

# MODIFIED ORGANOSILICAS FOR ADSORPTION OF SOME ORGANIC ACIDS

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## Abstract

The chemical modification of silica surface by nitrogen-containing organic reagents ( $\gamma$ -aminopropyltriethoxysilane, imidazole or N-vinyl-2-pyrrolidone) and also with hexamethyl disilazane and hydrocarbon oligomers was proposed for the enhancement of adsorptive capacity of silica in respect to monocarboxylic and bile acids. The calculation of the content of protonated and deprotonated groups on the surface of synthesized organosilicas with distinguished basicity of functional groups was performed using the program GRFIT for the model of diffuse layer. The contribution of hydrophobic and electrostatic interactions to the adsorption of organic acids was revealed. It has been established that the maximum of organic acids adsorption coincides with the value of pH at which the curve of increasing concentration of anion of organic acid and the curve of decreasing concentration of protonated functional groups of aminopropyl silica are intercrossed.

The development of new methods of synthesis of adsorbents having high selectivity in relation to organic acids is an important scientific and practical problem. The inorganic carriers, first of all silicic ones, are the most perspective for preparation of adsorbents for organic acids, as they have high chemical stability, do not swell at contact with solutions, have a sufficient thermal and bacterial stability.

The surface of hydroxylated amorphous silica contains weak-acid silanols as functional groups (the constant of ionization of silanol groups is of  $10^{-7}$ - $10^{-9}$ ). Therefore the adsorption of organic acids on a surface of hydroxylated silica is insignificant.

Chemical modification of silica surface is a handy method for directional change of its adsorption selectivity. The increase of silica adsorptive capacity with respect to organic acids may be achieved by introduction of basic groups onto surface layer of silica.

In present article a chemical modeling of the basic nitrogen-containing centers of various structure on a silica surface was carried out, and the adsorption of organic acids on synthesized organosilicas was studied.

The nonporous, amorphous, pyrogenic silica - aerosil (A-300) and macroporous silica - silochrome (C-80 and C-120) were used as the starting silica material (Table 1).

The chemical reagents - trichlorosilane (TCS),  $\gamma$ -aminopropyltriethoxysilane (APTES), 2,4,6-trichloro-1,3,5-triazine (TAZ), imidazole (Im), N-vinyl-2-pyrrolidone (VP), salicylic (Sal), benzoic (Benz),  $\alpha$ -picolinic (Pic), deoxycholic (DCA), glycocholic (GCA) and taurocholic acids (TCA) were used without additional purification.

The specific surface area of studied siliceous adsorbents was determined by two methods: 1) by the low temperature nitrogen desorption method using a GH-1gasometer; 2) from the data of methanol adsorption obtained in vacuum adsorptive laboratory equipment with spring quartz balance [1].

The concentrations of functional groups of hydroxylated silicas and silicas modified with basic groups were determined by potentiometric titration of weighted

portions [2]. Weighted amounts were 0.1 g, titrant was 0.1 M NaOH (or 0.1 M HCl) + 0.1 M NaCl; solution volume was 30 ml, contact time for silicas modified with basic groups was 4 h and that for hydroxylated silicas was 24 h. The correction on solubility of silica for equilibrium solutions (at  $\text{pH} > 9$ ) was introduced [3]. In case of hydroxylated silicas the titration was performed in dehydrated ethyl alcohol [4]. The constants of ionization of functional groups of silicas were calculated from results of potentiometric titration using the Henderson-Hasselbach equation:  $\text{pK} = \text{pH} + \lg(1 - \alpha) / \alpha$  for various degrees of ionization of surface  $\alpha$  [2,3,5]. The apparent constants of acidity  $\text{pK}_a$  were determined by extrapolation for  $\alpha \rightarrow 0$ .

The IR spectra of compacted plates of hydroxylated and modified silicas were recorded in the vacuum cell having  $\text{CaF}_2$  windows using the spectrophotometer IKS-29 over the interval from 4000 to  $1200 \text{ cm}^{-1}$ .

