RIGA TECHNICAL UNIVERSITY
Faculty of Material Science and Applied Chemistry
Chair of Chemistry

Vitalijs LAKEVICS

SORPTION CHARACTERISTICS OF LATVIAN CLAYS

Summary of Promotion Work

Scientific supervisor
Assoc, professor, Dr.habil.chem.
A.RUPLIS

Topicality of work

In connection with achievement in the field of material science at present a particular attention is paid to the properties of materials, which are in highly dispersed state. Porous solids - sorbents and catalysts have been investigated intensively. Currently their role in reducing of contamination of environment, weathering of construction materials and cultural monuments protection is realized.

Knowledge about properties of new highly dispersed systems (HDS) is deficient. A continuous addition to the knowledge is necessary because of emergence of more new materials as well new opportunities for using well-known materials in unconventional fields.

Investigation of properties of the novel materials determined their usage boundaries and deepens the understandings about relations between their structure and specific operation properties. The application of unconventional local natural clay minerals is theoretically motivated by HDS analysis from thermodynamic aspect.

On the course of geological processes the complicated chemical and physically chemical processes take place, resulting ensue in formation of widely distributed highly dispersed sedimentary rocks - clays.

Clays possess high reserve of potentially available free surface energy. One of the simplest ways to apply this energy reserve is using clays as the sorbents: adsorption on clays occurs spontaneously. Until now sufficient attention was not drawn to this.

Only in resent years investigation of sorption properties of Latvian clays has been started and some ways of their usage have been found.

The search for the catalyst support materials is actual for improvement of synthesis methods of important medical preparations and further development of theory of catalysis, which is tightly connected with investigation of adsorption - desorption mechanism and with problem of modification of sorbents.

Scientific significance

Sorption characteristics of the Latvian clay samples from several deposits (Nicgale, Vadakste) have been determined for the first time. The obtained results widen the data base of properties of Latvian clays.

Investigation of modified samples of Latvian clays shows that Latvian clays can be practically applied in such fields as waste water treatment to eliminate the organic contaminants; vegetable oils (rapeseed and other) bleaching.

Catalytic activity of Latvian clays in the synthesis of organic compounds as demonstrated for the first time.

By acidic treatment of Latvian clays it is possible to obtain sorbents, which can be used in chromatography practice.

Determination of surface characteristics of obtained sorbents (value of specific surface area, pore distribution, cation exchange capacity) enlarges data base and lets to widen the fields of their application in sorption and catalysis.

Determination of cation exchange capacity must be specially accentuated because of significance if this characteristic in analysis of migration of different unacceptable (toxic, radioactive) admixtures in over ground and subsoil waters in normal or catastrophe created situations, it will open up the new opportunities for scientific motivated usage of sorbents for waste water treatment.

Work tasks Investigation of the sorption and catalytic properties of some Latvian clays using experimental and theoretical methods.

Particular attention should be paid to the practical usage of obtained results, which are significant for Latvian national economy and environmental protection.

Work objectives Characterization of Latvian clay (Devonian, Quaternary and Triassic deposits) sorption characteristics (value of specific surface area, pore structure, cation exchange capacity). Preparation of new sorbents from Latvian clay samples deposits (thermal and acidic treatment, treatment with organic reagents for the obtaining organoclays). Demonstration of the catalytic properties of Latvian clays.

Theoretical definition of the obtained results should be based upon modern acknowledgement and internationally accepted standards in physical and colloid chemistry including recommendation of IUPAC committee.

Review of literature

For the realization of work objectives, the respective literature has been used. Literature sources are grouped in four parts:

First articles: experimental measurements of the surface characteristics (specific surface area, pore structure, thixotropy, ion exchange capacity); field of usage (water decontamination, elimination of air pollution, rapeseed oil bleaching); reviews, doctoral theses, latest works.

Review of literature has been comprised in historical sequence. It has been attempted to group the literature sources in accordance with the most significant matter (results obtained, ideas developed).

The first articles about surface characteristics of Latvian clays have been published in 1950s of the last century (works of professor J. Eiduks). First scientific work on sorption of organic dyes as Methylene blue, fucsine and other on the samples of Latvian clays has been published in 1951. A bit later sorption of organic dyes has been used to determine the crystal structure'of Latvian clay samples. In 1973 CH3OH vapour sorption on Latvian clay samples has been measured for the first time. It has been found that along with the elevation of treatment temperature of samples their specific surface area decreases.

