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Ionic liquids–based magnetic nanofluids as lubricants

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Abstract
In this paper, a kind of ionic liquid–based ferrofluid, which may be suitable as a prospective lubricant was synthesised. The nanosized magnetic particles dispersing in the ionic liquid were coated with a layer of designed surfactant containing ionic liquid unit with carboxylic acid group. Three ionic liquids, 1-ethyl-3-methylimidazolium tetrafluoroborate (C_2MIMBF_4), 1-butyl-3-methylimidazolium tetrafluoroborate (C_4MIMBF_4), and 1-hexyl-3-methylimidazolium tetrafluoroborate (C_6MIMBF_4), with the same anionic structure and cationic backbone were used as carrier liquid. The effect of cation alkyl chain length on the colloidal stability was checked qualitatively by direct observation and magnetic sedimentation. The lubrication performances of the stable ferrofluid were evaluated. Experiment result shows that stable ferrofluid can only be achieved for the ionic liquid C_6MIMBF_4 with the longest alkyl chain. Lubrication tests first evidence the benefits of ionic liquid–based ferrofluid as a new kind of magnetic lubricant, whose lubrication behaviour can be actively controlled by the application of magnetic field.

KEYWORDS
colloidal stability, ferrofluid, ionic liquids, lubrication

1 | INTRODUCTION

Ferrofluid (FF) is a colloidal suspension of single-domain magnetic particles dispersing in a carrier liquid.[1] These particles commonly have diameters between 5 and 20 nm and are composed of a magnetic material such as Fe_3O_4,[2] Ni-Fe,[3] and ε-Fe_3N.[4] To avoid agglomeration under magnetic and van der Waals forces, these particles are usually coated with long chain molecules (sterically) or decorated with charged groups (electrostatically).[5] As a carrier medium, a wide range of liquids have been used, such as organic solvent (heptanes, kerosene), inorganic solvent (water), and oil (synthetic ester, hydrocarbons).[6] Owing to a combination of the pronounced magnetic properties and fluidity inhering in classical liquids, these magnetic colloids have attracted wide interest and most of the successful applications are based on the advantage of the precise control over FF response using magnetic fields, such as mechanical seals, shock absorbers, separation, and optical devices.[7-10]

Lubrication is another important application for FF. It, serving as a new lubricant, is mainly based on the following properties[11-13]: (1) FF can be retained at the desired location by an external magnetic field but still possess fluidity. (2) Subjected to a magnetic field, the load capacity of the FF film can be improved. (3) With a proper magnetic field, it can be prevented from leaking; meanwhile, the dosage is small. Although FF as lubricant shows several advantages, the properties of the volatilization, flammability, and decomposition of the traditional carrier liquids could severely restrict its potential applications in specific areas, such as space environment.

Ionic liquids (ILs) are salts with melting points below 100°C.[14] Compared to conventional lubricants, ILs exhibit negligible volatility, nonflammability, and high thermal stability.[15] In addition, ILs show no migration property under temperature gradient.[16] These properties are highly desirable in lubrication, especially for the extreme conditions.[17] Meanwhile, these superiorities also make them possible as novel carrier liquids for FF synthesis. Since Oliveira et al[18] reported the ILs-based FFs consisting of bare γ-Fe_2O_3 and $CoFe_2O_4$ dispersed in ILs, several papers have been published.[19-26] For the highly ionic atmosphere inside ILs, the particle surface modification still remains a primary issue to achieve long-term colloidal stability. In addition, since the number of ILs is huge and their properties can be altered by varying the combination of used cations and anions, it could be a great challenge to synthesise proper and stable ILs-based FF, whose structure and properties can meet the lubrication requirements.

Till now, imidazolium-based ILs have received the most attention due to their excellent properties of stability, flexibility in molecular design, and ease of synthesis.[15] To realise the purpose of lubrication, 3 kinds of typical imidazolium ILs with a fixed anionic structure and cationic backbone were chosen as carrier liquids for the ILs-based FFs preparation. The effect of the alkyl side chain lengths on the colloidal stability against sedimentation is analysed. What is more, as a kind of magnetic lubricant, lubrication properties of the ILs-based FF with/without an external magnetic field were evaluated. To the best of our knowledge, it is for the first time on the use of IL-based FF as lubricant.

2 | EXPERIMENTAL DETAILS

2.1 | Synthesis of Fe_3O_4 particles, surfactant and FFs

Particle preparation: The Fe_3O_4 nanoparticles were prepared by the coprecipitation method (see in Figure 1). The molar proportion of salts (Fe^{2+}/Fe^{3+}) was 0.5 and excess $NH_3{\bullet}H_2O$ as precipitating agent was added into ferric salts solution with vigorous stirring. The suspension was heated up to 90°C for 1 hour to convert the hydroxides into magnetite. Then, the particles were separated from the solution by magnetic decantation and washed with distilled water several times to clear impurities. After removing the excess water by acetone, the slurry was dried at 50°C in vacuum for 1 hour to eliminate residual acetone.

