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RESEARCH ARTICLE

SYNTHESIS AND INVESTIGATION OF MODIFIED ACTIVE SILICA FILLERS

Raxmatullayev Lutfillo Suyarovich[1], Kiyomov Sharifjon Nozimovich[2], Fayziyev Jakhongir Bakhromovich[2], Ahmedov Orif[3] and Djalilov Abdulahat Turapovich[4]

1. Independent Researcher at the Tashkent Research Institute of Chemical Technology.
2. Doctor of Technical Sciences, Senior Researcher at the Tashkent Research Institute of Chemical Technology.
3. Uzkimyosanoat, KRICT DREKSIYASI LLC.
4. Doctor of Chemical Sciences, Professor, Academician, "Tashkent Scientific Research Institute of Chemical Technology LLC".

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Abstract

This article investigates methods for obtaining organic modifiers based on oleic acid for the surface modification of silicon-(IV) oxide. Diethanolammonium oleate was synthesized based on the acid-base interaction between oleic acid and diethanolamine. The molar ratio of OA:DEA = 1:1 was determined to be optimal for obtaining the modifier. It was established that the most effective synthesis conditions were a temperature of 85-90 °C and a reaction time of 2.0-2.5 hours. Under these conditions, the product yield was 98.55%, while the conversion of oleic acid reached 99.43%. The average acid value of the obtained diethanolammonium oleate was 0.84±0.02 mg KOH/g, and the content of free oleic acid was 0.423 wt.%.In addition, a modifier based on tetraethylammonium oleate was synthesized in two stages using oleic acid, NaOH, and tetraethylammonium bromide. During the ion-exchange stage, NaBr, formed as a by-product, was separated by vacuum filtration, which enabled purification of the target product. The practical chemical yield of tetraethylammonium oleate was 97.90%, while the process mass yield relative to the starting reagents was 75.39%.The obtained results demonstrate the potential of the synthesized oleate compounds as promising organic modifiers for the surface modification of silicon-(IV) oxide.

Introduction:-

In 1953, the American chemist Loring Coes first obtained modified silicon oxide through high-temperature and high-pressure synthesis from the mineral coesite. Later, in 1961, S. M. Stishov isolated silicon oxide from coesite, a rare, extremely hard, and dense tetragonal mineral found on Earth, at a temperature of 1200-1400 °C and a pressure of 10-16 MPa [1; p. 158054]. The article presents a method for obtaining spherical SiO_2 particles of uniform size through the hydrolysis and polycondensation of silicon alkoxides in an alcoholic medium in the presence of water and ammonia. It was shown that the particle size can be controlled by varying the concentration of tetraethoxysilane, the amount of water, the ammonia concentration, and the solvent composition. At the first stage of the process, the

Corresponding Author:- Raxmatullayev Lutfillo Suyarovich
Address:-Independent researcher at the Tashkent Research Institute of Chemical Technology.

silicon alkoxide undergoes hydrolysis with the formation of silanol groups, which subsequently undergo condensation to form a Si-O-Si siloxane network. At present, this method, known as the Stöber method, is one of the main laboratory methods for producing silica nanoparticles [3; pp. 972-1048].

This review article summarizes the results of studies on the preparation of SiO2 nanoparticles by the sol-gel method, control of their size and surface properties, organic modification, as well as their application in polymer nanocomposites. It was noted that as the particle size decreases, the specific surface area and surface energy increase. This promotes the ability of SiO_2 to interact with polymers; however, at the same time, it increases the tendency of the particles to agglomerate. The article demonstrates that well-dispersed nanosilica can improve the mechanical strength, elastic modulus, and thermal stability of polymers [3; pp. 1393458].

Silicon is an attractive platform for optoelectronic integration; however, its indirect band gap makes it a weak light emitter. This study demonstrated that thermal annealing of silicon (SiO_2) coatings prepared by the sol-gel method can significantly increase the intensity of photoluminescence (PL) associated with the silicon band gap. Samples annealed at 900 °C exhibited more than a fourfold increase in emission intensity in the region around 1160 nm [4; pp. 7826-7835].

This article demonstrates that several modified methods can also be used for the accurate determination of contact angles in experiments conducted on horizontal surfaces. Liquid droplets on a flat, freshly cleaned silicon oxide (wafer) surface are dynamically measured using the sessile drop method, while the liquid volume is increased or decreased [5; pp. 248-253].In the study, the process of obtaining SiO_2 nanoparticles by gradually adding sulfuric acid to a solution of water glass (sodium silicate) was investigated using small-angle X-ray scattering.

It was established that particle formation proceeds in three stages:-
accumulation of silicic acid monomers;
growth of primary SiO_2 particles;
aggregation and formation of a porous structure.

The hydrolysis and condensation processes of silicic acid were analyzed by monitoring electrical conductivity. It was shown that the precipitation rate and the mode of acid addition affect the particle size, porosity, and aggregate structure [6; pp. 117115].

In the article, the process of producing precipitated SiO_2 by neutralizing a sodium silicate solution with sulfuric acid was carried out in a 100-liter pilot reactor. The acid was introduced in two stages: in the first stage, until the gelation point was reached; and in the second stage, until the pH of the medium reached a value of 5. It was established that under conditions close to the gelation point, particle flocculation and interparticle bridging promote the formation of a porous SiO_2 structure. As the time to gelation and temperature increased, the BET specific surface area and pore volume decreased [7; pp. 27271-27303].

This study presents a comprehensive review of production strategies, properties, and advances in the field of optoelectronic devices based on the Si/SiO_2 system, as well as new materials used in this field. In addition, the study examines the potential applications of Si/SiO_2 in various areas, including light-emitting diodes, solar cells, photodiodes, and phototransistors. Overall, the article opens up new directions for research and further development in this rapidly growing field [8; pp. 138994].

