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Magnetically Induced Agitation in Liquid-Liquid-Magnetic Nanoparticle Emulsions: Potential for Process Intensification

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Microscopic mixing using magnetic nanoparticles (MNP) unveils exciting ramifications for process intensification in chemical engineering. This study explores the use of oil-in-water MNP emulsions to achieve mixing in a nonmagnetic continuous phase tantamount to that occurring in equivalent dilute ferrofluid suspensions. To assess the technique, measurements of the torque exerted by ferrofluid emulsions and suspensions of equal magnetic content were performed in rotating, oscillating, and static magnetic fields. Results show that momentum transfer is fairly alike in amplitude and proportionality for the two types of systems of equal magnetic content under the three types of magnetic fields. This implies that momentum of spinning nanoparticles in the emulsions is transferable to the oil droplets containing them which, in return is then transferred to surrounding nonmagnetic liquid. The magnitude of the resulting mixing allows for the foresight of a versatile MNP mixing technology completely separated from the target phase being mixed. *AIChE J*, 60: 1176–1181, 2014
Keywords: torque measurement, ferrofluid, emulsion, magnetic nanoparticle, mixing, process intensification

Introduction

Stable colloidal suspensions of magnetic nanoparticles (MNPs) continue to be broadly studied as these enable the modification of liquid properties, especially when submitted to external magnetic fields.[1,2] Indeed, they exhibit unique behavior compared to the bulk form of ferro or ferrimagnetic materials. The size-dependent properties of MNPs, especially their superparamagnetism that stem from their single-domain nature and their high-specific surface area are considered to form the basis for the design of novel magnetically stimulated techniques with multiple applications in chemical engineering, chemistry, biotechnology, and medicine.[3–6]

The modification and control of fluid properties principally stem from the transfer of electromagnetic energy from the MNPs to the liquid, resulting in the occurrence of noteworthy alterations of liquid magnetoviscous properties. For example, in a ferrofluid shear flow, it is known that an external magnetic field forces MNPs to spin asynchronously with respect to the local fluid vorticity of the fluid, resulting in an anisotropic modification of viscosity.[7] This behavior, known as rotational viscosity, was identified and studied using ferrofluid body torque measurements in a cylindrical Couette geometry.[8–11]

Recently, this energy transfer from the MNPs to the liquid has been put in use by converting the suspended particles into nanostirrers allowing control of mixing in nanoscale when the whole system is subject to rotating, oscillating, and static uniform magnetic fields (RMF, OMF, SMF).[12,13] In doing so, it has been shown that rotating MNPs under transverse RMF generates nanoscopic liquid eddies inducing enhancement of liquid transport properties beyond the conventional paradigm of molecular diffusion.[12,13]

However, conventional ferrofluids imply direct contact between surfactant-stabilized MNPs and a continuous liquid phase, for example, solvent. This represents a severe impediment to implement (bio)chemical transformations directly in ferrofluids. As a matter of fact, preserving the MNP colloidal stability despite occurrence of potentially unwanted chemical interactions between the stabilizing surfactants and desirable (bio)chemical transformations is far from being a trivial task. To avoid this possibility while still taking advantage of the magnetic, nanoscale mixing effect of MNPs, to promote mixing we propose the use of ferrofluid emulsions consisting of small immiscible ferrofluid droplets emulsified in a nonmagnetic continuous phase.[14,15] Currently, experimental evidence is lacking concerning magnetic torque transfer from the MNPs trapped inside the immiscible droplets of an emulsion to its surrounding continuous nonmagnetic phase under magnetic field stimulation. The possibility for such bottom-to-up momentum transfer, if objectified, is expected to open up a range of new process intensification applications where MNP-bearing liquid inclusions can serve to mix, without interference, nonmagnetic liquids where chemical transformations are running.

