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The synthesis and rheological characteristics of colloidal systems containing functional magnetic nanoparticles

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Abstract

Functional magnetic nanoparticles were synthesized by homogeneous nucleation from the solution of metal salts in the presence of functional oligoperoxide surfactants (FOS). FOS addition causes the decrease of the quantity of large particles and agglomerates. The presence of radical forming sites on the magnetic colloid surface provides the possibility of carrying out of grafted polymerization in a wide temperature range in the media of various polarities. As a result of homogeneous nucleation of the particles in the presence of oligomer surfactants the extremes of the particle size, dynamic viscosity and maximal value of FOS sorption are observed at the same FOS concentration in the solution. The dependences of dynamic viscosity of magnetic colloid suspensions modified by various amount of FOS on shear stress witness the formation of multi-layer functional shell with different orientation of polar functional groups and their different remoteness from the surface. The formation of new polymeric chains tethered to the colloid surface leads to breaking particle assemblies and provides both the aggregative and sedimentation stabilization of the magnetic fluids formed and targeted affinity to biological substrates.

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1. Introduction

At present hybrid polymer/metal or polymer/metal oxide colloidal beads with functional shell and magnetic properties are of great interest for application in biochemistry and cell biology as analytical reagents and for separation of pure cell culture and specific substances (proteins, nucleic acids) from their mixtures. The special requirements for these colloids are monodispersity and availability of tailored functional groups on the particle surface [1]. The obtaining of functional colloidal particles by the technique of homogeneous nucleation from the salt solutions in the presence of functional oligoperoxide surfactants (FOS) as templates and surface modifiers simultaneously provides both the control of particle size distribution and targeted functionality and reactivity of the particle surface [2,3].

Therefore, the synthesis of magnetic colloids with narrow size distribution and multi-layer functional shell by homogeneous nucleation from the mixture of Fe salt solutions in the presence of FOS as well as stable

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colloidal systems on their basis were the aim of these investigations.

2. Experimental

2.1. Synthesis

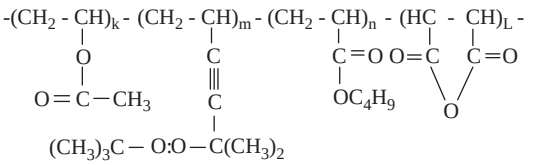
The nucleation process of Fe_3O_4 functional particles from the salt solution occurs in accordance with the reaction:

$$2FeCl_3 \cdot 6H_2O + FeCl_2 \cdot 4H_2O + 8NH_4OH \rightarrow Fe_3O_4 + 8NH_4Cl + 20H_2O$$

The solution of salt mixture (0.2 M $FeCl_3 \cdot 6H_2O$, 0.13 M $FeSO_4 \cdot 7H_2O$, Fe^{3+}/Fe^{2+} molar ratio = 3:2, excess of Fe^{2+} to stoichiometric ratio) was added to water–ammonia (fourfold molar excess of NH_4OH to stoichiometric ratio) solution of FOS at continuous stirring under N_2 atmosphere and 274–298 K. FOS concentrations are shown in Tables 1 and 2. Reagent concentrations were taken to obtain 2%wt or 5%wt suspensions of magnetite in reaction mixture. The reaction mixture was stirred for 5 h to reach the adsorption equilibrium of FOS. Then Fe_3O_4 particles were washed with distilled water, methanol and distilled water again to remove the solution of salt mixture and reversibly adsorbed FOS molecules. Purified suspensions were dried under vacuum and used for analysis and suspension preparing.

2.2. Characterization

The size and morphology of Fe_3O_4 particles were investigated by scanning electron microscopy (SEM) (Akashi ISI DS 130C microscope). X-ray diffraction analysis was carried out using "DRON-30" (CuKα irradiation). Amounts of adsorbed FOS and grafted copolymer were determined by elemental analysis. Sedimentation stability of suspensions was evaluated by measuring optical transmission (OT) of diluted suspensions vs. time and calculating $1/tg\alpha$, where α - slope angle of relation OT vs. time. The dynamic viscosity of Fe_3O_4 suspensions was measured using "RHEOTEST 2.1". The structures of the FOS used as templates and colloid surface modifiers are presented on the scheme below.



where $k = 11.5$–16.9%; $m = 44.2$–48.3%; $n = 22.6$–24.2%; $L = 14.7$–17.6%; Mn = 4500–5200 g/mol.

3. Discussion

These surface-active substances are highly soluble in water media in a wide pH range and form micelle-like structures in the solution at achieving definite FOS concentration. FOS addition causes the decrease of the quantity of large particles and agglomerates and as a result unimodal particles are formed predominantly and weight-average size of particles decreases sharply (Table 1). This can be explained by the displacement of the reaction of particle nucleation into micelle-like structures formed by FOS molecules, which are the templates determining the particle size distribution.

Some characteristics of the synthesis, colloidal-chemical and rheological properties of Fe_3O_4 functional nanoparticles and fluids on their basis are presented in the Tables 1,2 and Figs. 1–3. It is evident (Fig. 4) that FOS molecules are sorbed irreversibly onto the colloidal particles providing its tailored surface activation including the ability to initiate the reactions of grafted polymerization. The presence of polymer shell tethered to the particle surface and possessing the targeted affinity not only leads to the breaking particle assemblies (Fig. 5) but also provides the aggregative and sedimen-

Table 1
The characteristics of the synthesis and properties of Fe_3O_4 colloidal particles

	C_{FOS} (% wt) (in solution)	Fe_3O_4 concentration, (%wt)	T (K)	d_N[b] (μm)	d_W[c] μm	k_{pol}	A_{FOS} (mg/g)	A_{FOS} (mg/m^2)
1	—	5	298	0.185	0.325	1.76	—	—
2	0.62	5	298	0.208	0.242	1.16	87.9	15.9
3	0.25	2	298	0.199	0.229	1.15	95.2	16.4
4	0.25	2	274	0.225	0.270	1.20	90.8	17.8
5[a]	0.25	2	274	0.226	0.269	1.19	94.9	18.5

[a]Dosing insertion of the solution of salt mixture.
[b]Number-average particle size.
[c]Weight- average particle size.