Properties of silicas chemically modified by monodentate amines studied by conductometry

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The protonation of aminoalkyl groups covalently bonded on the silica surface was studied by the conductometric titration method. Porous varieties of silica can adsorb HCl from an aqueous solution. Conductometric titration was proposed for the determination of concentrations and constants of protolytic equilibrium of grafted amino groups. During HCl chemisorption the effect of temperature on the electric conductivity of suspensions of the modified silicas was studied.

Key words: conductometry, aminosilicas, concentration of immobilized groups, adsorption, equilibrium constant, protonation.

The main method for studying acid-base equilibria at the liquid—solid interface is pH-metry.[1] This method revealed specific features of protonation of organic bases covalently bonded on the surface of chemically modified silica (CMS).[2] However, the use of pH-metry to study protolytic equilibria of CMS does not allow one to distinguish processes that occur in solution from those occurring both in solution and at the interface. For instance, when a silica weighed sample (m = 0.1 g) with groups of alkylsulfonic acid ($C_{\rm H} = 0.1$ mmol g^{-1}) covalently bonded on the surface is suspended in water (V = 0.01 L), the pH of the suspension decreases to 3 ($[{\rm H}] \cdot 10^{-3} = C_{\rm H} \cdot m/V$).[3] The suspension of the nonmodified silica in a 10^{-3} M solution of sulfonic acid has the same pH. Therefore, when using pH-metry to study CMS, it seems important to be positive that the measured values reflect the interaction of the acid with immobilized groups rather than with products of desorption or CMS destruction. Ions capable of migrating make the main contribution to the electric conduction of aqueous suspensions of CMS. Therefore, adsorbed (mobile) and covalently bonded (immobile) molecules can easily be discriminated during conductometric titration.[1] In conductometric studies, adsorbed substances are protonated due to the interaction with acid and loose their ability to form hydrogen bonds with silanol groups. This results in their desorption into a solution and increases the electric conduction of the solution. At the same time, molecules covalently bonded on the support surface cannot migrate to the bulk even after protonation and, hence, the addition of acid to these CMS does not considerably increase the conduction of the suspension up to the equivalence point. The potential to use conductometric titration to study CMS is exemplified by determination of the concentration of aminopropyl groups grafted on SiO_2.[4]

The purpose of this work is to evaluate an ability of conductometric titration for studying protolytic equilibria at the water—CMS interface. For the study, we chose silicas with covalently bonded aliphatic amines, which differ by the concentration of immobilized groups and by the support nature and have known protolytic properties.[4—6]

Experimental

Conductometric titration of aqueous suspensions of CMS was carried out with an aqueous solution of HCl. To measure the electric conduction of CMS suspensions, a vessel with two parallel plates of platinum tin (Arrhenius cell) was used. A conductometric cell was temperature-controlled with an accuracy of ±0.2 °C for 0.5—1 h. After a constant temperature was maintained, the electric conductivity was measured at 13—75 °C. The tests with standard solutions of KCl in the concentration interval from 0.1 to 0.01 mol L^{-1} showed that the temperature gradient in the zone of temperature control and polarization phenomena at the electrodes are virtually absent. A change in the cell resistance during titration was determined using an R-5058 variable-current bridge at a working frequency of 1000 Hz. Suspensions in the Arrhenius cell were magnetically stirred. Titration was carried out in the absence of silica to find the dependence of the electric conductivity (κ) on the acid concentration.

The sorption characteristics of CMS were studied as follows. Silica (0.1—0.2 g) was added to a temperature-controlled cell for conductometric titration containing deionized water (16—25 mL). Then the suspension was stored for 24 h at ~20 °C and titrated with a 0.05 M solution of HCl in water. The electric conductivity was determined after sorption equilibration. The

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time needed to reach equilibrium changed from 15 min (near the equivalence point) to several seconds (after this point was achieved). Based on the data of direct conductometric titration of a suspension of nonmodified silica (blank entry), the dependence of κ on the proton concentration in solution $[H^+]$ was found. These values were used to determine the amount of the acid adsorbed by the nonmodified silica ($C^a{}_{HCl}$) using the equation

$$C^a{}_{HCl} = (C_{HCl} - [H^+])V/m,$$

where C_{HCl} is the total concentration of the added acid, mol L^{-1}; V is the total volume of the added acid, mL; m is the sorbent weighed sample, g.