Surfactant preparation: To achieve chemically stable FF, the bare particles should be coated with proper surfactant. In this paper, to avoid the volatility of traditional surfactants, the surfactant containing IL unit with carboxylic acid group was prepared via substitution

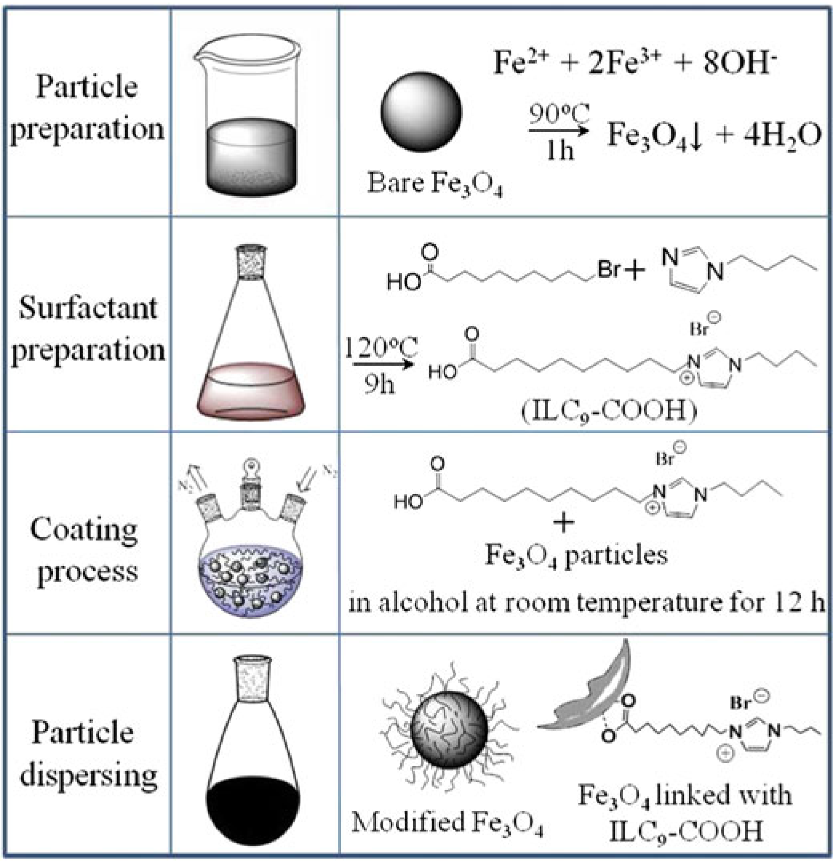

FIGURE 1 Schematic diagram of synthetic process [Colour figure can be viewed at wileyonlinelibrary.com]

reactions. The detailed synthetic process was described in the literature.[27] Simply, the appropriate 1-butylimidazole was mixed with the 10-bromodecanoic acid at 120°C for 9 hours to obtain the required surfactant, 1-butyl-3- (9-carboxydecyl)-1*H*–imidazol-3-ium bromide (ILC_9-COOH), shown in Figure 1.

Coating process: The modification process was performed by mixing surfactant ILC_9-COOH with freshly Fe_3O_4 nanoparticles in the mass ratio of 1:1 in ethanol at room temperature for 12 hours under the protection of nitrogen (see Figure 1). Then, the excess surfactant was removed by ethyl acetate and the ILC_9-COOH functionalized nanoparticles were dried at 80°C for 2 hours.

Particle dispersing: The final ILs-based FF was obtained by dispersing the coated nanoparticles in the ILs using the ultrasonic method at the frequency of 40 kHz for 2 hours. As shown in Figure 1, the carboxylic acid of the surfactant ILC_9-COOH could absorb on the surface of the magnetic particles. And the structure left is expected to dissolve with the carrier liquids.

To synthesise ILs based magnetic nanofluids as lubricant, 3 typical imidazolium ILs were chosen as carrier liquids. They were C_2MIMBF_4, C_4MIMBF_4, and C_6MIMBF_4 with the same anionic structure and cationic backbone. To make clear the effect of particle concentration on the lubrication properties, FFs with different particle mass percents were produced. For instance, a 5-wt% dispersion contains 0.5-g modified particles and 9.5-g pure ILs.

2.2 | Material characterizations

X-ray diffraction (XRD) pattern of the magnetic particles was obtained using an X'Pert PRO X-ray diffractometer (Panalytical) with Co Kα ($\lambda = 1.7889$ Å). The size and morphology of nanoparticles were determined using a JEM-200CX (JEOL) transmission electron microscope (TEM) operated at 200 kV. Fourier transform infrared (FT-IR) spectra of the particles (bare and modified) dispersed in KBr pellets were recorded on a NEXUS870 spectrometer (NICOLET). The suspension stability of samples was investigated by qualitative observations of the particle sedimentation with/without of a magnetic field. Before test, all the samples were redispersed by ultrasound to ensure equal initial conditions. Vibrating sample magnetometer LDJ9600 was used to measure the magnetic properties of the final stable FFs at room temperature.