Energy storage technology using phase-change materials (PCMs) is considered one of the most promising technologies for improving energy efficiency. The conversion of solar energy into thermal energy followed by its storage in PCMs is becoming increasingly important for enhancing energy efficiency [9; pp. 111524].

This study is aimed at developing a new type of composite material based on unsaturated polyester with enhanced flame resistance achieved through modification of the polymer matrix with nano- and micro-sized oxide particles, such as silicon dioxide, carbon-coated silicon dioxide, and aluminum oxide, in combination with widely used flame-retardant systems [10; pp. 8-19].

In the study, highly dispersed SiO_2 nanoparticles were obtained using sodium silicate and sulfuric acid in a membrane dispersion microreactor. The acid stream was introduced into the sodium silicate solution through a

microporous membrane in the form of fine droplets. This method ensured rapid and uniform mixing of the reactants, reduced local pH variations, and limited uncontrolled particle growth. The type and amount of surfactants, the reactant ratio, flow rate, and mixing conditions affected the morphology, specific surface area, and dispersibility of SiO_2 [11; p. 453].The article summarizes data on the formation, concentration, and thermal changes of hydroxyl groups on the surface of amorphous silicon dioxide.

On the SiO2 surface, the following groups are mainly present:-
isolated or single silanol groups - ≡Si-OH;
vicinal, i.e., silanol groups connected to each other by hydrogen bonds;
geminal groups - $=Si(OH)_2$;
siloxane bridges - ≡Si-O-Si≡.

During dehydration, physically adsorbed water is removed, whereas during dehydroxylation, condensation of silanol groups occurs, resulting in the formation of siloxane bonds. The possibility of rehydroxylation of the surface under the influence of water vapor has been substantiated [12; pp. 699-721].

The study comprehensively investigated the morphology, specific surface area, porosity, silanol group content, and water adsorption of fumed SiO_2 samples obtained under various production conditions. It was shown that fumed silica consists of primary spherical nanoparticles that combine into strong aggregates during high-temperature synthesis and subsequently form loose agglomerates. The synthesis temperature, gas flow rate, and reactant ratio affected the particle diameter, aggregate structure, and surface hydrophilicity. Samples with a high specific surface area are capable of forming a well-developed interfacial boundary with the polymer [13; p. 108889].

In the article, the aggregate structure of six different industrial samples of fumed SiO_2 was analyzed using small-angle X-ray scattering and three-dimensional modeling. It was quantitatively demonstrated that fumed SiO_2 aggregates have not a simple linear-chain structure but a branched fractal structure. The degree of branching, primary particle size, and fractal dimension of the aggregate determine the compaction, dispersibility, and rheological activity of the material. Branched aggregates can form a three-dimensional filler network within the polymer matrix, increasing the elastic modulus and viscosity [14; p. 2856].

In the review article, three main methods for preparing polymer-SiO_2 nanocomposites were analyzed:-
mechanical mixing of pre-prepared components;
conducting the sol-gel process within the polymer matrix;
in situ polymerization of the monomer in the presence of SiO_2.

It is emphasized that the effect of SiO_2 depends on the particle size, specific surface area, surface functional groups, degree of dispersion in the polymer, and interfacial adhesion. Good nanoparticle dispersion increases the mechanical strength, elastic modulus, thermal stability, and dimensional stability of the material. However, the agglomeration of hydrophilic SiO_2 in nonpolar polyolefins remains one of the main technological challenges [15; p. 152912].

In the study, high-density polyethylene was melt-mixed with hydrophilic and hydrophobic fumed SiO_2 having different specific surface areas. As the specific surface area of SiO_2 increased, interparticle interactions and the tendency of the particles to agglomerate increased. Hydrophobic SiO_2 with an organically modified surface exhibited better compatibility with polyethylene and was more uniformly dispersed within the matrix. The nanofiller affected the elastic modulus, thermal resistance, and thermomechanical properties of polyethylene. The results showed that the effectiveness of SiO_2 depends not only on its content but also on its specific surface area, degree of modification, and dispersion [16; p. 4457].

To obtain an organic modifier based on oleic acid and diethanolamine intended for use in the modification of the surface of silicon-(IV) oxide, a synthesis based on their acid-base interaction was carried out. As a result of proton transfer from the carboxyl group of the oleic acid molecule to the secondary amino group of diethanolamine, diethanolammonium oleate, an ionic compound, is formed.

