

## Hybrid Nanostructures Based on Layered Silicates and Nitrogen-containing Organic Compounds

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**Abstract**—Organic–inorganic hybrid nanostructures were prepared by treatment of synthetic layered silicates of the montmorillonite structure with aliphatic and aromatic amines. The interaction of organic compounds with the surface of layered silicates was studied by transmission electron microscopy, IR spectroscopy, and differential scanning calorimetry.

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Much researchers' attention is given today to the synthesis and study of hybrid organic–inorganic materials. Such structures combining characteristics of organic and inorganic substances open vast prospects for the development of new materials with diverse combinations of physicochemical and service characteristics.

Hybrid organic–inorganic structures based on layered silicates are very promising materials for various branches of industry. Thanks to specific structural features, layered silicate materials have properties important for practice, such as the capability for sorption, ion exchange, and catalysis. Efficient modification of the surface with organic compounds will expand the application fields of layered silicate materials. In particular, in some cases it is necessary that the surface of layered silicate materials be hydrophobic. Insofar as the majority of layered silicate materials are more or less hydrophilic under common conditions, the hydrophobic surface can be obtained by treatment with organic compounds. Preparation of such organosilicate complexes would allow the use of silicate materials as fillers for polymeric media and plasticizers.

Nanosized layered silicates can be prepared under hydrothermal conditions. Preparation of layered silicates in the nanodisperse state can open new prospects for their application. One of promising applications of such materials is preparation of polymer–inorganic nanocomposites. It is known that a composite containing only 2–3% of a natural clay material modified with organics shows considerably enhanced rigidity, strength, and barrier properties. It can be expected that

a nanosized synthetic filler would exert a still stronger effect on the properties of composite materials. At the same time, the use of nanosized silicate materials of various chemical compositions requires a new approach to modification of their surface with organic compounds. Because of the high degree of dispersity and the tendency of nanoparticles to agglomerate, it is necessary to study in more detail hybrid nanostructures and the mechanism of interaction of organic compounds with the surface of nanoparticles.

In this study we prepared and examined organic–inorganic nanostructures based on synthetic layered silicates and nitrogen-containing organic compounds.

Layered silicates used in this study as the base for preparing organic–inorganic nanostructures (for the composition of the samples, see table) belong to structural type 2:1 (according to the classification of layered and layered–ribbon silicates [1]) and have a stack structure consisting of one octahedral and two tetrahedral silicon–oxygen layers. Nonstoichiometric substitutions in the structure of such silicates are compensated by exchangeable cations in the interlayer space, which is capable of broad size variation upon intercalation of molecules of water or organic compounds. On the surface of layered silicates of this structure, there is a large set of active adsorption centers of different nature. It should be taken into account that a separate particle of layered silicates of this structural type has surfaces with different properties: two on the external side and one inside the crystal [2]. The basal and cleaved (torn edge of the crystal lattice) surfaces can be external, and the basal surfaces of separate layers that are affected by the adjacent layers can be

## Compositions and conditions of synthesis of layered silicates

Sample designation	Composition	Starting reactants	Hydrothermal treatment conditions		
			time, h	pressure, MPa	temperature, °C
1	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$	$\text{SiO}_2$ , $\text{MgO}$ , $\text{NaOH}$	1	70	250
2	$(\text{Al}_{1.33}\text{Mg}_{0.67})\text{Si}_4\text{O}_{10}(\text{OH})_2\text{Na}_{0.17} \cdot n\text{H}_2\text{O}$	$\text{SiO}_2$ , $\text{MgO}$ , $\text{Al}_2\text{O}_3$ , $\text{NaHCO}_3$	3	70	300

internal; these surfaces differ in the energy state from the external basal surfaces [2]. Along with active surface centers, the factor enhancing the adsorption ability of layered silicates of the montmorillonite structure is their tendency to form a secondary structure, so-called cryptostructure. The formation of a cryptostructure is accompanied by aggregation of smaller particles into coarse aggregates with a porous structure.

The electron micrographs of layered silicate samples in the initial state and after treatment with organic compounds are presented in Fig. 1. Figure 1a shows that the initial sample 1 has a secondary structure. Sample 2 contains a larger fraction of separate nanoparticles, not combined in coarse aggregates. Such differences may be due to the composition of the samples and to different size and synthesis conditions. Figures 1b and 1d–1f also show electron micrographs of samples 1 and 2 treated with hexadecylamine and diphenylamine. The structure of these samples does not undergo significant changes. Treatment of sample 2 with hexadecylamine led to the appearance of a secondary structure (Figs. 1d, 1e). This fact is indicative of the adsorption of hexadecylamine on the external surface of particles of sample 2, which led to their agglutination. Treatment of sample 2 with diphenylamine does not lead to such an effect.