The $[H^+]$ and $C^a{}_{HCl}$ values were used to plot the adsorption isotherm and its linear form. Sorption isotherms were reduced to a linear form,[7] and the dependence of $[H^+]/C^a{}_{HCl}$ on $[H^+]$ was plotted. The value inversely proportional to the slope of the linear region of the isotherm was taken as the protolytic equilibrium constant (pK_{exp}) for the interaction of the immobilized amino groups with protons.

The studied CMS with *p*-propylamine groups ($-NH_2$) covalently bonded on the surface were synthesized using a known procedure.[8] Different silicas (SiO_2) were used as matrices (Table 1): nonporous, Aerosil (A); mesoporous, silica gel (Sg); and macroporous, Silochrom (Sh).

Results and Discussion

It is commonly accepted[4] that a silica matrix does not adsorb an acid from an aqueous solution and, hence, suspending nonmodified silica in an aqueous solution of an acid should not affect its electric conduction. The data on the electric conductivity of aqueous suspensions of the nonmodified silicas (blank entry) of different genesis obtained at the acid concentration ranging from 0 to 0.005 mol L^{-1} and at certain solid phase/electrolyte solution weight ratios suggest the following.

1. For all types of silicas, κ depends linearly on C_{HCl}.

2. The blank entry with the nonmodified silica revealed that within the measurement error the slope of the linear plot of κ *vs.* C_{HCl} coincides with tanα only for a suspension of Aerosil. Therefore, a correction for the nonspecific adsorption of the acid with the silica matrix needs to be introduced into the data obtained for the porous silica modifications (Fig. 1).

Table 1. Modified silicas with the immobilized $-(CH_2)_3NH_2$ group

Sample	Designations	d^*/nm	S^{**}/m^2 g^{-1}
1	$Sg-NH_2$	—	300
2	$Sg-NH_2$	6	300
3	$A-NH_2$	0	50
4	$Sh-NH_2$	200	80

* Pore diameter.

** Specific surface area.

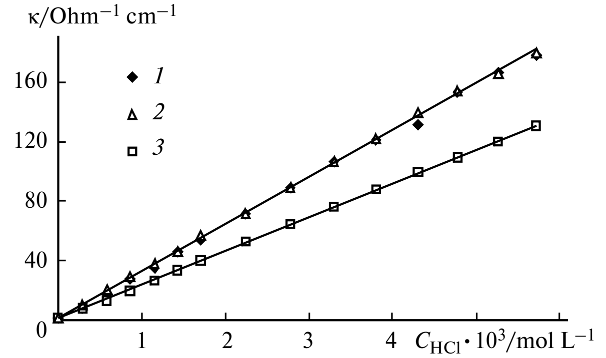


Fig. 1. Plots of κ *vs.* C_{HCl} for a solution containing no silica (*1*) and a suspension of nonmodified SiO_2: A (*2*), Sg (*3*).

Conductometric titration in the presence of a nonmodified support (silica gel or Silochrom) was additionally carried out to determine corrections required for the porous CMS. This blank entry made it possible to take into account the influence of the silica matrix on the adsorption of the acid by CMS.

Unlike the case of the nonmodified silica, the plot of the electric conductivity of a SiO_2-NH_2 suspension *vs.* acid concentration is nonlinear (Fig. 2). The substantial decrease in the conductivity of the SiO_2-NH_2 suspension compared to that of the nonmodified silica indicates that the acid interacts with the amino groups immobilized on the surface. The isotherms of acid adsorption were calculated from the data on conductometric titration of SiO_2-NH_2 (Fig. 3). Contrary to the isotherms obtained from the pH-metric measurements,[6] these are I type isotherms, and the saturation value corresponds to the concentration of the immobilized aminopropyl groups (Table 2). This supports the idea that the interaction of hydrochloric acid with the aminopropyl groups of the grafted phase does not involve destruction of the latter.