Thermal destruction of modified silicas was studied by use of thermal gravimetric analysis (Thermal analyzer Q-1500 D, conditions:  $T = 25-1000^\circ\text{C}$ ,  $\text{DTA} = 100 \text{ mV}$ ,  $\text{DTG} = 250 \text{ mV}$ ,  $\text{TG} = 20-50 \text{ mg}$ ,  $V = 10^\circ\text{C/min}$ ). The accuracy of determination of functional groups concentration was 5 % [6].

The adsorption of organic acids has been investigated under static conditions at  $20 \pm 1^\circ\text{C}$ . Exactly 0.05 g of silica was placed to 10 ml of acid solution (1 mmol of benzoic or  $\alpha$ -picolinic acid, 0.5 mmol of salicylic acid or 0.1 mmol of deoxy-, glyco- and taurocholic acid). Bile acids are not enough and slowly water-soluble, therefore their solutions were prepared by long heating and stirring (at low temperature) of the weighted amounts. In such a way solutions of bile acids with concentration of 0.1 mmol which is in 10-100 times less than critical concentration of micelle-formation were prepared [7]. Then the necessary pH value (in interval from 2 to 8) was positioned. The suspensions of hydroxylated and modified aerosils were at stirring during 1 h, and the suspensions of modified silochromes were under stirring for 24 h. Beforehand it was established that this time is sufficiently for achievement of equilibrium. Then pH value of solution was measured using universal ionometer EV-74. Further the suspension of silica was centrifuged (2000 rpm, 5 min), and equilibrium solution was separated. Afterwards the concentration of organic acid was determined by use of the spectrophotometer Specord M-40. The values of acid adsorption were determined as difference of acid concentrations in solutions before and after adsorption.

Organic amines belong to compounds having pronounced basic properties. The basicity of amines depends on structural factors and electron effects of substitutes. The aliphatic amines can be arranged in a series depending on their proton-acceptor ability:

primary amines < secondary amines < tertiary amines.

The basicity of heterocyclic amines containing nitrogen atom in cycle is less than that of aliphatic amines. Amides of acids are very weak bases. The addition of proton to amides takes place as a rule through the oxygen atom [8]. It may be expected that the nitrogen-containing groups of different structure grafted to silica surface will increase not only the affinity of organic acids to silica surface but also will determine the value and pH interval of adsorption depending on their structure.

In order to verify this supposition we have synthesized three silicas chemically modified by:

- aliphatic primary amino groups;
- functional groups containing five-member heterocycles with two nitrogen atoms;
- amide groups which are in five-member heteronuclear compounds.

Realization of chemical reactions onto surface layer was proved by IR spectral control of all steps of silica modification.

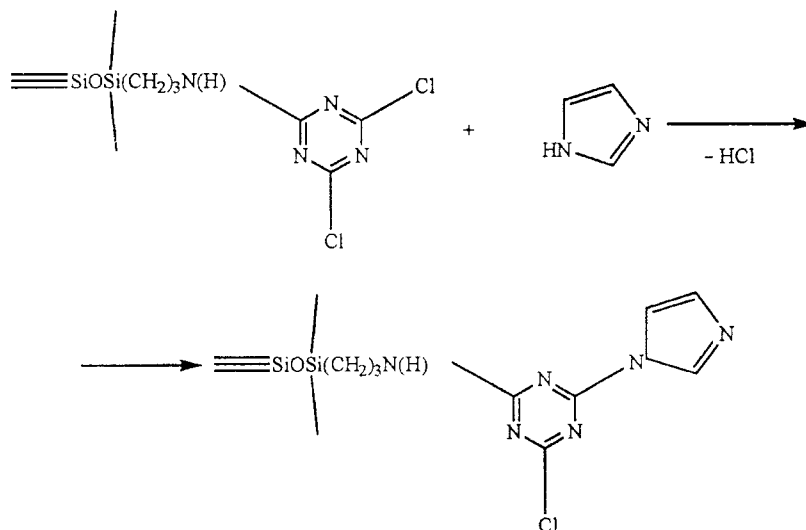
For synthesis of organosilica with aliphatic primary amino groups the known reaction of interaction of surface silanol groups with  $\gamma$ -aminopropyltriethoxysilane was chosen. The chemical fixation of aminopropyl groups on a silica surface was fulfilled in

conditions excluding formation of oligomers. The subsequent hydrolysis of ester groups and thermal treatment of modified silica at 150 °C have ensured the formation of additional siloxane bonds on the silica surface [9]. The obtained organosilica contains only aminopropyl groups. The basic physicochemical parameters of aminopropylsilica are presented in the Table 1.

