Russian Chemical Bulletin, Vol. 46, No. 3, March, 1997

# The influence of grafted functional groups on the adsorption properties of silica

*T. M. Roshchina,* V. Ya. Davydov, K. B. Gurevich, A. A. Mandrugin, and N. M. Khrustaleva*

*Department of Chemistry, M. V. Lomonosov Moscow State University,*
*Vorob'evy Gory, 119899 Moscow, Russian Federation.*
*Fax: 007 (095) 939 0129. E-mail:kulikov@gcms.chem.msu.su*

The adsorption properties of silica gel with grafted aminopropyl and guanidinoethanethiol (GET) groups were studied by the techniques of adsorption under static conditions and gas chromatography. It was shown that molecules capable of forming hydrogen bonds are adsorbed on all modified samples more weakly than on the initial silica gel. The grafting of GET radicals on the surface results in a noticiable increase in the dispersion interaction with adsorbed molecules. Calculation of the contributions of molecular groups to the constant of adsorption equilibrium showed that the thermodynamic characteristics of adsorption on aminosilochromes and aminosilicas with a polymeric layer of the modifying agent have similar values. Such adsorbents can be used for investigation of polar compounds, including organic bases.

**Key words:** silica, aminopropyl and guanidinoethanethiol grafted groups; gas chromatography; thermodynamic characteristics of adsorption.

Investigation of the surface properties of chemically modified silicas (CMS) by various techniques including adsorption and gas chromatography (GC) is necessary for directed synthesis of these materials.[1–3]

In the majority of works devoted to studying intermolecular interactions of CMS by adsorption methods, silochrome, the most chemically and geometrically uniform variety of the amorphous porous silica, was used as the starting support.[1,4–7] However, sorbents and catalysts of practical importance generally were obtained by the modification of silica gels whose advantages are first of all the high strength of particles and the possibility of controlling the surface areas and pore sizes over a wide range.[1,3]

In this work, the surface chemistry of silica gel and samples prepared from it by chemical grafting of aminopropyl and guanidinoethanethiol (GET) groups was studied by GC and adsorption methods under static conditions. The effects of the amount and nature of the grafted compound on the adsorption properties of modified materials were investigated. The method for calculation of the contributions of molecular groups to thermodynamic characteristics of adsorption (TCA) was used for quantitative evaluation of the properties of aminosilicas.

## Experimental

Silica gel KSK-1 with particles of 0.1—0.2 mm in size (Table 1) was used as the starting support (pilot plant of NIINP, Gorky). Aminosilicagels with different concentrations of the grafted groups were obtained by modification of silica with γ-aminopropyltriethoxysilane (APTES) in company "Biokhimmak". The samples with the grafted guanidinoethanethiol groups (samples 3 and 5) were synthesized by heterogeneous solvolysis of the derivatives of 2-amino-2-thiazaline; aminosilicas were used as their precursors (samples 2 and 4, respectively). It should be noted that the GET group grafted to the silica surface was stable for a long time, in contrast to the homogeneous analog (guanidinoethanethiol).[7,8]

The concentration of the grafted amino groups on samples 2 and 7 is close to a monolayer coverage, and the grafted layer of the polymeric type is formed on samples 4 and 8.[5,6] In order to study the effect of the surface properties of the starting supports on the characteristics of the modified samples, the data obtained previously for S-120 silochrome and aminosilochromes[5,6] were used in this work for a comparison.

The adsorption isotherms at 77 K were determined by a static method on a Micromeritix 2100D (USA) analyzer for

**Table 1.** Characteristics of samples

| Number of sample | Sample | $C$ | $S_{sp}$ |
|---|---|---|---|
| 1 | Silica gel (KSK-1) | | 80 |
| 2 | Aminosilica gel | 1.7 | 72 |
| 3 | GET-silica gel | | 75 |
| 4 | Aminosilica gel | 7.3 | 60 |
| 5 | GET-silica gel | | 63 |
| 6 | Silochrome | | 98 |
| 7 | Aminosilochrome | 2.5 | 87 |
| 8 | Aminosilochrome | 5.3 | 80 |

$C$ is the surface concentration of the $NH_2$ groups per nm$^2$; $S_{sp}$ is the specific surface area, m$^2$ g$^{-1}$

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 3, pp. 452—457, March, 1997.

measurement of porosity and specific surface area. The specific surface area of the samples ($S_{sp}$) was calculated from the $N_2$ adsorption isotherms with the BET method, suggesting that the area occupied by $N_2$ molecule in a monomolecular layer on the adsorbent surface is equal to 16.2 Å$^2$.

