Effect of composition on rheological behavior of iron oxides produced by hydrothermal method

Alan R. de Oliveira\textsuperscript{a}, Afshin Abrishamkar\textsuperscript{b}, Ewerton M. Veloso\textsuperscript{a}, Fernando C. de Oliveira\textsuperscript{c}, Jeferson G. Da Silva\textsuperscript{a}, Juliano R. Pereira\textsuperscript{a}, Renata Dini\textsuperscript{d}, Ângelo M.L. Denadai\textsuperscript{a,⁎}

\textsuperscript{a} Instituto de Ciências da Vida (ICV), Universidade Federal de Juiz de Fora, Campus Governador Valadares (UFJF-GV), Av. Dr. Raimundo Monteiro de Resende, 330, Centro, Governador Valadares, MG 35010-177, Brazil
\textsuperscript{b} Department of Chemistry and Applied Biosciences, Swiss Federal Institute of Technology (ETH Zurich), Vladimir-Prelog-Weg 1, 8093 Zurich, Switzerland
\textsuperscript{c} Departamento de Química e Metalurgia, Centro Federal de Educação Tecnológica de Minas Gerais (CEFET-MG), Campus Timóteo, Rua Dezenove de Novembro, 121, Centro Timóteo, MG 35180-008, Brazil
\textsuperscript{d} Departamento de Química, Universidade Federal de Minas Gerais (UFMG), Campus Pampulha, Av. Pres. Antônio Carlos, 6627, Pampulha, Belo Horizonte, MG 31270-901, Brazil

A R T I C L E  I N F O

Keywords:
Iron oxides
Colloidal suspension
Rheology
Hydrogen bonding

A B S T R A C T

The aim of the present work was to investigate the rheological properties of different iron oxides (Fe\textsubscript{2}O\textsubscript{3}, NiFe\textsubscript{2}O\textsubscript{4}, ZnFe\textsubscript{2}O\textsubscript{4} and Ni\textsubscript{0.5}Zn\textsubscript{0.5}Fe\textsubscript{2}O\textsubscript{4}) aqueous suspensions. The oxides were produced through mixing the respective metallic sulfates within a closed isothermal reactor at 100 °C and at pH =12, in an oxidant environment (provided by H\textsubscript{2}O\textsubscript{2} 0.63% w/v). The reactor was coupled with an adequate real-time data (RTD) acquisition system enabling measurement of temperature, pH and pressure. Obtained RTD data showed that once the isothermal conditions are reached, the pressure slowly decreases over time, which is a result of O\textsubscript{2} consumption through oxidation of Fe\textsuperscript{2+} to Fe\textsuperscript{3+}. To characterize the suspensions as a function of temperature and shear rate, the steady rheology was used. The results revealed that the effect of temperature on viscosity of all suspensions was insignificant while steady rheology showed pseudoplastic behavior for all ferrites. The magnitude of viscosity and pseudoplasticity turned out to be in agreement with the hydrodynamic diameters of particles complying with the order: NiFe\textsubscript{2}O\textsubscript{4} > Fe\textsubscript{3}O\textsubscript{4} > Ni\textsubscript{0.5}Zn\textsubscript{0.5}Fe\textsubscript{2}O\textsubscript{4} > ZnFe\textsubscript{2}O\textsubscript{4}. Finally, the rheological behavior of suspensions was attributed to the concentration of OH groups on the surface of particles and the hypothesis was effectively supported by DRX, FTIR and TGA/DTA measurements.

1. Introduction

Production of ceramic materials by wet routes, such as sol-gel syntheses [1,2], microemulsions [3], sonochemical [4], hydrolysis of precursors [5,6], flow injection syntheses [7], hydrothermal reactions [8,9] and coprecipitation [10–12] involves at least one liquid phase (e.g. aqueous solution), which leads to formation of a viscous suspension of these materials as a product.