In the Soviet time, great attention to the sorption characteristics of Latvian clays was not paid. Only in 1991, reports started to appear about Latvian clay surface characteristics. Systematic research has been made by A. Ruplis with collaborators. The results of works were summarized in his habil. doctor's dieses in 1998. Associate professor of LU, Rolands Bumans, also was involved in these works.

Carbon tetrachloride and hexane vapour sorption isotherms have been measured to determine the specific surface area and porous structure of ciay samples. In further works, other surface parameters were determined and their changes on acidic treatment of samples different Latvian clay samples were checked. Academic E. Gudriniece proposed the idea about the rapeseed oil purification using Latvian clays. A. Ruplis has shown mat acid treated Latvian clay samples can be successfully used for the rapeseed oil decolorization. In 1999, I was also involved in the investigation of sorption properties of Latvian clays by supervising of associate professor A. Ruplis.

Great attention is paid to the determination of Latvian clay samples cation exchange capacity (CEC) by using organic dyes as Methylene blue. Methylene violet.

At the same time, it has been found that Latvian clays can be used as catalysts in the synthesis of organic compounds. Next chapter of literature review deals with different usages of Latvian clays including purification of rapeseed oil.

At the end of 90-ies in literature, reviews concerning sorption properties of Latvian clays have appeared.

At the same time academician J. Freimanis developed his investigations about organoclays on the base of Latvian clays.

Analysis of literature leads to the following conclusions: during the last years most important and most advanced ways in investigations of Latvian clay surface characteristics are:

  1)determination of clay specific surface area;
  2)investigation of clay porous structure;
  3)determination of cation exchange capacity;
  4)characteristics of organoclays;
  5)catalytic characteristics of Latvian clays;
  6)practical usage of clays in waste water treatment;
  7)application of clays in treatment of vegetable and other oils from admixtures;
  8)clays as catalysts in synthesis and reactions of organic compounds.

Nevertheless, in comparison with achievements in clay sample investigation other countries contribution of Latvian scientists in is small and studies on colloid chemical characteristics of clays are at the beginning, in spite of indigenous significance of clays in management of different processes of environmental protection, as well as in their usage in new and nontraditional branches.

RESEARCH METHODS

Vapour sorption. A complete glass adsorption device provided with mercury traps and McBain-Bakr quartz spring balance has been used in vapour sorption measurements (Fig.l). The feature of the device is in using mercury traps instead vacuum taps (8). Vacuum taps can't be used when the sorption of organic vapours is studied, because most of them can dissolve in grease of vacuum taps.

Sorption characteristics were determined using McBain-Bakr quartz spring balance. Sorption pressure was measured by U-shape mercury gauge (1). Sorption amount was measured by changes of quartz spring lengths during adsorption and desorption. Both of values have been read by cathetometer. The sensitivity of method was about 2-3 mg/mm.

To keep clear the measuring part of the device from the pump oil vapours special traps (2) were filled with liquid nitrogen were used.

A U-tube filled with Au or Cd powder or foil separated the samples from the other part of the device to avoid the sorption of mercury vapour on the samples.

Before measurements the surface of sample must be cleared from the substances adsorbed from atmosphere. It was done by using of forevacuum (12) and diffusion (14) pumps at a pressure of 1×10^{-3} mm Hg.

If it is necessary the samples can be outgased in temperatures up to 400 C. We have used temperatures not higher than 50 C, to avoid the structural changes of clay surfaces.

