Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2017, **27**, 485–486

Mendeleev Communications

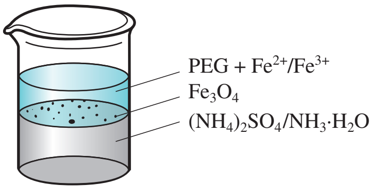
Synthesis of magnetic iron oxide nanoparticles at the interface of the polyethylene glycol–ammonium sulfate–water extraction system

Valery M. Shkinev,*[a] Yulia A. Zakhodyaeva,[b] Rustam Kh. Dzhenloda,[a] Olga B. Mokhodoeva[a] and Andrey A. Voshkin[b,c,d]

[a] *V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: vshkinev@mail.ru*
[b] *N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: yz@igic.ras.ru*
[c] *Institute of Fine Chemical Technologies, Moscow Technological University, 119571 Moscow, Russian Federation*
[d] *Moscow Polytechnic University, 107023 Moscow, Russian Federation*

DOI: 10.1016/j.mencom.2017.09.018

The synthesis of iron oxide nano- and microparticles in the PEG 3000–ammonium sulfate–water extraction system has been accomplished for the first time. Upon the addition of a solution of ammonia, iron oxide particles with sizes from 200 nm to 10 μm are produced at the interface. The phase composition of the obtained oxides consisting of magnetite with goethite impurity has been determined.



The magnetic particles of iron oxide are widely used in medicine[1] and technology.[2,3] Magnetite is most frequently produced in a homogeneous medium.[4–6] The synthesis of magnetite in organic solvent–aqueous solution extraction systems is known.[5,7] Extraction systems based on polyethylene glycol (PEG) have not been used previously to obtain magnetic particles. At the same time, these systems can be employed to recover metals from solutions.[8,9]

Systems based on water-soluble polymers have a number of advantages over conventional systems. Among them are the ability to dissolve extractable hydrophilic compounds, the conductivities of extracts, and the fact that the salt content of the PEG phase and the density of the phase decrease with the total salt content of the system.

The physicochemical characterization of the above systems has shown that the interface is between a uniform Langmuir layer of PEG molecules from the polymer and an aqueous salt solution.[10] In this case, the transport of ions occurs through channels and interaction proceeds near the boundary of the salt layer.[11] Note that there is a potential jump, which depends on the composition of the system and pH, at the interface. The permittivity of the phases is also different.

We found that solid particles could be produced only at a certain sequence of introducing reagents into the extraction system. The experiments were performed in a two-phase system containing 25 wt% PEG-3000 (Fluka), 25 wt% ammonium sulfate, and 50 wt% water, which was studied previously.[8–10] A mixed solution of iron(III) chloride (0.1 M) and iron(II) sulfate (0.05 M) was prepared in distilled water. The solutions were carefully poured onto Petri dishes.

As an example, Figure 1 presents the results of two parallel experiments performed using permanent magnets placed under the Petri dishes.

Iron oxide was obtained in 24 h. In experiment A, the oxide produced had no magnetic properties, as is evident from the distribution of a film on the surface of phases. In experiment B, the film on the surface of the phases completely repeated the contours of a magnet to indicate that particles in the film had magnetic properties (*i.e.*, under the effect of permanent magnets, particles were aligned according to magnetic lines).

The X-ray diffraction analysis of the magnetite (Fe_3O_4) samples, which was performed on a D2 Phaser diffractometer (Bruker) using CuKα radiation with $\lambda = 0.1548$ nm has shown that the experimental diffraction peaks completely correspond to the peaks of X-ray patterns from a computer databank for magnetite (Fe_3O_4). Consequently, the samples of particles obtained by our procedure at the phase boundary in the water–ammonium sulfate–polyethylene glycol extraction system consisted of a magnetite phase with a cubic crystal lattice. The samples also contained goethite impurities, as verified by the spectrum.

The size of particles in the dispersions of the produced samples in water was determined by static light scattering using a SALD 7500nano device (Shimadzu). Figure 2 shows that the dispersion

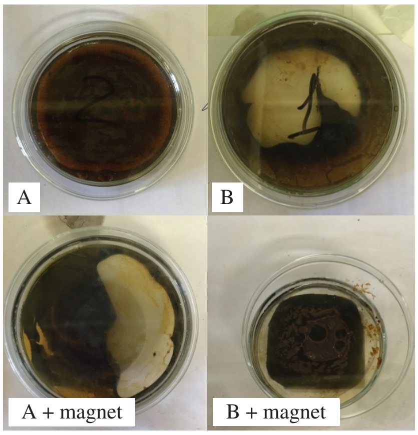


Figure 1 Samples in Petri dishes.