**Table 1**  
Physicochemical parameters of hydroxylated silicas and silicas modified by basic or hydrophobic groups

Sorbent	Starting silica	Specific surface area, m <sup>2</sup> /g	Functional group	Characteristic absorption bands in the IR spectrum (cm <sup>-1</sup> ) and their interpretation	Concentration of functional groups, mmol/g		Ionization constant pK <sub>a</sub>
					pH-titration	DTG-analysis	
1	Aerosil A-300	300	Silanol	3750 ν(Si-OH)	1.00	0.97	8.68
2	Silochrome C-120	118	Silanol	3750 ν(Si-OH)	0.40	0.43	7.85
3	Aerosil A-300		Pyrrolidyl	2990, 2955, 2930, 2885 ν(C-H); 1670 ν(C=O), 1490, 1480 ν(lactam ring); 1420, 1365 δ(C-H)	0.98	1.13	3.75
4	Silochrome C-120	112	Imidazolyl	1570 ν(C=C); 1445, 1545 ν(C-N) imidazole ring; 1470 δ(N-H) for secondary amino groups	0.25	0.22	4.55
5	Silochrome C-120	116	Aminopropyl	3375, 3315 ν(N-H); 2983, 2940, 2880 ν(C-H); 1590 δ(N-H); 1460, 1425, 1380 δ(C-H)	0.25	0.24	6.90
6	Aerosil A-380	375	Aminopropyl	3375, 3315 ν(N-H); 2983, 2940, 2880 ν(C-H); 1590 δ(N-H); 1460, 1425, 1380 δ(C-H)	1.52	1.28	6.80
7	Silochrome C-80	78	Trimethylsilyl	2970, 2930 ν(C-H)	-	0.3	-
8	Silochrome C-80	78	Hydrocarbon oligomer, trimethylsilyl	2970, 2920, 2870, 2860 ν(C-H)	-	0.5	-

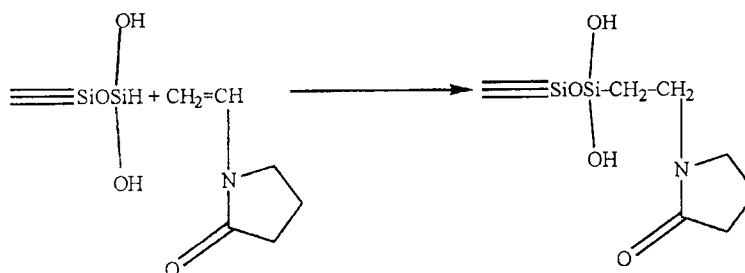
The method of chemical assembly was applied for preparing of organosilica containing five-membered heterocycles with two nitrogen atoms. Imidazole was used as bonded functional compound. Chemical immobilization of imidazole on a silica surface was carried out in three stages [10]. The first step is modification of silica surface by aminopropyl groups as described above. The second step is chemical interaction of surface aminopropyl groups with 2,4,6-trichloro-1,3,5-triazine. The chemical interaction of aminopropyl groups of modified silica with 2,4,6-trichloro-1,3,5-triazine was carried out with a yield of 100 %. At last the third step is the interaction between the silica modified by 2,4,6-trichloro-1,3,5-triazine and imidazole with subsequent hydrolysis of the third chlorine atom of symm.-triazine molecule:



This reaction has 100 %-yield as well. Thus, as a result of chemical assembly, the silica surface modified in three steps contains only imidazole groups (Table 1).