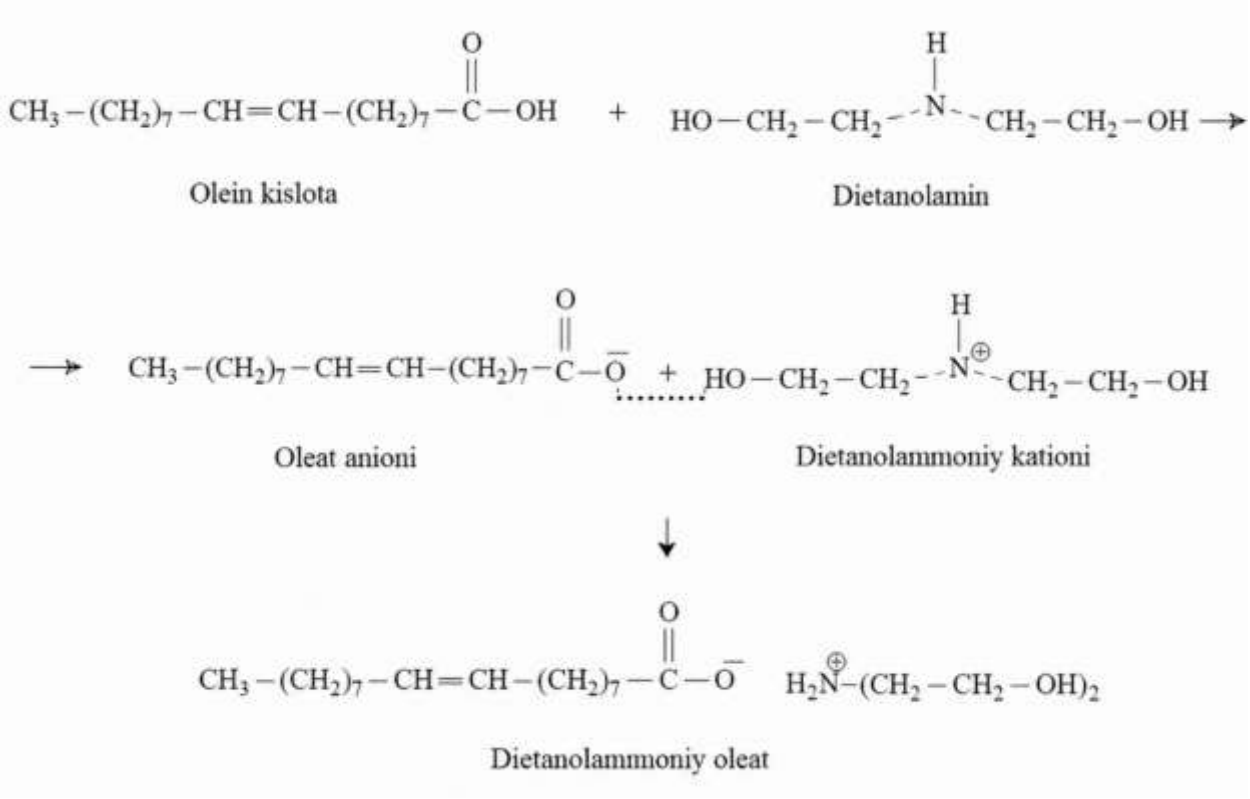

Fig. 1. Preparation of diethanolammonium oleate.

$C_{17}H_{33}COOH + HN(CH_2CH_2OH)_2 \rightarrow [C_{17}H_{33}COO]\text{-}[H_2N(CH_2CH_2OH)_2]^+$

For the synthesis, 10.00 g (0.03540 mol) of oleic acid and 3.70 g (0.03519 mol) of diethanolamine were placed in a 100 mL heat-resistant reaction vessel. The actual molar ratio of the reactants was 1.006:1.000, i.e., approximately 1:1.

The reaction mixture was continuously stirred using a magnetic stirrer while the temperature was gradually increased to 85-90 ℃. The process was carried out at this temperature for 2.0-2.5 h. During this period, the reaction mixture was observed to transform into a homogeneous, viscous state. After completion of the reaction, heating was stopped, and the resulting product was cooled to room temperature under continuous stirring. As a result, 13.50 g of the organic modifier OA-DEA was obtained.

The acid value of the organic modifier OA-DEA, determined in three parallel experiments, was 0.86, 0.82, and 0.84 mg KOH/g, respectively. The mean acid value was 0.84 ± 0.02 mg KOH/g, with a relative standard deviation of 2.38%. Based on the obtained value, the average content of free oleic acid in the product was determined to be 0.423 wt.%, corresponding to 0.0571 g in 13.50 g of the product. The average conversion of oleic acid was 99.43%. The closeness of the obtained value to the theoretically calculated value of 0.88 mg KOH/g confirms the effectiveness of the selected synthesis conditions.

Table 1.Effect of the molar ratio of oleic acid to diethanolamine on the formation of the organic modifier

№	Molarratio OA	Amount of DEA corresponding to 10.00 g of OA, g	Theoreticalconversionof OA, %	Theoretical residual OA, g	Theoreticalresidual DEA, g
1	1:0,80	2,98	80,0	2,00	-
2	1:0,90	3,35	90,0	1,00	-
3	1:1,00	3,70-3,72	≈100	≈0,06	-
4	1:1,10	4,09	100	-	0,37
5	1:1,20	4,47	100	-	0,74

In the practical experiment, at a molar ratio of 1:1, 10.00 g of oleic acid and 3.70 g of diethanolamine were used; the actual molar ratio was 1:0.994. According to the stoichiometric calculation, approximately 0.06 g of excess oleic acid may remain after the reaction.

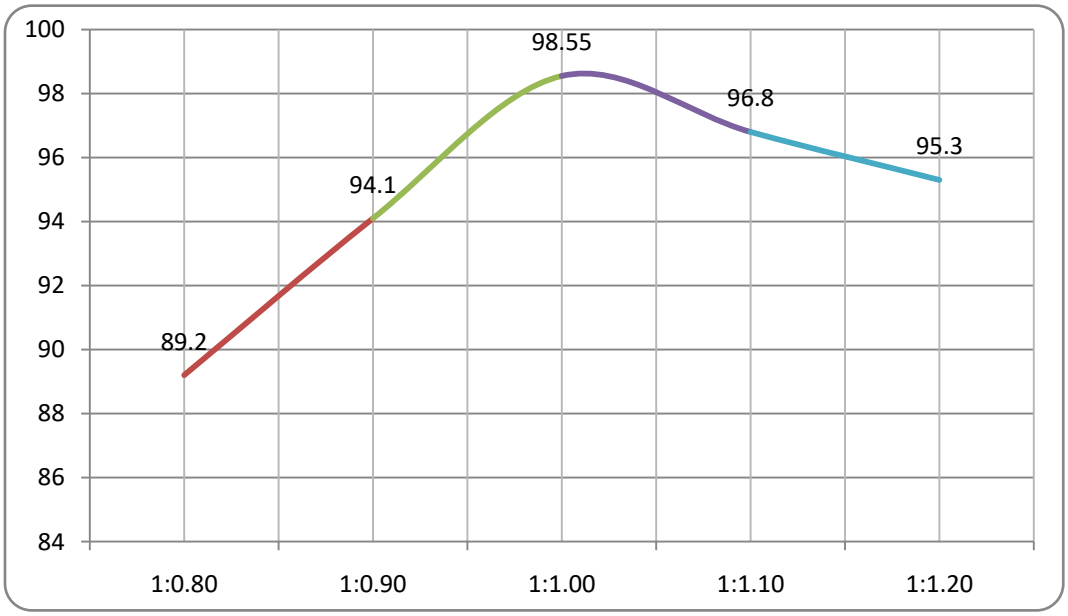

Fig. 2. Effect of the molar ratio of the starting materials on the formation of diethanolammonium oleate.

