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Adsorption of surfactants on superfine magnetite

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Superfine magnetite particles were obtained by chemical condensation. Their size can be varied by the magnetic field application and a change in the crystallization temperature. The X-ray diffraction and adsorption data suggested an increase in the crystallite size and a decrease in the value of limiting adsorption and specific area of magnetite with an increase in the temperature and magnetic field intensity. The nature of surfactants and solvents has a substantial effect on the adsorption process. The IR spectroscopic and equilibrium adsorption data showed that oleic acid has the highest affinity to the surface among the surfactants studied (stearic, oleic, and linoleic acids and sodium oleate). On going from carbon tetrachloride to hexane, the value of limiting adsorption of oleic acid decreases.

Key words: adsorption, surfactants, magnetite, adsorption isotherm, solvent, specific area, IR spectroscopy, magnetic field.

Adsorption of surfactants from various media on the surface of superfine iron oxides is of interest for syntheses of catalysts, paintwork ingredients, and magnetic adsorbents. In particular, superfine magnetite, being a typical ferrimagnetic, is widely used in manufacturing magnetic films and disks.

The purpose of this work is to study the influence of the nature of surfactants and solvents on adsorption processes on the magnetite surface and the magnetic field application and a temperature change during crystallization of magnetite on its crystal structure and specific area.

Experimental

Superfine magnetite was prepared by chemical condensation[1]

$$FeCl_2 \cdot 4H_2O + 2\ FeCl_3 \cdot 6H_2O + 8\ NH_4OH =$$

$$= Fe_3O_4 + 8\ NH_4Cl + 20\ H_2O.$$

The temperatures of the synthesis were 278, 298, and 348 K. During the synthesis, the reaction vessel was placed in the magnetic field with an induction of 0, 0.5, and 1.0 T. The resulting suspension was repeatedly washed with distilled water to pH 7. The removal of chloride ions was checked by the conductivity of washing waters, which was close after multiple washings to that of distilled water and equal to 10.6—12.2 μSm cm^{-1}.

The adsorption isotherms of oleic, stearic, and linoleic acids from solutions of CCl_4 and those of oleic acid from solutions in hexane at 298 K were studied (Fig. 1). Equilibrium concentrations of the acids were determined by IR spectroscopy using a Specord M-80 spectrophotometer from a change in the integral intensities of some characteristic absorption bands of acids in the corresponding solvents.[2] With this purpose, we preliminarily obtained the dependence of changing the integral intensities of absorption bands with an extreme at 2925 cm^{-1}, caused by stretching vibrations of CH_2 groups of acids in CCl_4, and bands with a maximum at 1710 cm^{-1} caused by stretching vibrations of C=O of carboxyl groups in hexane, on the concentration of acids. The integral intensity equal to the surface area of the band at 2925 or 1710 cm^{-1} was determined integrating the molar absorption coefficient in the specified limits of the wave number.

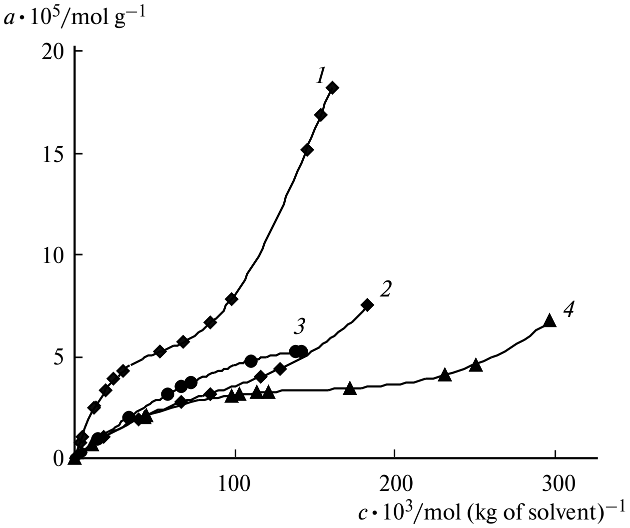

Fig. 1. Adsorption isotherms of oleic (*1*), stearic (*2*), and linoleic (*3*) acids from CCl_4 and of oleic acid from hexane (*4*) on the magnetite surface at 298 K.