Gas-chromatographic (GC) measurements were carried out on a Tsvet-100 chromatograph with a flame-ionization detector and $N_2$ as a carrier-gas. The columns used were 0.5 and 1 m in length and 2.5 mm in inner diameter. Prior to the study, all samples were heated for 20 h in an $N_2$ flow at 180 °C in the case of the starting silica and aminosilicas, and at 150 °C in the case of GET-silicas.

For all adsorbent samples, we determined the specific retention volumes per weight unit ($V_g$/mL g$^{-1}$) and per unit of surface area ($V_a$/mL m$^{-2}$) as well as the relative retention volumes $V_{rel}$ (with respect to *n*-nonane).

The values of specific retention volumes were calculated by the formula

$$V_a = t_c \cdot w/(m \cdot S_{sp}),$$

where $t_c$ is the adjusted time of adsorbate retention, $t_c = t_{adsorbate} - t_0$ (hold-up, $t_0$, was determined with respect to methane; it was equal to 11—19 s); $w$ is the space velocity of a carrier-gas, reduced to zero drop in the pressure in a column; $m$ is the weight of an adsorbent in a column; $S_{sp}$ is the specific surface area of an adsorbent. The $V_a$ values are equal to Henry's constants of adsorption equilibrium expressed as mL m$^{-2}$. The initial (the Henry region) differential molar heats of adsorption $q$ (below heats of adsorption) were calculated from dependences of the specific volumes on reverse temperatute; $q = -\Delta U$, where $\Delta U$ is the change in the differential molar inner energy during adsorption. The coefficients of selectivity for pyridine and isomeric dimethylpyridines were also determined as the ratio of $V_a$ for two compounds eluted successively from the column. All thermodynamic characteristics of adsorption were obtained at the nearly zero coverage of the surface.

The method to calculate the contributions of molecular groups to the constant of adsorption equilibrium was used for the quantitative evaluation of the properties of aminosilicas similarly to that employed in Ref. 9, 10. By using an additive scheme and taking into account that the molecular groups of the same type and the fragments of adsorbing molecules contribute equally to the constant of adsorption equilibrium on this adsorbent, the logarithm of the specific retention volume as a whole, $\ln V_a$, can be represented as the sum of contributions of the same type:

$$\ln V_a = \Sigma(\ln V_{ai}) \cdot n_i,$$

where $V_{ai}$ corresponds to the specific retention volume of the $i$ group, $n_i$ is the number of groups of the same type in the adsorbed molecule.

The contribution of each molecular group to adsorption ($\ln V_{ai}$) was determined by taking the experimental values of $V_a$ and calculating by the least squares method the system of linear equations that link $\ln V_a$ with the number of the $n_i$ groups of the same type. The $V_a$ values for *n*-alkanes ($C_6$—$C_{10}$) as well as for the compounds presented in Table 2 were used for calculation.

## Results and Discussion

As can be seen in Table 1, modification of the γ-APTES silica gel results in a decrease in the specific surface area of the samples: the higher concentration of the grafted compound, the higher the decrease mentioned. Similar changes in $S_{sp}$ are also observed for aminosilochromes. However, formation of the GET groups on the surface has practically no influence on the $S_{sp}$ values as compared to the corresponding aminosilica gels.

