure to air. Characterization of the oxidized nanofluids revealed the formation of an amorphous ferromagnetic ferric oxide phase, both in the absence of PVP (Fe<sub>2</sub>O<sub>3</sub>) and in its presence (Fe<sub>2</sub>O<sub>3</sub>-PVP). In contradiction of the general role of the surfactant to serve as a protective layer that prevents oxidation, PVP could not sufficiently prevent the surface oxidation of the Fe NPs. Similar instability of Fe NPs upon short-term exposure to air in the presence of a surfactant was observed by Guo et al.,<sup>24,25</sup> wherein the Fe nanocrystals were oxidized to Fe<sub>2</sub>O<sub>3</sub> even in the presence of the capping agent. The UV-visible spectra of Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>-PVP (Figure S5) showed the characteristic peaks at 454 and 452 nm, respectively.<sup>26</sup> Raman spectra revealed the formation of a- $Fe_2O_3$  (Figure 3). The Raman peak at 217 cm<sup>-1</sup> was assigned to the A<sub>1g</sub> mode, and the peaks centered at 280, 389, and 599 cm<sup>-1</sup> were attributed to the E<sub>g</sub> bands of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.<sup>27,2</sup>



Figure 3. Raman spectra of (a)  $Fe_2O_3$  and (b)  $Fe_2O_3$ -PVP nanofluids measured using a He–Ne laser (632.817 nm).

The X-ray photoelectron spectroscopy (XPS) survey spectrum of Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>-PVP shown in Figure 4a depicted predominant Fe 2p, C 1s, O 1s, and N 1s peaks. The increased content of O 1s, N 1s, and C 1s in Fe<sub>2</sub>O<sub>3</sub>-PVP evidenced the contribution of the surfactant (PVP). The XPS spectra of the Fe 2p core level (Figure 4b) further supported the formation of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. For both Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>-PVP samples, the peaks of Fe  $2p_{1/2}$  and Fe  $2p_{3/2}$  were indexed at 724.6 and 711.1 eV, respectively, along with the characteristic satellite peaks at 719 eV.29 The additional peak appearing at 732.8 eV may be assigned as a satellite peak for Fe  $2p_{1/2}$ .<sup>30</sup> The shape of the Fe 2p core spectrum and the existence of these  $\alpha$ - $Fe_2O_3$  peaks agree well with the reported XPS of the  $Fe^{3+}$  state.  $^{31}$  The O 1s peaks of both  $Fe_2O_3$  and  $Fe_2O_3-PVP$ presented in Figure 4c,d, respectively, show three distinct components: (i) the peak corresponding to the Fe–O bond is centered at 530.1 eV for Fe<sub>2</sub>O<sub>3</sub> and at 529.7 eV for Fe<sub>2</sub>O<sub>3</sub>-PVP. The higher intensity and binding energy of this peak for  $Fe_2O_3$  can be explained as resulting from the increased number of metal ions (Fe<sup>3+</sup>) strongly interacting with the lattice oxygen

in the absence of PVP. (ii) The increase in binding energy and intensity of the peak at 531.5 eV for  $Fe_2O_3$ –PVP compared to  $Fe_2O_3$  (531.2 eV) accounts for the interaction between the Fe atoms and the carboxyl groups (C==O), which is substantially higher in the case of  $Fe_2O_3$ –PVP as indicated by the higher peak intensity.<sup>32</sup> (iii) Moreover, the peaks at 533.3 and 533.5 eV are attributed to residual oxygen-containing groups such as O–H bonding, which could arise from Fe–OH or decanol; in the case of  $Fe_2O_3$ –PVP, it could originate from the surfactant molecules, indicated by the small increment (0.2 eV) in the observed electronic bonding energy.<sup>33</sup> The appearance of the N 1s peak (Figure 4e) at 399.9 eV in  $Fe_2O_3$ –PVP arises from the nitrogen of the PVP.