From engineering point of view, the fluidized product obtained by wet routes has a number of advantages including the greater facility of mixing as well as possibility of transport by pulping, diffusion and heat transfer through convection [13,14]. Moreover, the liquid phase is an ideal environment for the functionalization of particles [15,16], enabling a homogeneous contact between the reagents while maintaining their colloidal stability through the use of anti-flocculants compounds [17,18].

However, during the production of some classes of ceramics in given conditions, for instance ferrites in alkaline solutions, wet-synthesis spontaneously produces materials covered with hydroxylated groups such as hydroxides (M-OH) or oxide-hydroxides (MO-OH) [11,12]. These materials typically exhibit a more complicated behavior compared to synthetic materials, like polymers in aqueous environments [19–21].

One of the main factors contributing to such a complexity is the large number of possibilities for their surfaces to interact with the solvent under acid/basic equilibrium conditions, which is caused either by the amphoteric characteristic of some transition metals or by variety of oxidation states. This phenomenon results in several colloidal interactions [22], such as electrostatic forces, van der Waals forces and hydrogen bonding with solvent molecules, electrolytes or neighbored particles [23].
These interactions, depending on pH and electrolytes concentration, can directly affect the viscosity of iron oxide suspensions by induction of particles aggregation. For instance, due to the presence of strong attractive forces, goethite suspensions (α-FeOOH) at flocculated conditions can have viscosity values that are one to three orders of magnitude greater than those of the suspending fluid (water), even at solid volume fractions close to 0.1 [20].

Viscosity of a fluid is defined as the extent of its resistance against the gradual deformation by shear stress, corresponding to the informal concept of “thickness”. In other words, viscosity is a physical-chemistry property that depends on the size, shape, concentration and mutual interactions of both particles and their aggregates [24]. Thus, the knowledge of the rheological behavior of colloid suspensions is of great importance to understand how these particles interact and how their chemical structure affects their size, stability, mutual interactions and transport properties.

Rheological properties can be directly affected by varying the composition of iron oxides, particularly when OH groups can be incorporated on the surface of particles during the synthesis. Therefore, iron oxides containing doping ions such as Zn2+ or Ni2+, which form oxides with different stabilities, can lead to the formation of particles with suspensions having M-OH groups at different concentrations.

With respect to the fact that the wet synthesis of iron oxides is a globally widespread process, the present work aimed to investigate the effect of chemical composition of four stoichiometric iron oxides i.e. Fe3O4, NiFe2O4, ZnFe2O4 and Ni0.5Zn0.5Fe2O4 on the rheological behavior of their aqueous suspensions. To this end, the oxides were all prepared through coprecipitation method at 100 °C in an automatized isothermal reactor coupled with an appropriate real-time data (RTD) acquisition system for measurement of T (°C), pH and P (kgf/cm²). The structures of the oxides were analyzed through X-ray powder diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR).

Also, their thermal behavior was assessed by differential thermal analysis (DTA) and thermogravimetric analysis (TGA) measurements. Finally, the colloidal properties of the oxides in suspension were studied by means of dynamic light scattering (DLS), while the rheological properties were investigated by steady rheology through measuring the shear stress with respect to the temperature and shear rate.

2. Experimental details

2.1. Reagents

The metal sulfates (FeSO4·7H2O, NiSO4·6H2O, and ZnSO4·7H2O) were purchased from Merck Laboratory and the reagents NaOH and H2O2 (10% v/v) were obtained from VETEC. All reagents were used as received. The amounts of salts used for each synthesis are listed in Table 1.

2.2. Synthesis of iron oxides

The iron oxides were prepared through the coprecipitation reaction of their respective metal sulfate (or a mixture of several of them) in a highly alkaline and oxidizing environment. In order to precisely control the synthesis conditions, the reactions were carried out in an automatized isothermal reactor containing a stainless steel vessel of 1.2 L, coupled with a real-time data (RTD) acquisition system for measurement of temperature (°C), pH and pressure (kgf/cm²) (see Figs. S1–S3; Supplementary material).

