



Overcharging of magnetite nanoparticles in electrolyte solutions



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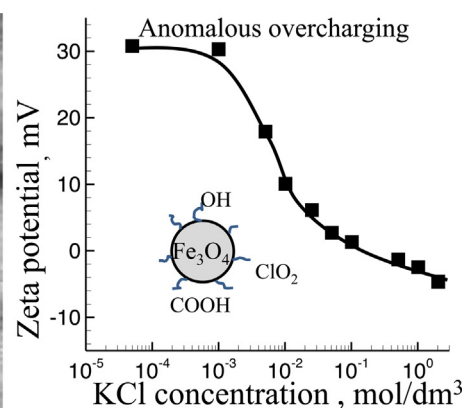
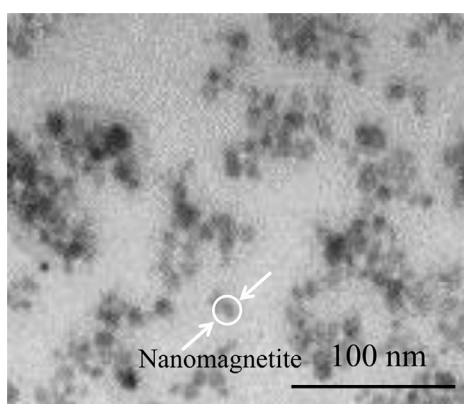
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HIGHLIGHTS

- Characterization of nanomagnetite (NM) particles obtained by different methods was done.
- Effect of pH and electrolytes on zeta potential of NM was studied.
- Anomalous overcharging of NM was observed and its mechanism was discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

The effect of electrolytes with mono-, bi-, and trivalent anions on the surface charge (ζ -potential) of magnetite nanoparticles was investigated. The nanoparticles of magnetite, Fe_3O_4 , were synthesised using different methods: a) coprecipitation of bivalent and trivalent iron sulphates at temperature $T = 25^\circ\text{C}$ (sample NM_1) and b) oxidation of rotating steel disk in distilled water at $T = 25^\circ\text{C}$ (sample NM_2) and at $T = 50^\circ\text{C}$ (sample NM_3). All samples were characterized using transmission electron microscopy, infra-red spectroscopy, by measurements of electrophoretic mobility and particle size distribution. Transmission electron microscopy data evidenced that primary particles in dried powder samples have quasi-spherical shape with mean diameters of $\approx 15\text{ nm}$ (NM_1), $\approx 80\text{ nm}$ (NM_2) and $\approx 70\text{ nm}$ (NM_3). From other hand data of particle size distribution analysis in aqueous suspensions at pH 6 indicated formation of aggregates of size of $\approx 30\text{ nm}$ (NM_1), $\approx 1200\text{ nm}$ (NM_2) and $\approx 520\text{ nm}$ (NM_3). Infra-red data also evidenced the presence of different functional groups in dependence on the protocol of synthesis. In presence of background electrolyte KCl (1 mM) the isoelectric point for all particles was in the interval pH 6.0–8.0. Adding of electrolytes with mono- (Cl^-), bi- (SO_4^{2-}), and trivalent (PO_4^{3-}) anions resulted in noticeable differences in behaviour of the ζ -potential and position of the isoelectric point for particles NM_1 , NM_2 and NM_3 . An increase of concentration of electrolytes always resulted in overcharging (changing from positive to negative charge) of particles NM_1 and NM_3 , whereas for particle NM_2 the overcharging was observed for both bivalent (SO_4^{2-}) and trivalent (PO_4^{3-}) anions. This behaviour cannot

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be explained by changes in the structure of electric double layer. The observed shifts of the isoelectric point and changes in the pH values in the presence of electrolytes reflected the impact of specific adsorption of anions on the ζ -potential of magnetite nanoparticles. Differences in pH values at which overcharging of nanoparticles took place can be explained by diverse structure of the surfaces of particles NM₁, NM₂ and NM₃.

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1. Introduction

Magnetite, Fe₃O₄, has the structure of spinel with two non-equivalent cations in crystalline structure, Fe²⁺ and Fe³⁺, which results in unique magnetic properties of this material [1]. Physical and chemical properties of nanomagnetite particles can noticeably differ from the behaviour of macroparticles of magnetite that is explained by “quantum size effects” [2]. The increased fraction of the ‘surface’ atoms with different coordination number and symmetry of the local environment is typical for nanoparticles. This results in unusual magnetic properties, for example, in giant magneto-resistance, magneto-caloric effect etc. Magnetization and magnetic anisotropy of nanoparticles can considerably exceed these properties for bulk samples, and huge differences in the Curie or Neel temperatures are observed for these states of the material [2]. Nowadays, practical applications of nanomagnetite particles became more and more extensive [3]. Nano-scale magnetite demonstrated exciting opportunities in a number of fields with applications in high gradient magnetic separators [4] for recovery of hazardous wastes, radioactive chemicals and toxic/carcinogenic metals [5–7], in medical magnetic resonance technologies as contrasting agents for clearer imaging of tissues and organs [8], in targeted drug delivery systems [9], as magnetic sensors [10] and replenishing catalysts [11].