Equilibrium measurements were made in constant temperature. The air temperature in sorption laboratory was $25,0 \pm 0,5$ °C. In twin quartz spring balances with samples were thermostated by water thermostat at temperature of $25.0 \pm 0.1°$ C. For the sample surface area determination such substances have been used molecules of which were bound physically to the surface. After desorption the weights of the samples have been returned to the initial position.
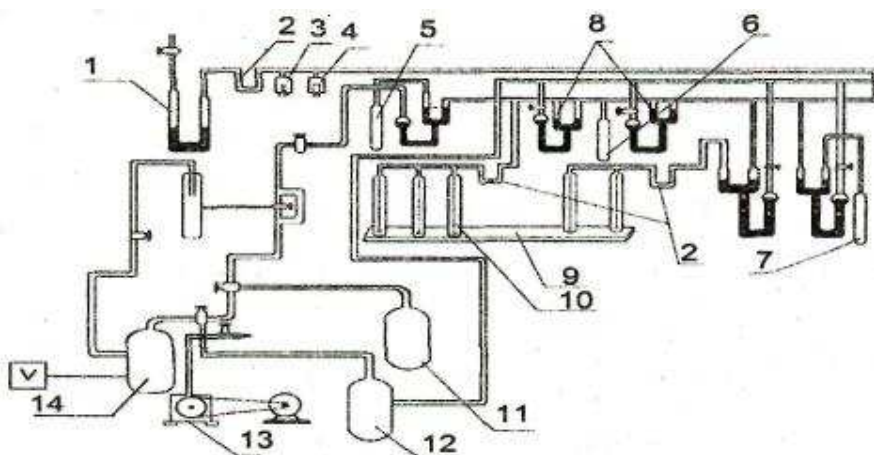
Fig.l. Scheme of the glass vacuum adsorption device with mercury taps and McBain-Bakr quartz spring balance: 1-U-shape mercury gage; 2-trap; 3,4-Manometric tubes; 5-Ampoule with methanol; 6-Ampoule with carbon tetrachloride; 7-Ampoule with n-hexane; 8-Mercury traps; 9-Water thermostat; 10-Quartz spring balances with samples; 11-Bottle; 12-Forevacuum bottle; 13-Forevacuum pump; 14-Diffusion pump.

Determination of catalytic activity A pulse microcatalytic device (Fig.2) has been used for determination of catalytic activity of Latvian clays. Catalytic conversion of 1,4-butanediol to the 2,3-dehydrofuran was realized in a small reactor (2) situated between evaporator (1) and chromatographic column (3). The carrier gas was argon.
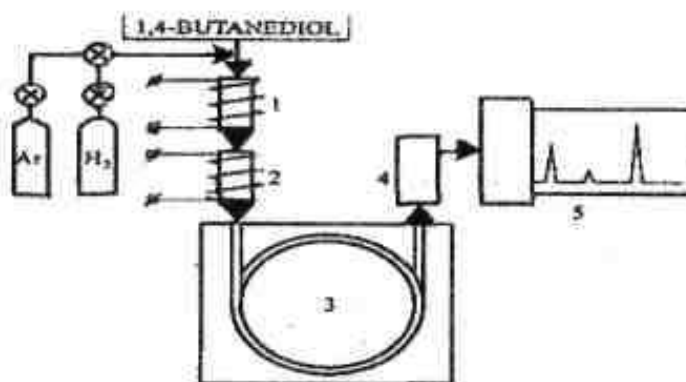

Fig.2. Scheme of the pulse microcatalytic device
1-Evaporator. 2-Reactor. 3-Chromatographic column. 4-Detector. 5-Recorders.

X-ray diffraction analysis X-ray diffraction analysis was used to determine the crystal structure of clay according to diffraction maxima. Moreover, in case of swelling clays it was used to determine of interplanar distances in clay samples before swelling and after it.

Chemical analysis Chemical analysis was used to determine the chemical composition of Latvian clays.

Sorption from water solutions For determination of adsorption isotherms of Methyl violet and Methylene blue in water solutions the Erlenmeyer flasks were used. Sorption medium was carried out by a shaker. Mixing was continued until the equilibrium state was achieved. The dye concentration changes were monitored by the photocolorimeter.

EXPERIMENTAL PART AND DISCUSSION

Latvian Devonian, Quaternary and Triassic deposit natural and modified clay samples were selected as the subjects of research. Devonian and Quaternary clays were swelling in water solutions, Triassic - swelling in water smectite type clays.

The sorption isotherms of these two groups of clay substantially differ probably due to the different sorption mechanisms. Catalytic characteristics of Latvian clays were compared with those taken from Russia deposit - Prosyanow kaolin. The sorption characteristics of natural and modified clay samples were ascertained in this investigation.

Clay samples were modified by thermal treatment (300 - 750 °C), acidic treatment and by treatment with organic reagents with the aim to obtain organoclays.

Isotherms of Carbon tetrachloride vapour sorption on the Quaternary clay samples

Carbon tetrachloride sorption isotherm on the natural clay sample from deposit Nicgale is shown in Fig.3. It is an isotherm for typical on Quaternary clays. On the X-axis the values of relative vapour pressure are plotted. On the Y-axis - the adsorption values.
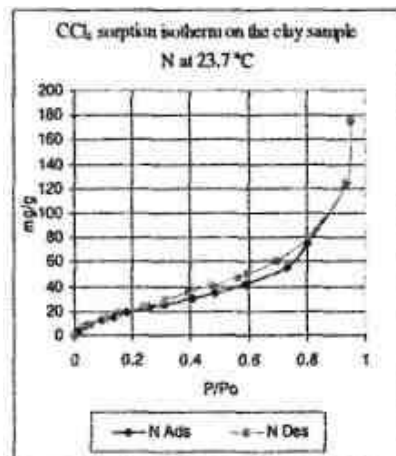

Fig.3. isotherm of Carbon tetrachloride vapour sorption on the natural clay sample from deposit Nicgale at 23,7°C.