Despite the rapid oxidation (2 days) of the Fe and Fe–PVP MNPs, the short-term chemical stability against oxidation and prolonged stability toward agglomeration in the case of the Fe–PVP nanofluids served our applications well. The in situ conversion of Fe(0) to oxidized Fe allowed measurements of both Fe and Fe<sub>2</sub>O<sub>3</sub> nanofluids under identical environments. With the exception of the chemical nature of the MNPs, all other properties of the Fe and Fe<sub>2</sub>O<sub>3</sub> nanofluids remained constant. This contributed to the small fluctuations in the measured data. However, the chemical instability limited the magnetic studies of the Fe and Fe–PVP NPs, which had to be performed on fresh samples.

Thermal conductivity measurements for the freshly synthesized Fe and aged Fe<sub>2</sub>O<sub>3</sub> nanofluids at a volume fraction of 0.061% were conducted as a function of temperature. Decanol was chosen as a base fluid owing to its relatively higher thermal conductivity and biocompatibility.<sup>34</sup> The effective thermal conductivity, calculated as the ratio of the thermal conductivity of the nanofluid  $(k_{nf})$  to the thermal conductivity of the base fluid  $(k_f)$ , is presented in Figure 5a for all samples. The highest thermal conductivity with respect to the rise in temperature was observed for Fe-PVP, with the lowest values obtained for the Fe<sub>2</sub>O<sub>3</sub> nanofluid in the absence of a surfactant. No significant difference in the effective thermal conductivity of Fe and Fe<sub>2</sub>O<sub>3</sub>-PVP is noted. The justification for the thermal conductivity data observed above is as follows: metals are known to be more efficient heat conductors than their oxidized counterparts. The superior thermal conductivity of metals is reflected in the Fe nanofluids (Figure 5a). Fe-PVP showed a 14.3% rise in thermal conductivity at 343 K, which is the highest enhancement observed among the measured nanofluids. With the rise in temperature, the thermal conductivity is increased, and in addition, the nanofluids with PVP displayed enhanced heat transfer to a greater extent than the nanofluids without PVP. This observation underlines the mechanism of Brownian motion, which plays a significant role in the overall thermal conductivity enhancement. Brownian motion is influenced by a higher temperature and a smaller particle size.<sup>35</sup> The presence of a surfactant is manifested in the smaller particle size and higher dispersibility. At elevated temperatures, the movement of the NPs is more pronounced, and Brownian motion becomes the governing factor for the thermal enhancement.<sup>36</sup> The effective thermal conductivity therefore increases in the following order: Fe–PVP ( $k_{\rm nf}/k_{\rm f}$  = 1.14 ± 0.0014) > Fe<sub>2</sub>O<sub>3</sub>-PVP ( $k_{\rm nf}/k_{\rm f} = 1.13 \pm 0.0011$ ) > Fe ( $k_{\rm nf}/k_{\rm f} =$  $1.12 \pm 0.0015$ ) > Fe<sub>2</sub>O<sub>3</sub> ( $k_{\rm nf}/k_{\rm f}$  = 1.11 ± 0.0016). The in situ (one-step) preparation of the nanofluids achieved in the present study demonstrated the highest enhancement in thermal transfer when compared to the data documented in the literature at maximum volume fraction (0.05%).<sup>8,9</sup> These



Figure 4. XPS spectra of  $Fe_2O_3$  and  $Fe_2O_3$ -PVP: (a) entire range, (b) high-resolution, (c) O 1s spectrum of  $Fe_2O_3$ , (d) O 1s spectrum of  $Fe_2O_3$ -PVP, and (e) N 1s spectrum of  $Fe_2O_3$ -PVP.



Figure 5. Variation of effective thermal conductivity ( $k_{nf}/k_f$ ) as a function of (a) temperature of Fe, Fe–PVP, Fe<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub>–PVP nanofluids and (b) as a function of volume fraction of ferric oxide nanofluids.



