Journal of Industrial and Engineering Chemistry xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Synthesis of stable iron oxide nanoparticle dispersions in high ionic media

Ehsan Nourafkan[a], Maryam Asachi[a], Hui Gao[a], Ghulum Raza[a], Dongsheng Wen[a,b,*]

[a] School of Chemical and Process Engineering, University of Leeds, Leeds, LS2 9JT, UK
[b] School of Aeronautic Science and Engineering, Beihang University, 100191, PR China

ARTICLE INFO

Article history:
Received 16 September 2016
Received in revised form 27 December 2016
Accepted 22 January 2017
Available online xxx

Keywords:
Iron oxide nanoparticles
Lithium bromide
Binary nanofluid
Reverse microemulsions
Ionic media
DLVO theory

ABSTRACT

A novel one-pot method was developed in this work to synthesize and disperse nanoparticles in a binary base fluid. As an example, stable magnetite iron oxide (Fe_3O_4) dispersions, i.e., nanofluids, were produced in a high ionic media of binary lithium bromide-water using a microemulsion-mediated method. The effects of temperature and precursor concentration on morphology and size distribution of produced nanoparticles were evaluated. An effective steric repulsion force was provided by the surface functionalization of nanoparticles during the phase transfer, supported by the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory. The formed nanoparticles exhibited a superior stability against agglomeration in the presence of high concentrations of lithium bromide, i.e., from 20 to 50 wt.%, which make them good candidates for a range of novel applications.

Introduction

Formulating stable nanoparticle dispersions (i.e. nanofluids) are fundamental to a wide range of applications, from materials processing, chemical reactions to heat transfer intensifications [1,2]. Most of the formation processes are based on a two-step method [3]. In this method, nanoparticles need to be produced first, followed by complicated processes including particle purification, separation, drying, packaging and storage, which produced many agglomerations. Such particles are then dispersed into a base fluid under suitable ionic or surfactant conditions [4]. Considering the close relationship between the structures and properties, the dispersed status of nanoparticles in the fluid plays a crucial role in determining the effective properties of the dispersion. The one-step method, which produces and disperses nanoparticle into the required fluid simultaneously, looks very appealing. Most of the one-step methods have been focused on dispersing particles into a single base fluid [3].

Microemulsions have recently received intensive interest for the synthesis of nanomaterials. The nanodroplets inside a microemulsion behave as energetic barriers that prevent ion–ion encounters of the precursors and surfactants around droplets, contributing to the steric stabilization of droplets [5]. Some surfactant molecules inside the droplets can also affect the growth of different facets of nanoparticles, leading to the production of particles with different morphologies and improved stabilities [6]. Different particle morphologies including spheres, rods and disks can be produced by properly adjusting the controlling parameters such as surfactant concentration, mole ratio of water to surfactant, oil and co-surfactant, and reaction temperature [7–9]. Such versatility makes microemulsion a promising method to produce particles with controlled size, shape, homogeneity, stability and functionalizing surface area. Microemuslisons have been successfully used to produce different iron oxide nanoparticles [10–12]. The research regarding the synthesis of stable nanoparticles in a high ionic media of lithium bromide (LiBr) solution, however, has never been reported.

Binary fluids have many unique applications in a variety of fields. For instance, LiBr–water binary is an effective working medium for absorption refrigeration systems and is suitable for many solar-based applications including solar thermal air conditioning [13,14]. It has been reported that dispersing suitable nanoparticles into a base fluid can trap more solar light energy and improve significantly the system energy efficiency [15]. Among various particles investigated, Alfaro et al. [16] experimentally showed that iron oxide nanoparticles were very promising in absorbing solar energy. However the stability of nanoparticles in a high ionic media of LiBr is a big challenge. The challenge lies on the dominance of the combined magnetic and van der Waals attractive

* Corresponding author at: School of Chemical and Process Engineering, University of Leeds, Leeds, LS2 9JT, UK.
E-mail address: d.wen@leeds.ac.uk (D. Wen).

http://dx.doi.org/10.1016/j.jiec.2017.01.026
1226-086X/

forces. Simply relying on the steric repulsion force in the ionic media, where electrostatic double layer (EDL) repulsions are insignificant, is difficult to achieve the stabilization. The ionic media would compress the EDL around nanoparticles and cause the formation of aggregates. Formulating stable nanoparticle dispersion in an ionic binary fluid becomes a key issue to advance its applications. Sesen et al. produced high stable super paramagnetic iron oxide nanofluids by functionalizing particles with a bilayer of lauric acid [17]. The experimental results showed that this type of nanofluids were able to improve heat transfer under both single and two phase conditions, and the stability of nanofluids could be improved by applying magnetic actuation [17,18]. There were a few prior studies investigated the stability of iron oxide nanoparticles in ionic strength media [19,20], but focused on the short term effect, i.e., a few days.

In this study, we present a novel one-pot microemulsion method to synthesize iron oxide nanoparticles with a narrow size distribution and robust surface functionalization. The proposed method provides a facile functionalizing strategy for separating nanoparticles from the oil phase. The functionalization includes the formation of a bi-ligand surfactant around nanoparticles during the phase transfer of nanoparticles from the oil phase to water phase after the reaction inside microemulsions. The bi-ligand layers serve as excellent steric stabilizers to prevent the flocculation and aggregation of nanoparticles. The long term stability of nanoparticles was analyzed in binary base fluids containing 20, 30, 40 and 50 wt.% LiBr salt and the results confirmed the prosperity of our new synthesis method. Investigation of the effect of temperature and precursor concentration on the morphology change is another aspect of novelty in current research.