As can be seen from the data in Fig. 3, the adsorption isotherms of the acid on SiO_2-NH_2 have the pattern of the Langmuir monolayer adsorption isotherm. Therefore,

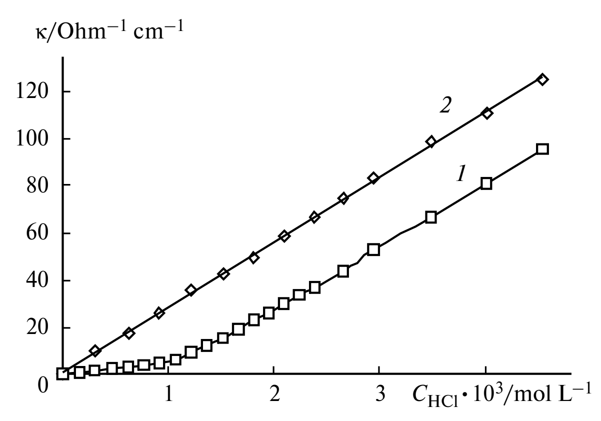


Fig. 2. Plots of κ *vs.* C_{HCl} of a suspension of sample **2** (*1*) and nonmodified silica of the same genesis (*2*).

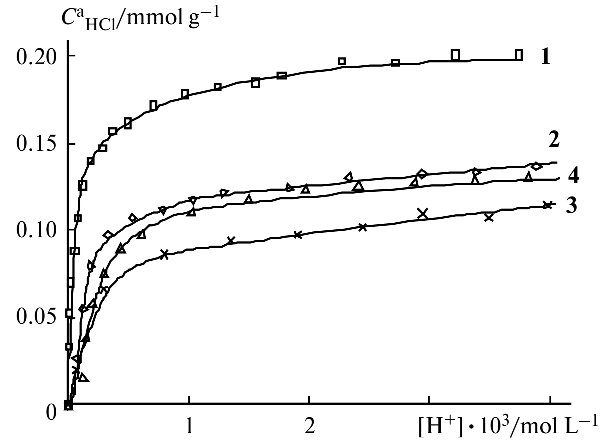


Fig. 3. Sorption isotherms of hydrochloric acid for samples **1**—**4**.

Table 2. Concentration of amino groups immobilized on the silica determined by pH-metric (C_L) and conductometric (*a*) titrations

Sample	C_L	*a*
	mmol g^{-1}	
1	0.18±0.01	0.18±0.02
2	0.12±0.01	0.13±0.02
3	0.08±0.01	0.10±0.02
4	0.11±0.01	0.11±0.02

the affinity of the adsorbent to an acid was determined by plotting a linear function of $[H^+]/C^a_{HCl}$ *vs.* $[H^+]$.

The transformation of the isotherms in the coordinates of the linear Langmuir equation (Fig. 4) showed that the experimental plots are linear not over the entire range of equilibrium concentrations. For instance, at $[H^+] = 10^{-5}$—10^{-4} mol L^{-1} the curves contain nonlinear portions (see Fig. 4, *a*). The straight linear portions cover (see Fig. 4, *b*) the equilibrium concentrations of the unbound acid in excess of 10^{-4} mol L^{-1}. This concentration range ($[H^+] > 0.1$ mmol L^{-1}) was used to determine the protolytic equilibrium constants (pK_{exp}^{cond}). In addition, the protonation constants were calculated for the studied sorbents from the data of pH-metric measurements (pK_{exp}^{pH}). As can be seen from the results of calculations (Table 3), the pK_{exp}^{cond} and pK_{exp}^{pH} values for the protolytic equilibrium of grafted amines are much lower than those for similar amines in solution ($pK = 10.74$),[9] which agrees with the earlier pH-metric results for aliphatic amines of different dentate character (see, *e.g.*, Ref. 10). The explanation includes the formation of arc structures on the CMS surface.[11]

