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Surfactant for Modification of Mineral Porous Materials and Their Porous Structure

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ABSTRACT. The processes of synthesis of quaternary ammonium salts (surfactants) based on oleic acid with subsequent study of the porous structure of the resulting organobentonites have been studied. Synthesis of surfactants was carried out in several stages, including ammonolysis of oleic acid, hydrolysis of amides, hydrogenation of nitriles, and alkylation of primary amines. Organobentonites were obtained by modifying bentonite with synthesized surfactants. The study of textural characteristics indicates a significant increase in the surface and the development of a porous structure after the modification of bentonite. Key parameters of textural characteristics were compared for different samples of organobentonites obtained using different surfactants. Samples of organobentonite obtained with various organic modifiers had different textural characteristics, which indicates the effect of the chemical composition of the organic modifier on the porous structure of the material..

KEYWORDS: Synthesis, quaternary ammonium salts, oleic acid, alkylbenzenes, ammonolysis, hydrolysis, hydrogenation, alkylation, organobentonite, textural characteristics, porous structure.

I.INTRODUCTION

In recent decades, the active interest of scientists and engineers in improving materials with unique properties and diverse applications has become an integral part of modern scientific and industrial activity. One of such promising materials is organobentonites, which are hybrid composites formed by combining natural clays with organic substances [1, 2].Organobentonites are attracting more and more attention of researchers due to their unique properties, such as high adsorption activity, stability and mechanical strength. These materials are widely used in various fields such as oil refining, environment, pharmaceuticals, catalysis and other industrial processes [3-5].

One of the key stages in the synthesis of organobentonites is the synthesis of quaternary ammonium salts (surfactants), which are used as an inclusion in the clay structure. This stage allows to improve the porous structure of materials and improve their functional properties. The creation of new surfactants (surfactants) is an urgent research problem in the field of chemistry and materials science [6, 7].

Surfactants whose synthesis is based on the use of oleic acid are of particular interest. The relevance of research in the field of creating surfactants based on oleic acid is due to several factors. First, oleic acid is an available and relatively inexpensive raw material, which provides the prospect of developing cost-effective surfactants. Secondly, oleic acid surfactants can have improved physicochemical properties such as surface activity, dispersing ability and emulsifying activity. This opens up opportunities for their use in various fields, including the food industry, pharmaceuticals, cosmetics, and others [8].

The process of synthesis of cationic surfactants (SAS) is based on the use of primary, secondary and tertiary amines, which have a significant hydrophobic part in their molecule. The synthesis of quaternary ammonium salts based on alkyl carboxylic acids, which are products of processing vegetable oils or synthetic fatty acids, is widespread in industry [9, 10].

The purpose of this article is to study the processes of synthesis of quaternary ammonium salts to create organobentonites and to study their porous structure. In the course of the study, the main methods for the synthesis of

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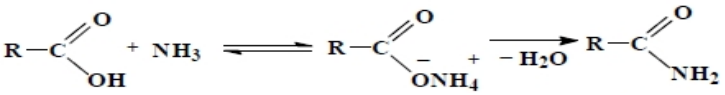
surfactants and their influence on the structure and properties of organobentonites were studied. In addition, experiments were carried out to analyze the porous structure of organobentonites.

II. SIGNIFICANCE OF THE SYSTEM

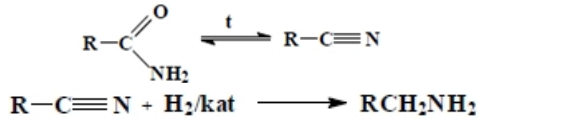
The processes of synthesis of quaternary ammonium salts (surfactants) based on oleic acid with subsequent study of the porous structure of the resulting organobentonites have been studied.The study of methodology is explained in section III, section IV covers the experimental results of the study, and section V discusses the future study and conclusion.

III. METHODOLOGY

Synthesis of alkyl and aryl-containing oleic acid salts. The synthesis of surfactants based on oleic acid is carried out in several stages. At the first stage, ammonolysis of oleic acid was carried out, i.e., the acid reacts with gaseous ammonia in the liquid phase to form ammonia soap. Then ammonia soap, as a result of thermal decomposition, forms an acid amide.

