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Preparation and structural characterization of nanosized magnetic solid-phase extractants

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Nanosized magnetic solid-phase extractants (SPEs) have been obtained by modifying magnetite with oleic acid and cetyltrimethylammonium bromide under microwave heating conditions; the structure of the surface layers of SPEs has been studied experimentally and confirmed by the calculation of the degree of sorbent surface coverage with modifying agent molecules.

Nanomaterials with modified surfaces are of interest due to their use as solid-phase extractants (SPEs) for the preconcentration of trace components from water in environmental analysis.[1–3] Due to high specific surface areas, the sorption of analytes on these SPEs is efficient even under batch conditions. Sorbent particles with magnetic properties can be simply separated by an external magnetic force to accelerate sample preparation in routine analysis. The key role in the solid-phase extraction of analytes plays a self-assembling ordered layer of organic molecules formed on the particle surface.

In spite of significant progress in the synthesis and application of magnetic nanoparticles (MNPs), the conditions for their preparation are often chosen empirically. To optimize the preparation of modified nanosized materials, the formation of an organic shell on the magnetic core was experimentally studied. As an example, we consider the sorption of oleic acid (OA) and cetyltrimethylammonium bromide (CTAB) by nanosized magnetite Fe_3O_4.

Magnetic SPEs were obtained by microwave synthesis.[4] Microwave radiation was chosen as a heating source because of its high temperature and time gradients and the selective interaction of microwaves with the components of reaction systems. We studied the structure of the surface layers of the materials obtained† and the possibility of optimizing the conditions of its formation.

The SEM images of modified magnetite nanoparticles are shown in Figure 1. MNPs were obtained at the molar ratios Fe_3O_4:OA = 1:1 and Fe_3O_4:CTAB = 1:2.5. Covered MNPs were homogeneous (with average diameters of about 40 and 140 nm, respectively). In addition to SEM data, the MNPs were characterized by IR spectroscopy and X-ray diffraction analysis.[4]

† Magnetite was synthesized and its surface was modified in a Discover SP-D microwave (MW) system (CEM Corp., USA). The HPLC determination of CTAB and OA was carried out on an LC-20 Prominence HPLC system (Shimadzu, Japan). For the CHNS analysis of samples, a Model 1108 CHNS-O analyzer (Carlo Erba, Italy) was used. Images of MNPs were obtained on a JEOL JSM-6700F scanning electron microscope (Japan).

Nanosized magnetite was synthesized under MW heating (10 min) at 80 °C by co-precipitation using ammonium hydroxide from a solution containing $Fe(NO_3)_3$ and $FeSO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O$ at the ratio Fe^{3+}/Fe^{2+} of 2:1. Magnetite was modified with OA by the addition of an ethanol solution of OA and heating for 10 min at 80 °C in a MW system. A further increase in the heating time did not change the residual concentration of OA in solution, *i.e.*, an equilibrium was reached. Modification with CTAB was carried analogously, but a surfactant was added in a water solution with pH 9–10.

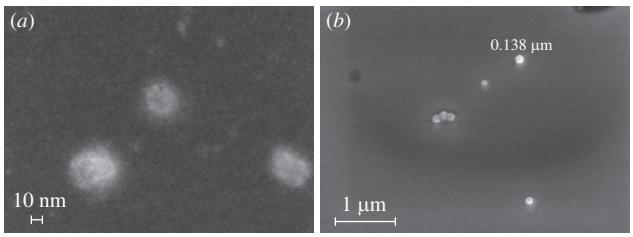

Figure 1 The SEM images of nanosized magnetite covered by (*a*) OA and (*b*) CTAB.

The sequential surface filling during the formation of a modifying layer is described by an expression which characterizes the structure of surface layers:[5] $Q = \theta Q_0$, where Q is the quantity of surfactant adsorbed (mol m^{-2}), θ is the number of layers on the surface of the sorbent; Q_0 is the quantity of surfactant adsorbed (mol m^{-2}) under the formation of a continuous surface (adsorption) monolayer: $Q_0 = (S_0 N_A)^{-1}$, where N_A is the Avogadro constant, S_0 is the surface area occupied by a surfactant molecule in a continuous surface monolayer (molecular area).[6]

The dimensionless quantity $\theta = Q/Q_0$ calculated as described above is numerically equal to the number of monomolecular surface layers. Adsorption of a surfactant on the surfaces of inorganic oxides is limited by the formation of a bilayer ($\theta_{max} = 2$),[5] when the first layer is mainly formed due to Coulomb attraction, and the second one is generated because of the hydrophobic interaction of the nonpolar tails of molecules in the first and second layers. The aggregates of mono- or bilayer structures formed in this process are specified as hemimicelles or admicelles, respectively.