Figures 2 and 3 show the IR absorption spectra of the samples. Strong absorption bands with maxima at 1000–1100 and 460–480  $\text{cm}^{-1}$  are due to Si–O vibrations in  $\text{SiO}_4$  tetrahedra. The bands at 2620–2630, 2850, and 1470–1480  $\text{cm}^{-1}$  are due to C–H vibrations, confirming the presence of organic compounds.

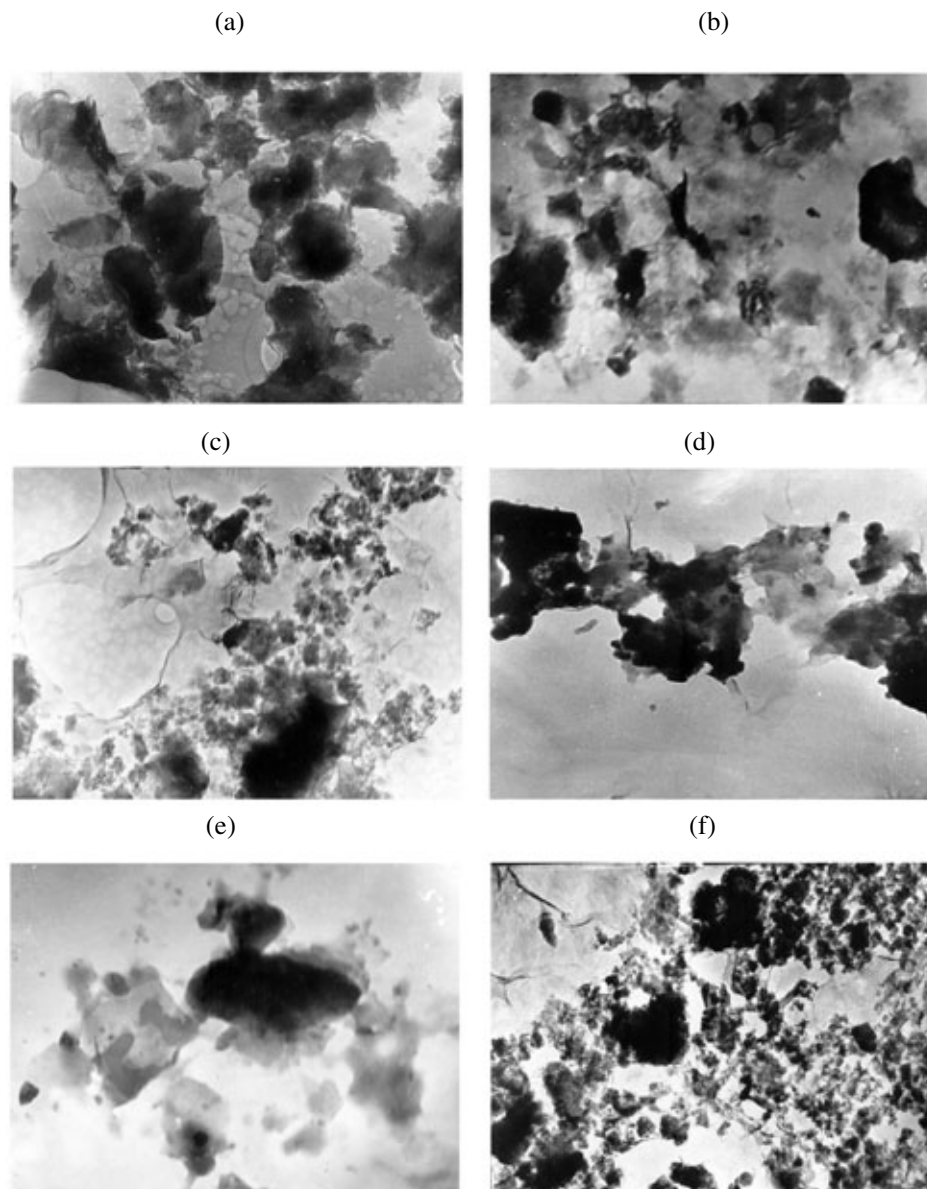
Important structural components of layered silicates are water of crystallization and hydroxy groups. A broad absorption band at 3400  $\text{cm}^{-1}$  corresponds to the stretching vibrations, and the band at 1640  $\text{cm}^{-1}$ , to the bending vibrations of adsorbed water molecules in the interlayer space of samples 1 and 2 before treatment with amines. In the IR spectra of samples 1 and 2 treated with hexadecylamine and diphenylamine, these absorption bands are absent, which indicates that the molecules of organic compounds entered into the

interlayer space and displaced from there the majority of water molecules.

