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The nature of the binding of high-molecular weight aminoammonium and quaternary ammonium salts with the amorphous silica surface

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Abstract

The adsorption of high-molecular weight aminoammonium salt $(C_{10}H_{21})_2N(CH_2)_2N(C_{10}H_{21})_3I$ and quaternary ammonium salts with different structure of hydrophilic and hydrophobic areas: $(CH_3)(C_{10}H_{21})_2N(CH_2)_2N(C_{10}H_{21})_3I_2$, $(C_{10}H_{21})_3N(CH_2)_6N(C_{10}H_{21})_3I_2$ and $(C_2H_5)_4NBr$ on amorphous silica (SG) has been investigated. The surface hydrate coating parameters of modified SG have been studied by the ^1H NMR spectroscopy technique applied to the frozen suspensions. The data obtained were used for identification of the nature of the modifying agent binding with SG surface. It was shown that beside dipole–dipole intramolecular dispersive interaction plays an essential role in high-molecular weight salts immobilization on SG surface. The binding of aminoammonium salt with the surface is also a result of hydrogen bound complexes formation between ternary amine nitrogen of salt and surface hydroxyl group. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Quaternary ammonium salts; SG; Binding water; Nuclear magnetic resonance

1. Introduction

Silicas (SG) modified by adsorption of high-molecular weight aminoammonium salt $(C_{10}H_{21})_2N(CH_2)_2N(C_{10}H_{21})_3I$ (I) and quaternary ammonium salts $(CH_3)(C_{10}H_{21})_2N(CH_2)_2N(C_{10}H_{21})_3I_2$ (II), $(C_{10}H_{21})_3N(CH_2)_6N(C_{10}H_{21})_3I_2$ (III) (QAS) were used for the preconcentration and determination of heavy metal traces in water [1,2]. The chemical-analytical properties of such SG do not practically differ from the properties of sorbents prepared via covalent grafting of modifying agent. This phenomena may be a result of strong QAS binding with SG surface and is an object of discussion for today.

The adsorption of high-molecular weight compounds onto SG may be accompanied by significant changes in the structure of the surface hydrate coating, because one molecule of such

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reagent can remove more than one water molecule from the surface [3–7]. If the free energy of interaction of the adsorbate molecules with binding water molecules or active centres of SG surface is low the changes in the structure of hydrate coating of SG are insignificant. In this case the molecules of modifying agent are concentrated on the outside of hydrate coating. When the free energy of such interaction is commensurable with the free energy of binding water intramolecular interaction, then partial removal of the weakly binding water from the surface will take place. If the free energy of one is higher than the free energy of interaction of binding water with the surface, then also the strongly binding water is particularly removed from hydrate coating. The strength of modifying agent binding with SG surface can be estimated on the basis of such changes [7].

One of the most convenient methods to study the structure of hydrate coating of SG is the registration of ^{1}H NMR spectra of silicas frozen suspensions [8]. Because the free surface energy of water molecules in the vicinity of the adsorbent/water interface is reduced owing to adsorption interaction, the water present at this interface freezes at temperature $T < 273$ K. The water subjected to a stimulated action of the adsorbent surface is in a quasi-liquid state and is observed in the ^{1}H NMR spectrum as a relatively narrow signal. At the same time the signal of crystalline ice as far as hydroxyl groups of the surface are not observed because of small (up to 10^{-6} s) times of transversal relaxation of protons in solids [9,10]. On the basis of intensity of ^{1}H NMR signal of water registered during a freezing–thawing process the thickness of the layer of non-frozen water may be determined. Earlier this method was used to study the nature of protein hydrolysate interaction with amorphous silica surface [11].

The aim of the present paper is the investigation of the nature of QAS binding with SG surface using the ^{1}H NMR spectroscopy technique applied to the frozen suspensions. QAS with different structures of hydrophilic and hydrophobic areas (I–III) and short chain quaternary ammonium salt $(C_2H_5)_4NBr$ (IV) were studied for these purposes.

2. Experimental

2.1. Materials

Water was purified according to Ref. [12]. The I-III with the substance content more than 95% were synthesised according to [13]. The IV was of analytical grade. The amorphous SG (A 300 Kalush, Ukraine) was used without additional purification. The aqueous suspensions were prepared by adding of different portions of water to fixed amount of nonmodified silica or SG modified with I-III (I-SG-III-SG). I-SG-III-SG were prepared by adsorption of water unsoluble I-III from hexane–toluene (1:1) mixture. The sorbents were dried at 353 ± 5 K to evaporate the solvents from SG surface. The silica loaded with IV (IV-SG) was obtained by adsorption from aqueous solutions. The samples of SG with zero amount of I-IV were prepared under the same conditions, respectively.