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The characteristics of adsorption isotherms were determined from the equation of the volume filling micropores theory (VFMT)[3,4]:

$$a = a_{\mathrm{m}}\exp\{-[(RT/E_{\mathrm{a}})\ln(c_{\mathrm{s}}/c)]^{n}\},$$

where a and c are the value of adsorption of the adsorptive and its concentration in a solution, respectively; c_{s} is the experimentally measured concentration of a saturated solution of the adsorptive equal to its limiting solubility; a_{m} is the value of limiting adsorption of the adsorptive calculated from the ratio $a_{\mathrm{m}} = V_{\mathrm{n}}/V_{\mathrm{m}}$; V_{n} is the volume of the pore system; V_{m} is the molar volume of the pure adsorptive; E_{a} is the characteristic energy of adsorption; and n is the parameter related to the structure of the pore system of the solid adsorbent. According to Dubunin´s classification for microporous adsorbents, $n = 2$.

Oleic and linoleic acids are completely mixed with $\mathrm{CCl_4}$ and, hence, the characteristics of adsorption isotherms were calculated under the assumption that a pure adsorbate is adsorbed in the pores of the adsorbent. In this case, the volume of the pore system was calculated using the formula

$$V_{\mathrm{p}} = (a_{\mathrm{m}}M_{\mathrm{A}})/\rho_{\mathrm{lA}},$$

where M_{A} and ρ_{lA} are the molecular weight and density of the liquid adsorptive, respectively.

The characteristics of the isotherms are presented in Table 1.

In order to determine the concentration region of a true solution[5] for the systems studied, the procedure of IR spectroscopic determination of the critical micelle formation concentration (CMC) was developed. Critical micelle formation concentration is the concentration of a surfactant at which spherical micelles are formed from monomeric molecules. The quantitative determination of CMC is based on a drastic change in some physicochemical properties (surface tension, electric conductivity, refractive index, *etc.*) at CMC.[5] For the determination of CMC, we obtained the plots of the integral intensities of some characteristics frequencies of fatty acids *vs.* their concentration in a specified solvent. These plots have a sharp inflection corresponding to CMC of these systems. The experimental CMC values are given below.

Acid—solvent	$\mathrm{CMC}\cdot10^3$ /mol (kg of solvent)$^{-1}$
Oleic acid—$\mathrm{CCl_4}$	2.40
Linoleic acid—$\mathrm{CCl_4}$	8.34
Stearic acid—$\mathrm{CCl_4}$	9.47
Oleic acid—$\mathrm{C_6H_{14}}$	12.1

The adsorption of sodium oleate from aqueous solutions was examined to study the influence of the magnetic field and temperature during synthesis of magnetite on its adsorption properties. The equilibrium concentrations of sodium oleate were determined by conductometric titration. The adsorption isotherms (Fig. 2) were plotted on the basis of the experimental data.