This conclusion is confirmed by the results of differential scanning calorimetry (DSC, Figs. 4–7). The results obtained show that the samples treated with the amines contain a smaller amount of sorbed water than the untreated initial samples. This follows from the differences in the weight loss and magnitude of the endothermic effects at about 100°C. Comparison of the TG curves of the initial and treated samples shows that the weight loss of the amine-modified samples in the range 200–700°C is caused by the presence of organic compounds adsorbed on various active centers of the surface. The weight loss at 200–400°C is attributable in part to the removal of free or weakly bound compounds. This is indicated by a pronounced endothermic effect at about 200°C in the thermograms of sample 1 (Fig. 4, curves 2, 3) treated with hexadecylamine; this effect is also characteristic of neat hexadecylamine. However, the intense weight loss in the temperature ranges 450–900 (sample 1) and 450–700°C (sample 2) suggests incorporation of organic compounds into the structure of layered silicates and formation of strong complexes decomposing only at high temperatures. Taking into account the absence of sorbed water in the interlayer space of the amine-treated samples, following from the IR data, we can conclude that we prepared organic–inorganic hybrid nanostructures containing organic compounds intercalated in the interlayer space in both the free and bound state, and also adsorbed on the external surface of the nanoparticles.

The results (TG and DSC data) of treatment with hexadecylamine of the initial sample 1 and of sample 2 pretreated with 1 M HCl are compared in Figs. 4 and 6. It is known [3] that acid treatment of layered silicates favors activation of their surface due to appearance of new active centers. Such a treatment might enhance the efficiency of interaction of hexadecylamine with the surface of silicate nanoparticles; however, Figs. 4 and 6 show that this effect is lacking.

The DSC curves show that the efficiency of treatments of layered silicates with the chosen aliphatic



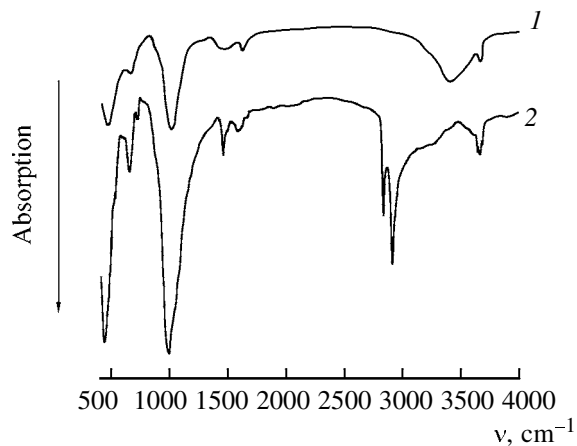
**Fig. 1.** Electron micrographs of samples: (a) sample 1, initial; (b) sample 1 treated with hexadecylamine; (c) sample 2, initial; (d, e) sample 2 treated with hexadecylamine; and (f) sample 2 treated with diphenylamine. Scale: 1 cm = 110 nm.

and aromatic amines is somewhat different. The TG curves show that hexadecylamine can be incorporated in the structure of both samples in a larger amount than diphenylamine. This result is consistent with the above-discussed results of the electron-microscopic examination, according to which treatment of sample 2 with hexadecylamine led to the formation of a cryptostructure, whereas treatment with diphenylamine did not have such an effect. Thus, hexadecylamine was adsorbed on both the external and internal surfaces of the silicate nanostructures, whereas the major fraction of diphenylamine was incorporated in the interlayer space of the samples. No significant

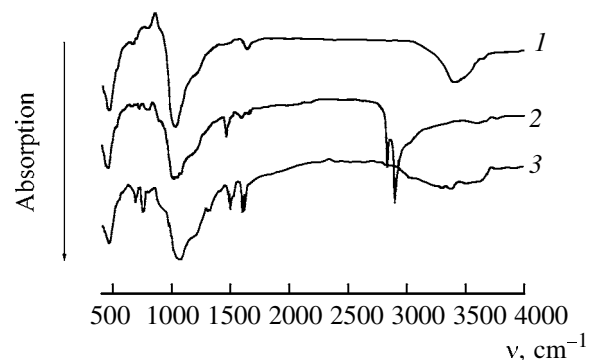
difference was observed in the efficiency of amine treatment of samples 1 and 2 having different composition and strongly differing in the cation-exchange capacity.

