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SURFACE MODIFICATION OF MONTMORILLONITE CLAY WITH ORGANIC MOLECULES

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ABSTRACT

In this paper, the organoclay was synthesized by the modification of the Na-montmorillonite from the deposit of Tagan (East Kazakhstan) with octadecylamine (ODA). Using X-ray phase analysis, the intercalation of ODA molecules in the interlayer spaces of the mineral was studied. The presence of ODA in the clay structure and the formation of hydrogen bonds in it after modification were confirmed by IR spectroscopy. According to the results of dynamic light scattering, a decrease in the particle size of montmorillonite after modification was shown. The TGA curves showed a decrease in the content of bound water in organoclay compared with the initial mineral. The determination of the contact angles made it possible to ascertain the substantial hydrophobization of montmorillonite and to create an optimal concentration of ODE causing this effect.

Keywords: Organo-clay, Octadecylamine, Hydrophobization of Montmorillonite, Montmorillonite modification.

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INTRODUCTION

Recently, hydrophobized clay minerals, the so-called organoclay, have attracted the great interest of scientists. This is due to their unique water-repellent and electron surface properties, due to which they can be found and are widely used in various fields: the production of paints, cosmetics, antibacterial, self-cleaning, non-freezing, energy-saving materials, targeted delivery of drugs, strengthening non-polar polymers, the separation of water-oil compositions, water purification, and others.[1-8]

Organoclay was synthesized in different ways. In principle, the general approach to producing organoclay is the replacement of inorganic montmorillonite cations (Na^+, Ca^{++}, Mg^{++}), which ensure the stability of the layered structure, by large organic cations of various nature. It was found that a cationic surfactant (usually a salt-based on a quaternary ammonium base), which contains, along with the hydrocarbon radical, also phenyl groups, has a stronger hydrophobic effect on clay compared to alkylammonium chloride. It has been shown that small additions of long-chain hydrocarbon to CTAB solutions enhance the hydrophobic effect of surfactants[9, 10]. The hydrophobization of galoisite nanotubes (GNT) was carried out by the adsorption of octadecylamine (ODA) from its solution in ethanol. It was found that pretreatment of GNT with a solution of dopamine hydrochloride and vitamin M enhances the hydrophobic effect of ODA, while the contact angles of contact with water are ~ 156°[11].

This study aimed to obtain hydrophobized forms of colloidal-dispersed fractions of Kazakhstan montmorillonite and to study its physicochemical properties.

EXPERIMENTAL

Synthesis of Organoclay

Organoclay clays were obtained by intercalation by sorption of surfactant ions into swollen layered silicates. For this, at room temperature, 1.0 g of finely grounded (up to 38-85 μm) dry montmorillonite

was introduced into a 500 ml solution of octadecylamine (ODA) in isopropyl alcohol of various concentrations and was intensively stirred for 12 hours. Then, the clay phase was separated from the suspension by centrifugation and dried at 80 °C for 2 h in a vacuum. The amount of adsorbed surfactant was calculated by the changes in its concentration after adsorption. The surfactant concentration in the solution before and after adsorption on montmorillonite was determined using a UV-74 UV spectrophotometer (China) at a wavelength of 375 nm.

Z-potential Measurement
The ζ potential of montmorillonite particles in its hydro suspensions was determined using a Malvern - NanoZS - Zetasizer device (Netherlands).

Fourier Transform IR Spectra were recorded on an FSM-1211 IR Fourier spectrometer.

Statistical wetting angles (θ) were determined on an LK-1 Goniometer (Russia) by layered montmorillonite powder on a glass surface. Each θ value is the average of three measurements. The measurement accuracy was ± 3°.

X-ray Phase Analysis
X-ray phase analysis (XRD) of the sodium form of montmorillonite and organophilic montmorillonite was performed using a Rikagu SmartLab diffractometer (Rikagu Corporation, Tokyo, Japan) on CuKα radiation in the range of 2θ 3-80°.

Thermal Properties of Montmorillonite
The mass loss of montmorillonite and organoclay was studied by thermogravimetric analysis using a Q500TAInstruments in the temperature range from 25 °C to 600 °C in air.