Consequently, we proposed to investigate the effects of different RMF, OMF, and SMF on the body torque exerted by MNPs inside oil-based ferrofluid emulsions and to compare them to water-based ferrofluids with the same magnetic content. Our analysis allowed quantifying the amplitude of the force exerted by excited MNP action inside ferrofluid

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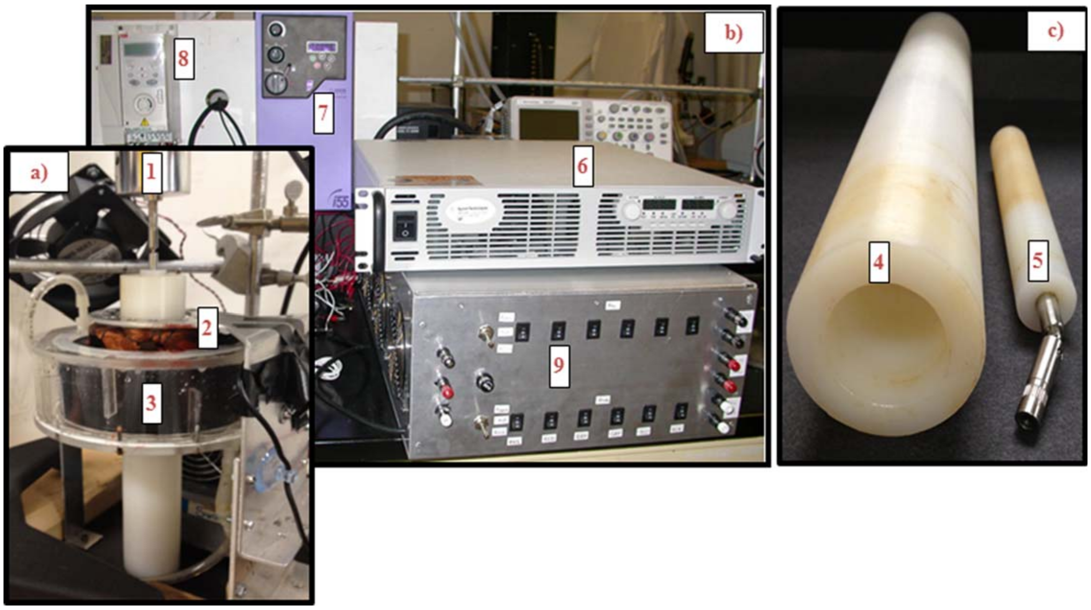

Figure 1. Torque measurements experimental setup and components (a) Magnet device, (1) Brookfield LVII+Pro viscosimeter, (2) magnet, (3) cooling jacket (b) magnet assembly and versatile power supply for (6) dc, (7) ac (8) RMF generation, (9) rectifier (c) ultrahigh density polyethylene rotating spindle, (4) custom-built container, (5) ultrahigh density polyethylene rotating spindle.

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emulsions under different magnetic fields. The torque measurement tests with dispersed MNPs in organic phase of oil-in-water emulsions subjected to RMFs demonstrate that the momentum of spinning MNP is transferable to the droplets, and then to the continuous phase of the emulsion with comparable intensity to that of the same MNPs content dispersed in aqueous conventional ferrofluids.

Methodology

Magnet

The tubular electromagnet utilized in the setup was designed and fabricated in collaboration with MotionTech LLC and Wingings. It is a two-pole three phase magnet, with bore dimensions of 55 mm in height and 45 mm in diameter (1) equipped with a Brookfield LVII+Pro viscosimeter (2) (Figure 1a). The magnet assembly consisted of a versatile power supply for direct current (6), alternating current (7), RMF generation (8), and a rectifier (9) (Figure 1b). This assembly is used to generate uniform RMFs, OMFs, and SMFs of moderate magnetic field intensity at the central vertical axis (up to 50 mT). The three identical coil pairs constituting the magnet can be energized separately or jointly in different configurations to generate the required magnetic field type. Because RMF emerges from the superposition of three OMFs that are 120° out of phase, the coils were energized by three balanced AC (alternate current) currents from a variable frequency drive (ABB, ACS150, 2.2 kW).In the case of OMFs, two-adjacent coils are fed by an AC current from an AC variable frequency drive (Invertek Drives, Optidrive E2). The same adjacent coils are connected to DC (direct current) current from a DC power supply (Agilent Tech, N8739A) to generate SMFs. Magnetic field frequency and strength is adjustable directly on the different power supplies. The temperature of the magnet solid part is controlled by a water-cooled jacket that encompasses the outer shell of the stator and is filled with a coolant circulating in and out from constant-temperature thermostated bath (Lauda, Model RKT20). More information on the specifications and design of the electromagnet are given elsewhere.[12]