2.2. Apparatus

^{1}H NMR spectra of binding water were registered on a high resolution spectrometer Bruker WP-100 SY (frequency 100 MHz; transmittance 50 kHz). A Bruker VT-1000 temperature controller was utilised to control the temperature in the detector up to ± 1 K. The intensity of the signal of non-freezing water was determined by an electronic integrator to an accuracy of ± 10%.

2.3. Procedures

Batch technique was used for the investigation of I-III adsorption onto SG. The value of adsorption was calculated using the following equation: $a = (C_i - [C]) \cdot V/m$, where a is the value of adsorption (mol g^{-1}); C_i, $[C]$ are initial and equilibrium concentration of QAS (mol l^{-1}) in hexane–toluene solution respectively; V is the volume of solution (l); m is the mass of the sorbent (g). The equilibrium concentration of QAS in organic solution was controlled spectrophotometrically by the absorbance of the ion-pair $(QAS)_2Co(SCN)_4$ [1].

The adsorption of water soluble IV from aqueous solution was investigated using ^{1}H NMR method [14]. For this purposes the dependences of non-frozen water content in frozen suspensions as a function of IV concentration in solution at fixed temperature were studied. The relative changes of signals intensity of adsorbed water in hydrate coating at various IV concentration were calculated as $I/I_0 = f(C_{IV})$, where I_0 is signal of water of non-frozen suspension, I is signal of water of frozen suspensions with various concentration of IV.

Content of water adsorbed on SG surface (C, mg g^{-1}) was determined by constructing the diagram presenting the ^{1}H NMR signal of water on the amount of water (x) added to previously weighed adsorbent by means of a microdispenser. The intersection of a graph of $I = f(C + x)$ dependence with the abscissa defines the adsorbed water content.

In order to avert the metastable states of water molecules formation the temperature dependences of signal intensity of non-frozen water were measured by heating the samples from 210 to 273 K.

The water binding with SG surface freezes at temperature below 273 K because the free energy of molecules of such water is lowered as result of surface influence. The value of free energy of binding water molecules (G) was determined using the temperature dependence of free energy of ice [11,15]. The decrease of the free energy of water molecules as the result of their binding with SG surface (ΔG) was calculated as: $\Delta G = G_0 - G$, where G_0 – the free energy of ice at 273 K. The total value of its changes (ΔG_Σ (mJ m^{-2})) on the base of $\Delta G = f(C)$ dependences was calculated as:

$$\Delta G_\Sigma = K \int_0^{C^0} \Delta G \, \mathrm{d}C$$

where K is a coefficient of proportionality, which is equal to 55,6/S, S- specific area of SG surface, C (mg g^{-1}) is an amount of binding water at ΔG and C^0-its content at $\Delta G \Rightarrow 0$. The percentage standard deviation of ΔG and ΔG_Σ determination was 20%.

The amount of strongly binding water (C^s) on SG surface and maximum value of the decreasing of free energy of its molecules (ΔG^s) were obtained by extrapolating the corresponding segment of the dependences $\Delta G = f(C)$ to the abscissa and ordinate axes respectively. The content of weakly binding water on the surface can be calculated as $C^w = C^0 - C^s$. The percentage standard deviation of determination of binding water content was 10%.

The absolute values of ΔG and C^s for non-modified SG are not the same because of different pre-treatment conditions of the sorbents. It may be caused by the polarisation of silica particles in the process of SG samples preparation [16,17]. But it is not important because of relative character of the dependences.

3. Results and discussion

The temperature changes of ^{1}H NMR spectra shape of water in the aqueous suspensions of SG and I-SG are presented in Fig. 1 (a, b). The signals observed in these spectra corresponded to water molecules subjected to a stimulated action of the silica surface. The data testified about the presence of non-frozen (binding) water on the surface of either modified or nonmodified sorbents, but the signals intensity of water for I-SG are lower than one for SG. The widening of the water signals in the spectra during the temperature decreasing is a result of the decline in the molecular mobility. The signals of aliphatic groups were observed in the ^{1}H NMR spectra of I-SG-III-SG suspensions only at QAS content on the surface $> 16.10^{-5}$ mol g^{-1}. But the intensity of these signals is low and weakly depends on temperature.

The ΔG dependences as a function of non-frozen water content for I-SG with different QAS content are represented on Fig. 2. The same dependences were obtained for II-SG and III-SG, too. Two segments on the all curves observed may be separated. The first segment (at significant ΔG changes) corresponds to the strongly and the second one (at low ΔG changes) to the weakly binding water content. The amount of strongly binding water, ΔG_Σ and maximum value of ΔG^s were calculated on the base of these dependences and summarised in the Table 1. The results ob-