In a typical synthesis, the salt was initially dissolved in 600 mL of water at room temperature (ca. 25 °C) and the solution was subsequently transferred to the metallic vessel of reactor. The solution was then heated up to 80 °C with stirring at 250 rpm while the reactor was kept open.

After 5 min that the system reached the temperature of 80 °C, 50 mL of a 20 mol/L NaOH solution was added into the reactor to produce the hydroxides according to Eqs. (1)–(3).

$$\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2(\text{s}) \quad (1)$$

$$\text{Ni}^{2+} + 2\text{OH}^- \rightarrow \text{Ni(OH)}_2(\text{s}) \quad (2)$$

$$\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2(\text{s}) \quad (3)$$

Subsequently, 50 mL of a 10% v/v H2O2 solution was added to the reactor, which was immediately closed and heated up to 100 °C. The reaction was carried out isothermally for 2 h under autogenerated pressure (Fig. S3; Supplementary materials).

H2O2 is known to be unstable at high temperatures and high pH values, and its decomposition reaction results in O2 as the main product [25]:

$$2\text{H}_2\text{O}_2(\text{l}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g}) \quad (4)$$

And in the presence of gaseous O2, Fe2+ is oxidized to Fe3+ through the global reaction [26]:

$$4\text{Fe(OH)}_2(\text{s}) + \text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 4\text{Fe(OH)}_3(\text{s}) \quad (5)$$

It is known that transition metal hydroxides undergoes a dehydration process at high temperatures (above 100 °C), leading to the formation of their respective oxides through a complex mechanism, which can be briefly expressed through the following reactions: [27–30]

$$\text{Fe(OH)}_2(\text{s}) \rightarrow \text{FeO}(\text{s}) + \text{H}_2\text{O}(\text{g}) \quad (6)$$

$$2\text{Fe(OH)}_3(\text{s}) \rightarrow \text{Fe}_2\text{O}_3(\text{s}) + 3\text{H}_2\text{O}(\text{l}) \quad (7)$$

$$\text{Zn(OH)}_2(\text{s}) \rightarrow \text{ZnO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \quad (8)$$

$$\text{Ni(OH)}_2(\text{s}) \rightarrow \text{NiO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \quad (9)$$

After the synthesis, the oxide suspensions were cooled down to room temperature and continuously washed with deionized water until their electrical conductivity values reached that of the input water (ca. 10 μS/cm). Then, suspensions containing iron oxides with the concentration of 0.01 g/mL were obtained by appropriate dilution. Finally, the suspensions were split into two aliquots, where the first one was dried and used for solid-state characterization and the second one was used to investigate the properties of the aqueous suspension, after fine adjustments of concentration.

2.3. Solid-state characterization

X-Ray Powder Diffraction (XRD) data were collected using a Bruker D8 DaVinci diffractometer, equipped with CuKα radiation, LynxEye linear Position Sensitive Detector, Ni-filter and Bragg-Brentano geometry. Data were collected between 10 and 100° in 2θ with step size of 0.02° and a count time of 1.0 s per step. A Soller slit with 2.5° of divergence and a 0.6 mm divergent slit were used. For all analyses a voltage of 40 kV and a current of 40 mA were applied to generate the incident radiation and all measurements were performed at room temperature (298 K). Infrared spectra were obtained in transmission mode using Perkin-Elmer Spectrum Two™ FTIR spectrometer. The samples were prepared in KBr pellets and...
measurements were carried out between 4000 and 400 cm\(^{-1}\) with 16 scans and resolution of 2 cm\(^{-1}\). Differential Thermal analysis (DTA) and thermogravimetric analysis (TGA) data were acquired for all iron oxides using a Hitachi TGA/DTA modulus (STA7200RV). The experiments were performed under a dynamic air atmosphere of 50 mL/min, a heating rate of 10 °C/min, and with sensitivity of 1.0 °C. For each experiment, approximately 5 mg of sample was used in an open platinum pan.