Taking into consideration reference data for S_0 (36–38 Å^2 per molecule),[7] the calculated Q_0 for OA and CTAB was 4.6 μmol m^{-2}. The specific surface area (100 m^2 g^{-1}) used in the calculations for bare magnetite was obtained by the averaging of published data.[8–15] Tables 1 and 2 and Figure 2 show the results obtained and adsorption isotherms in the θ–$C_{CTAB\,sol}$ coordinates.

The shape of adsorption isotherms corresponds to a characteristic curve for the adsorption of surfactants on the surfaces of inorganic oxides.[16] A region of saturation in the isotherms corresponds to θ = 1.2–1.3 for OA or 1.5–1.6 for CTAB (Figure 2); that is, adsorption is completed by the formation of a bilayer with a looser structure.

If the adsorption of ionic surfactants takes place, the sequential formation of hemimicelles and admicelles is accompanied by a surface charge permutation; for this reason, the surface electrokinetic potential is useful for studying the surface structure of

Table 1 Adsorption of CTAB on the magnetite (experimental data) and the number of surface layers (calculated).

Sample number	$C_{CTAB\,sol}$/ mol dm^{-3}	$C_{CTAB\,ads}$/ mg mg^{-1}	$C_{CTAB\,ads}$/ μmol g^{-1}	Q/μmol m^{-2}	$\theta = Q/Q_0$
1	1.50×10^{-5}	0.0174	47.7	0.477	0.10
2	4.58×10^{-5}	0.0152	41.8	0.418	0.09
3	5.63×10^{-5}	0.0500	137	1.37	0.30
4	7.96×10^{-5}	0.0790	217	2.17	0.47
5	1.72×10^{-4}	0.146	402	4.02	0.87
6	2.77×10^{-4}	0.257	705	7.05	1.5
7	9.47×10^{-4}	0.267	733	7.33	1.6

Table 2 Adsorption of OA on the magnetite (experimental data) and the number of surface layers (calculated).

Sample number	$C_{OA\,sol}$/ mol dm^{-3}	$C_{OA\,ads}$/ mg mg^{-1}	$C_{OA\,ads}$/ μmol g^{-1}	Q/μmol m^{-2}	$\theta = Q/Q_0$
1	3.71×10^{-5}	0.00953	33.7	0.337	0.07
2	9.18×10^{-5}	0.00408	14.4	0.144	0.03
3	9.48×10^{-5}	0.0132	46.8	0.468	0.10
4	7.99×10^{-5}	0.0274	97.1	0.971	0.21
5	1.55×10^{-4}	0.0263	93.2	0.932	0.20
6	1.47×10^{-4}	0.0485	172	1.72	0.37
7	2.05×10^{-4}	0.0921	326	3.26	0.71
8	1.72×10^{-4}	0.1213	430	4.30	0.93
9	2.46×10^{-4}	0.130	461	4.61	1.0
10	2.16×10^{-4}	0.168	598	5.98	1.3
11	3.31×10^{-4}	0.177	625	6.25	1.4