2.3 | Friction tests

The lubrication properties of the stable IL–based FFs were performed on a reciprocating sliding tribometer (Sinto Scientific, JAP). It consists of a bearing ball of 10 mm in diameter and a reciprocating disc, which are both made of nonmagnetic 304 stainless steels in consideration of its good corrosion resistance. The surface of the disc was sanded and polished with a final surface roughness, Ra, ranging from10 to 20 nm. To figure out the influence of external magnetic field on the lubrication property, a symmetric magnetic field distribution at the point contact was achieved by placing a bar magnet under the disc. And the length of the magnet was 10 mm, which fully covers the Hertz contact areas. The test conditions are listed in Table 1. For each test, the ILs-based FF was deposited in the vicinity of the contact centre at rest condition.

3 | RESULTS AND DISCUSSION

3.1 | XRD and TEM studies

The XRD pattern of Fe_3O_4 sample is displayed in Figure 2. A series of characteristic peaks in Figure 2 agree with the standard Fe_3O_4 powder (JCPDS 19-629). The peaks of spectrum are broadened because of tiny particle sizes. The *d* values calculated from the XRD spectrum were well indexed to the inverse cubic spinel phase of Fe_3O_4.

TABLE 1 Test conditions

Normal load, N	0.5
Stroke, mm	10
Sliding velocity, mm/s	10
Test time, s	400
Magnetic strength on disc surface, mT	0, 45, 105
Volume of FF, μL	5
Ambient temperature, °C	25 ± 2

Abbreviation: FF, ferrofluid.

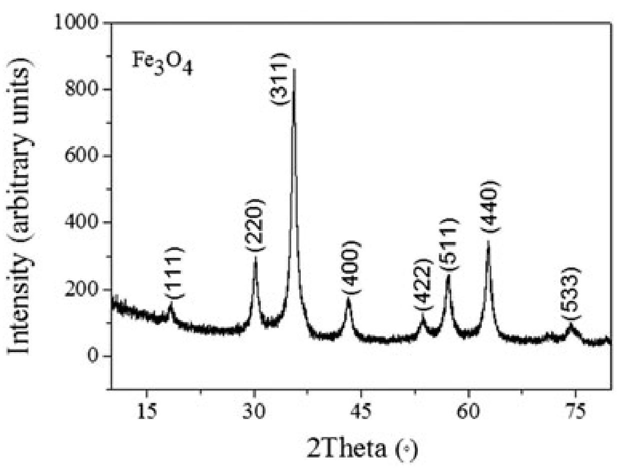

FIGURE 2 X-ray diffraction patterns of Fe_3O_4 powder

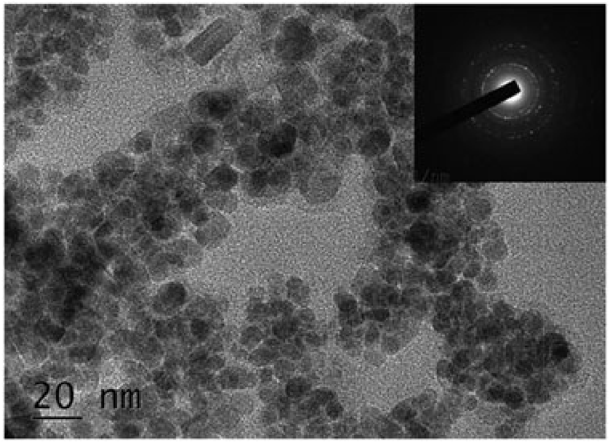

FIGURE 3 Transmission electron microscope image of the modified Fe_3O_4 particles. The inset presents the electron diffraction pattern of particles

Figure 3 shows the TEM of the modified Fe_3O_4 sample. Because of the magnetism, particle aggregation was observed. The shape of the particles is nearly spherical. The mean size is about 14 nm with a uniform and narrow distribution. The electron diffraction pattern suggests that the particles are in crystal structure of Fe_3O_4 according to observation of the diffraction rings.