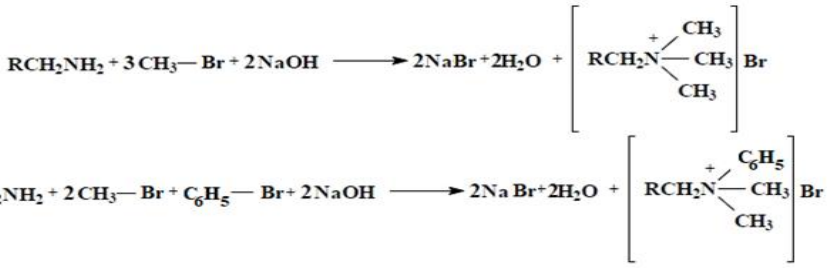


In the second stage, hydrolysis of amides or their destructive distillation in the presence of an Al2O3 catalyst at a temperature of 270-295°C was carried out, as a result of which oleic acid nitrile is formed, and then the nitriles were subjected to catalytic hydrogenation turning into primary amines.



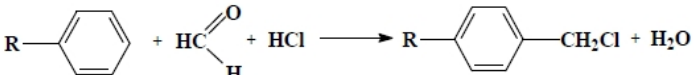
The addition of ammonia to the hydrogenation process leads to an increase in the yield of primary amine. The primary amine formed during the hydrogenation process reacts with the nitrile to form a secondary amine, releasing ammonia. When ammonia is introduced into the process, the formation of ammonia is suppressed, as a result, the formation of secondary and tertiary amines stops, which leads to an increase in the yield of primary amines [11].

At the final stage of the process, surfactants were obtained, which are used for the synthesis of organobentonites. This is achieved by alkylation of primary amines with appropriate alkylating or arylating agents such as methyl chloride or benzyl chloride. As a result, a quaternary salt of amines is formed.



Thus, the hydrogenation of nitriles proceeds using a nickel catalyst in an experimental setup, the yield of this product was at least 98%. The hydrogenation process was carried out under the following conditions: temperature in the range of 170-180°C, ammonia pressure 14-16 atm., hydrogen pressure 40 atm., total pressure 56 atm., the duration of the process was 2-2.5 hours. A nickel-aluminum catalyst was used as a catalyst.

Synthesis of alkylbenzyltriethylammonium salts. Alkylbenzenes, which are intermediate products in the production of sulfonic acid, were also used as an affordable and cost-effective raw material for the production of quaternary ammonium salts. At the first stage, the alkylbenzenes of the C11-C18 fraction were subjected to chloromethylation using formaldehyde and hydrogen chloride, and at the second stage, the condensation of alkylbenzyl chloride with a tertiary amine.



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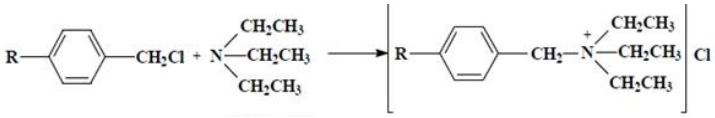

Synthesis of organobentonites. One of the main areas of research is the synthesis of organobentonites based on quaternary ammonium salts and Krantau bentonite [12]. Krantau bentonite, as a natural material, has unique properties such as high absorbency, good structural stability and hydrophilicity. In combination with quaternary ammonium salts, which are effective surfactants, bentonite is modified, improving its dispersing and adsorption properties.

To create organobentonite adsorbents, the existing known methods were applied [8]. The original sample of natural bentonite has passed the preparatory stage, including the removal of mechanical impurities, sand and water-soluble components by elutriation in distilled water. The resulting mass of bentonite was separated from the liquid by centrifugation and then dried at a temperature of 105ºC.