The results of the stoichiometric analysis showed that the OA molar ratio has a significant effect on the formation of the organic modifier. When the amount of diethanolamine is reduced to a ratio of 1:0.80-1:0.90, 1.00-2.00 g of free oleic acid may remain in the reaction system, which leads to an increase in the acid value of the product and adversely affects the stability of the subsequent modification process.

Table 2.Main experimental parameters of the organic modifier obtained at an OA molar ratio of 1:1

Parameter	Result
Oleicacid	10,00 g
Diethanolamine	3,70 g
Mass of the obtained product	13,50 g
Averageacidvalue	0,84 ± 0,02 mg KOH/g
Free oleicacid	0,423 mass.%
Conversionofoleicacid	99,43 %
Calculatedproductyield	98,55 %

Increasing the amount of DEA to molar ratios of 1:1.10-1:1.20 does not lead to an increase in the theoretical conversion of oleic acid. On the contrary, this results in the retention of 0.37-0.74 g of excess amine component in the reaction system and increases the consumption of reactants. At an OA molar ratio of 1:1, practically complete interaction of the starting components is achieved. Under these conditions, the average acid value was 0.84 ± 0.02 mg KOH/g, the conversion of oleic acid was 99.43%, and the calculated product yield was 98.55%. Therefore, an OA molar ratio of 1:1 was selected as optimal for obtaining the organic modifier.

Table 3.Effect of temperature on the yield of the OA-DEA organic modifier

№	Temperature, °C	Product yield, %	Process description
1	65-70	88,4	At low temperatures, the viscosity of the system increases, which slows down the interaction of the components.
2	75-80	94,6	Molecular mobility and mass transfer intensity increase, which promotes faster product formation.
3	85-90	98,55	The optimal temperature range; the maximum yield

			was established experimentally.
4	95-100	95,7	A further increase in temperature does not result in an additional effect; an increase in thermo-oxidative and technological losses is possible.

Increasing the temperature from 65-70 to 85-90 °C accelerates the formation of the OA-DEA modifier by reducing the viscosity of the reaction mixture, increasing the mobility of the components, and improving mass transfer. At a temperature of 85-90 °C, the experimental product yield was 98.55%. A further increase in temperature to 95-100 °C does not improve the efficiency of the process but may promote thermo-oxidative processes in the unsaturated fragments of oleic acid, darkening of the product, and increased process losses. Therefore, the temperature range of 85-90 °C was selected as optimal.

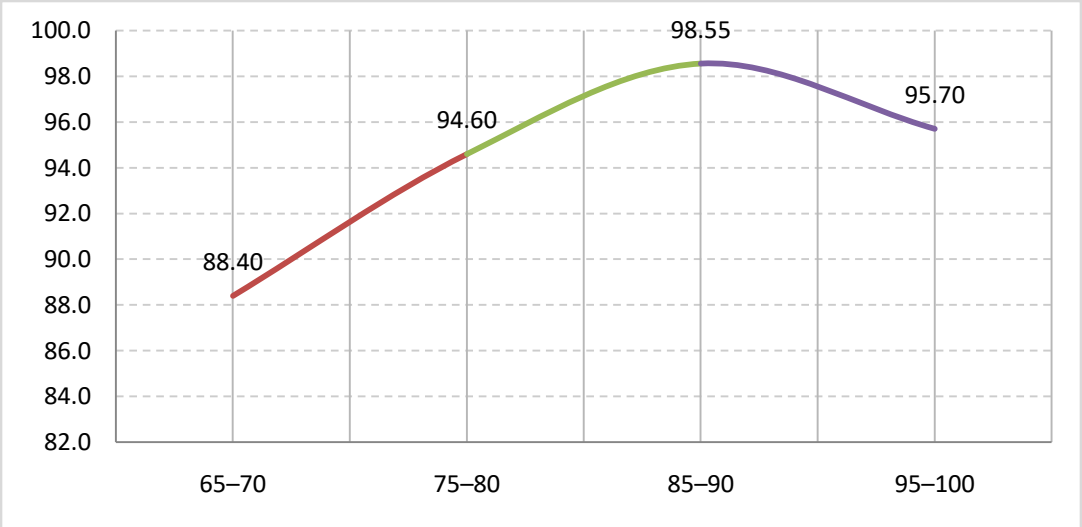

Fig. 3. Effect of temperature on the formation of diethanolammonium oleate

As the reaction time increases, the degree of interaction between oleic acid and diethanolamine molecules increases. In the 1.0-1.5 h interval, the process is likely not yet sufficiently complete; therefore, a relatively low product yield is expected.

Table 4.Effect of reaction time on the yield of the OA-DEA organic modifier

№	Reactiontime, h	Product yield, %	Process description
1	0,5-1,0	84,8	Within a short period of time, the degree of interaction between the components does not reach a sufficient level.
2	1-1,5	92,7	The extent of the reaction increases; however, the system has not yet fully reached the optimal state.
3	2,0-2,5	98,55	Optimal reaction time; maximum yield established experimentally.
4	2,5-3,0	96,1	A further increase in the process duration does not result in a significant increase in yield and is accompanied by increased energy consumption.

When the reaction was carried out for 2.0-2.5 h, the system approached the optimal state, with an experimental product yield of 98.55%. Increasing the process duration to 3.0 h did not provide any additional increase in yield but could lead to higher energy consumption and an increased likelihood of thermo-oxidative processes. Therefore, a reaction time of 2.0-2.5 h was established as optimal.