For fixation of amide groups on silica surface the solid-phase hydrosilylation method was used. N-vinyl-2-pyrrolidone was used as nitrogen-containing reagent. The chemical immobilization of N-vinyl-2-pyrrolidone has been fulfilled in two steps. The interaction between silanol groups and trichlorosilane tends to chemical bonding of silicon-hydride groups onto silica surface [11]. The obtained hydride silica was subjected to hydrolysis.

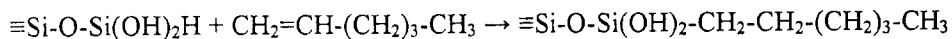
Hydrolysis of the surface chlorosilyl groups was undertaken to prevent the formation of hydrogen chloride and /or hydrochloric acid during the subsequent reaction of N-vinyl-2-pyrrolidone solid-phase hydrosilylation. Hydrogen chloride and hydrochloric acid promote side processes, such as acidic hydrolysis of silicon-hydride groups, hydrolysis and dimerization of N-vinyl-2-pyrrolidone [12]. Chemical reaction between silicon-hydride groups of hydride silica and N-vinyl-2-pyrrolidone was carried out without solvent and catalyst:



The polymerization of N-vinyl-2-pyrrolidone is a side reaction that takes place during the solid-phase thermal hydrosilylation. Formed polymer is adsorbed on the surface of hydride silica [13].

The synthesis of hydrophobic silica with trimethylsilyl groups was carried out in one step by reaction between free silanol groups of silica surface and saturated vapor of hexamethyldisilazane [9].

The preparation of hydrophobic silicon dioxide with hydrocarbon groups onto surface layer consists of four stages. The first step is the modification of silica surface by  $\equiv\text{Si-H}$  groups as described above. Then the addition of 1-hexene to surface of hydride silica (the solid-phase hydrosilylation) was fulfilled:



This reaction was effected at high pressure of reagent in stainless steel autoclave at 300 °C for 3 h without catalyst and solvent. Obtained organosilica was subjected to hydrolysis. At last the interaction of formed silanol groups with hexamethyldisilazane (endcapping) was carried out [9].

The synthesized organosilicas with basic nitrogen-containing and hydrophobic groups have high hydrolytic, chemical and thermal stability. They withstand prolonged contact with water and organic solvents (toluene, dioxane, benzene) in the Soxhlet apparatus and do not destroy under contact with mineral acids. The thermal destruction of modified layer of silica in air and in vacuum begins at 250 and 400 °C, respectively.

Some physicochemical parameters of silica modified by basic and hydrophobic groups are presented in the Table 1. The specific surface area of silicas during modifying regular decreases. The values of constants of ionization of silanol groups of initial silicas are according to literary data [14].

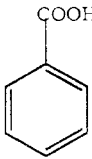
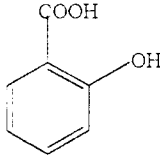
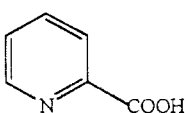
Constants of ionization of nitrogen-containing basic groups of modified silicas increase in sequence: aminopropyl > imidazolyl > pyrrolidyl. Constants of protonization decrease in the same one. As we supposed, the amide groups fixed on silica surface have the least basicity. The basicity of amide groups chemically immobilized on a silica surface is higher than that of aliphatic ones. It is slightly higher than the basicity of starting N-vinyl-2-pyrrolidone. It is known that the strengthening of basic properties of amide nitrogen can achieve by replacement of hydrogen atoms of amino group on methyl groups [8]. Besides the basicity of cyclic amides is higher than aliphatic ones. An increase of basicity of grafted amide groups in comparison with basicity of the starting modifier (N-vinyl-2-pyrrolidone), apparently, is caused by replacement of unsaturated vinyl group which is one of substituents at nitrogen atom in N-vinyl-2-pyrrolidone molecule on  $\text{CH}_2-\text{CH}_2$  - group of the silica surface as a result of solid-phase hydrosilylation reaction.

The basicity of grafted aminopropyl ( $\text{pK}_a = 6.90$ ) and imidazolyl groups is lower than that for aliphatic amines ( $\text{pK}_a = 10.7$ ) and starting imidazole ( $\text{pK}_a = 7.03$ ). The decrease of basicity is typical for functional organic groups bonded on silica surface. It is caused by introduction of the massive substituent (silica surface) in structure of functional reagent.