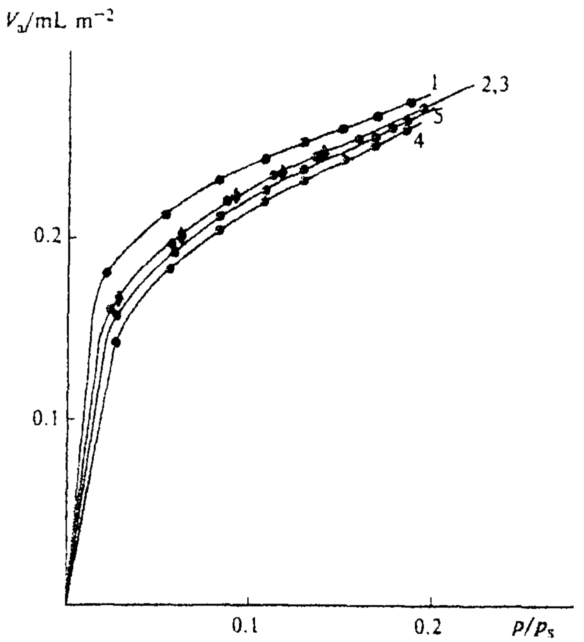

**Fig. 1.** The adsorption isotherms of nitrogen at 77 K on samples 1—5 (numbering of samples is presented in Table 1).

The adsorption isotherms of nitrogen on modified silicas in the whole range of pressures studied are positioned lower than those for the starting support (Fig. 1). Consequently, displacement and shielding of the surface hydroxyl groups of the starting silica gel lead to a decrease in the intermolecular interaction during $N_2$ adsorption on these surfaces. The increase in the amount of the aminopropyl groups on sample 4 also results in a decrease in nitrogen adsorption.

The adsorption isotherms of $N_2$ on the GET samples coincide or are positioned higher than those on corresponding aminosilica gels.

The results of study of the surface properties of the samples by GC are presented in Tables 2 and 3 and in Figs. 2—4. Chromatographic peaks for all test adsorbates on the modified samples are symmetrical, unlike those for the starting support. Hence, the presence of different functional groups does not affect negatively the uniformity of the materials obtained. For example, Fig. 2 demonstrates chromatograms of the compounds with the functional groups, including organic bases, on aminosilica gel. These data indicate the uniformity of the materials obtained. Examination of dependences of $\lg V_a$ on the number of the carbon atoms in the *n*-alkane molecule shows that when the surface coverages are

**Table 2.** The values of relative retention volumes $V_{rel}$ ($n$-nonane is the standard) and specific retention volumes $V_a$ (mL m$^{-2}$) at 403 K on the starting and modified samples 1—8

| Sample* | $V_{rel}$ | | | | | | | | $V_a$ |
|---|---|---|---|---|---|---|---|---|---|
| | Benzene | Toluene | Chloro-benzene | Diethyl ether | 2-Methyl-propan-2-ol | Acetonitrile | Nitromethane | Pyridine | $n$-Nonane |
| 1 | 0.85 | 1.95 | 1.58 | 8.80 | 23 | 7.74 | 3.56 | 80 | 0.18 |
| 2 | 0.45 | 0.98 | 1.25 | 1.35 | 9.09 | 2.17 | 1.59 | 21.7 | 0.28 |
| 3 | 0.32 | 0.69 | 0.89 | 0.90 | 6.08 | 1.36 | 0.93 | 13.54 | 0.40 |
| 4 | 0.29 | 0.54 | 0.81 | 0.15 | 0.70 | 0.34 | 0.41 | 0.88 | 0.24 |
| 5 | 0.23 | 0.42 | — | 0.11 | 0.75 | 0.31 | 0.30 | 1.29 | 0.80 |
| 6 | 0.31 | 0.67 | 0.64 | 2.75 | 6.83 | 1.69 | 0.69 | 25.30 | 0.28 |
| 7 | 0.32 | 0.73 | 1.04 | 0.53 | 3.30 | 0.82 | 0.75 | 6.20 | 0.37 |
| 8 | 0.28 | 0.55 | 0.83 | 0.15 | 0.71 | 0.28 | 0.39 | 0.87 | 0.23 |

* Numbering of samples is presented in Table 1.