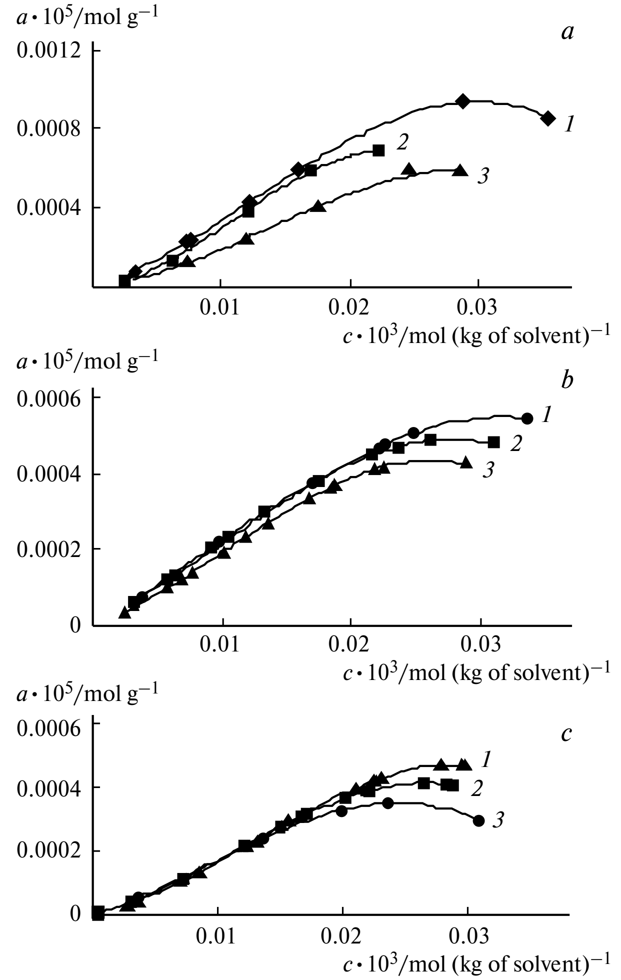

Fig. 2. Adsorption isotherms of sodium oleate from aqueous solutions on the surface of magnetite synthesized at 278 (*a*), 298 (*b*), and 348 K (*c*) and at a magnetic field induction of 0 (*1*), 0.5 (*2*), and 1.0 T (*3*).

According to the known classification of experimental isotherms of adsorption from solutions,[6] the adsorption isotherms obtained for sodium oleate on the magnetite surface refer to the L type. Isotherms of this type characterize adsorption processes with the parallel orientation of adsorptive molecules relatively to the adsorbent surface.

In solutions of ionogenic surfactants, the CMC value is numerically equal to the solubility[7] (c_{s}). Therefore, for calcula-

Table 1. Characteristics of adsorption isotherms of fatty acids at $T = 298$ K

Surfactant	c_{s}/mol (kg of solvent)$^{-1}$	a_{m}/mol g^{-1}	E_{a}/kJ mol^{-1}	V_{p}/cm^3 g^{-1}
Stearic acid (from $\mathrm{CCl_4}$)	0.40	$2.11\cdot10^{-3}$	13.05	0.244
Oleic acid (from $\mathrm{CCl_4}$)	3.54	$4.49\cdot10^{-1}$	8.55	142.0
Linoleic acid (from $\mathrm{CCl_4}$)	3.57	$1.07\cdot10^{-3}$	9.07	0.332
Oleic acid (from $\mathrm{C_6H_{14}}$)	3.54	$6.36\cdot10^{-4}$	9.40	2.02

Table 2. Characteristics of adsorption isotherms of sodium oleate from aqueous solutions on the surface of magnetite

T/K	c_s/mol (kg of solvent)$^{-1}$	$a_\mathrm{m} \cdot 10^3$/mol g^{-1}	E_a/kJ mol^{-1}	$V_\mathrm{p} \cdot 10^2$/cm^3 g^{-1}
288	0.45	2.19	5.79	4.44
293	0.61	1.67	6.95	3.53
298	0.95	3.24	6.72	7.39
303	1.30	2.62	7.74	6.43
308	1.42	1.92	8.71	4.83
313	1.50	2.21	8.55	5.64
318	1.55	3.20	7.86	8.25
338	1.60	1.49	9.19	3.88

tions of the adsorption characteristics, CMC of aqueous solutions of sodium oleate were experimentally determined from the dependence of the refractive index of the solution on its concentration at different temperatures. The break in this plot corresponds to the CMC of sodium oleate at the specified temperature. The c_s values (CMC) are presented in Table 2. It was established that the solubility of sodium oleate increased with temperature.

The characteristics of the adsorption isotherms of sodium oleate on the magnetite surface are presented in Table 3. The pore volume of the adsorbent (V_p) was determined using the average molecular weight of the adsorptive under the assumption that a saturated solution of the adsorptive is adsorbed in the pores of magnetite[6]

$$M_\mathrm{av} = X_\mathrm{A}M_\mathrm{A} + X_\mathrm{solv}M_\mathrm{solv},$$

where X_A and X_solv are the molar fractions of the adsorptive and solvent, respectively; M_A and M_solv are the molecular weights of the adsorptive and solvent.

$$V_\mathrm{p} = a_\mathrm{m}V_\mathrm{m},$$

where V_m is the molar volume of the adsorbate, $V_\mathrm{m} = M_\mathrm{av}/\rho_\mathrm{A}$.