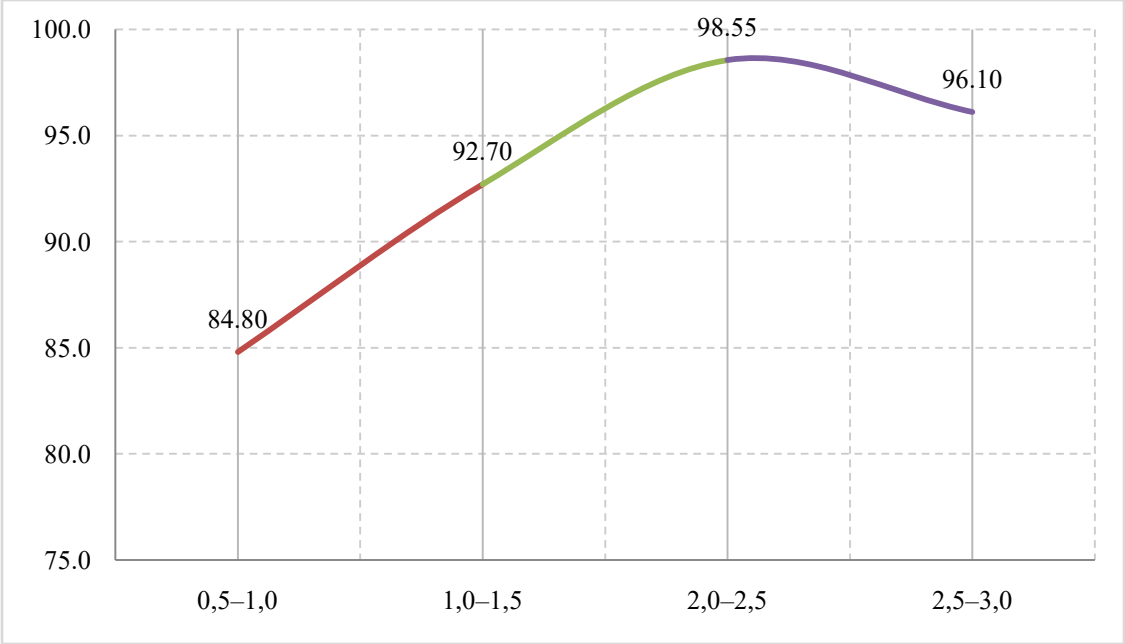

Fig. 4. Effect of reaction time on the formation of diethanolammonium oleate.

When evaluating the combined effect of temperature and reaction time on the preparation of the modifier at an OA molar ratio of 1:1, the optimal conditions were determined to be a temperature of 85-90 ℃ and a reaction time of 2.0-2.5 h. Under these conditions, the calculated product yield was 98.55%, the conversion of oleic acid was 99.43%, and the average acid value was 0.84 ± 0.02 mg KOH/g.

Methodology for Obtaining an Organic Modifier Based on Oleic Acid, Sodium Hydroxide, and Tetraethylam monium Bromide:-

The oleate-type organic modifier, tetraethylammonium oleate, was obtained in two stages. In the first stage, oleic acid was neutralized with sodium hydroxide to form sodium oleate, while in the second stage, the resulting sodium oleate was subjected to an ion-exchange reaction with tetraethylammonium bromide (TEAB). The aim of this process was to obtain tetraethylammonium oleate purified from inorganic salts by separating the sodium bromide formed during the reaction.

Stage I: $C_{17}H_{33}COOH + NaOH \rightarrow C_{17}H_{33}COONa + H_2O$

Stage II: $C_{17}H_{33}COONa + [(C_2H_5)_4N]Br \rightarrow [(C_2H_5)_4N]+[C_{17}H_{33}COO]^- + NaBr\downarrow$

According to the calculation results, the molar ratio of OA:NaOH was approximately 1.005:1.000:1.002, which practically corresponds to a ratio of 1:1:1. NaOH, having the smallest amount of substance (0.03275 mol), was taken as the limiting reagent.

Table 5. Stoichiometric Calculation of Reagents

Reagent	Mass, g	Molarmass, g/mol	Amountofsubstance, mol
Oleicacid	9,30	282,47	0,03292
Sodiumhydroxide	1,31	40,00	0,03275
Tetraethylammoniumbromide	6,90	210,16	0,03283

In a 100 mL heat-resistant reaction vessel, 9.30 g (0.03292 mol) of oleic acid was placed and heated to 65-70 ℃ under continuous stirring using a magnetic stirrer. In a separate vessel, 1.31 g (0.03275 mol) of NaOH was dissolved in a minimum amount of distilled water, after which the resulting alkali solution was gradually added to the oleic acid under continuous stirring.

The mixture was maintained at a temperature of 70-80 ℃ for 30-45 min. At this stage, neutralization of the carboxyl group of oleic acid occurred, resulting in the formation of sodium oleate.After completion of the neutralization, water was removed from the reaction medium under reduced pressure. According to the stoichiometric calculation, approximately 0.59 g of water should theoretically be formed at the first stage. After removal of the water, the mass containing sodium oleate was cooled to 40-50 ℃.

At the second stage, 6.90 g (0.03283 mol) of tetraethylammonium bromide was dissolved in dry acetone, after which the resulting solution was added to the sodium oleate. The reaction mixture was continuously stirred at 50-55 ℃ for 1.0-1.5 h, without allowing the temperature to exceed the boiling point of acetone. As a result, tetraethylammonium oleate was formed, while sodium bromide was released as a by-product.