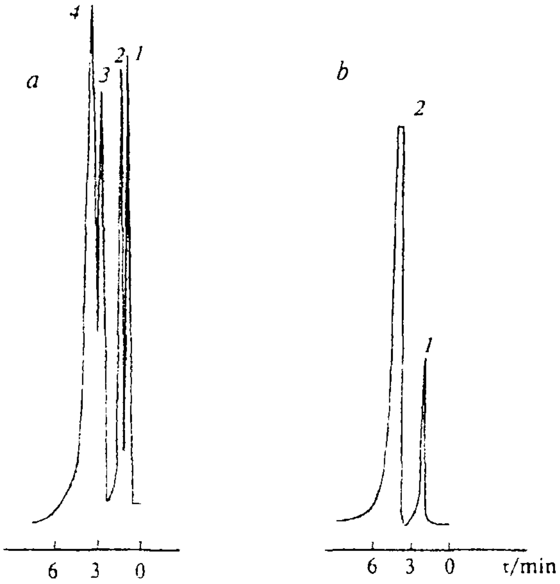

**Fig. 2.** Chromatograms for separation of heterocyclic compounds on aminosilica gel (sample 4, Table 1):
a) pyridine (*1*), 2,6-dimethylpyridine (*2*), 3,5-dimethylpyridine (*3*), 3,4-dimethylpyridine (*4*) ($T_{column}$ = 419 K, $w(N_2)$ = 0.52 mL s$^{-1}$); *b*) dioxane (*1*) and morpholine (*2*) ($T_{column}$ = 425 K, $w(N_2)$ = 0.124 mL s$^{-1}$). Column 1 m×2.5 mm.

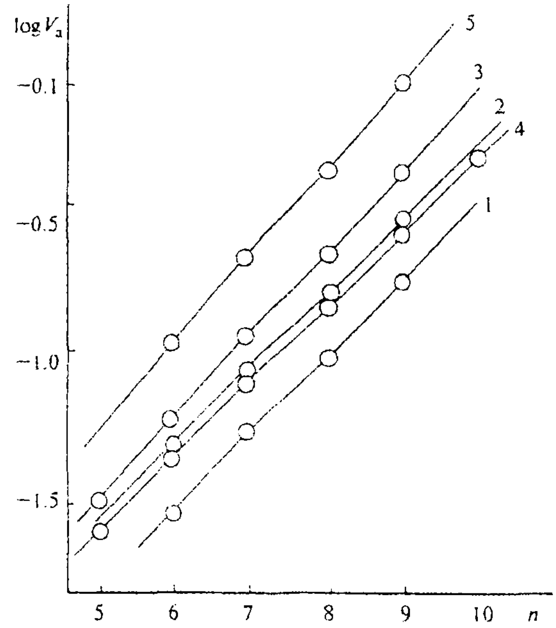

**Fig. 3.** Dependence of lg$V_a$ on the number of the carbon atoms $n$ in the molecules of $n$-alkanes on samples 1—5 at 403 K (numbering of samples see Table 1).

close to zero, saturated hydrocarbons, whose adsorption is only due to dispersion interaction with the surface of any composition, are retained most weakly on the starting silica gel (Fig. 3). Introduction of the aminopropyl groups leads to an increase in the $V_a$ values of $n$-alkanes. Stronger dispersion interaction with unsaturated hydrocarbons is observed on the samples with the grafted GET groups. The contribution of the $CH_2$ groups to the lg$V_a$ value is enhanced on the GET silica gels as compared to aminosilicas (0.29 and 0.25, respectively).

In our opinion, these results are evidence of the possibility of penetration of the adsorbate molecules to the grafted layer and hence, for the presence of additional "side" interactions with grafted radicals of various compositions; this is in a good agreement with the results of previous studies of CMS.[1,6]

The $V_{rel}$ values are the most convenient characteristic for the evaluation of the contribution of specific interaction to adsorption. It is seen from the data presented in Table 2 that the modification of the surface leads to a sharp increase in $V_{rel}$ of the compounds with the active functional groups. Thus, on going from the starting silica gel to nitrogen-containing samples, $V_{rel}$ values for pyridine drop by a factor of ~4 and later by a factor of 100 with increasing concentration of the grafted aminopropyl groups.