RESULTS AND DISCUSSION

Physico-chemical Properties of Organoclay
Figure-1 shows the diffractograms of the initial and octadecylamine-modified Na-montmorillonite (OG). The obtained diffraction patterns are characterized by a series of reflections typical of montmorillonites. The starting montmorillonite has an asymmetric basal reflection, corresponding to an interplanar distance of 13.84 Å. After treatment with an ODA solution, the basal reflex shifts to the left, and the interplanar spacing increases to 16.61Å. This effect may be due to the intercalation of ODA molecules with long hydrocarbon chains into the interpackage space of the layered silicate, which, accordingly, leads to its expansion. Similar results were obtained when studying the interaction of cetyltrimethylammonium bromide (CTAB) with montmorillonite from the Erzurum deposit (Turkey). It was found that the intercalation of surfactants with a long hydrocarbon radical into the interpackage space of the layered silicate is accompanied by space expansion by ≈0.2 nm. Also, a significant (≈50-fold) decrease in the specific surface area of clay was found. This effect can be explained by the aggregation of a certain part of clays as a result of neutralization of the negative charge on their surface by surfactant cations, which leads to a decrease in the mutual repulsion of particles of the same charged particles.[12-15]

IR spectra of Na-montmorillonite and organoclay (OC)
Figure-2 shows the IR spectra of Na-montmorillonite and organoclay (GO). An analysis of the IR spectrum of the OC shows the presence of specific groups in the composition of the starting montmorillonite with absorption bands characteristic of clays. A wide absorption band at an oscillation frequency of 1038 cm^{-1} and a small peek at 904 cm^{-1} are due to Si – O – Si bonds. At frequencies of 470 cm^{-1} and 527 cm^{-1}, vibrations of Me–O bonds (Me – metal) are observed. Noticeable peaks in the IR spectrum in the frequency region 3434 cm^{-1} indicate the presence of bound water in the structure of montmorillonite. Bending vibrations at 1538 cm^{-1} are characteristic of hydrogen bonds, which can be formed by both Si-OH groups of the mineral and water molecules present in the interlayer space of montmorillonite.

On the IR spectrum of the organic clay modified with ODA, peaks appear at frequencies of 1488.96 cm^{-1}, 1476.28 cm^{-1}, 1638.78 cm^{-1}, 3430.91 cm^{-1}, 914.93 cm^{-1}, which correspond to stretching vibrations of amine groups[10]. There are also vibrations at frequencies of 2853.71 cm^{-1} and 2926.94 cm^{-1}, related to stretching vibrations of CH bonds in – CH_3 and – CH_2 groups of ODA. All this is evidence of the presence of ODA molecules in the clay structure.[16]

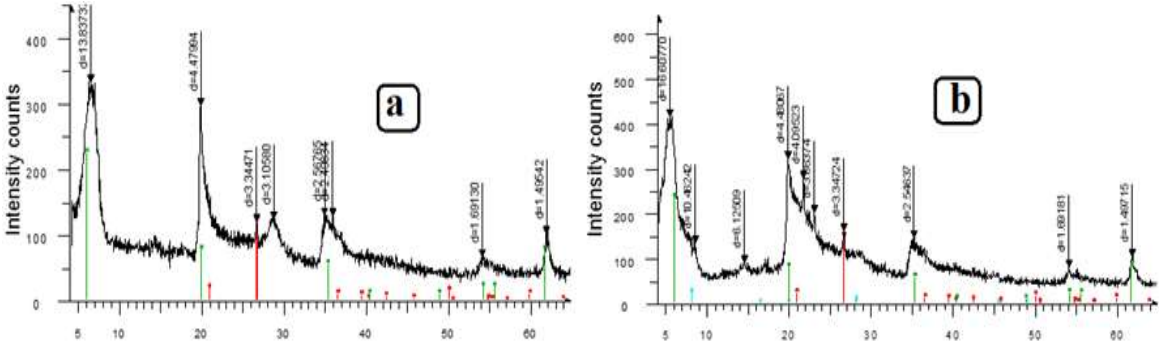

Fig.-1: Diffraction Patterns of Samples of (a)Sodium Montmorillonite and (b) Organoclay.