This procedure was also used for the determination of the pore volume of magnetite available for adsorption of stearic acid from solutions of CCl_4, because stearic acid, unlike oleic and linoleic acids, has the limit of solubility in CCl_4.

Table 3. Characteristics of adsorption isotherms of sodium oleate from an aqueous solution on the surface of magnetite synthesized under different conditions

Conditions of synthesis		$a_\mathrm{m} \cdot 10^3$ /mol g^{-1}	E_a /kJ mol^{-1}	$V_\mathrm{p} \cdot 10^2$ /cm^3 g^{-1}
T/K	B^*/T			
278	—	4.24	6.90	9.68
	0.5	3.37	7.25	7.69
	1.0	2.39	7.26	5.46
298	—	3.24	6.72	7.40
	0.5	2.39	7.38	5.46
	1.0	2.17	7.41	4.96
348	—	2.49	6.85	5.69
	0.5	1.88	7.34	4.29
	1.0	2.97	6.62	6.78

* Magnetic field induction.

Sodium oleate was adsorbed from aqueous solutions at temperatures in the interval from 278 to 358 K in order to elucidate the thermodynamic features of the adsorption of surfactants on the magnetite surface. As an example, five adsorption isotherms of sodium oleate are presented in Fig. 3. The characteristics of the adsorption isotherms at eight temperatures are given in Table 2.

The isosteric heat of adsorption was found from the experimental adsorption isosters plotted in the linear coordinates ($\ln c - 1/T$) at different temperatures (278—358 K) (Fig. 4).

In order to determine the mean size of condensed particles of the magnetic phase, the dispersion analysis of suspensions of magnetite synthesized under different conditions was performed. Dispersion analysis was performed by the microscopic method. The differential curves of size distribution of particles of magnetite synthesized at different temperatures and in different fields were plotted using the experimental data (Fig. 5).

Results and Discussion

For adsorption from CCl_4, the limiting value of adsorption of oleic acid is much higher than the corresponding value for stearic acid (see Table 1).

As can be seen in Fig. 1, the adsorption isotherm of linoleic acid lies above the adsorption isotherm of stearic acid. However, the a_m values of both acids are close. The

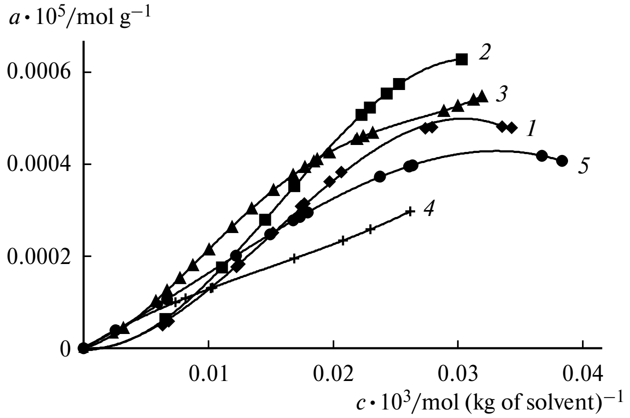

Fig. 3. Adsorption isotherms of sodium oleate from aqueous solutions on the surface of magnetite synthesized at 278 (*1*), 288 (*2*), 298 (*3*), 338 (*4*), and 358 K (*5*).

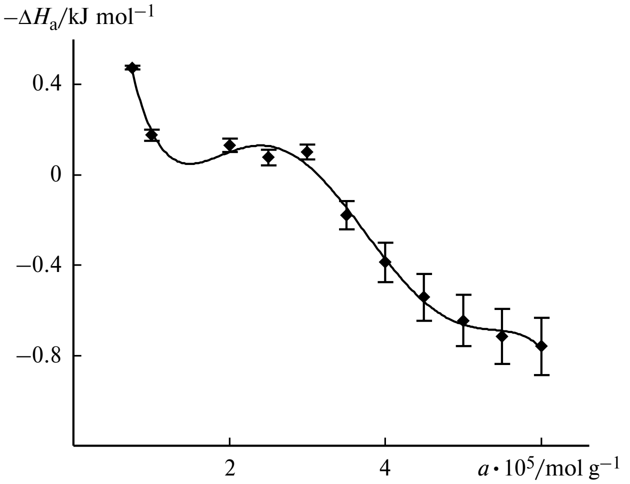

Fig. 4. Dependence of the isosteric heat of adsorption (ΔH_a) of sodium oleate on the value of adsorption (*a*).