It is seen from the adsorption values for molecules with electron density localized at any atoms or bonds

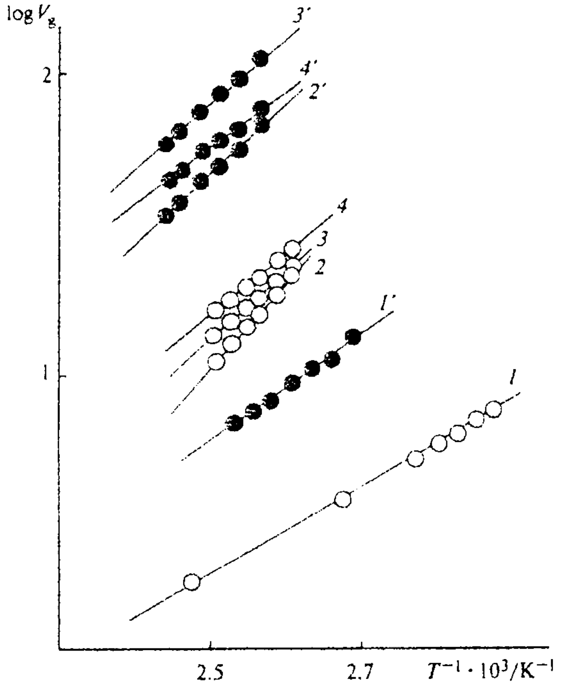

**Fig. 4.** Dependence of lg $V_g$ on reverse temperature (1/T) on aminosilica (1—4, sample 4, Table 1) and GET-silica (1'—4', sample 5, Table 1) for diethyl ether (1, 1'), 2-methylpropan-2-ol (2, 2'), pyridine (3, 3'), and n-nonane (4, 4').

that in the case of grafting GET groups, it is necessary to take into account not only the nature of a modifying agent but also the concentration of the grafted amino groups on the surface of the precursor of aminosilica gel (monolayer or "polymer" coverage). A decrease in $V_{rel}$ for the molecules capable of dipole-dipole interaction and of the formation of strong hydrogen bonds is observed on going from sample 2 (monolayer coverage) to the corresponding GET silica gel (Table 2). However, the heats of adsorption and the $V_a$ values for diethyl ether, 2-methylpropan-2-ol, and pyridine change slightly when the GET groups appear on the surface (the $V_a$ values for some adsorbates on samples 2 and 3, respectively, are equal to: 0.38 and 0.35 ($Et_2O$); 2.56 and 2.38 (Bu$^t$OH); 5.81 and 5.44 (Py)) (Table 3). This can be explained by the fact that the increase in the dispersion component is compensated by the decrease in the contribution of specific interactions. As was established previously by IR spectroscopy,[6] the silanol groups accessible to adsorption remain on the surface of silochrome containing the amount of the grafted aminopropyl radicals close to a monolayer (sample 7). Therefore, a decrease in the contribution of specific interactions on sample 3 can be ascribed to the formation of "arch" structure of the grafted layer, because the polar GET groups can normally interact with the surface residual silanol groups, thereby decreasing the accessibility of both SiOH and GET groups to adsorption.

**Table 3.** The heats of adsorption q on modified samples* 2—5, 8

| Adsorbate | q/kJ mol$^{-1}$ | | | | |
|---|---|---|---|---|---|
| | 2 | 3 | 4 | 5 | 8 |
| n-Heptane | 33 | 37 | 34 | 29 | 34 |
| n-Nonane | 39 | 48 | 40 | 37 | 45 |
| Diethyl ether | 57 | 58 | 29 | 32 | 35 |
| 2-Methylpropan-2-ol | 70 | 69 | 52 | 47 | 59 |
| Pyridine | 68 | 71 | 44 | 45 | 40 |

* Numbering of samples is presented in Table 1.