The adsorption of some monocarboxylic (benzoic,  $\alpha$ -picolinic and salicylic) and bile (deoxycholic, glycocholic and taurocholic) acids on a surface of starting hydroxylated silicas and synthesized organosilicas with basic or hydrophobic groups (Table 1) was investigated. Determination of organic acid concentrations in solutions before and after adsorption has been carried out by a spectrophotometry (on absorption of acids in UV region). Dependence of absorption spectra of acid solutions on pH previously was investigated. It has been established that the position and the intensity of absorption band maximum change from 230 nm ( $\epsilon$  11600) to 224 nm ( $\epsilon$  9000) for benzoic acid in interval of pH from 2 to 8. The alteration of maximum position from 303 nm (pH 2) to 296 nm

(pH 4-8) in the absorption spectrum of salicylic acid is observed. In this case the absorption band intensity remains practically constant,  $\epsilon$  3500. The absorption band at 264-265 nm in the spectrum of  $\alpha$ -picolinic acid is observed. Its intensity changes depending on pH. It is  $\epsilon$  800 at pH 3 (zwitter-ion exists mainly in solution) and  $\epsilon$  450 at pH 8 that corresponds to absorption of anion. The obtained data are in good agreement with literary ones. The concentration of bile acids was determined by method described in [15]. Chosen organic acids distinguish in values of ionization constants (Table 2). Figure 1 presents the distribution diagrams of acid-base forms of these organic acids in dependence on pH.

**Table 2**  
Some physicochemical properties of organic acids

Acid	pKa	lgK <sub>o/w</sub>
 benzoic	4.00 (COOH)	1.97
 salicylic	2.9(COOH) 13.1 (OH)	2.24
 $\alpha$ -picolinic	1.07 (COOH) 5.25 (NH <sup>+</sup> )	-1.98 (pH 2.0) -1.50 (pH 7.4)

The diagrams show that salicylic acid is present in a solution practically completely as anion within pH interval from 2 up to 8. Benzoic acid exists as both neutral form and anion. The concentration of anion of benzoic acid in solution becomes larger than neutral form at pH > 4.  $\alpha$ -Picolinic acid is mainly as zwitter-ion. The anion of  $\alpha$ -picolinic acid appears in solution at pH > 5. Thus, we had a good chance to compare the interaction of different form of organic acids (neutral molecule, zwitter-ion and anion) with silica surface.

The results of study of organic acids adsorption on starting and modified silicas are presented in Figs. 2-4. Benzoic and  $\alpha$ -picolinic acids practically are not adsorbed on a surface of initial silica. The change of their concentration in a solution after adsorption does not exceed an error of determination by spectrophotometric method. The adsorption of salicylic acid on hydroxylated silica is insignificant (up to 8 % of initial concentration). It does not practically depend on pH of initial solution. The anion concentration increases and neutral form decreases in initial solution of salicylic acid at pH > 2. The adsorption of salicylic acid decreases practically to zero at more high pH values when the dissociation of silanol groups of silica surface begins. The electrostatic repulsion prevents the adsorption. Apparently the adsorption of salicylic acid is conditioned by hydrophobic interactions.

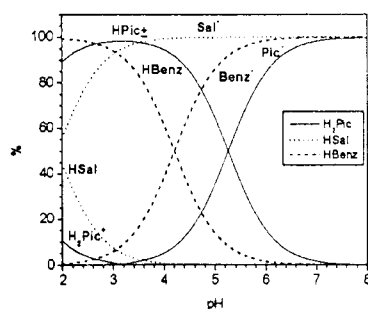


Fig.1. Distribution diagrams of benzoic, salicylic, and  $\alpha$ -picolinic acids.

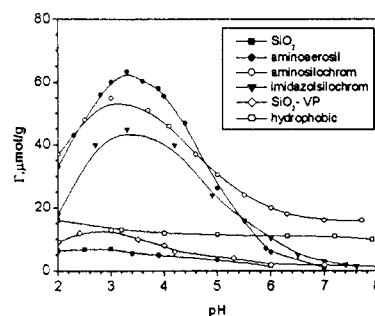


Fig.2. Adsorption of salicylic acid onto modified silica surfaces as a function of pH.