isotherm of adsorption of oleic acid from a CCl_4 solution is S-shaped. In the region of adsorptive concentrations lower than the CMC, the adsorption isotherm of oleic acid is satisfactorily described by the VFMT equation. The volume filling of magnetite pores occurs in this region. The value of adsorption increases at the adsorptive concentrations higher than the CMC. This can be related to a change in the orientation of molecules on the surface and polymeric coverage of the adsorbent surface. The inflections are not so pronounced in the adsorption isotherms of stearic and linoleic acids.

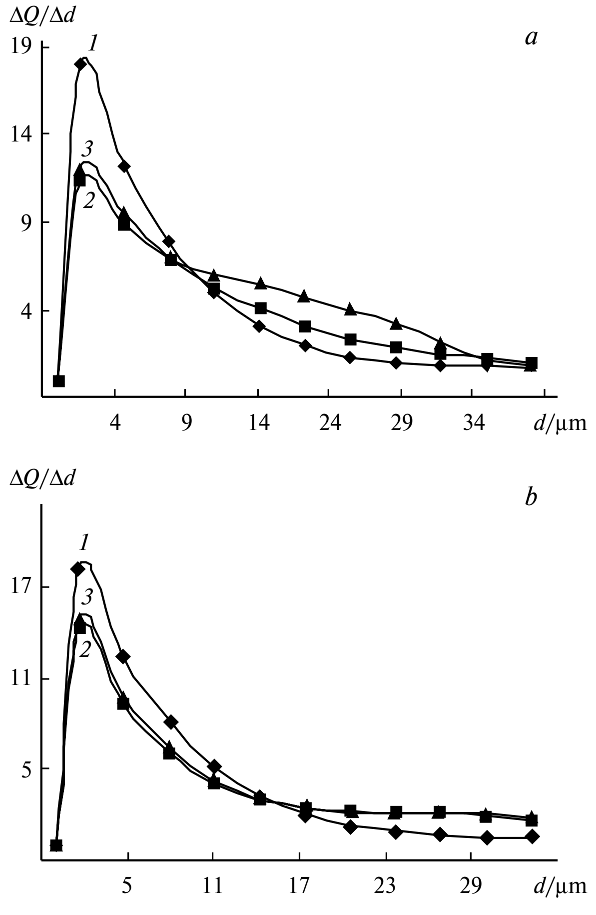

Fig. 5. Differential curves of size distribution of particles during synthesis of magnetite in the absence (*a*) and presence of (*b*) of the magnetic field at 278 (*1*), 298 (*2*), and 348 K (*3*).

In terms of decreasing values of limiting amount adsorbed, the fatty acids under study can be arranged in the following order: oleic > linoleic > stearic.

The replacement of CCl_4 by hexane results in a considerable decrease in the value of limiting amounts adsorbed. This is due to the difference in the solvating abilities of the solvents. As compared to hexane, CCl_4 is a solvent with a lower energy of intermolecular interaction (the dipole moment of the molecule is equal to zero) and a lower adsorption activity. The adsorption of oleic acid from hexane is hampered by solvation processes in both the solution volume and the surface layer of the adsorbent. This system also exhibits the competitive adsorption of oleic acid and hexane on adsorption sites of the magnetite surface.