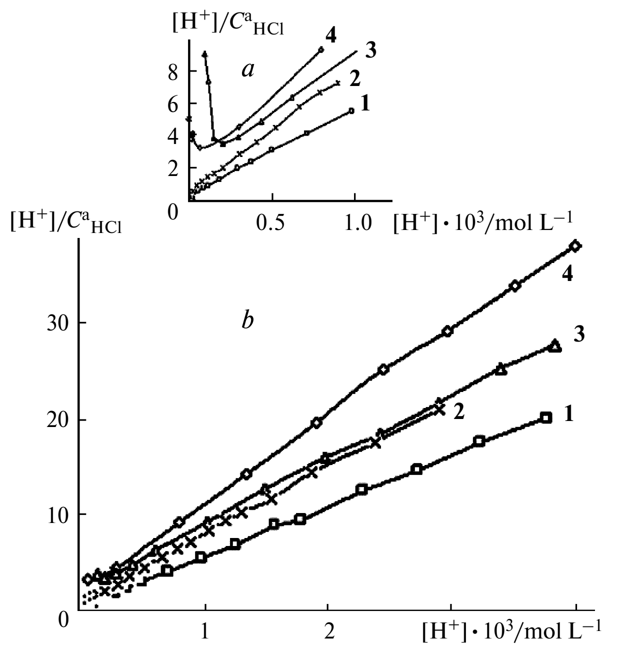


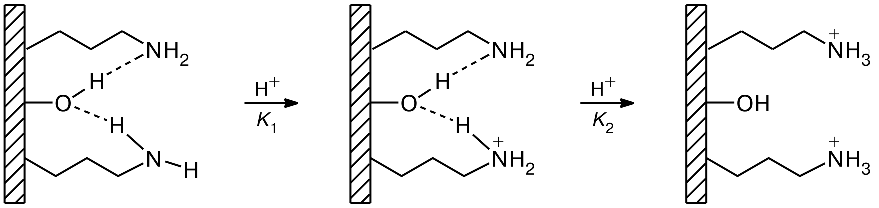
Fig. 4. Sorption isotherms of hydrochloric acid for samples **1**—**4** plotted in the linear coordinates of the Langmuir equation.

Table 3. Logarithms of the protolytic equilibrium constants for the silicas with covalently bonded propylamine groups obtained experimentally from the data of conductometry (pK_{exp}^{cond}) and pH-metry (pK_{exp}^{pH}) and theoretically calculated (pK_{calc})

Sample	C_L/µmol m^{-2}	pK_{exp}^{cond}	pK_{exp}^{pH}	pK_{calc}
1	0.9	3.97	—	5.2
2	0.4	3.84	—	4.9
3	3	3.62	6.31	6.5
4	0.55	3.56	6.22	5.0

The found values of pK_{exp}^{cond} and pK_{exp}^{pH} (see Table 3) differ strongly. The pK_{exp}^{cond} values are lower by almost three orders of magnitude than pK_{exp}^{pH}. The observed discrepancy is probably caused by the fact that our method is suitable for calculating surface processes that proceed *via* one step. At the same time, it is known[12] that the interaction of the monodentate immobilized amine with a proton is not a one-step process. It can be assumed that the protonation of the silica-grafted layer of monodentate alkylamines proceeds *via* two steps (Scheme 1) and can be described correctly only with the use of two equilibrium constants (pK_1 and pK_2). To explain specific features of protonation, one can use the model of cluster distribution of immobilized groups,[13] according to which neighboring reaction sites form a dimer. Proton addition does not destroy such an associate but protonates one amino group (pK_1) to decrease the basicity of the adjacent nonprotonated amino group. A decrease in the basicity of the grafted amino group adjacent to the protonated group can be explained by the influence of a positive charge, which is transmitted through a system of hydrogen bonds between the immobilized amino groups, silanol groups, and water (see Scheme 1). The addition of the second

Scheme 1



proton destroys the associate of the adjacent amino groups, which is accompanied by the protonation of the second NH_2 group (pK_2). The pK_2 value is by two—three logarithmic units lower than pK_1.