The hydrophobicity degree of molecule can be characterized by the constant of distribution between apolar solvent (*n*-octanol is the most frequently used) and water [16]. The salicylic acid is characterized by a small solubility in water and high constant of distribution in octanol/water system ( $P_{o/w} = 172$ ) in comparison with related compounds as a result of formation of intramolecular hydrogen bond [17]. It may suppose that what is known "hydrophobic expulsion" of molecules of salicylic acid occurs during adsorption from aqueous solution. The adsorption on solid surface is more preferable than the energy unfavourable solvation. Benzoic acid is not adsorbed on the silica surface despite the fact that it is in molecular form up to pH 4. Probably, the aqueous environment for benzoic acid molecules is more "preferable". The solubility of benzoic acid is better than that of salicylic one. The constant of distribution in octanol/water system ( $P_{o/w} = 74$ ) is essentially lower for benzoic acid [18].  $\alpha$ -Picolinic acid is characterized by some smaller constants of distribution in octanol/water system. It is  $\lg P_{o/w} = -1.98$  for zwitter-ion at pH 2 and  $\lg P_{o/w} = -1.50$  for anion at pH 7.4. The hydrophobic nature of adsorption of salicylic acid on a surface of high disperse silica is confirmed by the fact that only salicylic acid is adsorbed in noticeable quantity (larger than on starting silica) on silica modified by trimethylsilyl groups (hydrophobic silica). Benzoic and  $\alpha$ -picolinic acids practically are not adsorbed on the surface of hydrophobic silicon dioxide.

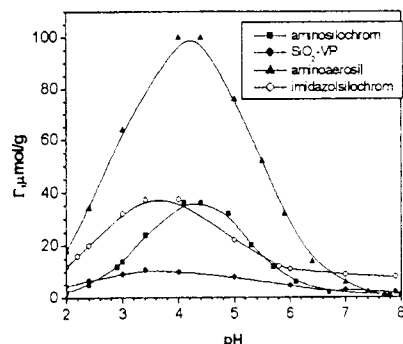


Fig.3. Adsorption of benzoic acid onto modified silicas as a function of pH.

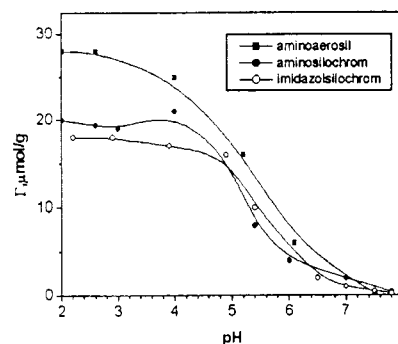


Fig.4. Adsorption of  $\alpha$ -picolinic acid onto modified silicas as a function of pH.

Salicylic and benzoic acids are adsorbed better on the silica surface modified by N-vinyl-2-pyrrolidone. The basic properties of amide groups of immobilized N-vinyl-2-pyrrolidone are not high. We have calculated the content of protonated and deprotonated functional groups on the silica surface using the program GRFIT for the model of diffuse layer [20]. It has been established that almost all pyrrolidyl groups at  $\text{pH} > 2$  are deprotonated and neutral. Therefore we have supposed that the adsorption of anion of salicylic acid which predominates in the solution at  $\text{pH} > 2$  and also the adsorption of neutral form and anion of benzoic acid depends not on electrostatic interactions but the hydrophobic ones as probably in the case of starting silica. The hydrophobicity of silica modified by N-vinyl-2-pyrrolidone is higher than that for hydroxylated silicon dioxide.

The adsorption of organic acids is much higher for silicas containing electron donor aminopropyl or imidazolyl groups. It should be noted that the adsorption on surface of silochrome containing aminopropyl groups is slightly smaller than that on the surface of aminopropylaerosil. However, it is possible to explain by smaller concentration of aminopropyl groups per unit of the surface and by smaller value of the specific surface area of silochrome compared with aerosil.

