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Note

How strongly do silanols interact with hydrocarbon solutes in gas chromatography?

J. NAWROCKI
Faculty of Chemistry, A. Mickiewicz University, 60-780 Poznań (Poland)
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Silylation of a silica surface leads to "deactivation" of the surface by suppression of its specific interactions. Even the most effective silylation cannot remove all the hydroxyls from the surface. The highest observed surface concentration of organosilyl groups on the surface does not exceed 4–4.5 μmol/m^2 (ref. 1) while the surface silanol concentration is said to be 8–9 μmol/m^2, so only *ca.* 50% of hydroxyl groups can be removed by silylation. The other 50% remain on the surface, and despite its inability to react (for steric reasons) it can interact. The remaining silanols are responsible for the so called "dual retention mechanism" in reversed-phase liquid chromatography (RPLC)[2,3]. It is possible to take advantage of these interactions by blocking them with strongly interacting amines[4,5], and they can also be used for an estimation of the strength of silanol interactions with various solutes in gas or liquid chromatography.

EXPERIMENTAL

A GCHF 18.3 gas chromatograph (Chromatron, Berlin, G.D.R.) equipped with a flame ionization detector was used with argon as a carrier gas. Stainless-steel columns (0.5 m × 4 mm I.D.) packed with silica gel (Machery-Nagel Kieselgel 60) modified by a 1:1 mixture of hexamethylcyclotrisiloxane (HMCTS) and hexamethyldisilazane (HMDS) were used.

A 10-μl Hamilton syringe was used to inject amines, and a 1-μl Hamilton syringe to inject benzene. Modification of the silica gel with the mixture was carried out as described in ref. 6.

RESULTS AND DISCUSSION

During the investigation of a silica surface modification with mixtures of silylating reagents, relatively poor results were noted for mixtures of HMCTS and HMDS[7]. The modified surfaces retained a considerable degree of specific interactions compared with surfaces modified by silazanes[6]. Two questions arose. (1) How many silanols are responsible for such substantial interactions? (2) How do the interactions influence the retention data?

To investigate these problems the strong interactions of amines with silanol

TABLE I

CHARACTERISTICS OF THE PACKING

Weight	*Modifier*	*% C*	$\frac{V_R\ (benzene)}{V_R\ (hexane)}$
3.483 g	A 1:1 mixture of HMCTS and HMDS	4.22	1.85 at 110°C

were utilized. As an example of a packing that shows some specific interactions, a silica gel modified with a 1:1 mixture of HMCTS and HMDS was chosen (Table I). The specific surface area of the unmodified silica was 330 m^2/g; the value for the modified silica was not measured, but it is known that very similar samples of the same silica modified with silazanes[6] had a specific surface area of *ca.* 260 m^2/g. It is

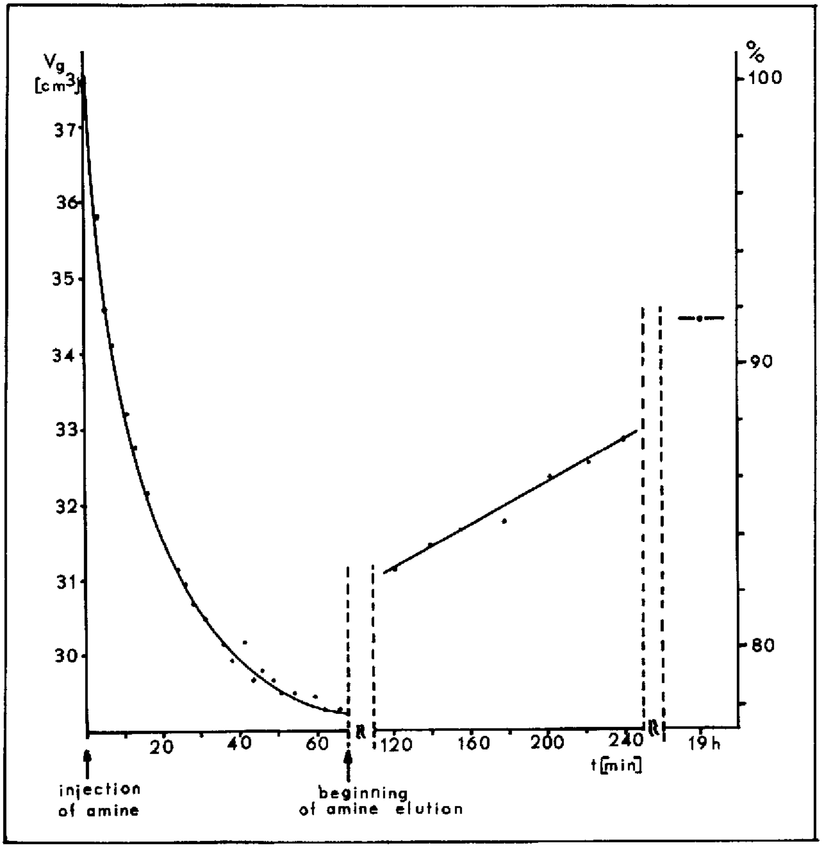

Fig. 1. The influence of *n*-butylamine (1.4 μl) on benzene retention. Column, 0.5 m × 4 mm I.D., packed with silica gel modified by the 1:1 mixture of HMCTS and HMDS; column temperature, 108°C; carrier gas, argon.

not known how many silanols remained on the modified surface, but the specific interactions of the packing were very clear —the retention volume of benzene relative to hexane at 110°C was 1.85, whereas for the much better deactivated silica surface[6] the value of 0.94 can be reached.