3.2 | FT-IR studies

Figure 4 shows the FT-IR spectrum of the bare and modified Fe_3O_4 particles. The characteristic absorption of Fe-O bond is close at 570 cm^{-1} for both bare and modified particles.[28] A broad band centred at about 3380 cm^{-1} is originated from the O—H stretching.[23,29] Comparing the bare particles, some new absorption peaks were found when the particle was modified with surfactant ILC_9-COOH. The absorption[29] at 2923 and 2850 cm^{-1} are usually assigned to the stretching vibration of CH_2. The absorption observed at 1153 cm^{-1} for modified particles is characteristic of C=N stretching vibration,[30] which indicates the existence of imidazolium. The peak at 1708 cm^{-1} was derived from the existence of the C=O stretch.[31]

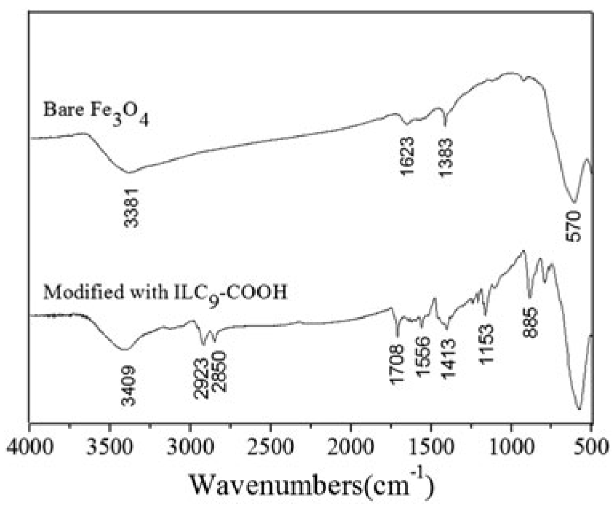

FIGURE 4 Fourier transform infrared spectra of bare and modified Fe_3O_4 particles

Two typical bands at 1556 and 1413 cm^{-1}, which indicates a complex reaction between magnetic particles and carboxylate groups, were ascribed to asymmetric and symmetric stretches of carboxyl group.[32] The result can be explained that the bonding pattern of the carboxylic acids on the nanoparticles surface was a combination of molecules bonded symmetrically and molecules bonded at an angle to the surface.[33] The wave number separation, Δ, between the 2 bands can be used to distinguish the type of the interaction between the carboxylate head and the particle. In this study, the Δ (1556 − 1413 = 143 cm^{-1}) is ascribed to bridging bidentate, where the interaction between the COO— group and the particle is covalent (see the scheme in Figure 1).[34] These results indicate that the synthetic surfactant ILC_9-COOH is chemisorbed onto the particles as a carboxylate.

3.3 | Stability studies

The stability of the FF depends on the thermal contribution and on the balance between attractive (van der Waals and dipole-dipole) and repulsive (steric and electrostatic) interactions.[35] Although Oliveira et al[18] reported stable IL-based FF consisting of bare magnetic nanoparticles, our previous experiments showed that bare particles are not stable in any of the 3 ILs. While for the modified particles, the results still varied since the ILs possess different structures.

The stability of nanofluids can be investigated using UV-VIS spectroscopy, dynamic light scattering, zeta potential, phase contrast microscopic and visual observation.[36] Taking account of the magnetic property of the Fe_3O_4 particles, the sedimentation process of the samples in the absence and presence of magnet are briefly investigated by visual observation and the obtained results are depicted in Figure 5.

When choosing IL C_2MIMBF_4 as the carrier liquid, although in the absence of magnet, the particle sedimentation was observed at the very beginning and obvious solid-liquid separation appeared as the time went by (Figure 5A, left). The Fe_3O_4 particles almost precipitate completely within 6 hours. In IL C_4MIMBF_4, similar result was found. The difference was that the sedimentation velocity of the particles/aggregates is apparently slowing down compared with that in IL C_2MIMBF_4. However, particles dispersed in IL C_6MIMBF_4 exhibited excellent stability over a period of