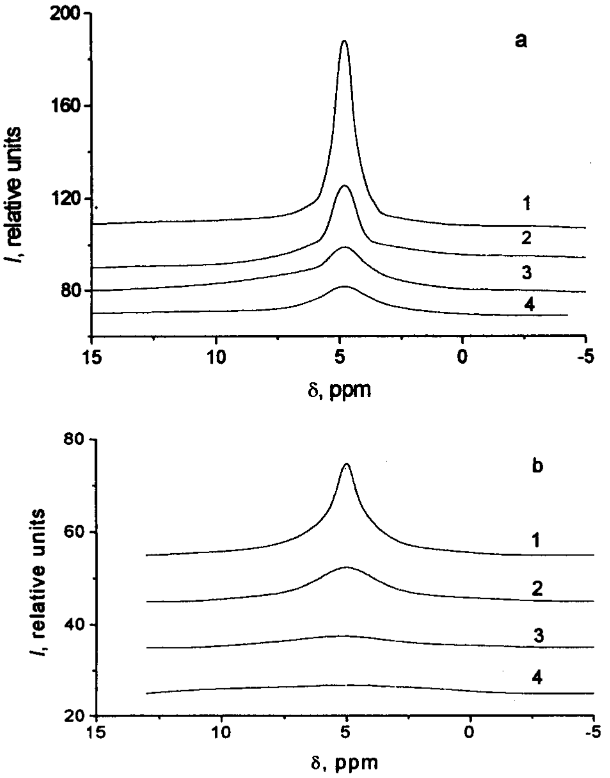

Fig. 1. Temperature dependences of ^{1}H NMR spectra of suspensions of SG (a) and I-SG (b). T K: 268(1), 265(2), 250(3), 220(4). Content of I on SG surface was 16×10^{-5} mol g^{-1}(b).

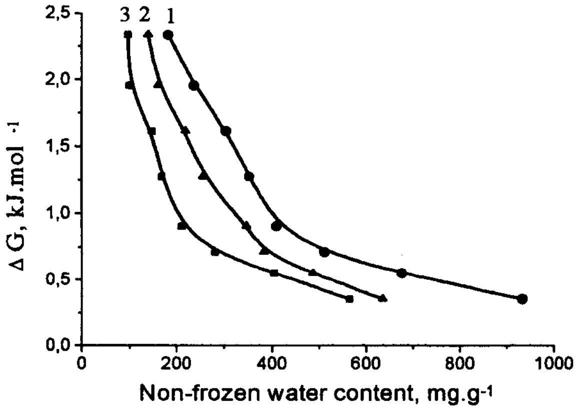

Fig. 2. The ΔG changes as a function of non-frozen water content on I-SG surface. Content of I, 10^{-5} mol g^{-1}:0 (1), 1.0 (2) and 16 (3).

tained (Table 1 and Fig. 2) show that ΔG^s, ΔG_Σ values and content of binding water decrease at increasing of I amount on SG surface. Data represented point out that the not only weakly but also strongly binding water is removed from the surface at QAS adsorption. This fact testifies about rather strong binding of I with SG surface.

Taking into account the fact that the positive charge of II and III is higher than one of I and molecule diameters (hydrophobic areas) of QAS increase in the row I < II < III it may be expected the decreasing of binding water content on the surface of sorbents in the row I-SG < II-SG < III-SG at equivalent QAS amount on the surface. The experimental data obtained show that the decreasing of one was observed in the row III-SG < II-SG ≅ I-SG. The stronger I binding with SG surface may be a result of hydrogen bound complexes formation between ternary amine nitrogen of I and surface hydroxyl group. It is also confirmed by the fact that I in contrast to II and III was removed from the surface by hydrochloric acid at pH < 3. It is probably caused by competitive interaction of ternary amine nitrogen of I with surface hydroxyl group and hydrogen ions in solution. Molecules of II and III have same charge and similar structure of hydrophobic areas. They differ only by distance between hydrophilic centres (2 and 6 CH_2-groups respectively). But ΔG_Σ and content of binding water on II-SG surface are some lower than ones on III-SG surface at equal QAS amount (Table 1). It may be a result of steric factors.

In order to test the role of dispersive intramolecular and electrostatic interaction during QAS immobilization onto SG surface the sorption of short chain QAS IV from aqueous solution was studied.

The intramolecular interaction and dispersive interaction between hydrophobic areas (alkyl chain) of IV molecules and ionised SG surface (aqueous solution at pH > 6) at monolayer formation may be ignored.