Shape, size and properties of nanomagnetite are controlled by the method of their synthesis [12,13]. By majority methods the synthesis is conducted in aqueous medium and the air oxygen is used as oxidizer. The pH of medium, the concentration of oxidizer [14], and the temperature [15] play important role during formation of nanomagnetite. Also nanomagnetite particles can be obtained using method of oxidation by air oxygen of rotating steel disk in distilled water [15]. Formation of nanomagnetite occurs at pH 4.0–6.5 [14], and it includes coagulation and condensation-crystallization mechanisms that were described in detail for formation of magnetite particles during aging of ferric hydroxide [12].

The surface charge (and ζ -potential) is a very important characteristic of nanomagnetite that determines the stability of nanofluids on the base of magnetite. The effects of adsorption of ions of heavy metals [16] and sulphate-ion [17], pH of medium [18,19] and temperature [20] on the ζ -potential of nanomagnetite were studied in previous works. However, detailed studies of overcharging processes of nanomagnetite as a function of the type and concentration of added electrolytes and of pH have never been performed before.

This work discusses the effect of electrolytes having mono- (Cl⁻), bi- (SO₄²⁻) and trivalent (PO₄³⁻) anions on the ζ -potential of nanomagnetite particles in aqueous suspensions prepared by different methods. The particles of nanomagnetite were synthesised using the method of coprecipitation of bivalent and trivalent iron salts at temperature $T=25^\circ\text{C}$ (sample NM₁) and method of oxidation of rotating steel disk in distilled water at $T=25^\circ\text{C}$ (sample NM₂) and at $T=50^\circ\text{C}$ (sample NM₃). The effects of specific adsorption of anions on the ζ -potential of nanomagnetite particles are discussed.

2. Materials and methods

2.1. Materials

The following chemical reagents of chemical grade purity were used: perchloric acid (Sigma-Aldrich, Saint Louis, USA), aqueous ammonia, bi- and trivalent iron sulphates (FeSO₄·903;4H₂O and Fe₂(SO₄)₃·903;6H₂O), sodium hydroxide, salts of KBr, KCl, K₂SO₄ and K₃PO₄ (all from Reanal, Hungary). Double distilled water was used to prepare salt solutions and suspensions. For adjustment of pH, perchloric acid and sodium hydroxide have been applied.

2.1.1. Synthesis of nanomagnetite

The particles of nanomagnetite, Fe₃O₄, were synthesised using different methods: by coprecipitation of bivalent and trivalent iron sulphates at temperature $T=25^\circ\text{C}$ (sample NM₁) and by oxidation of rotating steel disk in distilled water at $T=25^\circ\text{C}$ (sample NM₂) and at $T=50^\circ\text{C}$ (sample NM₃).

2.1.1.1. Sample NM₁. The method of coprecipitation of bivalent and trivalent iron sulphates mixture (with ratio 1:2 wt/wt) was used for synthesis of sample NM₁ [21]. The synthesis was done at room temperature, $T=25^\circ\text{C}$. The mixture of iron sulphates (16 g) was dissolved in 1 M aqueous solution of the perchloric acid (200 ml) and then 25 % wt solution of aqueous ammonia (20 ml) was very slowly added to the obtained mixture to precipitate iron oxides. Perchloric acid was used to avoid formation of hydroxide complexes [1,22]. Finally, the mixture was agitated with magnetic stirrer for 10 min at a rate of 180 rpm. The colour of the suspension became black as a result of formation of nanomagnetite particles.

The gel-like precipitate was isolated from liquid using a constant magnet and washed 3–4 times with distilled water. Precipitate (10.07 g) was added to 2 M aqueous solution of perchloric acid (200 ml), centrifuged and washed several times with distilled water to remove any residual reactant perchloric acid and to obtain neutral pH. Then suspension was ultrasonicated for 10 min using a UZD-22/44 ultrasonic disperser (Sumyprigor, Sumy, Ukraine). Finally, perchloric acid was added to suspension (pH 2.9) in order to avoid oxidation of nanoparticles. This method produces acidic (positively charged) nanoparticles of NM₁. The concentration of NM₁ in suspension was 8 mg/ml. The obtained suspension was stable against aggregation (for more than 1 year).

2.1.1.2. Samples NM₂ and NM₃. Samples NM₂ and NM₃ were obtained by method of oxidation of rotating steel disk. The steel E 235-B (Fe 360-B) with composition 97.0% Fe; 0.14–0.22% C; 0.05–0.15% Si; 0.4–0.65% Mn; ≤0.3% Ni; ≤0.05% S; ≤0.04% P; ≤0.3% Cr; ≤0.3% Cu; ≤0.08% As; ≤0.01% N has been applied [23]. At the start of each experiment the surface of steel disk was cleaned from oxidation layer using sequentially the sandpapers with different grits P36, P80, P400 [24,25], washed with 1 M solution of sulphuric acid and then washed thoroughly with distilled water [14,15]. The disk had radius $R=6$ cm, and it was partially dipped to the distilled

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