The pK_1 values of the aminosilicas is known[10] to depend linearly on the concentration of immobilized groups (C_L). For primary amines, this dependence is described by the equation[14]

$$pK_1 = 4.47 + 0.77C_L. \qquad (1)$$

Using the regression equation (1), one can calculate the theoretical protonation constants (pK_{calc}), which are given in Table 3 along with the experimental values. The pK_{calc} values differ slightly from the found p$K_{exp}{}^{pH}$ values and, hence, the dependence of p$K_{exp}{}^{pH}$ on the surface amine concentration is close to linearity.

The pK_2 values are related to the density of amino groups in the grafted layer.[6] Since the layer grafted on the aminosilicas most frequently has the cluster structure and its density is independent of the concentration of immobilized groups, the pK_2 values remain unchanged in a wide interval of concentrations of immobilized groups[1]: p$K_2 = 4.0\pm0.5$.

For the silicas modified by monodentate amines, the calculated protonation constants p$K_{exp}{}^{pH}$ and p$K_{exp}{}^{cond}$ have different physical sense. Therefore, they cannot describe the same process. If the above-considered theory on the possibility of protonation of immobilized groups in two steps is applied, it becomes evident that each step is described by its intrinsic constant pK_1 or pK_2. In this case, the p$K_{exp}{}^{pH}$ values (see Table 3) depend on C_L, they are almost the same as pK_{calc} and correspond to pK_1. The lack of correlation between p$K_{exp}{}^{cond}$ and the concentration of immobilized amino groups and a possibility to determine p$K_{exp}{}^{cond}$ as p$K_2 = 4.0\pm0.5$ suggest that the obtained p$K_{exp}{}^{cond}$ values correspond, most likely, to pK_2.

Thus, the sorption isotherm of the acid in the coordinates $[H^+]/C^a_{HCl}$—$[H^+]$ cannot be linear in the whole interval of changing the pH of the suspension (see Fig. 4). Under the conditions where the acidity of an aqueous suspension of the aminosilica changes in an interval of pH 5—9, protolytic equilibria on the CMS surface are described by one equation, while at pH < 4 they obey another equation. Since $[H^+]$ can easily be found from the measured value (pH) using pH-metry, two consecutive processes of protonation of the grafted layer of amino groups can be discriminated. When conductometric titration is used, the measured value is not directly related to $[H^+]$, which restricts the possibility of using this method to determine pK_1 of multistep processes.

Let us consider the data of conductometric titration on the influence of the temperature regime on the reaction of an acid solution with the aminosilicas. As can be seen from the data in Fig. 5, an increase in the temperature of the solution and suspension increases their electric conductivity. This phenomenon is usually explained by the effect of heating that involves a decrease in the viscosity of the suspension and, correspondingly, an increase in the ion mobility.[15] For electrolyte solutions, the temperature increase by one degree induces an increase in the conductivity by 2—2.5%.[15] Similar values were obtained for suspensions of the aminosilicas. Therefore, the response of SiO_2—NH_2 suspensions to heating is similar to that of solutions and no substantial changes in the structure of the grafted layer occur that affect the mobility of ions in the interface.

Thus, we have shown that the method of conductometric titration can successfully be used for studying protolytic equilibria at the solid—solution interface. Under certain conditions, the results agree with the data of pH-metry. It is proved that the treatment of SiO_2—NH_2

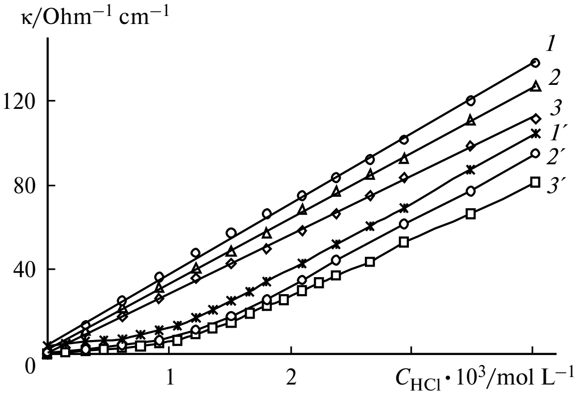


Fig. 5. Plots of κ *vs.* C_{HCl} of a suspension of SiO_2—NH_2 in water: blank entry (*1—3*), sample **2** (*1′—3′*) at temperatures 22 (*1*, *1′*), 45 (*2*, *2′*), and 55 °C (*3*, *3′*).

