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INVESTIGATION OF SMALL POPULATIONS OF REACTIVE SILANOLS ON SILICA SURFACES

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SUMMARY

A gas chromatographic method was used to reveal the importance of a small population of silanols on a silica surface in relation to the retention of both saturated and unsaturated hydrocarbons. The application of diethyl ketone instead of the previously applied amine as a titrant is recommended. The correlation of the surface concentration of reactive silanols with trace metal content is discussed.

INTRODUCTION

In previous papers[1–4] we showed that very small populations of active adsorption centres on silylated[1,3] and bare silica[2,4] can be responsible for a considerable part of the retention in gas chromatography (GC). The blockage of this population with amine molecules was shown to lead to a considerable improvement in column efficiency, which emphasized the importance of the silanol population on the adsorbent surface[3]. We expressed the belief that the active centres are the silanols.

Marshall and co-workers[5–7] showed that some small populations of silanols have a considerable influence on high-performance liquid chromatographic (HPLC) column efficiency. They concluded[6] that a chemically distinct group of associated silanols occur on a silica surface, and emphasized the high reactivity of the silanols.

The questions now arise of whether the sites are really silanols and why some of the silanols are more reactive than others. The silanols which occur on fully hydroxylated silica at a concentration of 8 μmol/m^2 (ref. 8) are believed to be the most important or the only adsorption sites on the silica surface under GC conditions[9,10]. Their importance in HPLC separations has also been recognized and emphasized[11,12].

It has been known for years that several kinds of silanols exist on a silica surface, namely "free" (isolated or single), "geminal" and "vicinal"[9]. These types of silanols were suspected to be associated with different retention (or reaction or adsorption) activities[9]. Snyder and Ward[13] postulated that two vicinal hydroxyl groups separated

by an optimum distance of 3.1 Å can form a so-called reactive hydroxyl site on the silica surface. The ratio of reactive to total hydroxyls varied from 0.71 for ordinary silica to about 0.02 for pyrogenic silica of the Cab-O-Sil type. Clark-Monks and Ellis[14] found that about 10% of hydroxyls formed so-called anomalous adsorption sites on a pyrogenic silica surface. Low et al.[15] showed that specially prepared silica may contain on the surface really anomalous adsorption sites capable even of effecting the dissociative adsorption of hydrocarbons. It was concluded that the sites are not silanols but some structural defects of the silica skeleton. The surface concentration of the sites was determined to be 0.28 μmol/m^2 [16]. Another strange property of silica was described by Krasilnikov et al.[17], who found a very small number of sites (0.0001–0.0002 μmol/m^2) to adsorb oxygen, but the nature of the sites was not discussed. These few examples are outlined to show that silica may contain some sites of an unusual adsorption strength.

However, Snyder and Poppe[18] assumed that under liquid chromatographic conditions non-free silanols would not contribute to surface inhomogeneity and the silanols would have a little effect on an overall retention. The various activities of the silanols can be manifested in their different acidities and reactivities with silylating reagents. Snyder[9,13,19] suggested a higher reactivity of vicinal silanols over the isolated groups. Miller et al.[20] reported the possibility of the formation of a hydrogen bond between geminal silanols. For this reason the geminal silanols can belong to the group of the reactive silanols. According to Miller et al.[20], a silylating reagent reacts preferentially with more acidic hydroxyls and the pH of the remaining silanols increases with increase in the modifier content on the surface. The silanols were said to be unevenly distributed on the surface and grouped in the form of clusters. Earlier the alkyl radicals on the reversed-phase (RP) HPLC phases were found spectroscopically to occur in clusters on the silica surface[21,22].

A wide diversity of silica surface acidities have been reported, with pK_a values of the silanols of 1.5[23], 5–7[24], 6–8[25], 7.1 $\pm$ 0.5[26], 9.5[27] and 10[28]. One of the possible reasons for such a diversity is contamination of the silica with traces of metals. These traces were found to be responsible for the difference in adsorption activity between chromatographic-grade silica and pyrogenic silica[29,30]. On the surface of porous glasses containing appreciable amounts of boron, two acidic centres were found, one with pK_a = 5.1 and the other with pK_a = 7. Centres having pK_a = 7 were identified as silanols whereas the other sites could not be identified as B–OH because this group is much less acidic[31].

It is known, however, that an insertion of a metal impurity into the silica network should form on the surface structural Lewis sites, which cause an increase in the acidity of neighbouring silanols[32]. Theoretical ab initio calculations led to a similar conclusion[33]. Adsorption of amines[34,35] and of furan[36] on a silica gel surface at very low coverages (ca. 0.1 μmol/m^2) proceeds with much higher heats of adsorption than that at higher coverages. These high values of the heats of adsorption were connected with the presence of Al, Fe or B impurities in the silica matrix[35–37]. Silica gel containing traces of Al also has catalytic acitivity[37].