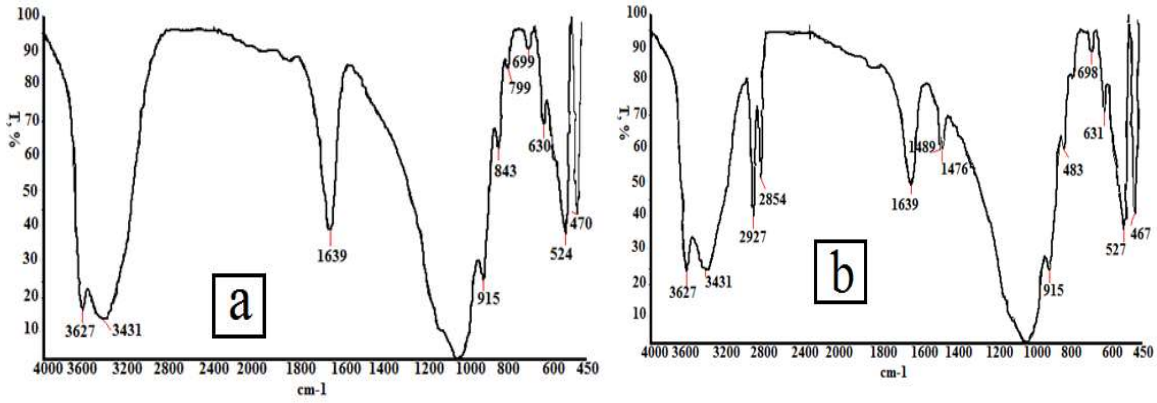

Fig.-2: IR Spectra of (a)Na-montmorillonite and (b) Modified ODA of Organoclay

Thermal Properties of Montmorillonite

On the derivatogram of Na-montmorillonite (Fig.-3a), an intense weight loss of the sample was detected at relatively low (up to 100 °C) temperatures. It can be associated with the removal of adsorption and interlayer water from montmorillonite. On the differential TGA curve of the original clay, a high peak is observed at low temperatures, in the range of 50-60 ° C, which may be associated with the separation of moisture from the surface of the silicate. A slight loss of water in the temperature range of 100-150 ° C may be associated with the release of bound water from the structure of montmorillonite. The amount of bound water, as expected, turned out to be less than adsorption. The loss of mass of the sample in the temperature range 460-500 °C can be explained by the destruction of the crystal structure of montmorillonite, i.e. partial amorphization of the mineral. It is common for layered silicates to form amorphous structures with increasing temperature.[16]

According to the derivatograms taken from organic clay modified by ODA(Fig.-3b), water loss begins, as in the case of the initial clay, at a temperature of 50-60 °C, however, this peak is inferior to the corresponding peak in the TGA curve of the original clay (Fig.-3a) as in width, and in height. This can be explained by evaporation of bound water. Second mass loss was observed in the temperature of 110°C to 300°C is 8%, which was explained to amide-imide reaction and loss of the methyl group in the organoclay. Similar trends were observed by authors when studying the thermal properties of organic materials[18]. The maxima at 350 °C and 450 °C are probably related to the transformation of the crystal structure of montmorillonite, i.e. the amorphization discussed above, similar to that described in[17]. From

the analysis of the differential curves of TGA, it follows that to avoid changes in the structure of montmorillonite, the temperature of their subsequent processing should not exceed 200-250 °C.

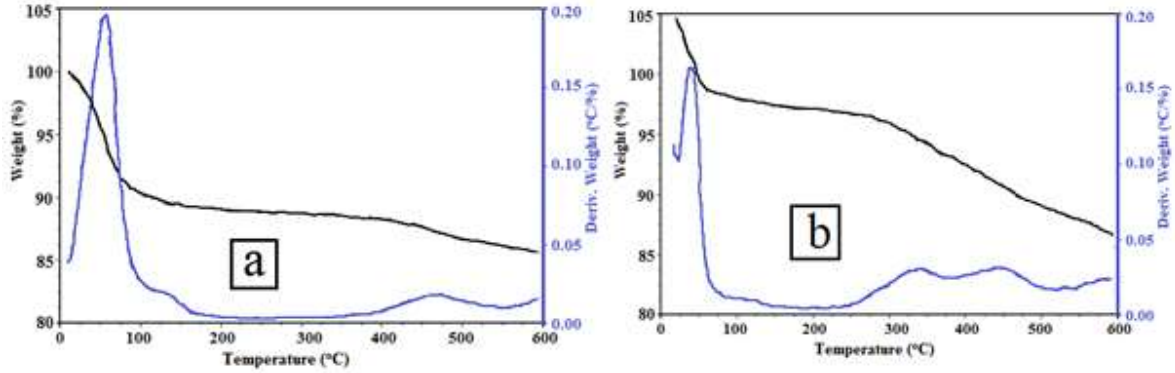

Fig.-3:TG Curves of (a)Na-montmorillonite and (b)Organoclay Modified with ODA.

The Size Distribution of Montmorillonite Particles

Since the introduction of surfactants into the interlayers' space of clays. It was important to determine the particle sizes of organoclay obtained by the modification of Na-montmorillonite ODA. Figure-4a and b shows the size distribution curves of particles of montmorillonite and its organophilic derivative.