**Figure 6.** Variation of effective thermal conductivity ( $k_{nf}/k_f$ ) as a function of magnetic field of (a) Fe<sub>2</sub>O<sub>3</sub> and (b) Fe<sub>2</sub>O<sub>3</sub>-PVP nanofluids at 0.01, 0.02, 0.03, 0.04, and 0.05% volume fractions.

findings open a new avenue to the enhancement of the thermal conductivity of nanofluids to direct nanofluid synthesis procedures toward single-step feasible approaches for increased heat transfer. The enhancement in thermal conductivity for  $Fe_2O_3$  nanofluids was also studied as a function of volume fraction at 303 K (Figure 5b). Unlike the previous findings in Figure 5a, at isothermal conditions (303 K) the thermal conductivity of

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 $Fe_2O_3$  rises with increasing volume fraction. The enhancement in thermal transport is 21.3 and 17.8% for  $Fe_2O_3$  and  $Fe_2O_3$ – PVP nanofluids, respectively. This is in accordance with our previous report and other literature, which proffered the heat transfer by conduction as a prevailing mechanism with the increase in volume fraction at constant temperature.<sup>37,38</sup>

The effect of the external applied magnetic field on the thermal conductivity of magnetic nanofluids with and without the surfactant was determined at different volume fractions of Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>-PVP nanofluids. As can be seen in Figure 6a, in the case of the  $Fe_2O_3$  nanofluid, an increase in heat transfer with the magnetic field was observed only at higher volume fractions (0.04 and 0.05%). The highest thermal conductivity is noted at 0.05% volume fraction-up to 34% enhancement in heat conductivity at the highest magnetic field (1120 G). At a higher volume fraction of NPs in the fluid, under the influence of the magnetic field, the NPs formed chainlike agglomerates in an attempt to move in the direction of magnetic field lines, causing higher heat conduction along the chains.<sup>13</sup> At lower concentrations of the Fe<sub>2</sub>O<sub>3</sub> nanofluid, with increasing magnetic field, the negligible amount of MNPs tended to accumulate on the walls of the sample holder, thereby depleting their concentration in the bulk liquid, as indicated by the lower thermal conductivity (decrease in % enhancement from 10.3 to 7.7% at 200 and 1120 G, respectively).<sup>39</sup>

The reported thermal conductivity data for the Fe<sub>2</sub>O<sub>3</sub>-PVP nanofluid (Figure 6b) illustrate a steady rise in thermal conductivity as a function of magnetic field representing an insignificant advancement in the thermal transport for all volume fractions. This can be justified as a deprived response of the MNPs to the external magnetic field by the PVP, which contributes diamagnetically to the base fluid. The mechanism for this steady rise in thermal conductivity with the magnetic field of the Fe2O3-PVP nanofluid can be related to the effective Brownian motion of the highly dispersed MNPs. This denies the formation of chain aggregates because of the interparticle repulsion forces. The absence of the phenomenon of a decrease in thermal conductivity as a function of magnetic field at low volume fractions, as observed for the Fe2O3 nanofluid (Figure 6a), can be supported by the same justification. Thus, from this analysis, it can be inferred that the magnetic field has no impact or a negligible impact on the thermal conductivity of magnetic nanofluids with high surfactant loading because of the negating effect of the diamagnetic surfactant.

The electrical conductivities of the fresh (Fe) and oxidized  $(Fe_2O_3)$  nanofluids were investigated with respect to the rise in temperature (Figure 7). Decyl alcohol (decanol) in its pure form showed negligible conductance, which increased upon the addition of the MNPs. The highest electrical conductivity of 143 nS cm<sup>-1</sup> at 65 °C was observed for the fresh Fe nanofluid. This is expected for a metal nanofluid owing to the notable electrical conduction of metallic iron. Thus, the observed enhancement in electrical conductivity is the net charge effect of the metallic NPs. The reduction in the electronic transport of surfactant-based nanofluids (Fe-PVP and  $Fe_2O_3$ -PVP) as compared to that of the pristine nanofluid is due to the retarding effect of the surfactant to the smooth flow of the charge carrier. The overall electrical conductivity (nS cm<sup>-1</sup>) increases in the order Fe (143) > Fe<sub>2</sub>O<sub>3</sub> (120) > Fe-PVP (109) >  $Fe_2O_3-PVP$  (95). These results imply that the electrical conductivity is the highest for the freshly



**Figure 7.** Electrical conductivity of Fe, Fe–PVP,  $Fe_2O_3$ , and  $Fe_2O_3$ –PVP nanofluids as a function of temperature.