The relative changes of signals intensity of adsorbed water as a function of IV concentration in suspension at four fixed temperatures are given in Fig. 3. The molecules of water soluble IV may be present both in solution and on the surface in equilibrium. The appearance of the dissolved sub-

Table 1
The influence of I-III adsorption on the characteristics of water binding with SG surface

Sorbent	QAS content (10^{-5} mol g^{-1})	C^s (mg g^{-1})	ΔG^s (kJ mol^{-1})	ΔG_Σ (mJ m^{-2})
SG	0	600	3.45	230
I-SG	0.1	571	3.24	230
I-SG	1.0	487	3.02	165
I-SG	5.0	424	3.03	143
I-SG	16	305	2.96	109
II-SG	20	296	3.28	121
III-SG	20	342	3.19	145

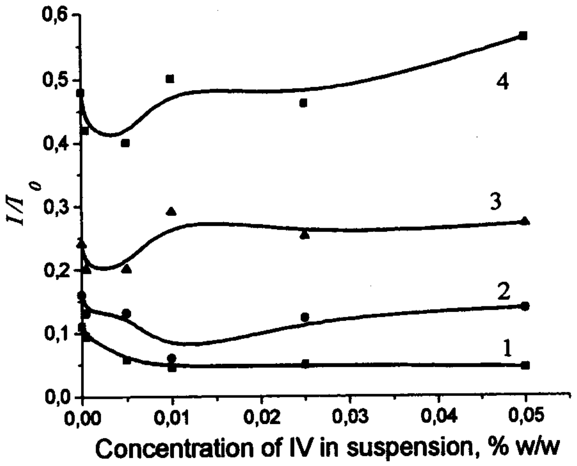

Fig. 3. The dependences of relative changes of signals intensity of binding water in frozen suspension on IV initial concentration at various temperature. *T*, K: 220 (1), 235 (2), 255 (3), 270 (4).

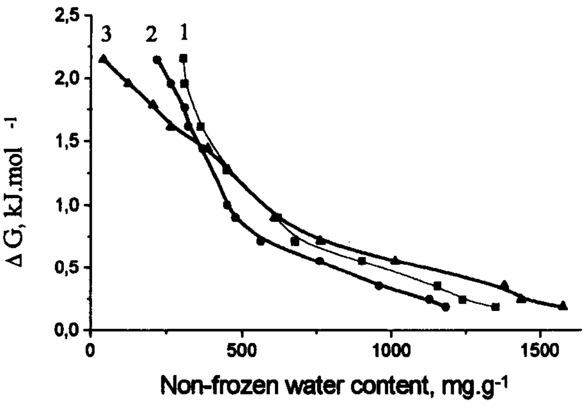

Fig. 4. The ΔG changes as a function of binding water content in frozen suspension of IV at its concentration (% w/w): 0 (1), 0.005 (2), 0.050 (3).

stances in solution is accompanied by increasing of volume part of non-freezing water [15]. The data obtained show that the increasing of IV concentration in aqueous solution up to 0.005% w/w was not accompanied by rising of signals intensity of non-frozen water. This fact testifies about full IV sorption in this concentration rage [14] and confirmed the important role of electrostatic interaction during IV fixation on SG surface.

The ΔG dependences as a function of non-frozen water content for silica suspensions with IV various concentration are represented in Fig. 4. Two segments corresponding to the weakly and strongly binding water may be separated on these curves as well as for QAS similar dependences. The amount of strongly binding water, ΔG_Σ and maximum val ue of ΔG^s were calculated on the base of these dependences. The results are given in the Table 2. The relative decreasing of ΔG_Σ and binding water content on SG surface during IV adsorption are less than for QAS (Tables 1 and 2). This fact may confirm weaker IV binding with SG surface compare to QAS. This phenomena may testify about essential role of intramolecular

Table 2
The characteristics of water binding with SG surface as a function of IV initial concentration in aqueous solution

Concentration (% w/w)	C^s (mg g^{-1})	ΔG^s (kJ mol^{-1})	ΔG_Σ (mJ m^{-2})
0	900	3.11	285
0.005	700	3.08	260
0.01	709	2.50	250
0.025	957	2.32	240
0.050	1079	2.19	270

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dispersive interaction during QAS immobilization onto SG surface.

The signal intensity of binding water and value of ΔG_Σ rise at IV concentration over 0.01% w/w (Table 2, Figs. 3 and 4, curve 3). It testifies about easy accessibility of hydrophilic centre of IV molecules for water molecules of liquid phase at increasing of IV content on SG surface. This fact may be caused by the formation of bilayer during IV adsorption as a result of intramolecular dispersive interaction [18].

4. Conclusions

It was found that I-IV adsorption on SG surface was accompanied by the significant changes of hydrate coating of the sorbent in the row I-SG $\cong$ II-SG $>$ III-SG. Taking into account the fact that molecule diameters of I-III are similar and the positive charge of I is smaller, the stronger I binding with SG surface is caused by hydrogen bound complexes formation. The comparison of changes of SG hydrate coating during QAS and short chain quaternary ammonium salt adsorption has shown that beside dipole–dipole intramolecular dispersive interaction play essential role in QAS immobilization on SG surface. The binding of short chain quaternary ammonium salt with hydrated SG surface during monolayer formation is mainly a result of electrostatic interaction.

The data obtained may be of practical interest for preparation and application of new modified sorbents with definite chemical-analytical properties.

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