The shape of adsorption isotherm is characteristic of multilayer adsorption (BET theory) and capillary condensation on the clay particle surface and external pore system, formed by clay particles and their aggregates. The shape of desorption isotherms is related to capillary evaporation from external pore system formed by clay particles.

The external pore system involves pores of different geometric profile: V-type, pores opened from the both sides ect. That's why hysteresis loop has been formed. The isotherms are characterized by narrow hysteresis loop. The shape of isotherms practically doesn't change in the course of thermal and acidic treatment. Only values of adsorption have been changed. The shape

of the sorption isotherms may be described as S-type (type II according to the IUPAC classification).
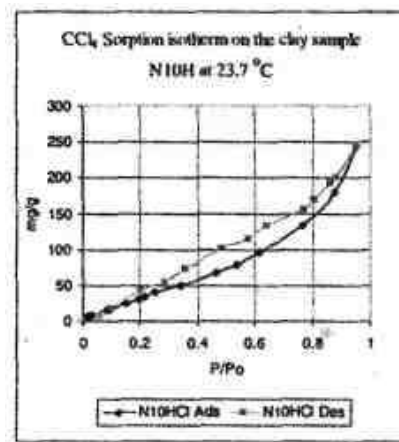

Fig.4. Isotherm of Carbon tetrachloride vapour sorption on clay sample from deposit Nīcgale at 23,7 ^{0}C, the treated by 10% HC1
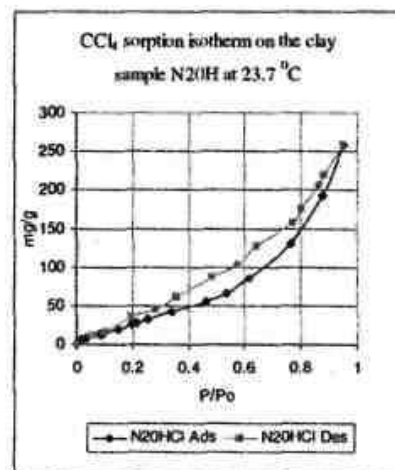

Fig.5. Isotherm of Carbon tetrachloride vapour sorption on clay sample from deposit Nīcgale at 23,7 °C, the treated by 20% HCl

As shown in Fig. 4. and 5. initial part of the adsorption isotherm burns to the linear. This observation testifies the equalization of clay surface energy.

S-type Carbon tetrachloride vapour sorption isotherm clay sample from deposit Nīcgale, modified by thermal treatment (300 - 750 ^{0}C) of the similar character have been determined.

S-type isotherms are described by the BET equation. The BET equation shows the dependence of adsorption on equilibrium pressure. On the basis of the adsorption isotherm the

energetic constants (c) monolayer capacity (a_m) and specific surface area (A) have been determined according to the BET equation.

The characteristics of investigated clays from deposit Nicgale which are calculated by the BET equation are reported in Table 1.

Table 1.

Change of a specific surface area (A) of clay samples from deposits Nicgale depending on temperature of processing and concentration of a hydrochloric acid

Sample	Energetic constants, c	Monolayer capacity a_m, mg/g	Adsorbent specific surface area A, m^2/g
N	17.75	19.4	23.8
N10H	13.5	35.2	41.4
N20H	14.1	28.1	33
N300	30.3	19.2	23.3
N500	30.1	19.0	22.7
N750	13.1	6.3	7.3

On the basis of obtained results we can conclude that specific surface area decreases with the elevation of the activation temperature. For the acid treated samples, the values of specific surface area are going through maximum as the concentration of acid increases.

Pore size distribution of the samples is important along with the value of specific surface area. To calculate the pore size distribution curves, desorption curves are preferably used, because the capillary evaporation seems to be a more significant factor than molecular desorption. The effective pore diameter (d) [cm] was calculated using a branch of hysteresis loop of desorption isotherm by Kelvin equation.