Sample	Mean particle size, nm	Cation-exchange capacity, mg-equiv/100 g
1	~50	10
2	~5	80

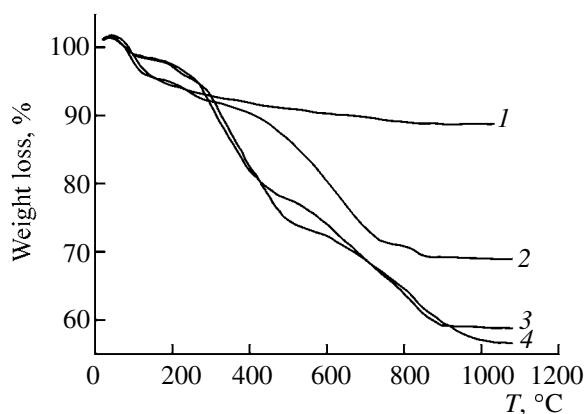
It is believed that the decisive factor in performing surface modification of layered silicates of the structural type 2:1 with organic compounds is the cation-



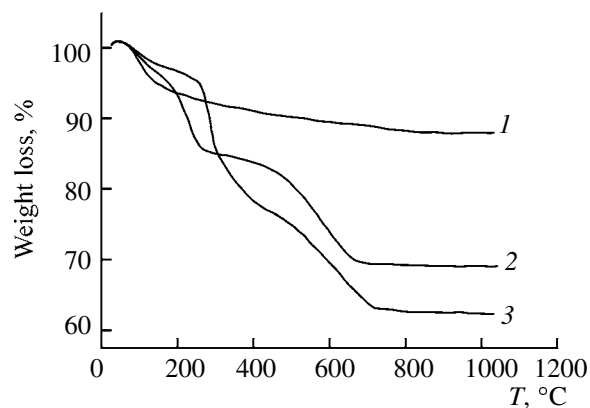
**Fig. 2.** IR absorption spectra of sample 1: (1) initial and (2) treated with hexadecylamine.



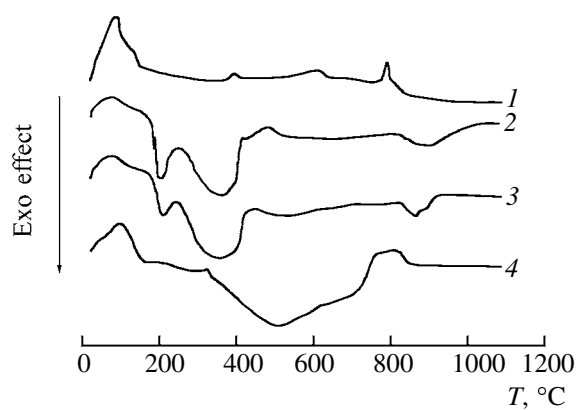
**Fig. 3.** IR absorption spectra of sample 2: (1) initial, (2) treated with hexadecylamine, and (3) treated with diphenylamine.



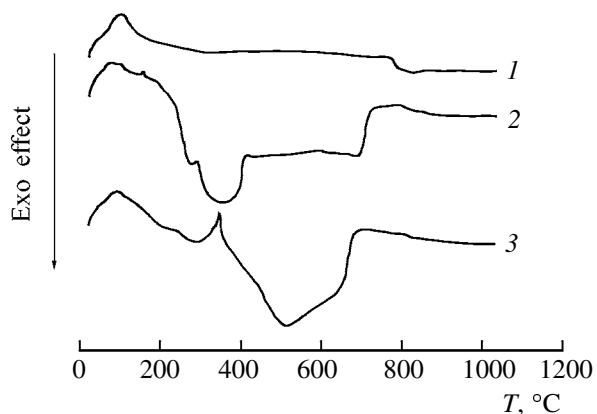
**Fig. 4.** Weight loss in heating of sample 1: (1) initial, (2) treated with diphenylamine, (3) treated with 1 M HCl and then with hexadecylamine, and (4) treated with hexadecylamine.



**Fig. 5.** Weight loss in heating of sample 2: (1) initial, (2) treated with diphenylamine, and (3) treated with hexadecylamine.



**Fig. 6.** DSC curves of sample 1: (1) initial, (2) treated with diphenylamine, (3) treated with 1 M HCl and then with hexadecylamine, and (4) treated with hexadecylamine.



