



Polyethyleneimine-modified iron oxide nanoparticles: their synthesis and state in water and in solutions of ligands

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Abstract

Water-soluble iron oxide nanoparticles (IONPs) are synthesized from oleate-stabilized particles (IONPs-OA) by replacing oleate moieties with 3,4-dihydroxybenzoic acid (3,4-DHB) and polyethyleneimine (PEI). Investigation of the obtained composite nanoparticles by TEM, SEM, and AFM methods demonstrated that the parent IONPs-OA particles have a narrow size distribution and that the size of the magnetite core (4.3 nm) was retained in the polyethyleneimine modified IONPs-PEI nanoparticles (4.5 nm). IONPs-PEI exist in the form of separate nanoparticles distributed in the bulk polymer matrix as well as elongated chains (up to 20 nm in length) consisting of 3–6 nanoparticles, and mostly in the form of large clusters (~150 nm). The NMR relaxometric properties of IONPs-PEI in the water at various pHs are determined. Relaxivity of such modified nanoparticles remains constant over a wide pH range (3–9) and decreases only in strongly alkaline solutions due to the destruction processes. In the presence of physiological amounts of NaCl (0.15 M), the relaxivity of IONPs-PEI solutions is reduced by 37%. The effect of the addition of various iron(III) chelators is analyzed. Tiron (disodium 4,5-dihydroxy-1,3-benzenedisulfonate) is the only ligand which destroys the polymer-bound IONP system in solution, dissolving the iron oxide core, while other ligands (3,4-DHB, 2,4-DHB, citric acid) do not reduce the relaxation of the composite aqueous solution. The developed polyethyleneimine-modified iron oxide nanoparticles can be regarded as a promising model of a contrast agent for magnetic resonance imaging (MRI).

Keywords Iron oxide nanoparticles · NMR relaxation · Polyethyleneimine modified nanoparticles · 3,4-Dihydroxybenzoic acid · Iron(III) chelators

Introduction

To date, great attention has been paid to the development of nanoscale materials and compositions on their basis both in solid form and in solutions [1, 2]. Such an interest is related to the unique optical and magnetic properties inherent to nanoscale materials, as well as their catalytic activity [3, 4]. Among the named characteristics, magnetic properties occupy a special place, and magnetic nanoparticles are of great importance for such areas as ecology, medicine, and materials science [5, 6].

The nanoparticle's magnetic properties are related to its size, shape, morphology, and composition, which determine the magnetic properties of the material itself. The latter is a key parameter since all substances interact with the magnetic field to some extent [7]. Since ferromagnetic materials show the strongest interaction with the magnetic field, they are preferable for producing magnetic nanoscale materials. Among iron compounds, magnetite is the most commonly used due to its high magnetization [8–10]. To date, a large number of methods are known for preparing nanoscale magnetite (IONPs), which allows to obtain nanoparticles of different sizes, shapes, and chemical nature of the surface, determining the variety of their application areas [11–16]. IONPs are now applied in immunology, in hyperthermia, as diagnostic tools and as detoxicants in medicine, as well as tools for drug delivery and cell separation [17–26]. At the same time, the use of IONPs in medicine imposes a large number of restrictions on the size of the particles and composition of the coating shells. With respect to the size, the IONPs are divided into three main categories based on their

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