The pore volume is an important parameter. It characterizes the quantity of sorbate, which can be taken up by sorbent at vapour pressures close to saturation. The total adsorbent pore volume of powdered materials is a conventional value, because capillary condensation and evaporation occur on the external surface of adsorbent. It can be found measuring the adsorption of saturated vapour. Vapour adsorption isotherms of the clay samples in these conditions asymptotically approaches to the Y-axis, therefore the total pore volume is evaluated by measuring adsorption in pressures, lower than saturated vapour pressure. Usually the sorbate vapour pressure was chosen in the relative pressure interval between 0, 90 and 0, 99.

Our calculations have shown that the pores of definite size are not found in most of samples. The maximum was not observed on pore size distribution curves. With this Quaternary and Devonian clays differ from Triassic clays.

By the mineralogical composition all of the Latvian clays are multimineral clays, nevertheless the clays of Quaternary and Devonian deposits are nonswelling in water solutions hydromicaceous type clays. Clays from Triassic deposit are swelling in water smectite type clays.

The values of total pore volumes of clays from deposit Nicgale are shown in Table 2.

Table 2.

The values of total pore volume of clays from deposit Nicgale

Clay sample	Adsorption at equilibrium pressure P/P₀=0.95, $a_{0.95}$ (mg/g)	Total pore volume V_{max} (cm³/g)
N	175	0.110
N300	121.3	0.072
N500	134.4	0.084
N750	76.3	0.048
N10H	243.7	0.153
N20H	257.9	0.162

The pore size distribution is uniform. There is no maximum on the pore size distribution curve. The total pore volume of investigated samples can be consider as relative parameter which might be used for comparison, because the absolute pore volume values depend on sorbate vapour equilibrium pressure.

The same regularities were experimentally found for Devonian (Kuprava deposit) and Quaternary (Priekule deposit) clay samples.

Isotherms of Carbon tetrachloride and n-hexane vapour sorption on Triassic clay samples.
Characteristic example of vapour sorption on smectite clays is shown in Fig. 6.
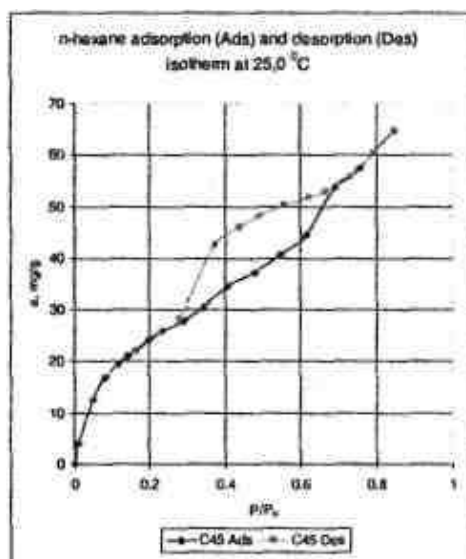

Fig.6. n-Hexane soiption isotherm on the natural clay sample C-45
from deposit Vadakste.

The n-hehane adsorption isotherm on clay sample C-45 has die S-type shape. It is similar to the adsorption isotherm for the hydromicaceous type of clays. However, desorption isotherm differs essentially from the desorption isotherm characteristic of hydromicaceous type of clays.

At a relative sorbate vapour pressure $P/P_0 = 0.3$ the smectite containing clays (Latvian Triassic clays, Vadakste deposit) are characterized by a typical slep on the desorption isotherm which is related to the capillary condensation and evaporation in the plane-parallel pore system. In this case we have to consider the internal pore system. It is formed, when smectite clays are swelling in water, when the distances between three- layer plates increase. During the drying process this structure is preserved more or less and the vapour molecule capillary condensation and capillary evaporation are observed there.

Adsorption isotherms on the modified clay samples also are the S-shape at (Fig.7 and 8).
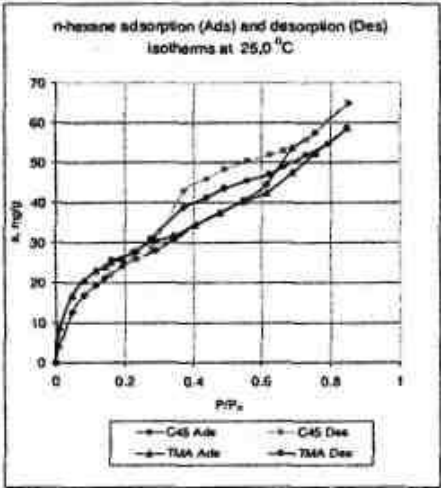