The dependence of adsorption of benzoic and salicylic acids on pH is a curve with maximum. Its position depends on nature of donor groups of adsorbent and monocarboxylic acid. It is due to distinction of constants of acidic dissociation of benzoic and salicylic acids, and also with distinction of constants of protonization for aminopropylsilica and silica modified by imidazole (Table 1). Protonated aminopropyl groups dominate on a silica up to pH 5 and protonated nitrogen atoms of imidazole prevail up to pH 3.5 as follows from calculation performed by the program GRFIT. Salicylic and benzoic acids at these pH exist in solution as anions, and  $\alpha$ -picolinic acid is as zwitter-ion. The electrostatic attraction facilitates adsorption of acid anions on the surface of silicas modified by electron donor functional groups. This interaction for  $\alpha$ -picolinic acid apparently is weaker because the negative and positive charges in zwitter-ion are close from each other. Thus, the attraction of differing charges is probable as well as the repulsion of the same ones.

Figure 5 presents curves of acid-base forms distribution for salicylic acid and those for protonated and deprotonated aminopropyl groups of aminopropylaerosil surface as a function of pH. The curve of pH-dependence of salicylic acid adsorption is given also.

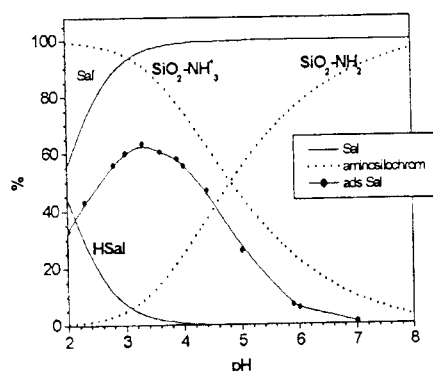


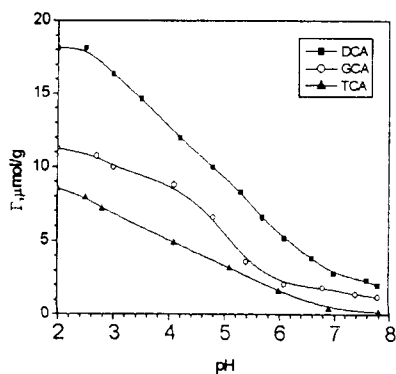
Fig. 5. Distribution diagrams of protonated and neutral aminogroups onto aminosilochrome surface, salicylic acid in solution and % of salicylic acid adsorption as a function of pH.

The maximum of acid adsorption practically coincides with pH value, at which curve of increasing concentration of anion and curve of downward concentration of

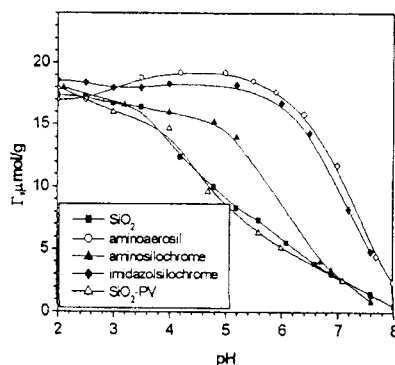


protonated surface aminopropyl groups are intercrossed. It testifies to determining role of the electrostatic contribution in adsorptive interaction.

All investigated bile acids (deoxycholic, DCA, glycocholic, GCA, and taurocholic, TCA, acids) are adsorbed on a surface of initial high disperse silica. The dependence of adsorption of bile acids on pH of aqueous solutions is presented in Fig. 6. As the pH of solution increases, the adsorption of bile acids decreases. The adsorption of bile acids at the same pH diminishes in sequence: DCA > GCA > TCA. In this sequence the solubility of acids and, hence, their tendency to hydration in aqueous solution increases. The decrease of adsorption of bile acids coincides with the reduction of quantity of nondissociated silanol groups and part of bile acids in molecular form. We have determined the dissociation constants of bile acids by potentiometric method for aqueous solution with ionic strength, which is near to 0. The pK values decrease in the same sequence: 5.6 for DCA, ~3 for GCA and ~2 for TCA.