In order to evaluate the effect of the nature of a modifying agent on the adsorption properties of the polymer-type samples 4 and 5 with high concentration of aminopropyl groups and nearly equal $S_{sp}$ values, let us consider the temperature dependence of $V_g$ for some compounds. It is seen in Fig. 4 that introduction of GET groups results in a sharp increase in the adsorption of all the compounds studied, which seems to be due to the increase in the length and polarizability of grafted groups. However, on the GET silica gel as compared to the corresponding aminosilica, the sequence of elution of pyridine with respect to n-nonane changes, and the straight line for 2-methylpropan-2-ol is positioned closer to the corresponding straight line for this hydrocarbon. The higher accessibility of the GET groups seems to play the main role in this case. This determines the relative increase in adsorption of an organic base and alcohol capable of forming strong hydrogen bonds. The results obtained are in good agreement with the data of Ref. 7 devoted to a comparative investigation of amino- and GET silochromes.

Table 3 shows the heats of adsorption on all modified samples. An increase in the concentration of the aminopropyl groups leads to a significant decrease in the q values for diethyl ether, pyridine, and 2-methylpropan-2-ol, confirming once more the complete substitution and shielding of the surface SiOH groups during the formation of the polymer-type coverage. However, unlike $V_a$ and $V_{rel}$, the difference in the q values for samples 4 and 5 is slightly noticeable. Thus, with the aid of GC one can follow the effect of the amount and chemical structure of a modifying agent on the change in the nature of intermolecular interactions in the CMS-based systems.

Aminosilicas are of the most interest for the study and analysis of various organic compounds by the GC method due to the uniformity of their surface as well as to the easy production, commercial availability, nonvolatility, and high thermal stability (to 200°C) of the grafted phase. Therefore, it is expedient to consider in more detail a comparison of the adsorption properties of silica gels and silochromes modified with APTES as well as those of the starting supports.

The ln $V_{ai}$ values calculated on the basis of an additive scheme with the use of Henry's constants of ad-

**Table 4**. The contributions of the molecular groups (as $\ln V_{ai}$) to $\ln V_a$ value at 403 K for the starting samples and aminosilicas

| Образец | —Me | —CH$_2$— | =CH— | =C— | —Cl | —O— | =C—OH | —CN | —NO$_2$ | =N |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Silica gels | | | | | |
| 1 | −2.8849 | 0.5685 | −0.3162 | 3.3929 | −3.0957 | 5.0652 | 10.047 | 3.1887 | 2.4117 | 4.22 |
| 2 | −2.6440 | 0.5741 | −0.3313 | 3.0131 | −2.4008 | 3.1748 | 8.8721 | 2.1530 | 1.8388 | 3.4167 |
| 4 | −2.7623 | 0.5848 | −0.4447 | 2.9408 | −2.3666 | 1.0026 | 6.5021 | 0.2787 | 0.4535 | 0.6673 |
| | | | | | Silochromes | | | | | |
| 6 | −2.7646 | 0.6056 | −0.4108 | 3.1454 | −2.8104 | 4.0436 | 8.7257 | 1.9881 | 1.1039 | — |
| 7 | −2.6575 | 0.6171 | −0.3534 | 3.0381 | −2.2387 | 2.4200 | 8.1122 | 1.4535 | 1.3481 | — |
| 8 | −2.7809 | 0.5831 | −0.458 | 2.9514 | −2.3214 | 0.9535 | 6.5101 | 0.0734 | 0.3696 | 0.7301 |

* Numbering of samples is presented in Table 1.

sorption equilibrium ($V_a$) are presented in Table 4. The contributions of hydrocarbon fragments (—$CH_3$, —$CH_2$—, and —CH=) are slightly dependent on the support or the amount of the grafted amino groups. However, the contribution of the functional groups to adsorption and the $V_{rel}$ values of polar compounds are much higher for the starting silica gel as compared to silichrome. A significant decrease in the contributions of the functional groups on going from the starting samples to modified samples and with increasing concentration of the grafted radicals. A comparison of the data of Tables 2 and 4 clearly shows that the above drop in the values of retention of the molecules capable of forming the hydrogen bond with the silanol groups is solely due to the decrease in the influence of the polar groups, because the contributions of the hydrocarbon groups change slightly. A decrease in $\ln V_{ai}$ of the functional group manifests to a considerably lesser extent for aminosilicas with a coverage close to a monolayer (from 1.7 to 2.3 $NH_2$ groups per nm$^2$) than that for the samples with a grafted "polymeric" film. Hence, the high concentration of the free silanol groups remaining on the surface of samples 2 and 7 after modification affects substantially both the $V_{rel}$ and $\ln V_{ai}$ values of the polar groups of molecules. Relatively low change in the contribution of the hydroxyl group to adsorption in the case of 2-methylpropan-2-ol seems to be due to the capability of a such group to form a strong hydrogen bond with both acidic silanol and basic amino groups.