Materials and experimental methods

Materials and characterization

Analytical grade materials including cyclohexane, sorbitane-monooleate (Span 80, HLB = 4.3), polyethylene glycol sorbitanmonolaurate (Tween 80, HLB = 15), propyl alcohol, sodium hydroxide, ferric chloride ($FeCl_3$), ferrous chloride ($FeCl_2$), LiBr and citric acid were purchased from Sigma-Aldrich and used without further processing.

The morphology and size distribution of produced Fe_3O_4 nanoparticles were analyzed by Transmission electron microscope (FEI Tecnai TF20 TEM). High resolution TEM (FEI Titan Themis 300), which is equipped with super-X EDX system with 4-detector, was used to study the crystal lattice and elemental composition of nanoparticles. Zeta potential and hydrodynamic size of nanofluids were analyzed using Malvern Zetasizer Nano-ZS (Malvern Instruments, UK) and the measurement of UV/vis absorption spectra of nanoparticles was performed by a UV 1800-spectrophotometer (Shimadzu Corporation, Japan). The stability of nanoparticles over flocculation and sedimentation was characterized by a dispersion analyzer centrifuge (LUMiSizer 6110, Lum GmbH, Berlin, Germany). Varian 240FS atomic absorption spectrophotometry (Varian Ltd, USA) was applied for the determination of iron oxide concentration.

Synthesis of iron oxide nanoparticles

Based on our previous experience [21], water/cyclohexane/Span 80-Tween 80/isopropyl alcohol were selected to form reverse microemulsions with the minimum average droplet size and polydispersity. The Massart co-precipitation method was used for the production of magnetite nanoparticles according to the following reaction [22]:

$$FeCl_2 + 2FeCl_3 + 8NaOH \rightarrow Fe_3O_4 + 8NaCl + 4H_2O \quad (1)$$

Table 1 shows the concentration and temperature condition of several experiment runs. The concentrations of other components were prepared based on chemical stoichiometry with ferrous chloride.

The reverse microemulsion was prepared by mixing 1 ml of deionized water containing $FeCl_3$ and $FeCl_2$ with a mixture of 8 ml cyclohexane, 0.05 g Span 80-0.45 g Tween 80 and 0.5 ml propyl alcohol for 1 h under magnetic stirring. 1 ml of sodium hydroxide solution as the precursor was added drop wise to the reverse microemulsion for a period of 10 min. The mixture was stirred over 4 h to reach the equilibrium. A trial was performed without using any surfactant in the mixture to compare with the reverse microemulsion method.

Results and discussion

Separation of nanoparticles

Fig. 1(a) shows the image of the final reactant dispersions for different experimental runs. The change in the color of final dispersion suggests the presence of different sizes of Fe_3O_4 nanoparticles. One trial was done with a water/alcohol/cyclohexane system without using any surfactant (Fig. 1(b)). The black color and adsorption of the suspension by a magnet show the formation of a magnetic fluid with large particle size.

In order to separate Fe_3O_4 nanoparticles from the reaction dispersion, a neodymium-samarium cobalt magnet (18 kg pull force) and a centrifuge (Thermo Scientific megafuge 16R) were tried. The dispersions were centrifuged for 30 min at the speed of 13,000 rpm. The comparison of the results before and after showed a negligible effect of the centrifugation effect on the separation of nanoparticles. Also, the efficiency of separation by a strong magnet was too low to have a good separation. The small size of nanoparticles and functionlization with surfactants show a great resistance of nanoparticles against separation by a centrifuge or magnet [23].

Phase transformation of nanoparticles

Phase transformation is another strategy for the separation of nanoparticles. During the phase transformation, the ligands on the surface of nanoparticles are modified to generate new binding ligands. The work of Sperling and Parak [24] showed that such modification could transfer the formed nanoparticles from the original nonpolar environment (i.e., organic phase) to a polar aqueous phase. In addition, the presence of ligand could also provide the colloid with an increased stability, e.g. by exchanging hydrophobic with the hydrophilic ligands.

Similar strategy was used in our experiments. Fig. 2(a) shows the dispersion of nanoparticles in an organic phase after the separation of reverse microemulsion in Case 2. By adding some droplets of acetic acid to the dispersion, iron oxide nanoparticles were transferred to the water phase (Fig. 2(b)). As schematically

Table 1
The condition of nanoparticle synthesis in different experiment runs.

Experimental run number	Ferrous chloride molarity	Temperature
Case 1	0.01	22 °C (Room)
Case 2	0.05	22 °C
Case 3	0.1	22 °C
Case 4	0.01	70 °C
Case 5	0.05	70 °C
Case 6	0.1	70 °C

Please cite this article in press as: E. Nourafkan, et al., Synthesis of stable iron oxide nanoparticle dispersions in high ionic media, J. Ind. Eng. Chem. (2017), http://dx.doi.org/10.1016/j.jiec.2017.01.026