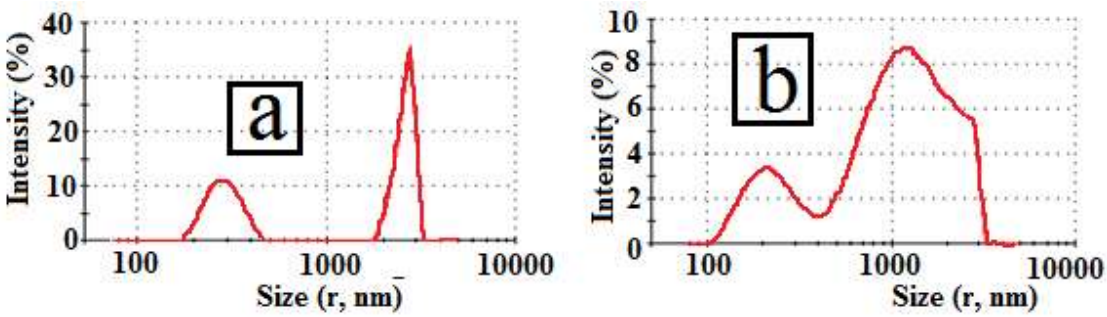

Fig.-4: The Particle Size Distribution of (a)Montmorillonite and (b)Organoclay, modified ODA.

As can be seen from Figure-4a, in Na-montmorillonite, the most probable particle size is 280 nm and 3000 nm, and the second peak is very sharp. In clay modified with ODA, the particle size distribution curves also have 2 curves: at 234 nm and 1400 nm (Fig.-4b). However, the attention is drawn to the different intensities of the distribution curves. The intensity of the curve in the maximum region for Na-montmorillonite is 11 and 35%, respectively, with the second maximum being sharp. This means that the size of most clay particles is in this area.

Static Contact Angles of Water on Na-montmorillonite and Organomontmorillonite

To confirm the effect of hydrophobicity during the modification of natural clay with octadecylamine, the wetting angles of the resulting organoclay were measured.

The contact angles of water wetting and photographs of a water droplet on the surface of montmorillonite and its modified ODA analogs are presented in Fig.-5. It should be noted that the samples are compressed particles, so they inevitably had a certain level of roughness. Since the clay particles were pressed under the same conditions, it can be assumed that the roughness of all the substrates was the same, and this factor should not be considered when interpreting the results. A drop of water on the surface of Na-montmorillonite, and samples modified with ODA at its low concentrations ($<1.25 \cdot 10^{-3}$ mol/L) in isopropanol, was instantly absorbed by the clay. With an increase in the concentration of ODA, its hydrophobic effect on the surface of montmorillonite increases. Clay treated with the relatively most concentrated solution (1 mol/L) of ODA leads to the formation of an almost superhydrophobic surface ($\theta = 157^{o}$).

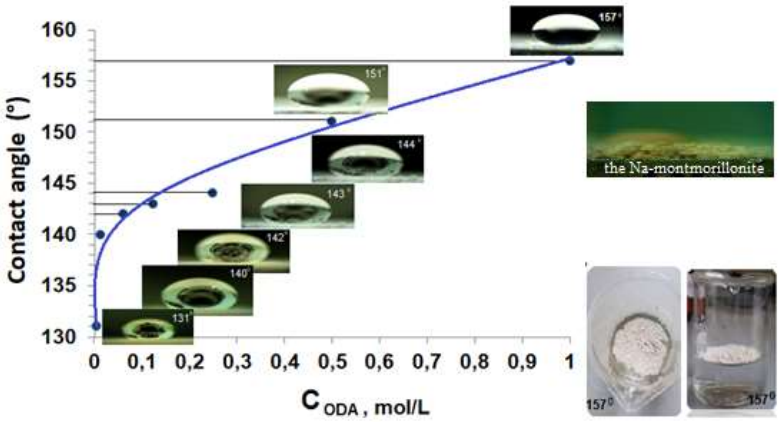

Fig.-5: Values of Water Contact Angles on the Surface of Pressed Na-montmorillonite Powders and Organoclay Samples Obtained at Different Concentrations of ODA

CONCLUSION

Thus, organoclayes were prepared by modifying montmorillonite with octadecylamine. The increase in the winter package space of montmorillonite during the processing of its ODE. By the XRD method, the intercalation of the surfactant into the interlayer spaces of montmorillonite was indicated. The reduction in particle size after a modification indicates a certain level of particle dispersion during processing. Changes in the clay structure after modification of the ODE are confirmed by IR spectroscopy (the appearance of peaks corresponding to stretching vibrations of amine groups). In the derivatograms of the initial and modified clays, two areas of sharp mass change were found: in the temperature range of 50-60 °C, due to the evaporation of loosely bound water, and 100-150 °C (removal of bound water), and the latter effect for organoclay is noticeably weaker. The mass loss at temperatures of 350 °C and 450 °C is associated with the transformation of the crystalline structure of clay.