2.4. Rheological behavior

Rheological behavior of iron oxides suspensions was investigated through steady flow rheometry in a controlled shear rate rheometer R-180 from Pro Rheo\(^\circ\). To this end, DIN standard 53019 measuring system, consisting of a cup \((d=26.03\text{ mm}, V=25\text{ mL})\) and a bob \((d=24.00\text{ mm}, h=36.00\text{ mm})\), was used. The experiments were performed as a function of temperature and shear rate \((\phi)\). The precise concentration of oxidized suspensions was gravimetrically determined by drying a known volume of suspensions (in triplicate). Once the solid content \((\text{in g/mL})\) was determined, the concentration of suspensions was adjusted to the desired value, which was 0.07 g/mL.

The temperature experiments were carried out at the constant concentration of 0.07 g/mL and constant shear rate of 1000 s\(^{-1}\). This shear rate value was used in order to guarantee the disruption of interparticle interactions by mechanical stress, enabling therefore the evaluation of effects of temperature on rheological behavior in the proximity of Newtonian regime. At this situation, the differences in viscosity values of iron oxides are mainly due to different hydrodynamic volumes of particles or small aggregates.

To perform these experiments, the rheometer cup was directly immersed in a thermostatic bath, which was heated from 20 to 60 °C with an average heating rate of 0.5 °C/min. To plot the relative viscosity curves as shown in Fig. 4B, the viscosity values of water were obtained from reference [31], as the sensitivity of rheometer was not high enough to measure the viscosity of low viscous fluids like water.

In the flow experiments, samples were initially pre-sheared for 2 min at 100 s\(^{-1}\) and they were then subjected to a loop of shear rate. Iron oxides suspensions were all sheared in duplicate from 100 to 1000 s\(^{-1}\) and then reversely from 1000 to 10 s\(^{-1}\) at 20 °C. In all systems, the shear rate was varied in linearly spaced steps that each took 30 s to complete. This range of shear rate was chosen due to two main reasons; firstly, because it partially covers the values typically for industrial mixing, and pipe flow [24]; and secondly, because this was the range where the rheometer showed better response for all samples. All data were collected and treated utilizing the software RHEASY\(^\circ\). Subsequently, they were exported to Microcal Origin 8.0 for further analysis.

2.5. Hydrodynamic diameter

As a measure of the size of particles, the average hydrodynamic diameter \((D_h)\) in aqueous solutions were measured by a Malvern Zetasizer Nano Series ZA particle analyzer, using polyethylene square cells. The samples were measured by a monochromatic light \((10\text{ mW He–Ne laser, wavelength }632.4\text{ nm})\), where the scattered light intensity was measured at an angle of 90°. \(D_h\) values were measured independently for five times and each value was achieved as the mean of 30 counts. All suspensions were prepared in ultrapure water, Milli-Q\(^\circ\), at solids content of 0.01 g/mL.

3. Results and discussion

3.1. Structural analysis

Ferrites are mixed iron oxides with the formula of MFe\(_2\)O\(_4\), with M usually being one of the first-row transition metals. These compounds adopt a crystal motif consisting of cubic close-packed (fcc) oxides (\(O^2−\)) with M and Fe\(^{3+}\) occupying the tetrahedral and octahedral holes, respectively. These structures, called spinels, can be formed in different types by incorporation of different cations. For example, the ZnFe\(_2\)O\(_4\) crystals are well-known to have a normal spinel structure with the tetrahedral M-sites occupied by Zn\(^{2+}\) ions and the octahedral sites by Fe\(^{3+}\) ions [4]. On the other hand, Fe\(_3\)O\(_4\) and NiFe\(_2\)O\(_4\) crystals typically have inverse spinel structures, where Fe\(^{3+}\) or Ni\(^{2+}\) ions occupy octahedral sites while Fe\(^{3+}\) ions are equally distributed between tetrahedral and octahedral sites [10,32]. Ni\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) is known to be a mixed spinel ferrite [33].