Ferrofluid emulsions

Oil-in-water type ferrofluid emulsions were prepared following a conventional procedure that has been proven to be an easy, cost effective, and reliable way to obtain stable emulsions.[14,16–19] The ferrofluid used in the emulsions is an oil-based ferrofluid (EMG 905 from Ferrotec) containing 8.1% by volume of Fe_3O_4 and the surfactant required to stabilize the oil-in-water emulsions is sodium dodecyl sulfate (SDS) of 99.9% purity from Bio-Rad. The first step of preparation consists of dissolving 5 g of SDS in 15 g of deionized water to produce a concentrated surfactant solution. A designated volume of this solution, necessary to obtain the final emulsion volume at 1.2 mmol/L of SDS, is then placed in a glass vial. To induce inversion during the emulsion preparation, this volume must be smaller than the volume of ferrofluid to be added, otherwise, only a fraction of the concentrated surfactant solution is initially placed in the vial and the rest is added later on. The next step consists of a very careful addition of the required amount of ferrofluid under constant mixing. Because the total volume at this point is relatively small, mixing is done using an ultrasonic bath (Ultrasonics Tru-Sweep model 275HTA) for 30 min. While maintaining mixing, the rest of the concentrated SDS solution or deionized water is then slowly and carefully added until inversion point, at which the completion to final emulsion volume with deionized water can be continued a little faster over the course of an hour. To finalize, the emulsion is transferred to a beaker and homogenized using an Omni Mixer Homogenizer for 3 h to reach maximum stability.[17] The droplet composition is obtained from EMG905 characterization (Table 1) and the size of droplets in the resulting

Table 1. Magnetic Properties of as-Received (Undiluted) Ferrofluids

Ferrofluid	EMG 905	EMG 705
Saturation magnetization, M_s	36.0 kA/m	18.7 kA/m
Initial susceptibility, χ_0	2.1	2.9
MNP volume fraction, ϕ	0.081 v/v	0.042 v/v
Median magnetic core diameter, d_p	12.4 nm	16 nm

emulsions, given in Table 2, is measured with a Zetasizer (Malvern, model Nano ZS). The initial mean diameter of the droplets was measured directly following preparation of the emulsions and the final mean diameter was measured once the tests were completed with a specific emulsion. In both cases, the samples were briefly agitated using a BR-2000 Vortexer from Bio-Rad prior to the measurements to ensure maximum homogeneity. The approximate number of MNP per droplet and the approximate mean distance between droplets were deduced from the initial size analysis data and the composition of the EMG 905 ferrofluid. Furthermore, the stability of the emulsions was assessed by the final mean diameter measurements shown in Table 2. An average size change of about 2.3% was determined after application of magnetic field and completion of the corresponding tests.

To verify the distribution of MNPs inside the droplets, the prepared emulsions were observed under a JEOL JEM1230 transmission electron microscope (TEM) and the images were captured using a wide-field digital camera. The procedure consisted of a single drop of the emulsion deposited on a copper grid covered with a formvar–carbon membrane. A typical TEM micrograph of droplet MNP cargo from an emulsion of 0.10% v/v magnetic content is illustrated in Figure 2. Agglomeration as shown in this figure, although caused by sample preparation, was reversible.

Colloidal MNP suspensions

Diluted colloidal MNP suspensions with magnetic contents equivalent to those of the produced emulsions are prepared using the commercial water-based ferrofluid EMG 705 from Ferrotec and deionized water. The magnetic properties of both ferrofluids (EMG 705, EMG 905) were measured by means of an alternating gradient magnetometer, MicroMag model 2900 (Princeton Instrument), at 298 K in low-field (for initial susceptibility, χ_0) and high-field (for saturation magnetization, M_s) asymptotes of magnetization curve. Using these values, the nanoparticle core diameter was estimated following a method proposed by Chantrell et al.[20] The results for the as-received undiluted ferrofluids are presented in Table 1.

Torque measurement

Torques measurements are carried out using a Brookfield LVII+Pro (model LVDV-II+P) viscometer positioned at the center of the opening in the vertical axis of the magnet bore (2) (Figure 1a). The viscometer is equipped with a custom built, ultrahigh density polyethylene rotating spindle (5) with a diameter of 17.65 mm (Figure 1c). A custom built container of the same material with an internal diameter of 27.45 mm (4) is placed inside the magnet containing 30 mL of ferrofluid. To initiate testing, the spindle is lowered into the liquid. The entire liquid (55 mm height) around the spindle is inside the magnet bore and exposed to the magnetic field.