synthesized metallic nanofluids and diminishes upon addition of the surfactant. Similarly, the oxidized Fe NPs passivate the electron-rich metallic surface, reducing the free electron cloud. As this is the first report on the electrical conductivity of Fe nanofluids, the results can be generalized as follows: the nanofluids of pristine and freshly prepared metallic NPs display the highest electrical conductivity, which is not achieved by any of its oxidized forms. Addition of the nonconductive surfactant decreases the electron conduction, which could be attributed to the charge delocalization within the long chain of polymer molecules. This study is still in its nascent stage, and further experimental data are anticipated to understand (i) the effect of physical stability against agglomeration and (ii) the role of particle functionalization by conducting polymers in the electrical transport.

The magnetization of  $Fe_2O_3$  and  $Fe_2O_3$ –PVP was analyzed by <sup>57</sup>Fe Mössbauer spectroscopy at room temperature (RT) and dc superconducting quantum interference device measurements. The RT Mössbauer spectra for both ferric oxide NPs are identical (within the uncertainty values) and for brevity, only the spectrum measured for  $Fe_2O_3$ –PVP is displayed in Figure 8. The pure doublet observed could be an indication of



Figure 8. Mössbauer spectra of Fe<sub>2</sub>O<sub>3</sub>-PVP at RT.

the superparamagnetic phase of the MNPs<sup>40</sup> and definitely proves the absence of any sizable permanent long-range magnetic moments in the Fe sites. The deduced hyperfine parameters are as follows: isomer shift (IS) = 0.32(1) mm/s, the quadrupole splitting (QS) =  $1/2e^2Qq = 0.91(1)$ , and a width of 0.62(1) mm/s. The relatively large width corresponds to the size distribution of the Fe<sub>2</sub>O<sub>3</sub>-PVP NPs. Both IS and QS values are in fair agreement with the values reported for 10 nm  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> at RT.<sup>41</sup>



Figure 9. Isothermal magnetization curves of (a) Fe<sub>2</sub>O<sub>3</sub> and (b) Fe<sub>2</sub>O<sub>3</sub>-PVP measured at 6 and 5 K, respectively.



Figure 10. FC and ZFC data of (a)  $Fe_2O_3$  and (b)  $Fe_2O_3$ -PVP measured in an applied field of 250 Oe. The bifurcation curves of FC-ZFC at 250 Oe are shown for (c)  $Fe_2O_3$  and (d)  $Fe_2O_3$ -PVP. (e) Hysteresis curve of  $Fe_2O_3$ -PVP was measured at 5 K and exhibited a coercivity of 850 Oe.

The isothermal magnetization M(H) curves measured at 5 and 6 K are depicted in Figure 9a,b, respectively. M(H) first increases linearly up to 5–6 kOe and then tends to saturate. The M(H) plots clearly reveal an admixture of two components and can be fitted as  $M(H) = M_s + \chi_p H$ , where  $M_s$  is equal to 9.6 and 8.3 emu/g for Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>-PVP, respectively, which is the intrinsic magnetic phase contribution, and  $\chi_p H$  is the linear paramagnetic part. Similar curves are observed at RT, and the  $M_s$  values are 5.7 and 4.7 emu/g, respectively (Figure S6). The slight loss in magnetization observed for Fe<sub>2</sub>O<sub>3</sub>-PVP is attributed to the diamagnetic contribution of the surfactant.<sup>42</sup>