The X-ray-diffraction patterns of synthesized iron oxides are shown in Fig. 1. As the figure demonstrates, all of them showed broad Bragg peaks in DRX, indicating low crystallinity. This behavior is commonly found in iron oxides produced by wet routes and without thermal treatment [34,35]. All ferrites exhibited cubic spinel phase with major XRD peaks around 30°, 35°, 43°, 53°, 57° and 63°, ascribed to the (220), (311), (400), (422), (511) and (440) planes. These XRD patterns are attributed to the Ni\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) phase (JCPDS: 52–0278), Fe\(_3\)O\(_4\) phase (JCPDS: 89–0691), ZnFe\(_2\)O\(_4\) phase (JCPDS: 82–1049), and NiFe\(_2\)O\(_4\) phase (JCPDS: 86–2267). The presence of other phases is also shown for the Ni\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) ferrite shows peaks at 2θ=11.4° and 23.2°, ascribed to the \(\gamma\)-NiOOH phase (JCPDS: 06-0075), while Fe\(_3\)O\(_4\) and NiFe\(_2\)O\(_4\) ferrites show smaller XRD peaks at 21.3°, 33.3°, 36.7°, 40.2° and 41.1° that are attributed to the presence of \(\alpha\)-FeOOH (goethite) (JCPDS: 29-0713).

The FTIR analysis helps to identify the spinel structures, functional groups and chemical substances adsorbed on the surface of particles. Fig. 2 depicts the FTIR spectra of the four iron oxides recorded between 4000 and 400 cm\(^{-1}\). The main vibrations are summarized in Table 2. In all samples, broad bands are observed in two ranges of 510–750 cm\(^{-1}\) and 360–500 cm\(^{-1}\), due to the vibrations of metal iron–oxygen at the tetrahedral sites (Fe–O\(_{\text{tet}}\)) and octahedral sites (Fe–O\(_{\text{oct}}\)), respectively [34,36].

In the FTIR spectra, broadband peaks with the maximum at around 3400 cm\(^{-1}\), corresponding to the stretching of hydroxyl groups coordinated on the particles, are ascribed to the presence of M–OH [37]. Adsorption of water on the samples is also confirmed by the bending mode of water molecules \((\delta_{\text{H-O-H}})\) around 1630–1650 cm\(^{-1}\) [34]. The Fe\(_3\)O\(_4\) and NiFe\(_2\)O\(_4\) oxides still show bands at around 3210, 895 and 796 cm\(^{-1}\), which are associated with the stretching of in-plane and out-of-plane bending of O–H bonds of \(\alpha\)-FeOOH [38,39]. Ni\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) shows bands around 1464 cm\(^{-1}\) attributed to the O–H bending modes of OH lattice.
In order to evaluate the dehydration profile of iron oxides as well as their ability to incorporate different amounts of OH groups and water molecules, thermal analysis of TGA and DTA were performed as shown in Fig. 3.

For all samples, only two major events are observed within the range of studied temperatures. An initial loss of mass with a not well defined range of temperature is related to the departure of adsorbed water molecules and small molecules like CO$_2$. These events are commonly found in iron oxides synthesized via wet routes [37,40]. Furthermore, all iron oxides exhibit another subsequent and greater mass loss, which is attributed to the dehydration caused by breakdown of M-OH groups.

Only for the Fe$_3$O$_4$ a well-defined range of loss of mass is found, which is from around 190–307 °C. For the other three ferrites, this phenomenon also starts at a defined temperature; however, the finishing temperature is not clear. The presence of a clear finishing temperature for Fe$_3$O$_4$ is probably due to the higher homogeneity of its chemical composition, which contains lower amounts of Fe$_2^+$-OH and Fe$_3^+$-OH groups. In the other iron oxides, the number of M$_x$(OH)$_y$ possibilities with different bond energies is greater, and thus, a less defined range of decomposition is to be expected. The main temperatures of mass loss events obtained from TGA curves are summarized in Table 3.