**Fig. 6.** Adsorption of bile acids onto highly disperse silica as a function of pH.



**Fig. 7.** Adsorption of deoxycholic acid onto modified silicas as a function of pH.

On the basis of these data we have supposed that bile acids are adsorbed mainly in molecular form on nondissociated silica surface forming adsorptive complexes of composition ( $\equiv\text{Si-OH-HCA}$ ). The adsorption curve of bile acids has been calculated using the program GRFIT. It appeared that the calculated curve and experimental one do not coincide. The better correspondence is observed with the formation of complex ( $\equiv\text{Si-OH-CA}^-$ ) between silanol groups and anion of bile acid also. Despite of the increase of concentration of anion with pH increasing, the adsorption of bile acid decreases. It is associated with the appearance and the accumulation of negative charges on surface as a result of the dissociation of silanol groups. Motive power of adsorption, apparently, is the "hydrophobic expulsion" of molecules of bile acids from a solution. The adsorption on silica surface is energy more favourable than solvation in aqueous solution. However, it does not exclude the fact that adsorptive complex has formed as a result of hydrogen bonds between silanol groups of surface and suitable functional groups of bile acids. The introduction in molecule of cholic acid of such substituents as glycine or taurine results to increase of solubility of bile acid, that is, to decrease of hydrophobicity. Indeed, the investigated acids are characterized by different values of the constants of distribution between n-octanol and water:  $\lg P_{o/w}$  is 4.7-4.2 for DCA, 2.28-1.89 for GCA and 2.06-1.59 for TCA. The values of distribution coefficients estimated with various methods by authors of the program ChemDraw are presented. From all bile acids investigated by us deoxycholic acid is the most weak and hydrophobic. Apparently, therefore it is adsorbed better than other bile acids. The hydrophobic character of adsorption of bile acids is

confirmed by results of the study of influence of ionic strength on adsorption value. The adsorption of DCA from solution in 0.05 M NaCl in acid region increases practically up to 100 %. Then the adsorption value (after pH > 5) becomes less than it from solutions with ionic strength ~ 0. The addition of electrolyte results to the enhancing of the "hydrophobic expulsion" from solution (effect of salting out). Therefore the molecular form of bile acid is adsorbed better from electrolyte solution. The corresponding salts of bile acids are much better dissolved in water and are better solvated. Therefore bile acids as anions are worse adsorbed on a silica surface preferring an aqueous environment.

On the basis of obtained data we have assumed that the adsorption of bile acids would increase by use of adsorbents with electron donor groups on a surface which have tendency to the protonization. The adsorption of deoxycholic acid on the surface of silicas modified by aminopropyl-, imidazolyl- and pyrrolidyl groups was studied. The introduction of electron donor groups tends to increase of adsorption and expansion of pH interval in which it was carried out (Fig. 7). The calculated concentrations of the protonated and neutral groups of amino- and imidazole-containing silochromes were compared with values of deoxycholic acid adsorption on its surfaces. It appeared that the adsorption of deoxycholic acid on the surface of imidazole-containing silica is observed even in that pH region where the positive charged functional groups of surface is absent completely. Apparently, the surface of silochrome as a result of modification by imidazole becomes more hydrophobic. It results to increase of adsorption of deoxycholic acid. The modifying of silica surface by N-vinyl-2-pyrrolidone practically does not influence on value of deoxycholic acid adsorption.

It should be noted that the adsorption of deoxycholic acid also increases on the surface of hydrophobic silicas modified by trimethylsilyl groups or hydrocarbon oligomers as compared with adsorption on starting silica.

Thus it has been shown that the modification of silica surface with electron donor or hydrophobic functional groups increases its adsorptive capacity in relation to monocarboxylic and bile acids. The role of hydrophobic and electrostatic interactions is revealed at adsorption of organic acids on a surface of hydroxylated silicas and silicas modified by nitrogen-containing basic groups. It has been established that the contribution to adsorption of electrostatic interactions between anions of organic acids and protonated functional groups of the surface of organosilicas rises as the proton acceptor ability of functional groups increases.

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