To establish a comparison base, the first series of tests are performed in the absence of any magnetic field. The spindle rotation speeds ranged from 0.0036 to 3.571 s^{-1}. After an initial stabilization time of 20 s for each set, 25 consecutive data points two seconds apart are collected. Data acquisition, performed by Brookfield Rheocalc software, must be carefully monitored during the tests in order to avoid external disturbances that may oscillate the spindle and affect the measurements.

The RMFs and OMFs generated have 100 Hz frequency and 31.4 kA/m intensity. Once the field is applied, a short delay is required for torque measurement stability in the absence of any shear. Once the baseline is set, the spindle rotation speeds are fixed from the lowest value to the highest, and every set ends with a final stabilization period in order to attain the initial torque baseline. For both field types, tests are performed with the initial setting and the inverse setting on the power supplies. This modification simply changes the direction of the current circulation in the coils.

The SMF tests are performed using different magnetic field intensities, ranging from 10.4 to 36.7 kA/m. During those tests, the spindle is never allowed to rest whereas a magnetic field is applied to avoid the chance of droplets coalescence or particle agglomeration in the solutions. However, as observed by Bibette,[14] no droplet coalescence is observed

Table 2. Characterization of Magnetic Liquid-Liquid-MNP Emulsions

Magnetic Content	Mean Droplet Diameter	MNP/ Droplet	Mean Distance Between Droplets
0.10% v/v	158.2 nm	311	1275 nm
0.25% v/v	144.6 nm	237	859 nm
0.50% v/v	128.8 nm	168	765 nm

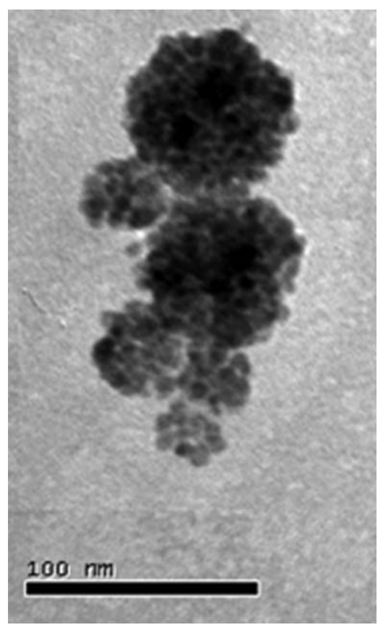

Figure 2. TEM micrograph of droplets with their MNP cargo from the emulsion of 0.10% v/v magnetic content.

The reversible agglomeration shown was caused by the sample preparation.