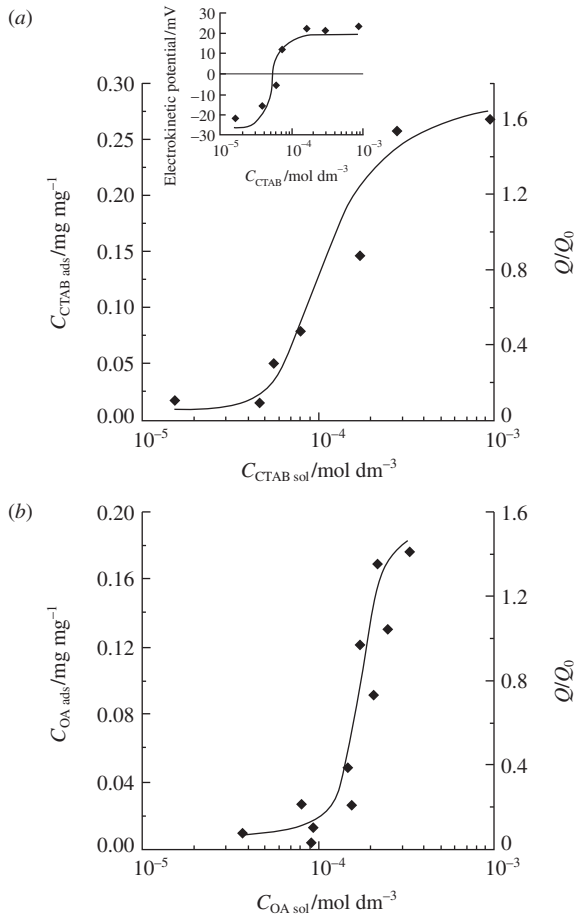

Figure 2 Adsorption isotherms of (*a*) CTAB and (*b*) OA on magnetite in the coordinates of $Q = f(C_{CTAB\,sol})$ and $\theta = Q/Q_0 = f(C_{CTAB\,sol})$. Insert: the dependence of the electrokinetic potential of Fe_3O_4 covered by CTAB on the concentration of CTAB.

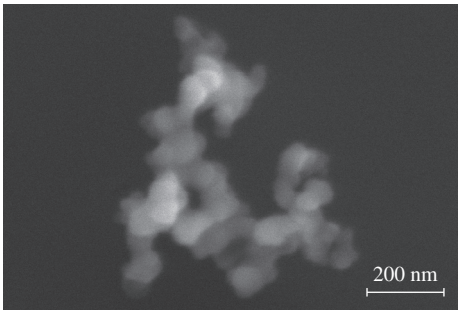

Figure 3 SEM image of the nanoparticles of Fe_3O_4 covered by OA and mercaptopropionic acid.

particles. The results for ζ-potentials obtained for various magnetite : CTAB ratios are given in Figure 2. A comparison of curves in Figure 2(*a*) and 2(*b*) shows that, in the area of equilibrium CTAB concentrations from 2×10^{-5} to 7×10^{-5} mol dm^{-3}, the formation of a surface monolayer occurs, whereas a surface bilayer is formed in a range from 7×10^{-5} to 3×10^{-4} mol dm^{-3}.

The CHNS analysis of Fe_3O_4 modified with OA‡ revealed that the OA content of the sample is ~14 mol%.§ A similar conclusion can be made from the data on OA adsorption. As follows from Table 2, the magnetite particle is covered with a tightly packed monolayer of OA molecules ($\theta = 1$) at an adsorption value of 0.130 mg mg^{-1}, or 11 mol%, which is close to the CHNS results. Note that the test samples are hydrophobic, being well-dispersed in organic solvents (toluene, hexane, kerosene, *etc*.). Thus, experimental data on the elemental analysis of the particles and data obtained from the constructed adsorption isotherm coincide satisfactorily; this allows us to consider the MNPs synthesized as hemimicelles with a tight monolayer of OA molecules on the magnetite surface.

To confirm a validity of the procedure used for the calculation of the degree of surface coverage, it was applied to published data on surfactant adsorption for magnetite–saturated and unsaturated carboxylic acids[17–21] and silica gel–cationic surfactant¶ like CTAB systems.[22–30] It was found that, for both systems, the calculated value of θ was higher than 1.3 only in a few cases, and it was lower than the theoretically predicted maximum of $\theta = 2$. This fact can be explained by the existence of steric barriers in the formation of a surfactant monolayer. The use of nanosized sorbent particles resulted in maximum values of θ; in coarser particles, the steric barriers are usually associated with the porous structure of sorbents. In these cases, a looser layer is formed ($\theta = 0.4$–0.9). Moreover, OA affords a more closely packed layer than that of saturated carboxylic acids. Thus, the chosen method of the microwave synthesis and modification of nanosized MNPs provides a greater structural order of modifying layers in addition to a shortened time of synthesis (in some cases, it takes dozens of hours[31,32]) and a better uniformity of particles. It is believed that it is promising to obtain new nanosized SPE materials with the surface layer of targeted structure. Such materials are valid for the effective and fast preconcentration of trace components from water solutions. For example, an SPE sequentially modified with oleic and mercaptopropionic acids (Figure 3) was successfully used for the determination of heavy metals in water, and an SPE with a layer of CTAB molecules was an appropriate sorbent for the extraction of aromatic pollutants from water.[4]

‡ Initial molar ratio Fe_3O_4 : OA was 1 : 1, an excess OA was eliminated later.
§ OA percentage in the sample was calculated from the carbon content.
¶ For cationic surfactants, the data on their adsorption on magnetite were not found, and the well-studied CTAB–silica gel system was chosen for a comparative analysis.

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