The process of modifying bentonite, including cation substitution, was carried out as follows: enriched bentonite with a particle size of less than 0.5 mm was flooded with distilled water, to which 1% of soda ash was added by weight of dry clay. The mixture was stirred for 2 hours at 50° C. using a magnetic stirrer. After that, the bentonite was filtered and washed to remove residual CI-ions (checking was carried out by adding an AgNO3 solution). Then the bentonite was placed in an oven and dried for 2 hours at 100-105ºC.

Preparations of organobentonite were obtained with various ratios of inorganic and organic raw materials. The dried clay was mixed with an aqueous solution of surfactants (heptadecyltrimethylammonium bromide (HDTMAB), diheptamethyltrimethylammonium bromide (DGDDMAB), heptadecylphenyldimethylammonium bromide (HDPDMAB), alkylbenzyltrimethylammonium bromide (ABTMAB)) at a concentration of 0.1 mol/L. In order to ensure the convenience of working with the solution, in order to avoid the formation of a thick gel-like liquid, which makes the process difficult, the concentration of the surfactant was limited. The modification process was carried out with constant stirring at a speed of 600 rpm for 1-6 hours at temperatures from 20 to 60ºC. The consumption of the modifier was from 5 to 30% by weight of dry clay. Quantitative determination of the content of the modifier was carried out using thermogravimetric analysis.

The mixture obtained after modification was washed to remove residual surfactant and separated from the liquid phase by centrifugation. The liquid phase obtained from the centrifuge was analyzed for the presence of surfactants by the foam multiples method.

As a result of the experiments, the optimal amount of surfactant was derived, which is no more than 3.5% by weight of sodium montmorillonite for GDTMAB, GDFDMAB and no more than 4% for ABTMAB and DGDDMAB in suspension. Probably, the amount of surfactant needed is primarily related to the cation exchange capacity of the clay (CFU). However, the available data show that large amounts of surfactants can be located in the interlayer surface of layered montmorillonite due to the formation of micelles from molecules. The adsorption of amine molecules on the interfacial surface during mixing of the organoclay suspension and as a result of the occurrence of the effect of adsorption decrease in clay hardness, due to which further dispersion of clay aggregates occurs, as well as the penetration of amines to newly formed surfaces, is established. Water, being the most surfactant in relation to clay, facilitates the process of adsorption reduction in strength and dispersion of clay. Probably, it is the formation of micelles that increases the adsorption activity of organobentonites with respect to various organic substances and increases the hydrophobicity of the initial bentonite.

The mixture obtained after modification was washed from the residual amine and separated from the liquid phase by centrifugation. The isolated solid phase was dried at 90°C for 2 hours until air-dry. The synthesized samples of organobentonites based on GDTMAB, GDFDMAB, ABTMAB, and DGDDMAB are conditionally named OB-1, OB-2, OB-3, and OB-4, respectively.

Definition of porous structure. To determine the characteristics of the porous structure, the method of low-temperature nitrogen adsorption at 77 K was used on a Quantachrome Nova 1000e static-type adsorption unit at the Institute of General and Inorganic Chemistry of the Academy of Sciences of the Republic of Uzbekistan. Before measurements, the samples were pretreated in vacuum at a temperature of 100°C for 12 hours. The partial pressure value was up to 0.995 P/P0. Curves of adsorption and desorption of nitrogen were measured in the range of partial pressures from 0.005 to 0.995 P/P0. The BET method was used to process the adsorption curves. Micropore volume was determined using the t-Plot method and mesopore volume was determined using the Barret-Joyner-Halenda (BJH) method. The average pore diameter was estimated by the formula Dav=4V/S using the BET method

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IV. EXPERIMENTAL RESULTS

The main physicochemical parameters of these samples were determined, which are given in Table. 1.

Table 1.
Main physical properties of organobentonites.