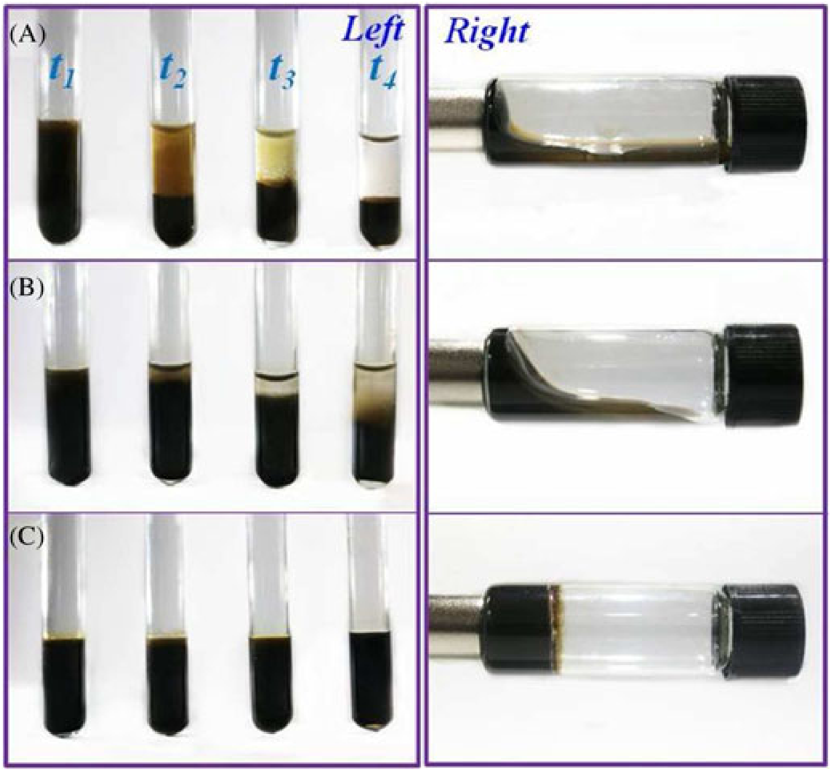

FIGURE 5 Suspension stability of modified Fe_3O_4 particles with 10 wt% in ILs with different alkyl side chain lengths as carrier liquids. A, C_2MIMBF_4, B, C_4MIMBF_4, and C, C_6MIMBF_4. The left is in the absence of magnet, where t_1, t_2, t_3, and t_4 refer to pictures taken at $t = 0$, 2, 4. and 6 h, respectively; the right is in the presence of a magnet ($H = 350$ mT), and the picture is taken after 30 min of magnetic field application [Colour figure can be viewed at wileyonlinelibrary.com]

6 hours without the observation of aggregation and precipitation (Figure 5C, left).

To further ensure the stability of the particles dispersed in the 3 ILs, samples were exposed to an external magnetic field, as shown in the right of Figure 5. Sample using IL C_2MIMBF_4 as carrier liquid proved to be unstable suspension, showing very fast sedimentation under a magnet. Phase separation also happened in IL C_4MIMBF_4, but the separating velocity got slower. Again, particles dispersing in IL C_6MIMBF_4 remained permanently stable.

Figure.6 reveals the stability of the FFs with different particle contents dispersing in IL C_6MIMBF_4. After 30 days, all the samples did not suffer any sedimentation under letting stand or external magnetic field. According to the results obtained, the samples choosing IL C_6MIMBF_4 as carrier liquid can be regarded as true (stable) IL-based FF.

The reason why colloid stability is affected by the length of alkyl side chain is still under investigation. Here, the phenomena might be analysed from both macro and micro aspects. Macroscopically, the natural settling velocity of the particles in the ILs can be evaluated roughly from Stokes law[37]:

$$v = \frac{(\rho_1 - \rho_2) g d^2}{18\eta}, \tag{1}$$

where ρ_1 is the density of particles, ρ_2 is density of carrier fluid, g is the gravitational acceleration, d is the diameter of particle, and η is the viscosity of the carrier fluid. For the imidazolium ILs, longer alkyl chains in imidazolium cations lead to the considerable increment of ILs viscosity.[15] Obviously, the IL C_6MIMBF_4 possesses much higher viscosity (300 mPa·s at 25°C) than C_2MIMBF_4 (41 mPa·s

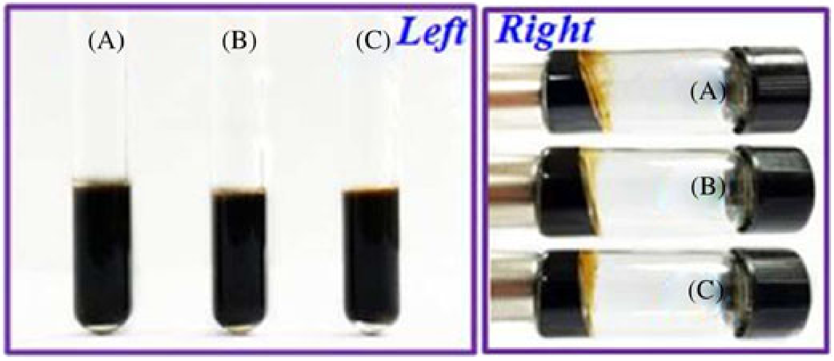

FIGURE 6 Effect of particles concentration on the suspension stability using IL C_6MIMBF_4 as carrier liquid. A, 5 wt%, B, 10 wt%, and C, 20 wt%. The left is in the absence of magnet; the right is in the presence of a magnet ($H = 350$ mT) and the pictures are taken after 30 days [Colour figure can be viewed at wileyonlinelibrary.com]

at 25°C) and C_4MIMBF_4 (98 mPa·s at 25°C), the colloid with C_6MIMBF_4 as dispersion medium remains excellent stability (against sedimentation) under gravity.