Fig.7. n-Hexane sorption isotherms on the natural and modified by TMA clay samples from deposit Vadakste.
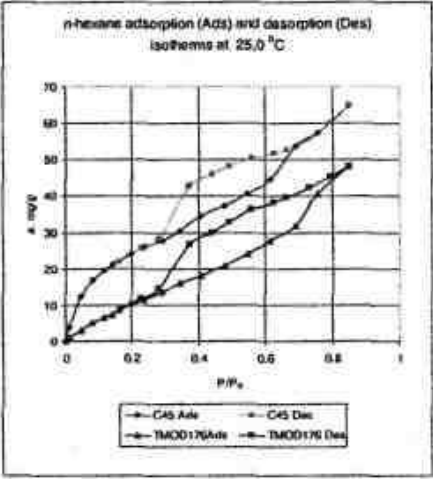

Fig.8. n-Hexane sorption isotherms on the natural and modified by TMOD176 clay samples from deposit Vadakste.

Hexane and carbon tetrachloride adsorption isotherms on natural clay C-45 sample represent themselves curves convex towards the equilibrium pressure axis in the low-pressure range (Fig. 9, 10). Such an isotherm shape is qualified for the sample specific surface area calculations according to the internationally standardized BET procedure.
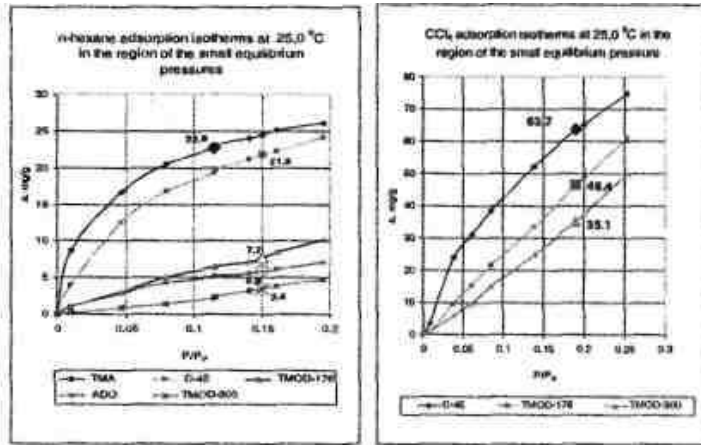

Fig. 9 *n* -Hexane adsorption isotherms at 25 °C in the region of the small equilibrium pressures.
Fig. 10. Carbon tetrachloride adsorption isotherms at 25°C in the region of the small equilibrium pressures.

Consequently, the experimental points of these isotherms fit a straight line in the BET equation coordinates within sufficiently wide range of relative equilibrium pressure ($h=P/P_0$, where P - equilibrium pressure in the given point of the isotherm; P_0 - the saturated vapour pressure of the sorbate at 25.0 °C (Fig. 11,12).
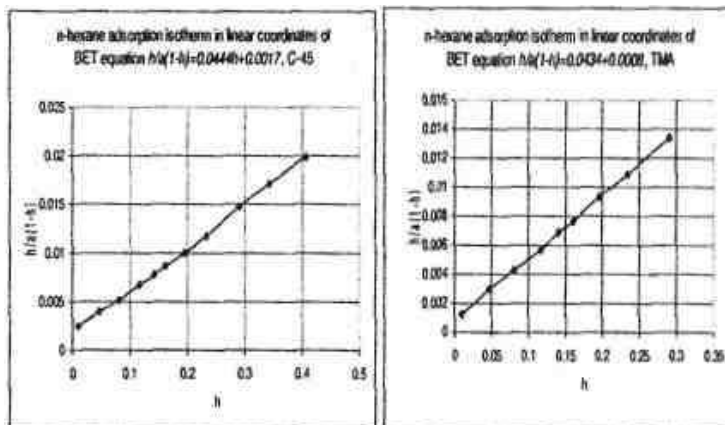

Fig. 11 n-Hexane adsorption isotherm on C-45 in linear coordinates of BET equation h/a(1-h) = 0.0444h+0.0017.
Fig. 12 n-Hexane adsorption isotherm on TMA (tetramethylammonium modified clay) in linear coordinates of BET equation h/a(l-h) = 0.0434h+0.0008.

Clay modification with organic ammonium cations produce significant changes in the nature of sorbate adsorption isotherms. Thus, the isotherms within small equilibrium pressure intervals lose out their convexity and produce nearly straight lines (Fig. 11, 12) evidencing that the clay surfaces after the modification have become energetically homogenous. According to the BET theory, the magnitudes of the vapor adsorption heats are close to the vapor condensation heat values, and such shaped isotherms, consequently, are not applicable in the calculations of the sample specific surfaces areas.