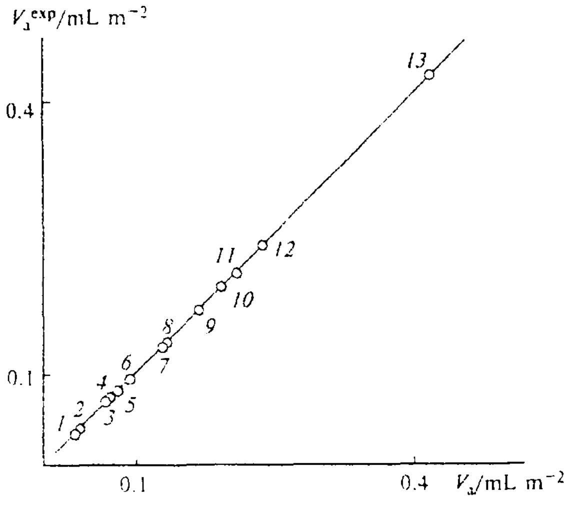

**Fig. 5.** Correlation between the calculated and experimental $V_a$ values at 403 K on aminosilica (sample 4, Table 1) for diethyl ether (*1*), *n*-hexane (*2*), benzene (*3*), *n*-heptane (*4*), acetonitrile (*5*), nitromethane (*6*), toluene (*7*), *n*-octane (*8*), 2-methylpropan-2-ol (*9*), chlorobenzene (*10*), pyridine (*11*), *n*-nonane (*12*), and *n*-decane (*13*).

In spite of differences in the properties of the starting supports, the formation of a dense uniform layer of a modifying agent allows aminosilicas with very close surface properties to be obtained; both the $V_{rel}$ and $q$ values presented in Tables 2 and 3 and the contributions of the molecular groups to the constant of adsorption equilibrium confirm this fact (Table 4). As follows from Fig. 5, which presents both the $V_a$ values calculated on the basis of an additive scheme and experimental values for 13 compounds obtained on sample 4, the contributions of the molecular groups to Henry's constant of adsorption equilibrium reflect adequately the extent of their participation in the adsorption process.

Thus, the contributions of the molecular groups and fragments to the constant of adsorption equilibrium can serve as a very informative quantitative characteristic of intermolecular interactions and adsorption properties of the materials under study.

These results made it possible to use aminosilica gel and aminosilochrome with a dense grafted layer (more than 5 $NH_2$ groups per nm$^2$) for the study of the adsorption of a series of organic bases and the effect of chemical structure of heterocycles on the retention values by the example of isomeric dimethylpyridines (DMPy). Table 5 presents the $V_a$ values and the heats of adsorption of these compounds on samples 4 and 8. Introduction of the methyl groups to the pyridine molecule results in a significant increase in these thermodynamic characteristics of adsorption. An increase in $V_a$ and $q$ correlates with an increase in the dipole moment rather than with the basicity of the compounds. Considerably lesser $V_a$ and $q$ values for 2,6-DMPy as compared

**Table 5.** The values of $V_a$ (mL m$^{-2}$) at 419 K, $q$ (kJ mol$^{-1}$) and coefficients of selectivity $\alpha$* at 419 K on aminosilica gel (4), aminosilochrome (8), and Chromosorb-103 (Chr-103, 463 K)

| Adsorbate | p$K_a$ | $\mu$/D | 4 | | | 8 | | | Chr-103 |
|---|---|---|---|---|---|---|---|---|---|
| | | | $V_a$ | $q$ | $\alpha$ | $V_a$ | $q$ | $\alpha$ | $\alpha$ |
| Pyridine | 5.23 | 2 | 0.15 | 44 | | 0.11 | 40 | | |
| | | | | | 1.47 | | | 1.91 | 1.81 |
| 2,6-DMPy | 6.72 | 1.78 | 0.22 | 49 | | 0.21 | 46 | | |
| | | | | | 2.14 | | | 2.05 | 2.04 |
| 3,5-DMPy | 6.15 | 1.85 | 0.47 | 54 | | 0.43 | 51 | | |
| | | | | | 1.23 | | | 1.23 | 1.26 |
| 3,4-DMPy | 6.46 | 2.58 | 0.58 | 57 | | 0.53 | 54 | | |