DTA curves also exhibit the same events for the iron oxides as those observed in TGA measurements. In fact, the desolvation and dehydration are both endothermic phenomena, due to the absorption of energy required to breakdown the hydrogen bonds of adsorbed H$_2$O and the covalent bonds in M-OH groups.

Based on these thermograms, the order of the capability of iron oxides to bind water molecules, OH groups and structural water molecules can be sorted as NiFe$_2$O$_4$ > Ni$_0.5$Zn$_0.5$Fe$_2$O$_4$ > ZnFe$_2$O$_4$ > Fe$_3$O$_4$. This order can be explained by the Gibbs free energy value calculated for the reaction in Eq. (10) (the reverse path of Eqs. 6–9), suggesting that nickel cation has a greater ability to form hydroxides, which is resulted from its greater affinity to OH groups: Ni(OH)$_2$ ($\Delta_rG^\circ$=−7370 J/mol) < Zn(OH)$_2$ ($\Delta_rG^\circ$=+1730 J/mol) < Fe(OH)$_3$ ($\Delta_rG^\circ$=+2196 J/mol) < Fe(OH)$_2$ ($\Delta_rG^\circ$=+8740 J/mol).

$$\text{M}_x\text{O}_{y+z} + y\text{H}_2\text{O}(s) \rightarrow x\text{M(OH)}_{2y+1}(s), \text{ at } 25^\circ\text{C}$$

(10)

### Table 2
Summary of the main FTIR absorption bands for iron oxides (Fe$_3$O$_4$, NiFe$_2$O$_4$, ZnFe$_2$O$_4$ and Ni$_0.5$Zn$_0.5$Fe$_2$O$_4$).

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>Fe$_3$O$_4$</th>
<th>NiFe$_2$O$_4$</th>
<th>Ni$_0.5$Zn$_0.5$Fe$_2$O$_4$</th>
<th>ZnFe$_2$O$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_{M-O}$</td>
<td>574</td>
<td>559</td>
<td>587</td>
<td>549</td>
</tr>
<tr>
<td>$\nu_{M-O}$</td>
<td>400</td>
<td>406</td>
<td>399</td>
<td>399</td>
</tr>
<tr>
<td>$\delta_{M\text{-}OH}$ in-plane FeOOH</td>
<td>796</td>
<td>798</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>$\delta_{M\text{-}OH}$ out-plane FeOOH</td>
<td>894</td>
<td>894</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>$\delta_{H\text{-}O}$ water</td>
<td>1655</td>
<td>1635</td>
<td>1630</td>
<td>1633</td>
</tr>
<tr>
<td>$\nu_{H\text{-}O}$ water</td>
<td>3433</td>
<td>3416</td>
<td>3467</td>
<td>3412</td>
</tr>
</tbody>
</table>

### Table 3
Summary of the main loss of mass for iron oxides (Fe$_3$O$_4$, NiFe$_2$O$_4$, ZnFe$_2$O$_4$ and Ni$_0.5$Zn$_0.5$Fe$_2$O$_4$).

<table>
<thead>
<tr>
<th>Thermal transition</th>
<th>Thermal transition (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiFe$_2$O$_4$</td>
<td>Fe$_3$O$_4$</td>
</tr>
<tr>
<td>Water desorption</td>
<td>30–120 °C</td>
</tr>
<tr>
<td>Dehydration</td>
<td>130–310</td>
</tr>
<tr>
<td>percentage loss</td>
<td>7.3%</td>
</tr>
<tr>
<td>Total loss of mass</td>
<td>19.3%</td>
</tr>
</tbody>
</table>

Fig. 3. A) TGA and B) DTA curves for iron oxides.
As previously mentioned, viscosity is an important physical-chemical property that is directly dependent on the intermolecular interactions, and consequently, on the chemical structure of the components of a suspension. In this work, the suspensions of Fe3O4, NiFe2O4, ZnFe2O4, and Ni0.5Zn0.5Fe2O4, synthesized under the same operational conditions, were all characterized by steady rheology in order to evaluate the effect of composition and amount of hydroxyl groups, incorporated on the surface of these oxides, on their flow properties. These structural differences can lead to a change of morphology (size, shape, and effective volume fraction) in the aggregates of dispersed phase; resulting in variations of the flow properties of the dispersions.