The magnitudes of the samples specific surface areas were estimated on the basis of assumption that the sorbate molecules produce a monomolecular layer at the same equilibrium pressures as those for unmodified clay C-45, e.g., when during the vapor adsorption h equals 0.15 for n-hexane and 0.19 for carbon tetrachloride (Fig. 9, 10).

Considering the isotherms of different organoclays, the sample containing tetramethylammonium cation (TMA) provides an exception. For this compound, the convex isotherm within the region of small pressures (Fig. 9) indicates somewhat larger adsorption values than for the unmodified sample C-45. The experimental data within the linearized BET coordinates also produce a straight line allowing the correct evaluation of the specific surface area value for the organoclay TMA as well (see Fig. 12 and Table 3).

As shown in Table 3, the specific BET-surface area of the unmodified Vadakste clay (C-45) and its TMA organoclay derivative are of the same order of magnitude as specific surface areas of many smectite (montmorillonite) clay samples.

Table 3.

The parameters of specific area *(A)* calculation for the organoclay samples and C-45 natural clay sample.

Samples	A, m^2 / g		BET method					
			n-C_6H_{14}			CCl_4		
	n-C_6H_{14}	CCl_4	h interval	a_m, mg/g	C	h interval	a_m, mg/g	C
[(CH$_3$)$_4$N] Br 120%	81,6	-	0,01 - 0,29	22,6	55	-	-	-
Vadakste C-45	79,1	75,2	0,01- 0,41	21,9	26,9	0,070-0,452	63,7	14,3

Samples	A, m^2/g		Extrapolation method			
			n-C_6H_{14}		CCl_4	
	n-C_6H_{14}	CCl_4	h	a_m, mg/g	h	a_m, mg/g
[(CH$_3$)$_3$ NC18H$_{37}$]Br 176%	27,8	54,1	0,15	7,7	0,19	46,4
ADO[(CH$_3$N(C$_8$H$_{17}$)$_3$]Br	21,3	-	0,15	5,9	-	
(CH$_3$)$_3$ NC$_{18}$H$_{37}$Br 300%	12,3	41,7	0,15	3,0	0,19	35,5

The modifying of clays by tetramethyl-(TMA), trimethyloctadecyl- (TMOD) and methyl-trioctyl-(ADO) ammonium bromides essentially changes the clay surface

(hydrophilic) surface is transformed into the oleophilic surface, n-hexane vapour sorption decreases in series of modified TMA>TMOD>ADO; this can be explained by cation structure (length, branching). Larger cations block up the plane - parallel pores. Carbon tetrachloride and n-hexane vapour sorption on organoclays increases in the region of larger of equilibrium pressures. It can serve as evidence that organoclays may adsorb the oleophilic molecules (petroleum, oils) from the water/oil emulsions and water solutions. Data about the carbon tetrachloride vapour sorption corroborate the possibility of organic cations to fix the structure of plane - parallel pores. The specific volumes of pores admitting the capillary condensation or evaporation processes were evaluated on the basis of the theory of capillary condensation. If the sorbent contains a plane-parallel pore system (as presumably is the case of our experiments) in which concave meniscus of sorbate can be formed, the pore specific volume V(l) may be calculated as the sorbate quantity difference Aol between the two characteristic points of the desorption isotherm — a_s (the beginning of the step on the isotherm) and a_b (the bottom point of the hysteretic loop), Therefore the total specific pore volume can be calculated as the sorbate quantity difference $\Delta a2$ between the two characteristic points of the desorption isotherm - a_2 (the upper point of the hysteresis loop) and a_b (the bottom point of the hysteretic loop). The results of calculations are shown in Tables 4 and 5.

Table 4.

Evaluation parameters of n-hexane adsorption isotherms, 25 ^{0}C

Sample code	The characteristic points of hysteresis loops								
	The upper, a_2			The step, a_s			The bottom, a_b		
	h	Sorbate specific quantity, by		h	Sorbate specific quantity, by		h	Sorbate specific quantity, by	
		Weight ,mg/g	Volume, cm^3/g		Weight, mg/g	Volume, cm^3/g		Weight ,mg/g	Volume, cm^3/g
C-45	0.69	53.6	0.0663	0.39	42.0	0.0636	0.28	28.3	0.0426
TMA	0.75	52.4	0.0793	0.39	39.0	0.0591	0.26	30.0	0.0454
TMOD-176	0.85	48.2	0.0730	0.39	28.5	0.0432	0.28	13.0	0.0197
ADO	0.70	18.7	0.0283	0.37	14.6	0.0211	0.28	8.0	0.0121
TMOD-300	0.76	35.0	0.053	0.39	20.0	0.0303	0.20	5.0	0.0076

Table 5.