with an aqueous solution of the acid does not produce CMS destruction associated with the desorption of grafted groups. It is found that the porous modifications of silica can adsorb the acid from an aqueous solution. Therefore, it is reasonable to use the nonporous modifications of SiO_2 when studying the protonation of the immobilized layer, because porous supports affect the amount of the sorbed acid. In the case of the porous supports (silica gel and Silochrom), a correction with allowance for acid adsorption by the silica matrix is advised. Conductometric titration enables one to determine the concentration of grafted amino groups and calculate protolytic equilibrium constants on the surface with grafted amino groups from the data of conductometric titration. Using this method, the temperature effect on the electric conductivity of suspensions of the modified silicas in the acid can be monitored.

References

1. V. N. Zaitsev, *Kompleksoobrazuyushchie kremnezemy: sintez, stroenie privitogo sloya i khimiya poverkhnosti* [*Complexing Silicas: Synthesis, Structure of Grafted Layer, and Chemistry of Surface*], Folio, Khar´kov, 1997, p. 240 (in Russian).
2. V. N. Zaitsev, A. K. Trofimchuk, and V. V. Skopenko, *Teor. Eksp. Khim.*, 1983, **38**, 564 [*Theor. Exp. Chem.*, 1983, **38** (Engl. Transl.)].
3. S. A. Alekseev, V. N. Zaitsev, and J. Fraissard, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 348 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 364].
4. V. V. Skopenko, A. K. Trofimchuk, and V. P. Kaminskii, *Ukr. Khim. Zh.* [*Ukrainian Chemical Journal*], 1982, **43**, 1136 (in Russian).
5. V. D. Oleinik and V. N. Zaitsev, *Adsorption Sci. Technol.*, 1999, **17**, № 1, 65.
6. V. D. Oleinik, V. L. Budarin, and V. N. Zaitsev, *Functional Materials*, 2000, **7**, 855.
7. Ya. I. Gerasimov, V. P. Dreving, and E. N. Eremin, *Kurs fizicheskoi khimii* [*The Course of Physical Chemistry*], Khimiya, Moscow, 1964, **1**, 624 (in Russian).
8. Yu. V. Kholin, V. N. Zaitsev, S. A. Mernyi, N. D. Donskaya, and L. N. Chistyakova, *Ukr. Khim. Zh.* [*Ukrainian Chemical Journal*], 1993, **59**, 910 (in Russian).
9. A. E. Martell and R. M. Smith, *Critical Stability Constants*, Plenum Press, New York—London, 1974—1983, **1—5**.
10. Yu. V. Kholin, *Zh. Neorg. Khim.*, 1996, **41**, 459 [*Russ. J. Inorg. Chem.*, 1996, **41** (Engl. Transl.)].
11. G. S. Caravajal, D. E. Leyden, G. R. Quinting, and G. E. Maciel, *Anal. Chem.*, 1988, **60**, 1776.
12. Yu. V. Kholin, V. N. Zaitsev, and S. A. Mernyi, *Ukr. Khim. Zh.* [*Ukrainian Chemical Journal*], 1993, **59**, 910 (in Russian).
13. V. N. Zaitsev, V. V. Skopenko, Yu. V. Kholin, and N. D. Donskaya, *Zh. Obshch. Khim.*, 1995, **65**, 529 [*Russ. J. Gen. Chem.*, 1995, **65** (Engl. Transl.)].
14. Yu. V. Kholin, V. N. Zaitsev, S. A. Mernyi, and O. A. Varzatskii, *Zh. Neorg. Khim.*, 1995, **40**, 1325 [*Russ. J. Inorg. Chem.*, 1995, **40** (Engl. Transl.)].
15. T. A. Khudyakova and A. P. Kreshkov, *Konduktometricheskii metod analiza* [*Conductometric Method of Analysis*], Vysshaya Shkola, Moscow, 1975, 207 (in Russian).

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