Initially, the effect of temperature on the viscosity of suspensions was evaluated through flow-temperature analysis depicted in Fig. 4. For these experiments, the suspensions with the concentration of 0.07 g/mL and shear rate of 1000 s⁻¹ were prepared and measured within the temperature range of 20–60 °C. This range of temperatures was chosen due to its wide applicability in industrial processes.

Fig. 4A demonstrates that the viscosity of ferrites actually undergo an insignificantly and approximately linear change with temperature, not complying with the exponentially decreasing profiles predicted by Arrhenius model (Eq. (11)) [29]:

\[ \eta = \eta_\infty e^{\frac{E_a}{RT}} \]  

(11)

Therefore, the nonlinear fitting commonly used for determination of the flow activation energy \(E_a\) and asymptotic viscosity \(\eta_\infty\) was not used. The rates of viscosity change over temperature \(\frac{\eta}{dT}\), determined by linear fitting of curves in Fig. 4, are listed in Table 4.

It is important to highlight that the viscosity of water strongly decreases with increasing temperature as a result of the breakdown of hydrogen bonds. Thus, in order to consider this phenomenon in the suspensions, the temperature dependence of the relative viscosity, \(\eta_{rel}\), was also investigated, which was obtained by Eq. (12):

\[ \eta_{rel} = \frac{\eta_{1000}}{\eta_{20}} \]  

(12)

As shown in Fig. 4B, \(\eta_{rel}\) increases with temperature for all ferrites due to reduction of water viscosity. Within the temperature range investigated, the magnitude of increase was approximately 70%, 129%, 70% and 112% for NiFe2O4, Fe3O4, Ni0.5Zn0.5Fe2O4 and ZnFe2O4 respectively. These different values confirm that the structural effects connected to particle aggregation are differently important for each system.

The greatest increase in the \(\eta_{rel}\) values was observed for the two systems where the \(\eta_{1000}\) values were practically unchanged (Fe3O4 and ZnFe2O4). On the other hand, in the two systems with highest modulus of \(\frac{d\eta}{dT}\), the \(\eta_{rel}\) values were offset due to reduction of water viscosity, and thus, had lowest increase with the temperature.

These differences were attributed to the presence of nickel in these iron oxides (specially NiFe2O4), which has the highest capability to form hydrogen bonds, as described above. Thus, it is hypothesized that the concentration of hydrogen bonds in the nickel-based iron oxides must be sufficiently high, so that the small aggregates resulting from particle-particle and particle-solvent interactions would still exist in the suspension therefore enabling the suspension to bear the high shear rate (1000 s⁻¹) and high temperatures.

Figs. 5A and B show the flow and viscosity curves of the suspensions measured at 20 °C and 0.07 g/mL of solids, while being sheared from 100 to 1000 s⁻¹ and then reversely from 1000 to 100 s⁻¹.

As Fig. 5B evidently implies, all suspensions exhibit pseudoplastic behavior as the viscosity decreases upon increase of the shear rate. Moreover, the magnitude of viscosity follows the same order observed in the temperature-dependent viscosity experiments, where NiFe2O4 has the greatest viscosity value.

In order to quantify the non-Newtonian characteristics of the fluids, the flow curves are modeled using the Ostwald de Waale model (Eq. (13)), where \(\tau\) is the shear stress, \(K_c\) is the consistency index (that is a measure for the viscosity of a non-Newtonian fluid), \(\phi\) is the shear rate and \(n\) is the behavior index, parameter used to quantify the non-Newtonian behavior (\(n=1\), Newtonian; \(n<1\), pseudoplastic; and \(n>1\), dilatant).

\[ \tau = K_c\phi^n \]  

(13)

For all the fluids \(n\) was lower than unity, confirming the pseudoplastic behavior. This behavior suggests that the aggregates of particles in the suspensions were broken down into smaller flow units by the applied forces, so that the resistance to flow was reduced, leading to the lower viscosity values as the shear rate was increased.