The IR spectroscopic data for magnetite, sodium oleate, and fatty acids under study obtained before and after adsorption are given in Table 4. The IR spectra of sodium oleate in the volume phase and adsorbed state are presented in Fig. 6. The broad band in the spectrum of magnetite in the region from 3200 to 3600 cm^{-1} is attributed

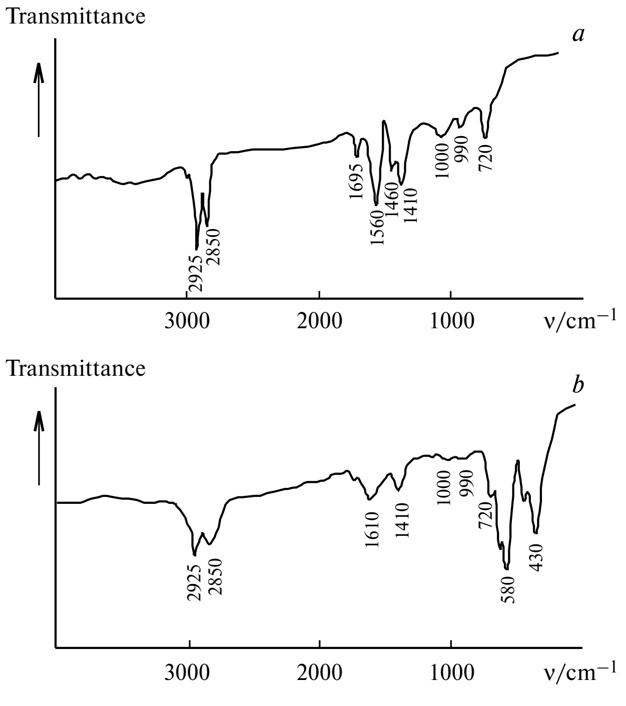

Fig. 6. IR spectrum of sodium oleate in the volume phase (*a*) and in the adsorbed state on magnetite (Fe_3O_4) (*b*).

Table 4. Main frequencies (ν/cm^{-1}) in the IR spectra of the studied substances before (ν) and after adsorption (ν')

ν	ν'	$\Delta\nu$	Assignment of bands[4] *
		Magnetite	
580, 430	580, 430	0	Vibrations of crystalline lattice of magnetite
	Stearic, oleic, and linoleic acids		
3020	3020	0	ν(C—H) in C=C—H
2960	2960	0	$\nu^{as}(CH_3)$
2925	2925	0	$\nu^{as}(CH_2)$
2870	2870	0	$\nu^{s}(CH_3)$
2850	2850	0	$\nu^{s}(CH_2)$
1710	—	—	ν(C=O)
1650	1650	0	ν(C=C)
1465	1460	5	$\delta(CH_2)$
1450	—	—	$\delta^{as}(CH_3)$
1440	—	—	$\nu(CH_2$—CH=C)
1420	1410	10	$\nu(CH_2$—CO)
1375	1350	25	$\delta^{s}(CH_3)$
1285, 1250, 1240	1265, 1230, 1220	20	Vibrations of the COOH group in acids
1090	1150, 1090, 1000	—	ν(C—C)
940	940	0	δ(OH)
720	720	0	ν(CH=CH)
		Sodium oleate	
1695	—	—	ν(C=O)
1560	—	—	ν^{as}(C=O)
1460	1460	0	$\nu(CH_2$—CH=C)
1420	1420	0	$\nu^{s}(CH_2$—CO)
1090	1110	20	ν(C—C)
720	720	0	ν(CH=CH)

* The following designations were used: ν and δ are stretching and bending vibrations, respectively; s and as are symmetric and antisymmetric vibrations, respectively.

to the absorption of adsorbed water.[8] The broad bands with maxima at 580 and 430 cm^{-1} correspond to vibrations of the Fe^{III}—O and Fe^{II}—O bonds in the crystalline lattice of magnetite. The integral intensities of these bands are in a ratio of 2 : 1, which corresponds to the stoichiometric ratio of tri- and bivalent iron oxides. No changes in bands in this region are observed during adsorption.

As can be seen from the data in Table 4, adsorption results in some changes in the spectra of the surfactants. For example, the absorption bands at 1710 cm^{-1} (oleic acid) and 1695 cm^{-1} (sodium oleate), which are assigned to stretching vibrations of C=O of the carboxyl group, disappear in the spectrum of the adsorbed surfactants. In the spectrum of sodium oleate in the adsorbed state, the bands at 1300—1750 cm^{-1} broaden and the peaks at 1560 and 1460 cm^{-1} degenerate. These data indicate the formation of adsorption complexes of the surfactants on the magnetite surface. The surfactant molecules displace water molecules from the magnetite surface, which is corroborated by the disappearance of the adsorption bands at 3200—3600 cm^{-1}.