After completion of the reaction, the mixture was cooled to 20-25 ℃. The solid NaBr formed was separated by vacuum filtration, and the precipitate was washed 2-3 times with a small amount of cold dry acetone. Acetone was removed from the combined filtrate by distillation under reduced pressure at 40-50 ℃. The resulting residual product was dried under vacuum at 45-50 ℃ until a constant mass was reached. As a result, 13.20 g of an organic modifier based on tetraethylammonium oleate was obtained.

The chemical yield was determined as the ratio of the actual mass of the target product obtained to its theoretical mass calculated from the stoichiometric reaction equation. Since NaOH was the limiting reagent, the theoretical amount of tetraethylammonium oleate was 0.03275 mol.
$m_{na}z = 0{,}03275 \times 411{,}71 = 13{,}48$ g
$\eta_{kim} = (13{,}20 / 13{,}48) \times 100 = 97{,}90$ %

Thus, the chemical yield of tetraethylammonium oleate was 97.90%. This value was taken as the actual chemical yield of the target product, determined relative to its theoretical amount.
$m(NaBr) = 0{,}03275 \times 102{,}89 = 3{,}37$ g
$m(H_2O) = 0{,}03275 \times 18{,}015 = 0{,}59$ g
$Y_{massa} = (13{,}20 / 17{,}51) \times 100 = 75{,}39$ %

The total mass of the initial reagents is 17.51 g. A portion of this mass is released as NaBr (3.37 g) and H_2O (0.59 g), which are not incorporated into the target product. Therefore, the yield of 13.20 g of the target product relative to the total mass of the initial reagents is 75.39%. This value characterizes the technological mass yield of the process rather than the chemical yield.

Physicochemical Analysis of the OA-DEA Modifier - Bis(2-hydroxyethyl)ammonium Oleate:-
The most diagnostically significant regions of the spectrum are the bands observed at 1594.63 and 1404.18 cm-1. They correspond to ν_as(COO^-) and ν_s(COO^-), respectively, representing the asymmetric and symmetric stretching vibrations of the carboxylate anion.

The difference between these bands is:-
$\Delta\nu = 1594{,}63 - 1404{,}18 = 190{,}45 cm^{-1}$
The presence of bands in the 1500-1650 cm-1 region and around 1400 cm-1, characteristic of carboxylate groups, is indicative of the presence of an ionized carboxyl group.

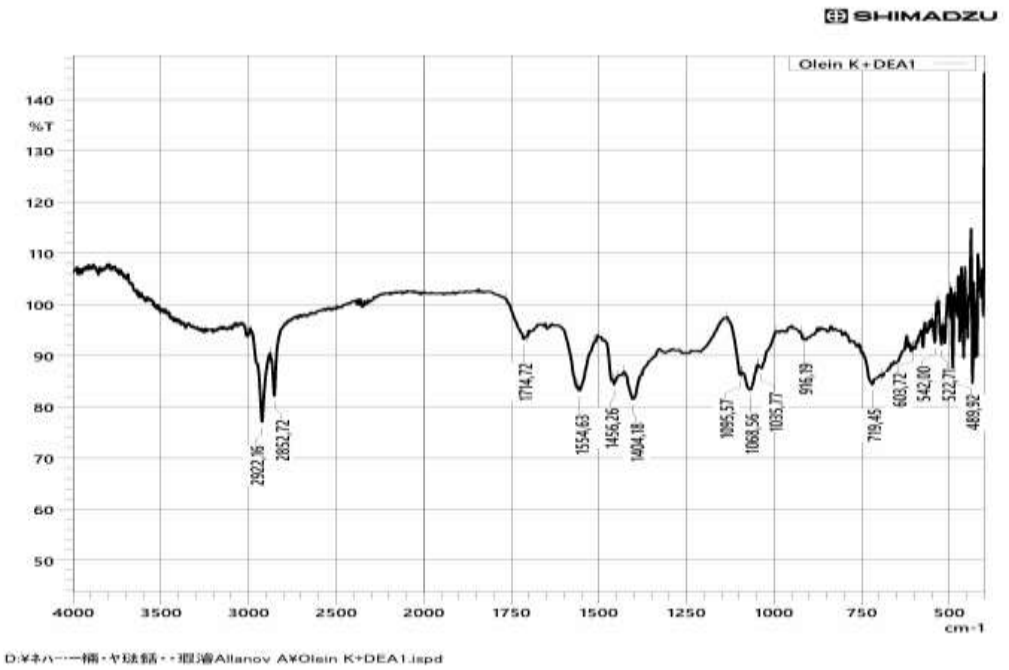

Fig. 5. FTIR Spectrum of the OA-DEA Modifier - Bis(2-hydroxyethyl)ammonium Oleate.

In the FTIR spectrum of the OA-DEA organic modifier, absorption bands are observed at 2922.16 and 2852.72 cm^{-1}, characteristic of the asymmetric and symmetric stretching vibrations, respectively, of aliphatic -CH_2- groups in the oleate fragment. The intense bands at 1594.63 and 1404.18 cm^{-1} correspond to the ν_as(COO^-) and ν_s(COO^-) vibrations, respectively, of the carboxylate group, indicating ionization of the carboxyl group of oleic acid and the formation of an ion pair with the diethanolammonium cation. The Δν value between these bands is 190.45 cm^{-1}.

The bands in the 1095.57-1035.77 cm^{-1} region are associated with C-O bond vibrations in the diethanolamine fragment, whereas the absorption band at 719.45 cm^{-1} is attributed to the rocking vibrations of -$(CH_2)_n$- groups in the long aliphatic chain. At the same time, the retention of the C=O absorption band at 1714.72 cm^{-1} indicates the presence of a small amount of free or incompletely ionized oleic acid in the product. The obtained FTIR spectroscopic results confirm that the interaction between OA and DEA predominantly proceeds via acid-base neutralization rather than an amidation reaction, resulting in the formation of the major portion of the product in an ionically associated form, namely bis(2-hydroxyethyl)ammonium oleate.