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REFERENCES

1. Q. Xu, W. Zhang, C. Dong, T.S. Sreeprasad, Z. Xia, *Journal of The Royal Society Interface,* **13,** (122)2016, **DOI:**10.1098/rsif.2016.0300
2. Q.Q. Shang, Y.H. Zhou, *Ceramic International,* **42,** (7)2016, **DOI:**10.1016/j.ceramint.2016.02.105
3. C.Y. Peng, S.L. Xing, Z.Q.Yuan, J.Y. Xiao, C.Q.Wang, J.C. Zeng, *Applied Surface Science,* **259,** 2012, **DOI:**10.1016/j.apsusc.2012.07.118
4. Z.W. Wang, Y.L. Su, Q. Li, Y. Liu, Z.X. She, F.N. Chen, L.Q. Li, X.X. Zhang, P. Zhang, *Materials Characterization,* **99,** 2015, **DOI:**10.1016/j.matchar.2014.12.004
5. W.T. Cao, Y.J. Liu, M.G. Ma, J.F. Zhu, *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* **529,** 2017, **DOI:**10.1016/j.colsurfa.2017.05.064
6. S. S. Kozhabekov, A. A. Zhubanov, and Zh. Toktarbay, *Oil & Gas Science and Technology - Rev. IFP Energies nouvelles,* **74**, (28)2019, **DOI:**10.2516/ogst/2019004
7. Kaldibek Zh. Abdiyev, Zhexenbek Toktarbay, Akbota Zh. Zhenissova, Mariamkul B. Zhursumbaeva, Raya N. Kainazarova, Nuraje, Nurxat, *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 480, 2015, **DOI:**10.1016/j.colsurfa.2015.04.025
8. A. M. Shala Abazi, B. H. Durmishi, F. S. Sallaku, H. S. Çadraku, O. B. Fetoshi, P. H. Ymeri and P. S. Bytyçi, *Rasayan Journal of Chemistry,* **13,** (1)2020, **DOI:**10.31788/RJC.2020.1315344
9. Yerbol Dauletov, Nurxat Nuraje, Kaldibek Abdiyev, Zhexenbek Toktarbay, & Maryamgul Zhursumbaeva, *Journal of Surfactants and Detergents*, **22,** (5)2019, **DOI:**10.1002/jsde.12283

10. O. Yessimova, S. Kumargaliyeva, M. Kerimkulova, K. Mussabekov and Zh. Toktarbay, *Rasayan Journal of Chemistry*, **13**, (1)2020, **DOI:**10.31788/RJC.2020.1315566
11. K. J. Shah, M. K. Mishra, A. Shukla, T.Imae, D. O. Shah, *Journal of Colloid and Interface Science*, **407,** (2013), **DOI:**10.1016/j.jcis.2013.05.050
12. S. Solarski, S. Benali, M. Rochery, E. Devaux, M. Alexandre, F. Monteverde, P. Dubois, *Journal* of *Applied Polymer Science*, **95,** (2)2005, **DOI:**10.1002/app.21254
13. Mariana, F. Mulana and L. Juniar, *Rasayan Journal of Chemistry*,**13,** (1)2020, **DOI:**10.31788/RJC.2020.1315377
14. K.Z. Abdiyev, Z. Toktarbay, A.Z. Zhenissova, M.B. Zhursumbaeva, R.N. Kainazarova, *Polymer Science Ser B.,* **57**, 217–223(2015), **DOI:**10.1134/S156009041503001X
15. Jaiveer Singh, Arti Jangra, Jai Kumar, Keerti Rani and Ramesh Kumar. *Rasayan Journal of Chemistry*, **13**(1), 105-111(2020), **DOI:**10.31788/RJC.2020.1315382
16. R. Dewi, H. Agusnar, Z. Alfian and Tamrin. *Rasayan Journal of Chemistry,* **13(1),** 382(2020), **DOI:**10.31788/RJC.2020.1315523
17. Damiyine, A. Guenbour and R. Boussen. *Rasayan Journal of Chemistry*, **13(1),** 448(2020), **DOI:**10.31788/RJC.2020.1315588
18. Akhmetzhan Ayatzhan, Ayezkhan Tashenov, Abeu Nurgeldi, Ospanova Zhanar, Toktarbay Zhexenbek, Abdiyev Kaldibek, Nuxat Nuraje, *Polymers for Advanced Technologies*, 1-7 (2020) **DOI:**10.1002/pat.4999

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