The surfactant molecules in the adsorbed state are subjected to the field of the solid surface, which is manifested as a shift of several characteristic bands to the low-frequency region.[9] For oleic acid this shift is 5—25 cm^{-1}. It is also noteworthy that the intensity of the peak at 1410 cm^{-1} increases significantly compared to the intensity of this peak for the volume phase of the acid. In addition, new peaks at 850 and 1160 cm^{-1}, assigned to out-of-plane bending vibrations of the CH_2 groups, appear in the spectrum of oleic acid adsorbed from CCl_4 solutions.

It was established in the work that the character of the adsorption isotherms depends on the conditions of synthesis of magnetite (see Table 3). For example, an increase in the magnetic field induction (from 0 to 1 T) and the temperature of synthesis decreases the value of limiting amount adsorbed. The characteristic adsorption energy (E_a) is a parameter of the microporous structure and qualitatively related to the micropore size. The increase in the characteristic energy (see Table 3) is likely explained by a decrease in the pore volume. The value of the pore volume of magnetite (~10^{-2} cm^3 g^{-1}) implies its microporous structure. This value decreases with both the temperature increase and an increase in the magnetic field induction.

The data in Fig. 3 and Table 2 indicate that the process of adsorption of sodium oleate on magnetite is complicated. For example, the value of amount adsorbed is expected to decrease with temperature; however, the a_m value increases at temperatures as low as 278—298 K. In the opinion of some researchers,[10,11] this change is due to the formation of clusters by the adsorbate in micropores. As a result, in cavities the surface is deformed and aggregates decompose.[11] The process of surface deformation is endothermic, and this contribution to the total adsorption process can be determining and results in changes in the values of adsorption. As can be seen in Fig. 4, the adsorption process is exothermic at small amounts of the adsorbed substance. The observed thermal effect becomes positive with adsorption.[10,12] This is probably associated with high positive heats of desolvation of the adsorbate and adsorbent, processes of deformation of the adsorbent surface, and association of the adsorbate in the adsorption layer.

The size distribution curves for particles of magnetite synthesized under different conditions (see Fig. 5) are similar in shape and have a maximum at 0.5—2.0 μm. For the particles synthesized in the absence of a magnetic field, the height of the maximum decreases with an increase in the temperature of synthesis, *i.e.*, polydispersity of the system increases. An increase in the temperature of

Table 5. Parameters characterizing the properties of the magnetite surface

Conditions of synthesis		$S_{sp}{}^a$/m^2 g^{-1} (15%)^d	RSA^b (%) (2%)^d	R^c/Å (5%)^d
T/K	B/T			
278	0	103	140.9	56.6
	0.5	56	127.8	66.2
	1.0	68	107.4	70.4
298	0	129	100.0	76.0
	0.5	100	98.2	76.2
	1.0	88	96.4	77.3
348	0	52	65.7	90.3
	0.5	64	62.1	90.6
	1.0	65	59.8	92.5

[a] Determined from the low-temperature adsorption of argon.
[b] Relative specific area, in the calculation of which a suspension of magnetite synthesized at 298 K was used as the reference sample.
[c] Size of crystals.
[d] Variation coefficient.

synthesis from 278 to 298 K results in the enlargement of the particles, and the magnetic field application has no substantial effect on a change in the dispersity of the system.

The results of X-ray diffraction and adsorption studies of the crystal structure and specific area are presented in Table 5.

It has previously been found that the magnetic field application significantly decreases the specific area of the crystallites that formed[1] but has no effect on the crystalline lattice of magnetite.[13] The increase in the temperature of synthesis from 298 to 348 K decreases the specific area more than twofold. The influence of the conditions of synthesis of magnetite on its specific area is confirmed by the X-ray diffraction data. It has been established[1] that the magnetic field application considerably decreases the specific area of formed crystallites, while the crystalline lattice of magnetite remains unaffected. An increase in the temperature of synthesis leads to a decrease in the specific area and crystallite growth.

The magnetic field and temperature action during synthesis of magnetite increases the polydispersity of the system and decreases its specific area to decrease the adsorption of the surfactant by magnetite.

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