From microcosmic point of view, a possible schematic for the stabilisation mechanisms is presented in Figure 7 and the detailed explanation might be as follows. (1) Compared with IL C_2MIMBF_4 and C_4MIMBF_4, IL C_6MIMBF_4 with the longer alkyl side chain are more flexible, which can produce stronger push-through forces towards the protective layers aggregating around the Fe_3O_4 particles[38] (see in Figure 7) This kind of push-through force between carrier liquids and coating layers gives rise to repulsive interactions, which guarantee colloidal stability. (2) The long cationic alkyl chain generates the strongest repulsive solvation force, which can lead to a longer-range repulsion for particle stabilisation.[39] (3) Ionic liquids with longer alkyl chains are more liable to form a densely packed structure due to more enthalpy gain[15]; thus, longer alkyl chain provides greater steric repulsion between the Fe_3O_4 particles. Therefore, it is believed that besides the influence of particle surface modification, the size of the alkyl chains of cations is an important parameter affecting the stabilisation of the nanoparticles in the ILs.

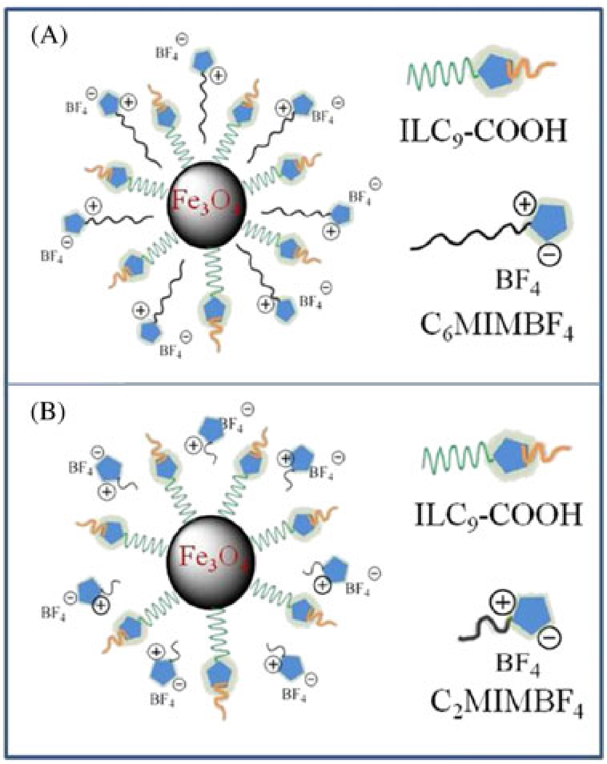

FIGURE 7 Schematic representation of the modified nanoparticle in ionic liquids (ILs) with different lengths of alkyl chains A, in IL C_6MIMBF_4 and B, in IL C_2MIMBF_4 [Colour figure can be viewed at wileyonlinelibrary.com]

3.4 | Magnetic studies

The behaviour of FF is mainly determined by their magnetic properties. Figure 8 exhibits the hysteresis loops of stable FF with different particle mass fraction dispersing in IL C_6MIMBF_4. As can be seen, the magnetization of the FF increases with the increasing of the particle mass fraction.

In FF, each particle can be regarded as a thermally agitated permanent magnet in the IL. The magnetization M of the FF can be described by the well-known Langevin law[40]:

$$M = M_S\left[\coth\alpha - \frac{1}{\alpha}\right], \quad \alpha = \mu_0 mH/kT, \tag{2}$$

where $M_s = M_d\Phi$ is the saturation magnetization when all magnetic dipoles with magnetic particle volume V_p and magnetization M_d having moment $m = M_dV_p$ tend to align parallel to the magnetic field H under the action of thermal agitation kT. μ_0 is the magnetic permeability of vacuum, and Φ is the fraction of magnetic nanoparticles in FF. With the increase of particle mass fraction, the number of magnetic dipoles per unit volume increases. Thus, the higher of the particle mass fraction, the larger of the magnetization.

In addition, the curves of the 3 ILs-based FF samples exhibit no coercivity and remanence, showing a classical superparamagnetic behaviour, similar as an ideal case of the paramagnetic state. This behaviour could be understood by the action of an extra relaxation process (the Brownian relaxation associated with the rotation of the

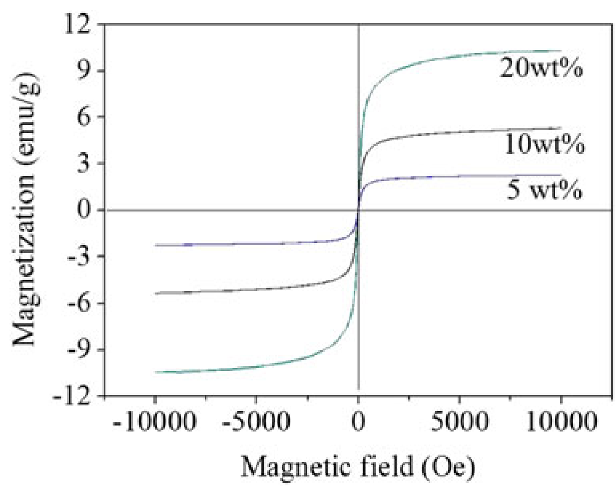

FIGURE 8 Hysteresis loops of stable ferrofluids with different particle mass fraction dispersing in ionic liquid C_6MIMBF_4 [Colour figure can be viewed at wileyonlinelibrary.com]

magnetic aggregates in the liquid). As pointed in ref.,[41] the superparamagnetic behaviour assures a reversible magnetic performance of the suspension, which will help to preserve the colloidal stability even after a magnetic field is applied.

