

## Water transverse relaxation rates in aqueous dispersions of superparamagnetic iron oxide nanoclusters with diverse hydrophilic coating



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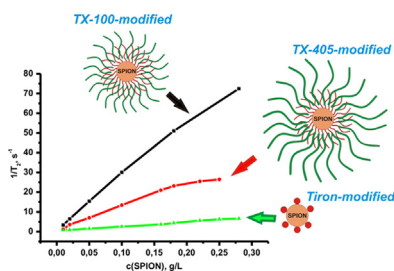
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### HIGHLIGHTS

- Hydrophilic coating of oleate-coated SPIONs by surfactants and triblock copolymers.
- Self-assembly of surfactants onto oleate layer is more predominant than ligand exchange.
- Structure of amphiphilic molecules affects clustering of SPIONs within hydrophilic coating.
- Particular effect of outer zone versus nearest one on relaxivity of hydrophilic SPIONs.
- Counter-ion interactions with ATP induce changes in relaxivity of surfactant-coated SPIONs.

### GRAPHICAL ABSTRACT

The effect of the hydrophilic external layer on the relaxation rate of iron oxide hydrophilic nanoclusters.



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### ABSTRACT

The article introduces transverse relaxation rates of water protons in the aqueous hydrophilic colloids synthesized on the basis of the oleate-coated iron oxide nanoparticles (17 nm) with non-ionic and cationic surfactants, triblock copolymers, polyethyleneimine (PEI) and 4,5-dihydroxybenzene-1,3-disulfoacid disodium salt (Tiron) as hydrophilic components. The IR spectroscopy, atomic force and transmission electron microscopy, along with dynamic light scattering data were obtained to evaluate the content of the hydrophilic coating, the clustering of iron oxide nanoparticles within the hydrophilic covering and the aggregation of hydrophilic nanoclusters. The analysis of the obtained results together with transverse relaxation rates under various concentration, counter-ion and temperature conditions reveals the particular importance of the water molecules diffusion in the outer hydrophilic layer versus the nearest to the iron oxide core layer. The obtained results reveal the counter ion binding with the charged hydrophilic iron oxide colloids as a route to affect the water transverse relaxation rates by biorelevant anionic substrates such as adenosine triphosphates.

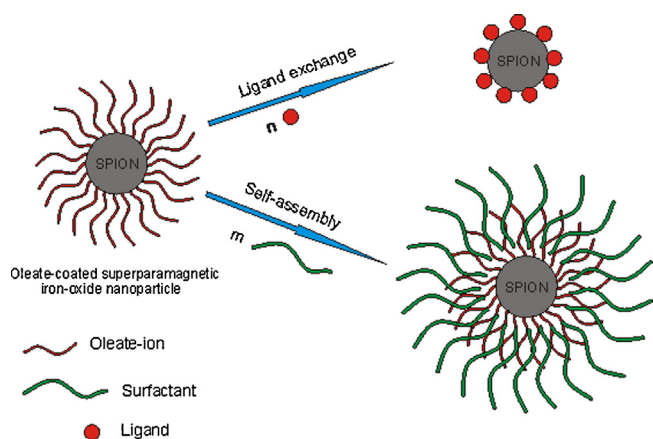
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### 1. Introduction

Superparamagnetic iron oxide nanoparticles (SPIONs) are a top of current interest today due to their applicability in medicine [1–6]

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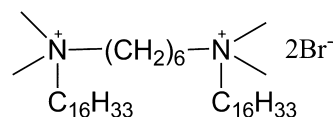


**Scheme 1.** Two possible surface recoating pathways for oleate-stabilized SPIONs.

and catalysis [7,8]. The colloid stability of SPIONs in aqueous media results from their encapsulation into the hydrophilic shell through various modes of surface coverage, such as polymer deposition [9–11], surfactant self-assembly [12–14] and silica coating [15–17]. The synthesis of hydrophilic SPIONs can be performed through the direct coating of iron oxide nanocrystals by hydrophilic molecules [18,19], although this way suffers from some drawbacks, such as broad particle size distribution and relatively low crystallinity of the nanoparticles. The synthesis of the oleate-stabilized SPIONs is the route to gain in the well-controlled shape/size uniformity and highly crystalline single-domain structures, but it should be followed by the recoating of oleate-stabilized SPIONs with hydrophilic molecules [13,14,18,20–22].