Physicochemical Analysis of Tetraethylammonium Oleate:-

The presented FTIR spectrum sufficiently confirms the formation of tetraethylammonium oleate, as the spectrum simultaneously exhibits absorption bands characteristic of the carboxylate group and the long hydrocarbon chain of the oleate anion, as well as absorption regions corresponding to the ethyl and C-N fragments of the tetraethylammonium cation.

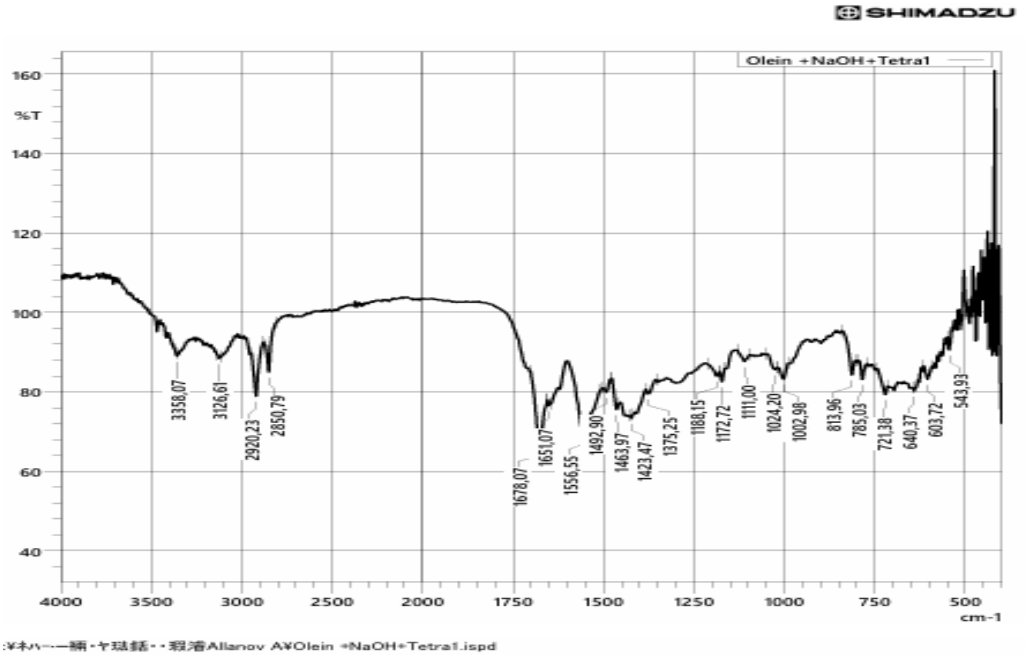

Fig. 6. FTIR Spectrum of Tetraethylammonium Oleate

In the FTIR spectrum of tetraethylammonium oleate, intense absorption bands are observed at 2920.23 and 2850.79 cm^{-1}, characteristic of the asymmetric and symmetric stretching vibrations, respectively, of -CH_2- groups in the long aliphatic chain. The absorption band at 1651.07 cm^{-1} is assigned to the stretching vibrations of the C=C bond in the oleate fragment. The most diagnostically significant features of the spectrum are the bands at 1556.55 and 1423.47 cm^{-1}, corresponding to the ν_as(COO^-) and ν_s(COO^-) vibrations, respectively, of the carboxylate anion. The Δν value between these bands is 133.08 cm^{-1}. The absence of a pronounced C=O band at ~1710 cm^{-1}, characteristic of free oleic acid, indicates the predominant conversion of the carboxyl group into the ionized oleate form. The deformation vibrations of CH_2 and CH_3 groups in the 1492.90-1375.25 cm^{-1} region, as well as the vibrations of C-N bonds and the alkyl skeleton in the 1186.15-1008.98 cm^{-1} range, confirm the presence of the tetraethylammonium cation. The intense band at 719.28 cm^{-1} corresponds to the rocking vibrations of the long -$(CH_2)_n$- chain. The obtained FTIR spectroscopic results provide scientific evidence for the formation of an ion pair consisting of an oleate anion and a tetraethylammonium cation.: - $[(C2H5)4N]+[C17H33COO]^-$

Thermal Decomposition of Tetraethylammonium Oleate Based on the Thermogravimetric Curve:-

At the initial stage, occurring in the temperature range of 20.54-160.66 ℃, the mass loss amounts to only 4.75%, which is mainly attributed to the removal of physically adsorbed moisture, residual solvent, and low-molecular-weight volatile components. Based on this, it can be assumed that the main structure of the modifier retains relative thermal stability up to approximately 160 ℃.

The main thermal decomposition is observed in the temperature range of 160.14-316.05 ℃, with a mass loss of 69.32%. This stage is associated with the thermal degradation of the tetraethylammonium cation, as well as the decomposition of the long hydrocarbon chain of the oleate fragment. For tetraalkylammonium salts, thermal decomposition depends significantly on the nature of the cation and counterion, with the main degradation generally occurring in the medium-temperature range.

In the subsequent temperature range of 316.05-601.77 ℃, an additional mass loss of 17.93% was recorded. This stage corresponds to the secondary decomposition of more thermally stable organic and carbon-containing fragments remaining after the initial degradation. At a temperature of approximately 600 ℃, about 8% of the initial sample mass remains as a residue.