3.5 | Lubrication studies

Representative frictional curves lubricated with stable FF using IL C_6MIMBF_4 as carrier liquid are shown in Figure 9A. The experiment started by bringing the bearing ball into contact with the disc in the presence of fixed volume of FF. After applying a normal load, the translation stage was moved in the lateral direction and the friction forces were recorded. The friction coefficient is the ratio of the friction force and the normal load. It can be note that the coefficients with/without of the magnetic field are both in the range of 0.06 to 0.1. Obviously, the magnetised IL-based FF exhibits the lower friction coefficient with a smaller fluctuation.

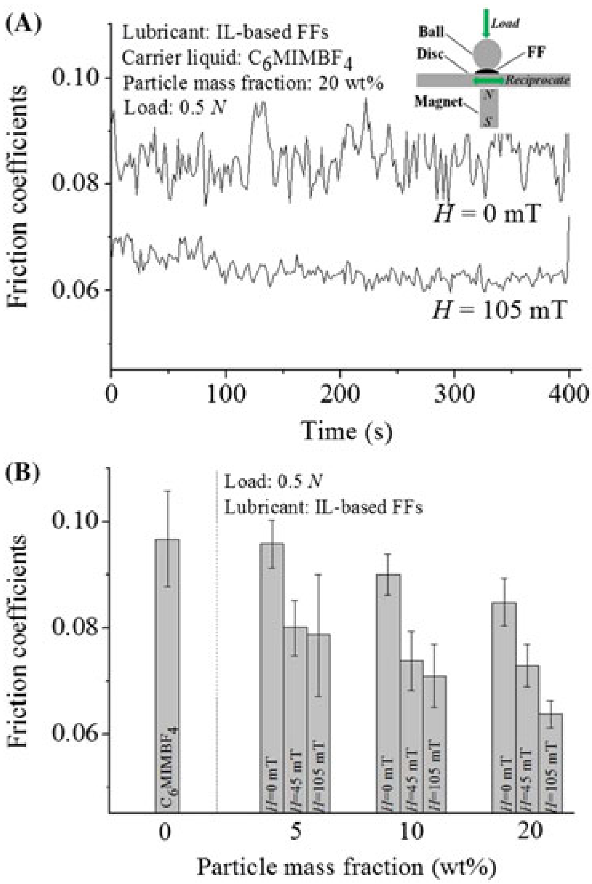

FIGURE 9 A, Friction curves lubricated with ionic liquid (IL)–based ferrofluid (FF) in the absence/presence of magnetic field; B, variations of friction coefficients lubricated with IL and IL-based FFs at the load of 0.5 N under different external magnetic fields [Colour figure can be viewed at wileyonlinelibrary.com]

Figure 9B presents the effects of external magnetic field and particle concentration on lubrication performance, where the data of IL C_6MIMBF_4 is pooled together. The maximum friction coefficient of 0.096 was obtained for the pure IL C_6MIMBF_4. Interestingly, the coefficients decreased gradually with the increase of the particle mass fraction for the FFs under zero magnetic field condition. When introducing magnetic field on the disc, the friction reduced significantly and it also declined with the increase of the magnetic field strength. The higher of particle mass fraction it was, the greater the influence of magnetic field it displayed. Given the above, it can be confirmed that the surface magnetic field and particle fraction are the key factors affecting the lubrication behaviour of IL-based FFs.

In the absence of magnetic field, the particles are homogeneously distributed in the carrier liquid (see in Figure 10, left) and the rheological behaviour of FFs is similar to those of conventional lubricants. However, for a given IL, the viscosity of the IL-based FFs is mainly determined by the concentration of the suspended magnetic material.[42] The increment of the viscosity is beneficial to increasing the load capacity of the lubrication films, so as to reduce direct contact between the surface asperities, which are helpful to reduce friction.

In the presence of a magnetic field, the lubrication behaviour of IL-based FF may firstly affected by the magnetoviscous behaviour. Upon field application, the magnetic moment of nanoparticles will be attracted partially to the external field (see in Figure 10). The chain-like structures formed by the Fe_3O_4 particles may further increase the viscosity,[43] and the higher particle concentrations in the IL, the more arranged microstructures could be formed. In addition, the higher magnetic field strength may result in the more ordered microstructure. It means that, the higher particle content and magnetic field strength, the more viscosity of FF. As mentioned before, in the mixed film lubrication regime, the increase of lubricant viscosity will contribute to decrease the direct contact of the surface asperities and achieve lower friction.