The effect of SPIONs on transverse relaxation rates ( $1/T_2$ ) of water protons results from the translational diffusion of water molecules in the inhomogeneous magnetic field surrounding the SPIONs, thus the nearest surrounding of SPIONs greatly affects their relaxivity [23,24]. The magnetization of SPIONs should be mentioned as another factor affecting the transverse relaxation rates of their aqueous dispersions. The works [13,21,22,25] exemplify the decrease in effective magnetic moment of SPIONs due to a non-collinear spin structure originated from the interaction between iron ions and amphiphilic molecules at the interface of nanoparticles. The diffusivity of water molecules and the thickness of an impermeable surface coating of SPIONs should be also noted as the factors affecting  $1/T_2$  values [18]. The work [26] introduces two zones surrounding the superparamagnetic core which greatly affect the transverse relaxivity of water molecules in hydrophilic colloids of SPIONs. The nearest to the iron oxide core layer, where water molecules are excluded, is called the exclusion zone. The outer zone is composed of the hydrophilic or charged moieties in which proton diffusion is assumed to be slower than in a bulk water. The full exclusion of water molecules from the nearest to the iron oxide layer is rather questionable and their diffusion should be significantly restricted in comparison with the outer layer. Two recoating mechanisms of the oleate-stabilized SPIONs by hydrophilic molecules are represented in the literature, which are the ligand exchange [9,14,26–29] and the supramolecular assembly of surfactant or amphiphilic molecules onto the oleate layer of SPIONs [10,21,30–32]. These alternative mechanisms which are schematically represented in Scheme 1 can provide diverse effect on the magnetization of SPIONs, the thickness of the nearest and the outer layers, as well as on the diffusion of water molecules within them.

As it was demonstrated by Qin et al. [31] the supramolecular self-assembly of the triblock copolymer F127 onto oleate-coated SPIONs provides the insignificant effect on their magnetization,



**Scheme 2.** Dicationic surfactant 16-6-16.

while more significant changes in magnetic properties were observed under the ligand exchange [28]. The length effect of polyethyleneoxide chain of PEGs on the magnetic relaxivity of water protons in aqueous colloids of SPIONs coated by PEGs [26] reveals the diffusion of water molecules in the outer layer as an important factor affecting the  $1/T_2$  values. Thus the analysis of magnetic relaxation rates of hydrophilic SPIONs in the correlation with the structure of hydrophilic components can shed light on both the morphology of the hydrophilic coating and the routes of its optimization.

The literature data indicate that the agglomeration of SPIONs is very often outcome of their hydrophilization [22]. The agglomeration of SPIONs is highlighted in the literature as the additional factor affecting the magnetic relaxivity of their aqueous dispersions [33–36]. The effect of SPIONs agglomeration on their superparamagnetic properties can result in both increased [33,37,38] and decreased [23,24]  $1/T_2$  values due to ferromagnetic and antiferromagnetic interparticle interactions. Thus agglomeration of SPIONs should be taken into account when  $1/T_2$  values are analyzed in the correlation with the coating layer morphology.

The above-mentioned diversity of factors affecting the relaxivity of the aqueous dispersions of hydrophilic SPIONs raises the problem of the relative importance of these factors. Thus the present work is aimed to find out a correlation between magnetic relaxation data in hydrophilic colloids of SPIONs with the identity of the coating and aggregation behavior of colloids. The use of the oleate-coated SPIONs recoated by hydrophilic compounds enables to remain the particle size distribution and their crystallinity on the same level. The choice of the hydrophilic molecules is affected by their diverse abilities to self-assembly with oleate layer and to coordinate with iron oxide core. In particular the supramolecular assembly onto the oleate layer should be predominant mechanism for surfactants with poor affinity to iron ions. The series of triblock copolymers with various architecture of poly(ethyleneoxide) (PEO) and poly(propyleneoxide) (PPO) blocks, namely (PEO)<sub>13</sub>(PPO)<sub>30</sub>(PEO)<sub>13</sub> (L64), (PPO)<sub>9</sub>(PEO)<sub>23</sub>(PPO)<sub>9</sub> (10R5) and (PEO)<sub>20</sub>(PPO)<sub>70</sub>(PEO)<sub>20</sub> (P123), Triton X-100 and Triton X-405 (TX-100 and TX-405) and dicationic surfactant (16-6-16, Scheme 2) have been chosen as amphiphilic compounds able to supramolecular assembly with oleate layer. The probability of the ligand exchange mechanism correlates with a complex ability of coating compounds with iron ions.

Thus both polyethyleneimine (PEI) and 4,5-dihydroxybenzene-1,3-disulfoacid disodium salt (Tiron) with greater complex ability toward iron ions [39,40] exemplify coating molecules with higher ligand exchange contribution. It is worth noting nevertheless that both recoating mechanisms are anticipated for non-ionic surfactants, triblock copolymers and PEI due to their abilities to form both multiple coordination bonds with iron ions on the iron oxide surface [26] and supramolecular assemblies with oleate layer. The agglomeration of the SPIONs under their hydrophilization is analyzed by atomic force microscopy (AFM) and dynamic light scattering (DLS) methods. The IR spectroscopy analysis is applied to reveal the presence or displacement of the oleates from the hydrophilic coating of SPIONs. The electrokinetic potential measurements are performed to reveal the charging of SPIONs due to the recoating by the above-mentioned hydrophilic molecules.

The effect of counter ions including AMP, ADP, ATP on the transverse relaxation rate of SPIONs coated by PEI and 16-6-16, as well

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