* The $\alpha$ values were determined as the ratio of the $V_a$ values for two elutions of compounds nearest in time.

to 3,5-isomer are due to shielding of heteroatom with $\alpha$-methyl radicals. The data presented in Table 5 again emphasize the proximity of the adsorption properties of the samples with the dense aminopropyl coverage even relative to strongly polar and reactive organic bases.

The data of Table 5 show that with respect to selectivity of the separation of nitrogen-containing heterocycles, aminosilicas with a dense layer of a modifying agent are not inferior to the polymeric sorbent Chromosorb-103, one of the best sorbents for the analysis of amino compounds. The results allow us to conclude that the formation of the dense structure of the grafted layer on the surface of silica makes it possible to obtain uniform sorbents with reproducible properties even when silica gel that is in fact unsuitable to gas chromatography of polar compounds is used as the starting support.

## References

1. G. V. Lisichkin, G. V. Kudryavtsev, A. A. Serdan, S. M. Staroverov, and A. Ya. Yuffa, *Modifitsirovannye kremnezyomy v sorbtsii, katalize i khromatografii* [*Modified Silicas in Sorption, Catalysis, and Chromatography*], Khimiya, Moscow, 1986, 247 p. (in Russian).
2. A. V. Kiselev, *Mezhmolekulyarnye vzaimodeistviya v adsorbtsii i khromatografii* [*Intermolecular Interactions in Adsorption and Chromatography*], Vysshaya Shkola, Moscow, 1986, 360 p. (in Russian).
3. V. A. Tertykh and L. A. Belyakova, *Khimicheskie reaktsii s uchastiem poverkhnosti kremnezyoma* [*Chemical Reactions with the Participation of the Surface of Silica*], Naukova Dumka, Kiev, 1991, 264 p. (in Russian).
4. N. K. Shoniya, S. M. Staroverov, Yu. S. Nikitin, and G. V. Lisichkin, *Zh. Fiz. Khim.*, 1984, **58**, 702 [*J. Phys. Chem. USSR*, 1984, **58** (Engl. Transl.)].
5. V. Ya. Davydov, T. M. Roshchina, N. M. Khrustaleva, and A. A. Mandrugin, *Zh. Fiz. Khim.*, 1993, **67**, 2428 [*J. Phys. Chem.*, 1993, **67** (Engl. Transl.)].
6. V. Ya. Davydov, A. A. Mandrugin, Yu. G. Morozova, T. M. Roshchina, and G. N. Filatova, *Zh. Fiz. Khim.*, 1992, **66**, 736 [*J. Phys. Chem.*, 1992, **66** (Engl. Transl.)].
7. V. Ya. Davydov, A. A. Mandrugin, T. M. Roshchina, V. M. Fedoseev, and M. M. Shishkina, *Vestn. Mosk. Univ., Ser. 2, Khimiya*, 1993, **34**, 361.
8. A. A. Mandrugin, V. M. Fedoseev, S. N. Khomutov, A. A. Rodyunin, and Yu. A. Leshchev, *Khimiya geterotsikl. soedin.*, 1987, 1572 [*Chem. Heterocycl. Compd.*, 1987, 11 (Engl. Transl.)].
9. V. Ya. Davydov, G. N. Filatova, E. Smolkova-Keulemansova, and Yu. Zima, *Chromatographia*, 1988, **25**, 1059.
10. V. Ya. Davydov, T. M. Roshchina, G. N. Filatova, and N. M. Khrustaleva, *Vestn. Mosk. Univ., Ser. 2, Khimiya*, 1995, **36**, 518.

*Received May 20, 1996;*
*in revised form November 11, 1996*