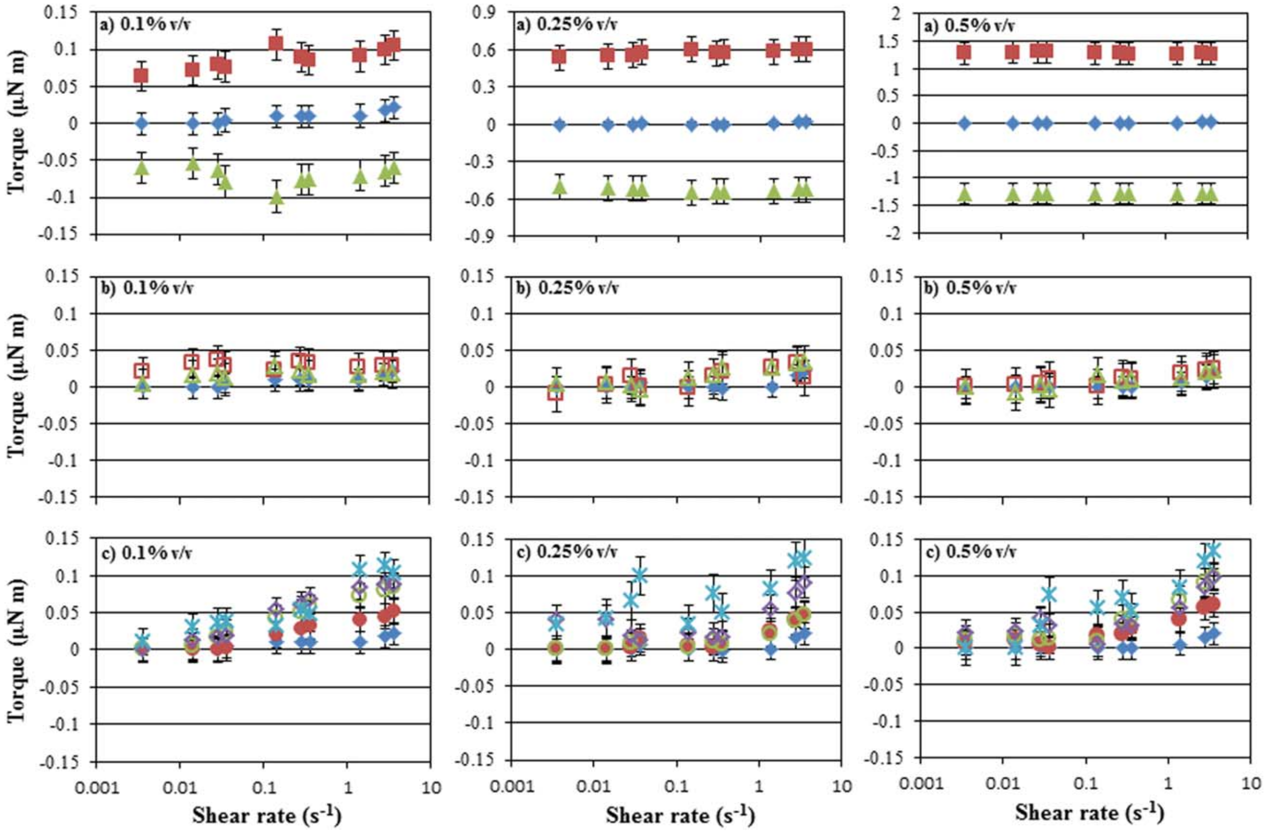

Figure 3. Required torque to attain fixed-shear rates under different magnetic fields for colloidal suspensions of MNPs (a) RMF of 3.14 kA/m at 100 Hz; ■ = RMF in counterrotation with spindle; ▲ = RMF in corotation with spindle; ◆ = no field; (b) OMF of 3.14 kA/m at 100 Hz; □ = initial OMF; △ = inverse OMF; ◆ = no field; (c) ● = SMF of 10.4 kA/m; ○ = SMF of 15.7 kA/m; ◇ = SMF of 26.1 kA/m; ✱ = SMF of 36.7 kA/m; ◆ = no field.

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following the different tests because of the stabilizing effect of the surfactant, the small droplet size, and the low concentration of MNPs. Apart from that, the testing procedure is identical to the one followed for the other types of magnetic fields.

For every solution, the tests with the three different field types are performed successively starting with the absence of magnetic field, and going on with RMF, OMF, and finally SMF. This procedure is followed to minimize the impact of potential variations that could occur between different experimentation periods. The static fields are the last to be tested because they are the ones harboring the highest potential for emulsion and suspension stability disruption. During the tests, close monitoring of the coils temperature and spindle stability is required to ensure quality results. Sudden changes or inconsistencies can indicate a need for adjustment in one of the different mobile pieces of the setup or the presence of coalescence or sedimentation inside the sample.

Visualization

To visualize the mixing action inside the prepared emulsions, an image acquisition setup using microscopy was devised. First, a model 500 LumaScope^{TM} from Etaluma (CA) was disassembled and the objective was inverted to allow for its insertion inside the electromagnet bore. Then, microslides (100 μm × 1.0 mm × 50 mm slits) were filled with an emulsion sample and placed flat at the center of the magnet, under the objective. Using standard bright field settings of sample illumination via transmitted white light across the 100 μm slit thickness, images were collected with a 100× objective at 0.2 s intervals with the focus plane placed 70 μm with respect to the slit upper face. The resulting images, with a field of view of 260 × 160 μm^2 and a pixel size of 0.2 μm, were then strung together to create short videos demonstrating the movement inside the fluid under a RMF and in its absence.

Results and Discussion

Figures 3 and 4 depict variations as a function of imposed shear rate of torque measurement results in colloidal suspensions of MNPs and in ferrofluid emulsions, respectively, with an equivalent magnetic content under the variety of different magnetic fields types and conditions. The vertical bars in Figures 3 and 4, representing the standard deviation on measured torques where typically repeat tests extended up to five fold, allow judging the level of scatter with respect to deterministic effects due to magnetic field properties and shear rate conditions.