A very rough calculation allows the estimation of the total number of hydroxyl groups on the unmodified silica surface: 3.5 g × 330 m^2/g × 8 $\mu mol/m^2$ ≈ 9240 μmol. Even if half the hydroxyl groups are deactivated by the MCTS–HMDS mixture there with still be a vast amount of silanols left on the surface. Injection of a known amount of an amine should block an equivalent number of surface hydroxyl groups, because a 1:1 mechanism can be assumed.

At a column temperature of 110°C, the amine slowly moves along the column. The amine retention time obviously depends on the amount of amine and it is over 50–70 min. The retention time of a hydrocarbon is much shorter. Thus it is possible to check how the blocking of silanols by the amine influences the retention time of the hydrocarbon solute. Starting with the amine injection, the subsequent injections of benzene reveal a decrease of the retention time. This might be explained by the

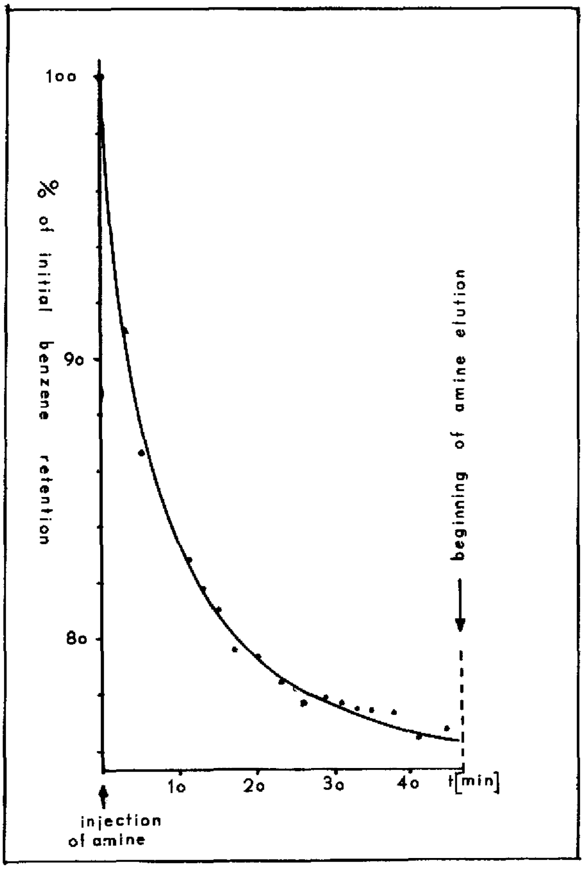

Fig. 2. The influence of diethylamine (1.6 μl) on benzene retention. Conditions as in Fig. 1, except column temperature, 110°C.

movement of amine along the packing bed to block the strongest adsorption sites in the column. Fig. 1 shows a curve of benzene retention volume changes *vs.* the time elapsed since the injection of *n*-butylamine.

The injection volume of *n*-butylamine was as low as 1.4 μl. This is equal to 14.2 μmol, and the same amount of silanols could be blocked. Assuming that about 50% of the hydroxyl groups had been deactivated with the silylating mixture, only about 0.3% of the silanols could be masked by the amine. This means that as few as 0.3% of the hydroxyl groups are responsible for over 20% of benzene retention. The *n*-butylamine is eluted from the column after *ca.* 66 min; after a further 50 min the recorder sets a new baseline but the amine is still eluting from the column. During that time the retention of benzene slowly increases as more and more hydroxyl groups unblock. After 19 h from the amine injection the benzene retention has returned to *ca.* 91.6% of the initial value: this means that some of the *n*-butylamine is chemisorbed. Conditioning at 270°C returns the retention to its the initial value.

A similar phenomenon was observed when diethylamine was applied instead of *n*-butylamine: 1.6 μl of diethylamine decreased the retention of benzene to 78% of the initial value (Fig. 2).

CONCLUSIONS

All these results are preliminary and further work is in progress, but it was very surprising to find that such a small amount of hydroxyl groups, 14.2 μmol, or roughly *ca.* 0.3% of all silanols present, can be responsible for *ca.* 20% of benzene retention. This means that some hydroxyl groups can interact much more strongly than others, or that they are different from the others (there are single, vicinal, and geminal silanols on the silica surface) or that they are much more accessible than the others.

Such a high reactivity of some (relatively few) silanols could explain apparent differences between various types of liquid chromatographic packing despite their similar carbon coverage. It is hoped that the method presented here will allow an evaluation of the distribution of retention sites on both modified and unmodified silica surfaces.

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