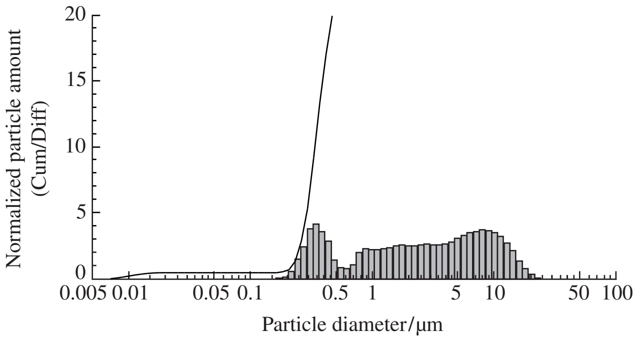


Figure 2 Particle size distribution in the sample of magnetite.

consists of particles with sizes from 200 to 500 nm with a maximum at 350 nm and a set of particles from 1 to 10 µm.

The results can be interpreted based on the two-stage mechanism of magnetite production in a homogeneous medium[4] and the synthesis of magnetite in the extraction system of a solution of di-*n*-propylamine in cyclohexane and an aqueous ammonia solution.[6] The interface of the extraction system based on PEG consists of a layer of polymer molecules.

The first reaction (the nucleation stage) is the fastest, and the linear molecule of $FeOOH_{(s)}$ is formed in all versions of the synthesis:

$$Fe^{3+} + 3OH^- \rightarrow FeOOH_{(s)} + H_2O. \tag{1}$$

The subsequent reaction (2) is slower and heterogeneous, and it proceeds in the Langmuir layer at the interface:

$$2FeOOH_{(s)} + Fe^{2+} + 2OH^- \rightarrow Fe_3O_{4\,(s)} + 2H_2O. \tag{2}$$

The synthesis of magnetite practically occurs in a template of PEG molecules; due to this, magnetite is formed only when iron salts are introduced into the PEG phase. At the subsequent aggregation stage of magnetite nanoparticles [reaction (3)], the particle size depends on solution ageing time (the growth stage). Particles with sizes of up to 10 µm can be produced for 24 h.

$$n\,Fe_3O_4 \rightarrow (Fe_3O_4)_n \tag{3}$$

Thus, iron oxide nano- and microparticles in the PEG-3000–ammonium sulfate–water extraction system were synthesized, a solution of ammonia being used as a precipitating agent. The iron oxide particles with sizes from 200 nm to 10 µm were produced at the interface. The magnetic particles consisted of magnetite with a goethite impurity. The thus obtained nanocomposite material can be used for drug delivery applications.

This study was supported by the Russian Foundation for Basic Research (project nos. 16-03-00106_a, 16-03-00528_a and 16-33-00214_mol_a), the Presidium of the Russian Academy of Sciences (project no. 0088-2015-0127) and, in part, by the Russian Foundation for Basic Research and the Moscow city Government (project no. 15-33-70004 'mol_a_mos').

References

1 M. Kempe, H. Kempe, I. Snowball, R. Wallén, C. R. Arza, M. Götberg and T. Olsson, *Biomaterials*, 2010, **31**, 9499.

2 N. V. Lukashova, A. G. Savchenko, Yu. D. Yagodkin, A. G. Muradova and E. V. Yurtov, *Met. Sci. Heat Treat.*, 2013, **54**, 550 (*Metalloved. Term. Obr. Metal.*, 2012, no. 10, 60).

3 S. P. Gubin, Yu. A. Koksharov, G. B. Khomutov and G. Yu. Yurkov, *Russ. Chem. Rev.*, 2005, **74**, 489 (*Usp. Khim.*, 2005, **74**, 539).

4 I. Martínez-Mera, M. E. Espinosa-Pesqueira, R. Pérez-Hernández and J. Arenas-Alatorre, *Mater. Lett.*, 2007, **61**, 4447.

5 J.-H. Wu, S. P. Ko, H.-L. Liu, S. Kim, J.-S. Ju and Y. K. Kim, *Mater. Lett.*, 2007, **61**, 3124.

6 K. Tao, H. Dou and K. Sun, *Colloids Surf., A*, 2008, **320**, 115.

7 E. N. Golubina, *Dr. Sci. Thesis*, Moscow, 2015.

8 V. M. Shkinev and B. Ya. Spivakov, in *Uspekhi analiticheskoi khimii* (*Advances in Analytical Chemistry*), ed. L. K. Shpigun, Nauka, Moscow, 2007, pp. 315–321 (in Russian).

9 A. A. Voshkin, V. M. Shkinev and Yu. A. Zakhodyaeva, *Russ. J. Phys. Chem. A*, 2017, **91**, 226 (*Zh. Fiz. Khim.*, 2017, **91**, 227).

10 V. M. Shkinev, *Dr. Sci. Thesis*, Moscow, 2013.

11 L. M. Kardivarenko, V. M. Shkinev, V. V. Bagreev and B. Ya. Spivakov, *Zh. Neorg. Khim.*, 1995, **40**, 701 (in Russian).

Received: 9th February 2017; Com. 17/5171