For each MNP concentration under every magnetic field, the quasi-plateaus exhibit the same amplitude and the measured torque increases with increasing the magnetic content in the liquid. More specifically, the similarities in amplitude and stability of the RMF test results indicate that the momentum of spinning MNPs inside the emulsions is

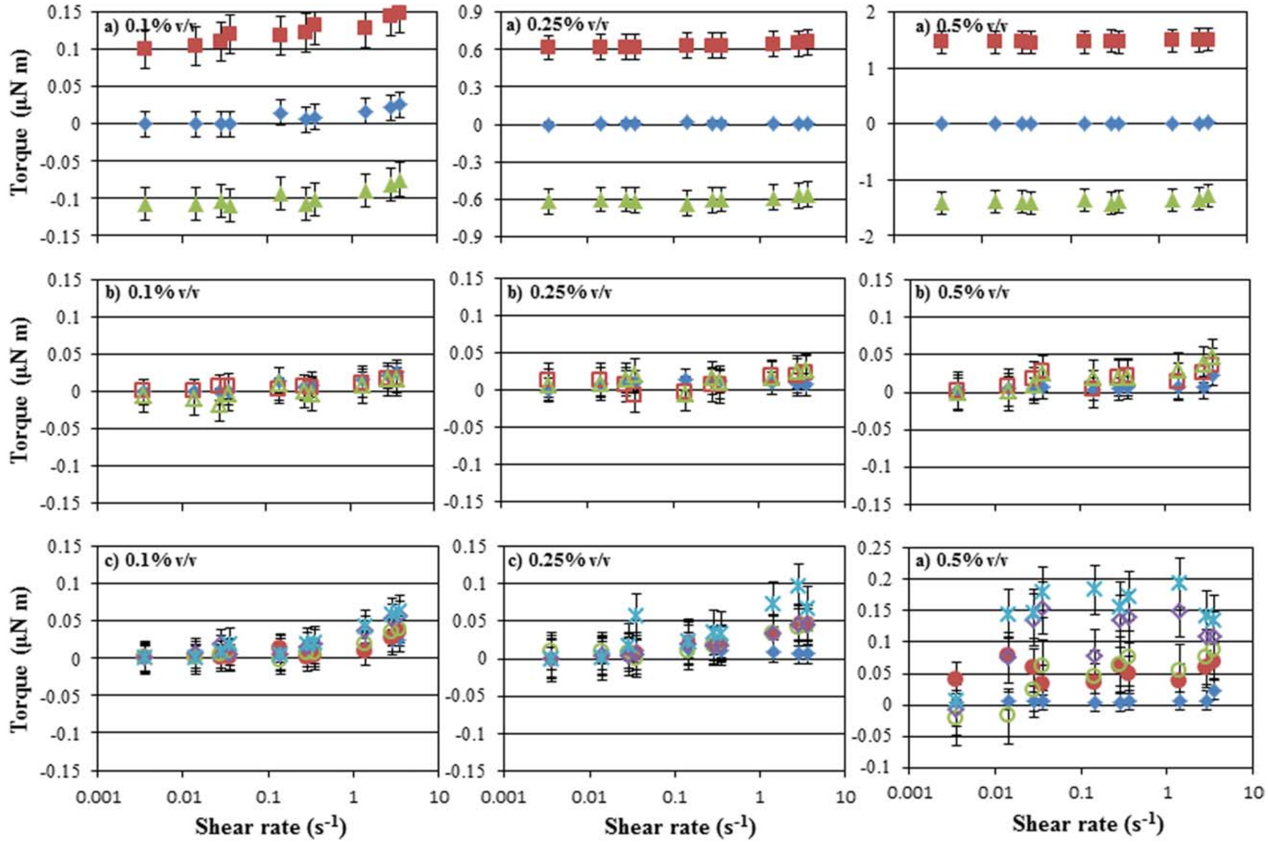

Figure 4. Required torque to attain fixed-shear rates under different magnetic fields for oil-based ferrofluid emulsions (a) RMF of 3.14 kA/m at 100 Hz; ■ = RMF in counterrotation with spindle; ▲ = RMF in corotation with spindle; ◆ = no field; (b) OMF of 3.14 kA/m at 100 Hz; □ = initial OMF; △ = inverse OMF; ◆ = no field; (c) ● = SMF of 10.4 kA/m; ○ = SMF of 15.7 kA/m; ◇ = SMF of 26.1 kA/m; ✱ = SMF of 36.7 kA/m; ◆ = no field.