The temperature dependence of the magnetization was measured in an applied magnetic field of 250 Oe using viawarming field-cooling (FC) and zero-FC (ZFC) processes between 5 and 300 K (Figure 10). The peaks in the ZFC branches are observed at 92 and 71 K for Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>-PVP, respectively (Figure 10a,b). The bifurcation of the FC-ZFC branches at 128 and 116 K, respectively, is considered as the blocking temperature of the materials  $(T_{\rm B}$ , see Figure 10c,d). The shape of the FC magnetization curve at lower temperatures below the ZFC peak determines the behavior of the MNP in the nanofluid. An increasing FC magnetization in the above-mentioned region indicates an absence of interparticle interactions, whereas a nearly constant or saturating FC curve is associated with strong interactions between the suspended NPs. From Figure 10a,b, it is imperative to note that the surfactant-based nanofluids lack the interparticle interactions, resulting in a decrease in  $T_{\rm B}$  (116 K) because of a reduced anisotropy contribution from the surfactant matrix around the NP.<sup>11</sup> The absence of the surfactant also depicts a flat FC curve for  $Fe_2O_3$  NPs in turn, leading to a higher  $T_B$ value (128 K). The small rise in the blocking temperature of Fe<sub>2</sub>O<sub>3</sub> can also be attributed to the slightly higher particle size and decreased random fluctuations of uncapped MNPs at low temperatures.

The combination of Figures 9 and 10 implies that both  $Fe_2O_3$  and  $Fe_2O_3$ -PVP NPs are composed of two magnetic components: (1) a major component of  $Fe_2O_3$  with a  $T_B$  of around 120 K and (2) a minor magnetic phase, probably magnetite ( $Fe_3O_4$ ). The  $M_s$  for bulk  $Fe_3O_4$  at RT is 96 emu/ g.<sup>43</sup> This means, from the current magnetization ( $M_s$ ) values at RT (5.7 and 4.7 emu/g), that the minor phase ( $Fe_3O_4$ ) in both materials is around 5–6%. The full hysteresis curve of  $Fe_2O_3$ -PVP at 5 K (Figure 10e) shows a small coercive field  $H_c$  of 850(20) Oe. The extrapolated  $H_c$  at 6 K for  $Fe_2O_3$  ( $T_B = 128$  K) is 1250(50) Oe.

No coercivity is observed at RT (Figure S6), indicating that the coercivity is attributed to the major magnetic phase and that both NPs are in superparamagnetic state. The lower magnetization values observed in the M(T) plots are expected for the MNPs of the nanofluid on account of their distinct behavior in the base liquid.<sup>44</sup> The individual NPs, due to their small size and dispersed nature, behave as single-domain magnets exhibiting superparamagnetism. This causes a low hysteretic response (at 5 K) of the MNPs where each particle behaves as a magnet, free to fluctuate while the atomic moments are ordered with respect to each other.

The absence of magnetic phase (sextet) in the Mössbauer spectrum arises from the tiny amount of the (probably  $Fe_3O_4$ ) particles (below the threshold of the Mössbauer technique), which are magnetic at RT. The bulk might have a blocking temperature lower than the RT. This tiny amount of magnetic particles attracts the rest of the material by adhesive forces.

The surfactant effect on the Mössbauer spectra and magnetization of the MNPs is influenced by the surface Fe ions. The surfactant impedes the magnetization of the surface ions, resulting in a small decrement in the saturation moment.<sup>45</sup> However, the loss in magnetization is negligible owing to the large amount of PVP used in the synthesis of the MNPs in this study. Thus, this paper concludes that the stability of the magnetic nanofluids can be enhanced substantially with the addition of a capping agent with only a trivial shift in their magnetism.

## CONCLUSIONS

A feasible one-pot synthesis of magnetic nanofluids was successfully achieved with and without the PVP surfactant. This synthesis route resulted in an enhancement of their thermal conductivity compared to previous reports. In addition, the thermal transport as a function of external magnetic stimuli was described, emphasizing the effect of the stabilizer. The electrical conductivity of all nanofluids-both Fe and Fe<sub>2</sub>O<sub>3</sub>-showed a significant enhancement over the base liquid. A possible mechanism for the deviation in the electrical transport in the presence of PVP is described. The indepth measurements of the magnetism of the Fe<sub>2</sub>O<sub>3</sub> nanofluids clarified the discrepancies regarding their role in the presence of a surfactant. To summarize, the present investigation formulates a clear understanding of the properties of the magnetic nanofluids, which have not been previously scrutinized. This study also sheds light on important issues that require further exploration.

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b05433.

Experimental and characterization details, XRD and Raman spectra, images of the magnetic nanofluids after 4 months, UV–visible plot, and magnetization curves at RT (PDF)

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#### Notes

The authors declare no competing financial interest.

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