The order of pseudoplasticity and consistency index was found to be: NiFe2O4 > Fe3O4 > Ni0.5Zn0.5Fe2O4 > ZnFe2O4, which is, in a more quantitative way, depicted in Figs. 6A and 6B.

In order to improve the understanding of the rheological data, dynamic light scattering measurements were used to determine the
hydrodynamic diameter ($D_h$) of the particles and the obtained data were correlated with the viscosity data. Fig. 7 shows the $D_h$ data for the particles in aqueous suspensions at 0.01 g/mL of solid.

The particle sizes are in good agreement with all the rheological parameters ($K_c$, $n$, $d\eta/dT$) of iron oxides suspensions and, with the exception of Fe$_3$O$_4$, also with the concentration of hydroxyl groups, as shown by TGA analysis. This outcome suggests that the strong and attractive solute-solute (M-O-H—OH-M) or solute-solvent (M-O-H—OH$_2$) hydrogen bonds are responsible for the aggregation and the hydration of particles/aggregates. Also, this proves that the rate of these interactions directly defines the size of particles/aggregates and rheological behavior of their suspensions.

However, in terms of the physical chemistry parameters evaluated herein, an anomalous behavior is observed for Fe$_3$O$_4$ compared to other compounds. It exhibited lower hydroxylation degree among all oxides, though had intermediate values of $D_h$ and rheological parameters. And there are several reasons for why this compound and its aqueous suspensions show this sort of behavior that justify such anomalies. As shown by FTIR and TGA data, this iron oxide incorporated the lowest amount of hydroxyls. Consequently, weaker solute-solvent interactions are expected, so that hydrogen bonding is less probable. However, unlike the doped iron oxides, the more homogeneous structure of Fe$_3$O$_4$ contributes to the "exchange interactions" in the solid state, giving rise to an intense ferromagnetic attraction [42]. These interactions lead to a greater rigidity in these particles, and hence, increasing the viscosity of their suspension.

### 4. Conclusion

In this work, it is shown that different iron oxides synthesized through coprecipitation method (wet route) and under the same reaction conditions, exhibit different amounts of OH groups, as a measure of the remaining amount of M(OH)$_x$, in the following order: NiFe$_2$O$_4$ > Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ > ZnFe$_2$O$_4$ > Fe$_3$O$_4$. This trend is consistent
with the Gibbs free energy data of M(OH)₂ formation reported in literature (from their oxides), demonstrating that Ni(OH)₂ is the most stable hydroxide and also explaining the wider dehydration range for NiFe₂O₄, as shown in TGA measurements. With the exception of Fe₃O₄, where the strong ferromagnetic forces affect the size of particles/aggregates, the hydrodynamic diameter and all rheological parameters of the suspensions are proven to be proportionally dependent on the concentration of hydroxyl groups. And this finding is believed to be due to the ability of these iron oxides to establish hydrogen bonds among them as well as with the solvent. In this regard, in the present study is evidently demonstrated that the concentration of OH groups in particles/aggregates is a crucial key to determine the viscosity of iron oxides suspensions.

Acknowledgments

The authors are grateful to the Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG: APQ-00435-14, APQ-01293-14 and APQ-03536-16), Centro Federal de Educação Tecnológica de Minas Gerais (CEFET-MG), Universidade Federal de Juiz de Fora (UFJF–PROPG), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq: 310175/2014-3, MCT/CNPqNANO: 550321/2012-8) and Financiadora de Estudos e Pesquisas (FINEP: 0633/13). The authors also thank the Departamento de Química of Universidade Federal de Juiz de Fora for X-ray facilities. This work is a collaborative research project with members of Rede Mineira de Química (RMQ-MG) supported by FAPEMIG (Project: CEX - RED-0010-14).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ceramint.2017.03.005.

References