Sample	Bulk density, g/sm^3	Humidity, %	true density, g/sm^3
OB-1	1,10	13,65	2,22
OB-2	1,07	12,40	2,20
OB-3	1,13	14,15	2,20
OB-4	1,02	10,83	2,08

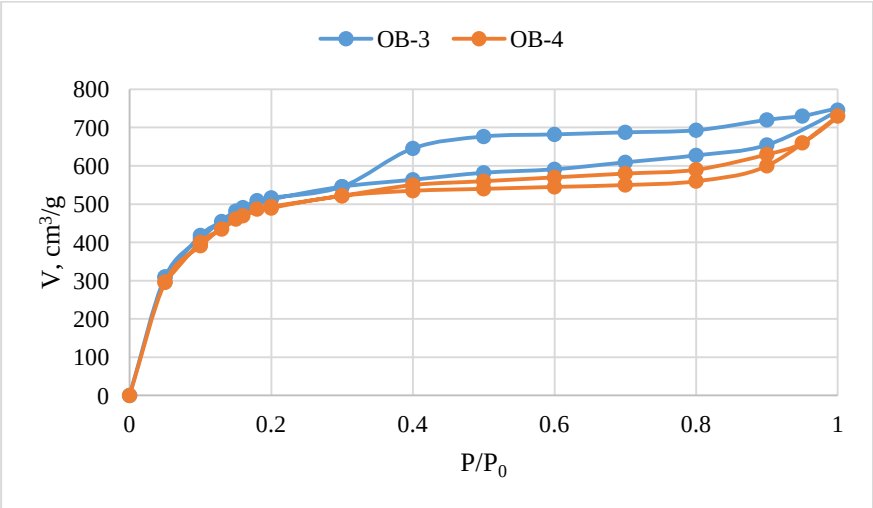
The presented table contains data on the main physical properties of organobentonites obtained on the basis of bentonite from the Krantau deposit using various organic modifiers. The values of bulk density, moisture content and true density for each sample (OB-1, OB-2, OB-3, OB-4) are given. Bulk density values range from 1.02 to 1.13 g/cm3. This indicates a different density and degree of compaction of organobentonites. Higher bulk densities may indicate a more compact material structure.

The moisture content of the samples varies from 10.83 to 14.15%. This value reflects the moisture content of the material and can affect its properties, including flow, rheology, and stability.

The true density of organobentonites is in the range from 2.08 to 2.22 g/cm3. This value reflects the mass per unit volume of the material without regard to porosity. Higher true density values may indicate a denser material structure.

Comparison of data between samples makes it possible to evaluate differences in the physical properties of organobentonites depending on the applied organic modifiers. Further analysis of these data and their relationship with other characteristics of organobentonites may help in understanding the effect of modification on their properties and possible applications.

In this study, special attention is paid to the surface characteristics of the created organobentonites, which are important properties of sorbents. The nitrogen adsorption isotherms obtained in the course of adsorption processes are shown in Figs. 1



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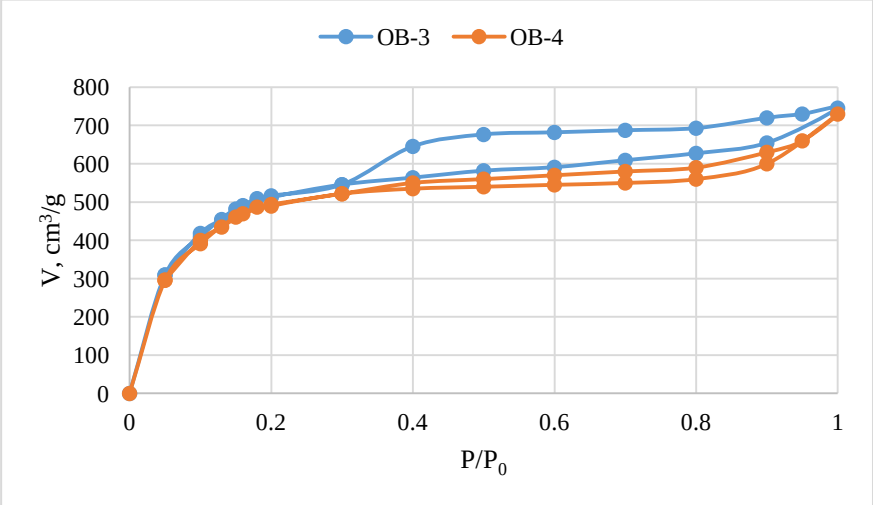

Rice. Fig. 1. Nitrogen adsorption isotherms on the studied samples.