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successively transferred to the ferrofluid droplets containing them and then to the continuous phase of the emulsion. This fact infers that the momentum transfer at the liquid–liquid interface between the organic and aqueous phases of the emulsion occurs with an efficiency comparable to the one taking place at the solid–liquid interface in the colloidal suspensions of MNPs, resulting in an analogous effective mixing in both types of solutions. RMF results (Figures 3a and 4a) are also symmetrical for corotating and counterrotating fields which is in accordance with the literature.[10]

The physical interpretation put forward that the MNPs spinning under the effect of a RMF are the cause of a cascade of events mediated by the oil droplet rotational movements which in turn convey momentum (and motion) to the continuous phase can best be appreciated from the video animation files "AIC_15105_VideoEmulsion_RotMagField_ON (100Hz_31.4kAm-1)" and "AIC_15105_VideoEmulsion_Rot MagField_OFF" (see Supporting Information) acquired with the LumaScope system with the liquid–liquid magnetic emulsions placed inside transparent microslides. The videos compare 6-s image sequences acquired at 5 Hz of the same 0.10% v/v magnetic emulsion, respectively, under RMF ($f = 100$ Hz, $H_0 = 31.4$ kA/m) and without magnetic field. When the magnetic field is off, the static character of the liquid–liquid emulsion is evident. On the contrary, enabling the RMF led to the emergence of many eddy-like constellations or dynamic packets of dark nodules, approximately 5 μm in size, that are endowed with composite internal-external movements. The nodules, consisting in all likelihood of reversibly coalesced groups of oil droplets, highlighted at least for some of them, the existence of an internal rotation. This, in addition to the external coherent rotations clearly visible in the aqueous continuous phase of the enclosure, sheds light into a peculiar mechanism driving mixing of the continuous phase via MNP-laden oil droplets. These movements are ascribed to a transfer of momentum between the MNPs to the surrounding droplet and then to the surrounding fluid. It will be interesting for future studies to develop rigorous mathematical formulations to describe the momentum transfer from the nanoparticles to the oil droplet to its interfacial boundary with the aqueous continuous phase ultimately to the bulk of this latter phase.

In the case of OMFs (Figures 3b and 4b), no significant difference is observed when comparing tests in the absence of magnetic field to the ones where it is applied. Indeed, as explained by Hajiani and Larachi,[13] MNP relaxation time is sufficiently short to allow random reorientation of the magnetic dipoles in the midst of OMFs oscillating cycles, resulting in zero spatially averaged torques when the field is reoriented and the MNPs are magnetized once again. In sum, OMFs do not bring the particles/droplets in a synchronous spin in colloidal suspension or in ferrofluid emulsion and hence they are not able to exert a measurable torque on the rotating spindle of the viscometer.

Under SMFs (Figures 3c and 4c), a torque increase is detected in higher magnetic content and stronger magnetic field for both types of solutions. This effect can be attributed to the MNPs magnetic moment alignment in the magnetic field direction, essentially locking them in position. From this action a resistance emerges against fluid displacements due to MNP rigidity toward movement.[13] Consequently, the apparent viscosity increases resulting in a measured inflationary torque at each shear rate. However, the possibility of reversible droplets or formation of MNP chain-like assembly in the emulsions and suspensions when subject to SMFs for extended periods complicates the obtainment of stable measurements.[14] Such assemblies create momentarily nonuniform magnetic concentration in liquid and are able to faintly sway the spindle. Consequently, the ensuing data points get more dispersed with increasing magnetic content concentrations.

Conclusions

In summary, this study elicits the effects of different magnetic fields on the torque exerted by MNPs in oil-in-water ferrofluid emulsions and allows for the comparison with diluted colloidal suspensions of the same MNPs with equivalent magnetic content. Similar suspensions having previously been studied in comparable conditions by Rinaldi et al.[10] and in mixing applications by Hajiani and Larachi,[13] the presented comparison permits the assertion that for an equivalent magnetic content, stable ferrofluid emulsions, and colloidal MNP suspensions provide very similar effective mixing under magnetic field. With regard to RMFs, this similarity means that the momentum developed by spinning MNPs inside emulsion droplets is transferable not only to the droplets but also to the surrounding liquid medium. Based on these results, it is then possible to envision the development of versatile techniques of MNP-based microscopic mixing using ferrofluid emulsions to keep the continuous phase to be mixed completely separated from the nanostirrers.

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