Besides the viscosity, the supporting force of the IL-based FF under the magnetic field could be the other important factor. The magnetization of the fluid interacts with the external magnetic field to produce attractive forces on each particle. This kind of attractive magnetic force shows itself as a body force on the liquid. The attractive force (F_m) on FF per unit volume can be written as[44]

$$F_m = \mu_0 M \nabla H, \tag{3}$$

where μ_0 is magnetic permeability of vacuum; M is the magnetization of FF; and ∇Hrepresents the gradient of

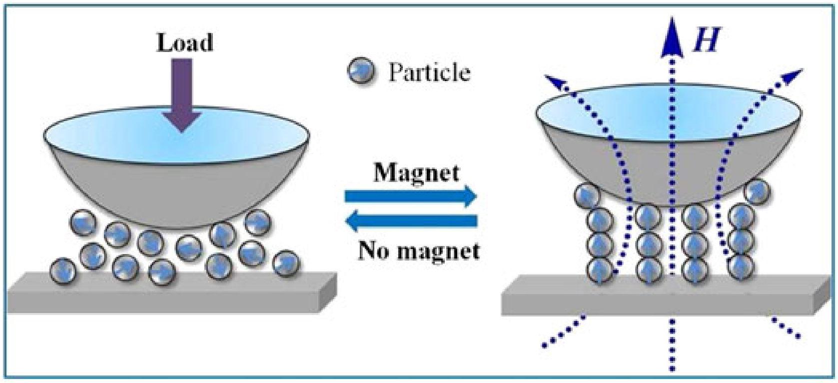

FIGURE 10 Schematic representation of the interactions between magnetic particles dispersed in carrier liquid in the absence (left) and in the presence (right) of a magnetic field [Colour figure can be viewed at wileyonlinelibrary.com]

magnetic field. In general, the magnetization (M) of the magnetic material is a function of temperature and the applied magnetic field. Considering the isothermal condition and linear behaviour of the FF, Equation 3 can be written as

$$F_m = \mu_0 \chi H \nabla H, \tag{4}$$

where χ is susceptibility of FF, and H is the external magnetic field strength.

The IL-based FF experienced the magnetic body force can generate extra magnetic supporting force acting on the upper ball. According to Equation 4, the body force depends on the magnetic response of the fluid and the strength of the magnetic field. As a result, the higher particle concentration and external magnetic field can get larger body force or magnetic supporting force, which helps further to reduce the direct contact between the friction pairs, especially in the mixed film lubrication.

Regarding the influence of magnetic response, Figure 8 reveals that the ILs-based FF is extremely sensitive to the strength of the applied magnetic field for low field values.[45] That could be the reason why the coefficients decreased more obviously when the external magnetic field changes from 0 to 45 mT. Therefore, when using IL-based FF as a new kind of lubricant, it is possible to actively control its lubrication behaviour by the application of magnetic fields.

4 | CONCLUSIONS

Considering the comprehensive advantages of ILs and FFs, stable ILs-based FF was synthesised for its potential application in lubrication. The magnetic particles in this study were decorated with a designed surfactant, which contains moieties that resemble the carrier liquid to increase the compatibility. Besides, the effect of alkyl side chain lengths of the ILs on the colloidal stability is pointed out. More importantly, the present authors believe that it is for the first time to report on the lubrication behaviours of stable ILs-based FFs.

Experimental results showed that the synthesised surfactant with carboxylic acid groups chemically binds to the surface of magnetite. Interestingly, the coated particles can only be dispersed stably in the IL C_6MIMBF_4 with the longer alkyl side chain. The higher viscosity of the IL C_6MIMBF_4 could be the reason of macro respect. Aside from that, the combined effects of the push-through force, the solvation and steric forces could be the stability mechanism in micro.

Friction tests first showed that the ILs-based FF presents better lubricity than carrier liquid (pure IL). The friction reduction may be ascribed to the increased viscosity due to the presence of the suspended particles when unexposed in magnetic field. Meanwhile, the lubrication property of ILs-based FF was also affected by the particle content and the external magnetic field. It seems that the excellent lubrication property of IL-based FF in the presence of magnetic field could be dominated by the magnetoviscous behaviour as well as the extra magnetic supporting force.

Further study is under way to synthesise FFs using other type of ILs as carrier liquids. A comprehensive lubrication performance of the ILs-based FFs should be conducted. The potential applications of the magnetic lubricant may be considerable, and may include some new magnetically controlled lubrication systems, especially for the extreme operating conditions on account of their high temperature stability and low vapour pressure.

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