The processing of the obtained isotherms by the corresponding adsorption equations contributed to obtaining the values of the textural characteristics of coals, which are given in Table. 2.

Table 2.

Textural Characteristics of Initial Bentonite and Organobentonite Samples

Sample	KP	OB-1	OB-2	OB-3	OB-4
S_{sp}, m^2/g*	66,51	465,58	506,06	461,33	418,56
S_{sp}, m^2/g**	251,25	2757,21	3081,03	2800,92	2507,53
t-Plot (outer surface), m^2/g	57,12	1576,51	2544,56	2313,23	2212,66
V_a, sm^3/g	0,091	0,113	0,229	0,210	0,200
V_b, sm^3/g	0,183	0,382	0,680	0,618	0,566
Pore size, Å	112,558	90,636	27,819	28,984	25,189
Average particle size, Å	29,221	14,328	15,281	18,256	15,125
Average micropore size, Å	6,358	4,969	5,443	5,156	5,216

* - *according to BET;*
** - *according to Langmuir.*

Tab. 2 shows the textural characteristics of samples of the original bentonite (BR) and organobentonites (OB-1, OB-2, OB-3, OB-4). These characteristics were obtained by processing the adsorption isotherms with the corresponding adsorption equations. The specific surface area for organobentonites is significantly higher than for the original bentonite, which indicates a significant increase in surface area after modification. The sequence of decrease in specific surface according to BET corresponds to the series OB-2>OB-1>OB-3>OB-4>CR. Therefore, the type of modifier and its amount affect the porous structure of the obtained organobentonite adsorbent. Based on the studies carried out, it can be concluded that samples of OB-2 organobentonite obtained by modifying Krantau clay (KR) with hexadecylphenyldimethylammonium bromide have higher characteristics compared to other samples. . This is confirmed by the obtained data on the surface and porous structure of materials.

The lowest values of the specific surface were found in the sample obtained on the basis of diheptadecyldimethylammonium bromide. This is probably due to the increased density of the organic modifier in the interlayer space of the clay, which prevents the development of the porosity of the system. A denser packing of alkyl radical molecules between clay layers reduces nitrogen adsorption, as a result of which the specific surface decreases.

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On the other hand, the introduction of an aryl-containing radical can lead to disorder in the modifier layers due to the size, structure, and low polarity of the hydrocarbon radical. This changes the porous structure of montmorillonite clay and can lead to an increase in the specific surface area of the samples.

t-Plot (outer surface), m2/g, reflects the specific surface area of only the outer surface of the sample. An increase in the value for organobentonites is also noticeable. Samples of organobentonites have large values of meso- and macropore volumes, which indicates their developed porous structure compared to the original bentonite.

Samples of organobentonites have higher values of pore volume and micropore volume. Also, organobentonites have smaller pore and micropore sizes, which once again indicates a higher porosity and a more complex structure after modification.

V. CONCLUSION AND FUTURE WORK

In general, the results of this study show that the choice of organic modifier plays an important role in the formation of the porous structure of organobentonites. The study of the processes of synthesis of quaternary ammonium salts - surfactants and the study of their porous structure allows you to optimize the synthesis and improve the properties of materials for various technological and industrial applications.

The results of the study indicate a significant increase in the specific surface and the development of a porous structure after the modification of bentonite with organic modifiers. This makes organobentonites potentially effective materials for various adsorption and technical applications.

The results obtained can be used for further improvement of the synthesis and application of organobentonites in various technological processes and industrial fields.

In general, this study provides valuable information on the effect of organic modifiers on the porous structure of organobentonites for the further development of scientific research in this direction.

The studies made it possible to reveal the optimal conditions for the synthesis and obtaining a more porous material when using ammonium in the process of hydrogenation of nitriles. The use of a nickel catalyst and certain temperature conditions also significantly affected the yield of primary amines, which is important for obtaining the final product, organobentonites.

The results obtained can be useful for further improvement of the synthesis and application of these materials in various technological processes and branches of science for the creation of porous materials.

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