**Fig. 7.** DSC curves of sample 2: (1) initial, (2) treated with diphenylamine, and (3) treated with hexadecylamine.

exchange capacity. This quantity is determined by incorporation of cations in the interlayer space to compensate negative charges arising from nonstoichiometric substitutions in lattices of layered silicates, and also to compensate charges arising on crystal faces and cleaved surfaces. Sample 1 is a layered silicate whose octahedral layer (magnesium–oxygen–hydroxide layer) has no isomorphous substitutions. Its cation-exchange capacity is determined only by the noncompensated charge on the cleaved surfaces and is relatively low. In the octahedral layer of sample 2, a part of Mg is replaced by Al, which increases the cation-exchange capacity.

Despite the low cation-exchange capacity, sample 1 was efficiently treated with aliphatic and aromatic nitrogen-containing compounds. The results showed that organic compounds in the structure of sample 1 are in the bound state. This fact indicates that the ion exchange with interlayer cations in the structure of layered silicates is not the only mechanism of the interaction of organic compounds with the internal surface of silicates of the structural type 2:1; thus, formation of organic–inorganic hybrid complexes requires further study.

## EXPERIMENTAL

To prepare organic–inorganic hybrids, we used layered silicate nanoparticles of the montmorillonite structure. The synthesis was performed under hydrothermal conditions. The composition of the nanoparticles and the conditions of their synthesis are given in the table. The choice of the synthesis conditions and methods for studying silicate nanoparticles are described in detail in [4].

The mean particle size was determined by electron microscopy and also from the X-ray diffraction data using the Scherrer formula [5]. The cation-exchange capacity of the silicates was estimated by one of the methods commonly used for determining the exchange capacity of strongly acidic cation exchangers [6]. The sodium form of the silicate samples was converted to the calcium form by placing the sample in 0.1 N CaCl<sub>2</sub> solution. The calcium content of the equilibrium solution was determined by EDTA titration. The equilibrium exchange capacity (mg-equiv g<sup>-1</sup>) was calculated from the difference between the calcium content of the initial and equilibrium solutions.

The synthesized layered silicates were intercalated with hexadecylamine C<sub>16</sub>H<sub>33</sub>NH<sub>2</sub> and diphenylamine C<sub>12</sub>H<sub>10</sub>NH (Merck Schuchardt OHG).

The organic molecules were intercalated into the structure of layered silicates by the procedure suggested in [3] for the surface modification of clay minerals and based on the ion exchange. A 0.6-g portion of hexadecylamine or diphenylamine was mixed with 0.6 ml of concentrated (37%) HCl and 20 ml of distilled water. The resulting solution was added to 50 ml of an aqueous suspension containing 1.5 g of silicate nanoparticles. The mixture was thoroughly stirred at 80°C for 1 h, after which the precipitate was filtered off and repeatedly washed with cold and hot (80°C) water and dried.

The amine-modified layered silicates were examined by transmission electron microscopy (EM-125 electron microscope,  $U_{acc}$  75 kV), IR absorption spectroscopy (Specord M-80 spectrophotometer), and differential scanning calorimetry (STA 429 calorimeter, Netzsch).

## ACKNOWLEDGMENTS

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## REFERENCES

1. Kukovskii, E.G., *Osobennosti stroeniya i fiziko-khimicheskie svoistva glinistykh mineralov* (Structural Features and Physicochemical Properties of Clay Minerals), Kiev: Naukova Dumka, 1996.
2. Aripov, E.A. and Agzamkhodzhaev, A.A., *Aktivnye tsenry montmorillonita i khemosorbtsiya* (Active Centers of Montmorillonite and Chemisorption), Tashkent: Fan, 1983.
3. Komarov, V.S., *Adsorbtsionno-strukturnye, fiziko-khimicheskie i kataliticheskie svoistva glin Belorussii* (Adsorption-Structural, Physicochemical, and Catalytic Properties of Belorussian Clays), Minsk: Nauka i Tekhnika, 1970.
4. Golubeva, O.Yu., Korytkova, E.N., and Gusarov, V.V., *Zh. Prikl. Khim.*, 2005, vol. 78, no. 1, p. 26.
5. Rusakov, V.V., *Rentgenografiya metallov* (X-ray Diffraction Analysis of Metals), Moscow: Atomizdat, 1977.
6. Soldadze, K.M., Pashkov, A.B., and Titov, V.S., *Ionoobmennyye vysokomolekulyarnyye soedineniya* (Macromolecular Ion Exchangers), Moscow: Izd. Khimicheskoi Literatury, 1960.