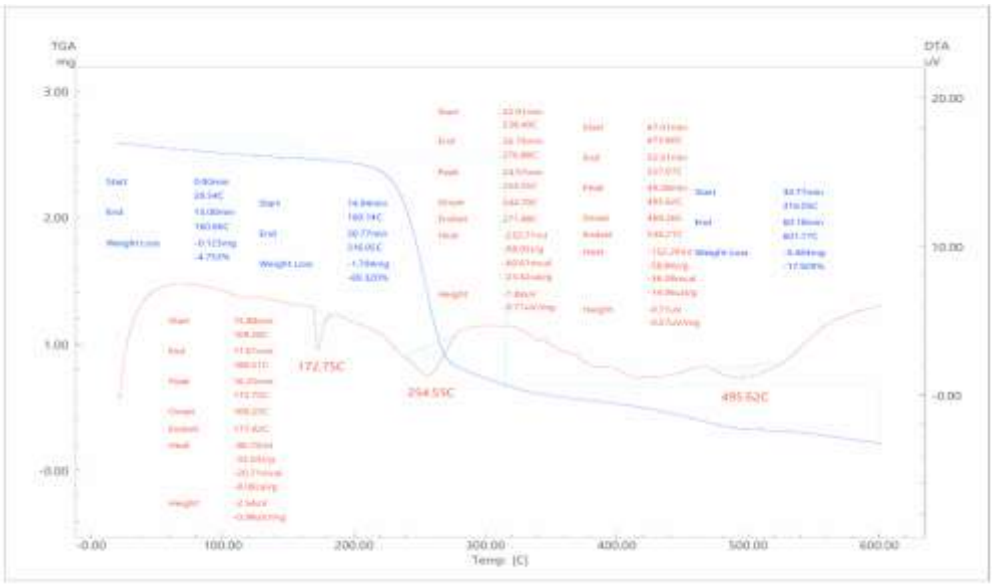

Fig. 6. Derivatogram of Tetraethylammonium Oleate

Thermal effects are observed on the DTA curve at temperatures of 172.75, 254.55, and 495.62 °C. The most pronounced thermal effect at 254.55 °C coincides with the region of maximum mass loss established from the TGA data and corresponds to the main stage of thermal degradation of the tetraethylammonium oleate structure. The thermal effect at 495.62 °C is likely associated with the secondary decomposition of the remaining thermally stable organic and carbon-containing fragments.

The TGA/DTA results showed that tetraethylammonium oleate retains relative thermal stability up to 160 °C, with the main stage of its thermal decomposition occurring in the range of 160-316 °C, while the maximum thermal effect is observed at approximately 254.55 °C. The established thermal characteristics substantiate the feasibility of using the selected relatively low-temperature processing conditions when applying this modifier for the organic modification of the SiO_2 surface.

Conclusion:-

As a result of the conducted study, effective methods for obtaining two ionic organic modifiers based on oleic acid-bis(2-hydroxyethyl)ammonium oleate and tetraethylammonium oleate-for the modification of the silicon dioxide-(IV) surface were developed, and their physicochemical properties were evaluated. It was established that bis(2-hydroxyethyl)ammonium oleate is formed as a result of an acid-base interaction between oleic acid and diethanolamine, accompanied by ionization of the carboxyl group. The optimal technological conditions for obtaining the modifier were determined as an OA molar ratio of 1:1, a temperature of 85-90 °C, and a reaction time of 2.0-2.5 h. Under these conditions, the product yield was 98.55%, the conversion of oleic acid was 99.43%, and the acid value was 0.84 ± 0.02 mg KOH/g.

It was established that variation of the OA molar ratio directly affects the composition of the product and the efficiency of the synthesis. A reduction in the amount of diethanolamine relative to the stoichiometric ratio leads to an increase in the content of free oleic acid, whereas the use of excess diethanolamine increases reagent consumption without a significant increase in product yield. From this perspective, a ratio of 1:1 was recognized as optimal in terms of rational consumption of the reaction components and ensuring a high degree of conversion. The results of studying the effect of temperature and reaction time showed that increasing the temperature does not provide additional process efficiency, which substantiates the technological feasibility of maintaining a temperature of 85-90 °C and a reaction time of 2.0-2.5 h.

Tetraethylammonium oleate was obtained by a two-stage synthesis: at the first stage, oleic acid was neutralized with NaOH to form sodium oleate, and at the second stage, the latter was subjected to an ion-exchange reaction with tetraethylammonium bromide. As a result of the process carried out at a practically equimolar OA:NaOH ratio of

1:1:1, 13.20 g of tetraethylammonium oleate was obtained with a chemical yield of 97.90%. Removal of the NaBr formed from the reaction medium made it possible to obtain the target ionic modifier in a relatively purified form.

The FTIR spectroscopic analysis confirmed the presence of carboxylate anions in both modifiers. For bis(2-hydroxyethyl)ammonium oleate, the main diagnostic features were the bands at 1594.63 and 1404.18 cm^{-1}, while for tetraethylammonium oleate, the corresponding bands were observed at 1556.55 and 1423.47 cm^{-1}, corresponding to the ν_as(COO^-) and ν_s(COO^-) vibrations. The absence of a pronounced C=O band characteristic of a free carboxyl group in the FTIR spectrum of tetraethylammonium oleate indicates the predominant conversion of oleic acid into its ionized form. The obtained results confirm the predominance of acid-base neutralization and ionic association over the amidation reaction during the synthesis.

The TGA/DTA results showed that the thermal characteristics of tetraethylammonium oleate exhibit a stepwise pattern. The minor mass loss in the temperature range below 160 ℃ indicates sufficient thermal stability of the modifier up to this temperature. The main degradation occurs in the range of 160-316 ℃, with the maximum thermal effect observed at approximately 254.55 ℃. The additional mass loss in the range of 316-602 ℃ is attributed to the further thermal degradation of organic and carbon-containing fragments remaining after the initial decomposition.

Overall, the obtained results demonstrate the possibility of producing bis(2-hydroxyethyl)ammonium oleate and tetraethylammonium oleate based on the oleate anion in high yields. The established structural and thermal characteristics confirm the formation of the ionic structure of the synthesized modifiers. The determined optimal synthesis conditions, as well as the relatively high thermal stability of tetraethylammonium oleate up to 160 ℃, scientifically substantiate the possibility of using these compounds as promising modifying reagents for the organic modification of the silicon dioxide-(IV) surface.

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