Sample specific pore volumes

Sample code	Specific pore volume, cm³ /g	
	Total, *V(2)*	Of plane - parallel pores, V(l)
C-45	0.0237	0.021
TMA	0.0334	0.0137
TMOD-176	0.0533	0.0235
ADO	0.0162	0.0090
TMOD-300	0.0454	0.0227

Adsorption of Methyl violet from water solutions

Latvian Quaternary clay samples from deposit Nicgale, natural and modified by sulfuric (oxalic) acid, have been studied. The results are shown in Table 6.

Table 6.

Adsorption ability of clay samples

Sample code	Maximum value of Methyl violet adsorption, G, mg/g	Cation exchange capacity, mg-eq./g
N	14.3	0.036
N3S	9.5	0.024
N25S	5.5	0.014
N3SS	9.6	0.024
N25SS	12.0	0.03

The obtained results show that acidic treatment causes the decrease of cation exchange capacity.

Catalytic characteristics of Latvian clays

The catalytic activity of clays from the Kuprava, Nicgale and Priekule deposits and that of kaolinite from the Prosyanovo (Russia) deposit were investigated in 1,4-butanediol dehydration. Clays and kaolinite show rather high catalytic activity.

The preheating at 750 °C causes the decrease of the clay catalytic activity; on the contrary the catalytic activity of kaolinite turns out to be increased. Treatment with 18% HCl increases the activity of all the catalysts. It was found that the catalytic activity of the studied catalysts depends on their specific surface area.

CONCLUSIONS

1. Sorption characteristics of powdered Latvian and Russian clay samples have been investigated. Hydromica containing clay samples from the Nicgale, Kuprava, Priekule deposits and kaolinite from the Prosyanovo deposit clay samples were treated thermally at 300 - 750 °C. Clay samples from deposit Nicgale were treated by sulfuric, oxalic, muriatic acid (bounds of acid concentration 3-25 %). Smectite - containing clays from the Vadakste deposit were treated by tetramethyl-, trimethyloctadecyl- and methyl-trioctylammonium bromides.

2. Carbon tetrachloride adsorption-desorption isotherms or n-hexane adsorption-desorption isotherms and Methyl violet adsorption from water solutions have been measured experimentally for the surface characterization.

3. The specific surface area decrease from 23,8 to 7,3 m^2/g, when the temperature of activation is increased from 23,7 ^{0}C to 750 ^{0}C. Values of specific surface area were calculated according to the BET procedure. For the acid-treated samples, the values of specific surface area are going through maximum as die concentration of acid increases. For example, for clay samples from deposit Nicgale the values of specific surface area change from 23,8 m^2/g to 41,4 m^2/g and back to 33,0 m^2/g.

4. The cation exchange capacity is decreased for the samples treated with sulfuric and oxalic acid. Obtained results are practically applied for the sorbent optimization for rapeseed oil bleaching.

5. Generalizing the obtained hither to experimental results and using literature origins concerning the organic vapour physical adsorption on Latvian clay samples and desorption from them in isothermal conditions it is possible to make the following conclusions:

   adsorption - desorption isotherms form the closed hysteresis loops;

   adsorption isotherms of natural clay samples can be divided in two groups.

   Hydromica - containing clays (Latvian Quaternary and Devonian clay deposits) are characterized by the S-type adsorption isotherms (type II according to the IUPAC classification) and have the same shape of desorption isotherms.

   Smectite - containing clays (Latvian Triassic clay deposits) are characterized by typical slep on the desorption isotherm. Modern capillary condensation theory explains this phenomenon by die capillary evaporation from the pore system, made by the plane - parallel plates.

6. .Natural clay samples modification by acidic treatment or realization of the cation-exchange reactions in order to synthesize organoclays causes diminishing of the curvature of initial part of adsorption isotherm. The initial part of isotherm burns to the linear. Observation testifies that clay surface energy is somewhat equalized. Solid disperse materials with equalized surface energy cause interest for chromatography as sorbents or solid supports of constant phase. This offers possibility for the usage of Latvian clays in nontraditional branches.

7. The activity of the catalysts and the reaction selectivity, were proved to depend on their specific surface area. The obtained results are used further for the determination of catalytic reaction mechanism.

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