An adverse influence of traces of metals on chromatographic separations has been reported. Methods of removing the metals from GC supports have been described[38]. Verzele et al.[39] showed by nuclear activation analysis that chromatographic-grade silica gels may contain a variety of impurities totalling 0.1–0.3%.

Removal of trace metals was shown to improve HPLC separations[40]. The contents of trace metals in HPLC packings was briefly reviewed by Verzele[41].

Other important papers published recently are those by Köhler and co-workers[42,43] and Mauss and Engelhardt[44]. Köhler and co-workers pointed out that the undesirable adsorption of basic compounds is caused by relatively few isolated silanols with high acidity. A very small amount (*ca.* 10 nmol) of N,N-diethylaniline was found to deactivate the strongly adsorbing sites. They concluded that an unidentified concentration of bonded-phase ligand is apparently required to modify the few residual, deleterious, acidic silanol groups that remain even on a fully hydroxylated silica surface. We hope that this and our previous papers[1–4] will help to determine the surface concentration of these strongly adsorbing sites. Mauss and Engelhardt[44] also emphasized the responsibility of the acidic, isolated silanols for adsorption of basic molecules while hydroxyl-containing solutes interact mainly with vicinal hydrogen-bonded silanols.

The problem of the small, reactive population of silanols was discussed in details in a recently published review by Nawrocki and Buszewski[45].

The aim of this paper is to report the further development of the method of gas-phase titration described previously[1–4] and particularly attempts to correlate the results of the method with those obtained by neutron activation analysis and to apply compounds other than amines as the titrants. The influence of the blockage of the strongest adsorption sites on the retention of *n*-alkanes is also discussed.

EXPERIMENTAL

A GCHF 18.3 gas chromatograph (Chromatron, Berlin, G.D.R.) with a flame ionization detector was used. Argon was used as the carrier gas. Kieselgel 60 (Machery, Nagel & Co., Düren, F.R.G.), particle size 0.12–0.15 mm, extracted with 20% hydrochloric acid, was examined. Experiments on the adsorption of amines on the silica surface were carried out in stainless-steel columns (0.5 m × 4 mm I.D.). For other experiments silanized glass columns (1 m × 3 mm I.D.) were used.

n-Butylamine (BDH, Poole, U.K.) was distilled before use and methanol, acetone and diethyl ketone (all from POCh, Gliwice, Poland) were of analytical-reagent grade and were used as received. Water was doubly distilled in a quartz apparatus.

A 10-μl syringe (Hamilton, Bonaduz, Switzerland) was used for injections of amines, water, methanol, acetone and diethyl ketone and a 1-μl syringe for the injections of hydrocarbons. Usually 0.5 μl of hydrocarbon vapour was injected.

The dead volume of the column was calculated by the method of Ambrus[46] from the total retention volumes of C_5–C_9 *n*-alkanes. The specific surface area and mean pore diameter of the silica were determined by means of a Sorptomat 1700 instrument (Carlo Erba, Milan, Italy) from nitrogen adsorption data at liquid nitrogen temperature and the BET equation.

Neutron activation analysis (NAA) conditions for the silica were as follows: sample and standards were irradiated in the Dalhousie University SLOWPOKE-2 reactor (DUSR) using either an inner site for thermal neutron irradiations or the cadmium site for epithermal neutron irradiations. The reactor flux for inner sites was maintained at $5 \cdot 10^{11}$ n cm^{-2} s^{-1}. Approximately 100 mg of silica sample were used as

this allowed reproducibility while maintaining a manageable activity. Short- and medium-lived nuclides were determined by irradiating the sample in the cadmium-shielded site for 4 min, allowing them to decay for 8 min and counting for 10 min. The cadmium site was used to reduce the high activities due to ^{24}Na, ^{38}Cl and ^{28}Al. Long-lived nuclides were determined by irradiating in an inner site for 7 h, allowing a decay of approximately 3 days and counting for 12 h. The samples were counted on either a Canberra 60-cm^3 Ge(Li) detector or an Aptec planar 500-mm^2 hyperpure germanium low-energy photon detector. The detectors were coupled to a Tracor Northern TN-11 or Canberra Jupiter Series 80 multi-channel analyser, respectively. Corrections for the production of ^{28}Al due to the $^{28}Si(n, p)$ ^{28}Al reaction were made, and also for the production of ^{27}Mg from the $^{27}Al(n, p)$ ^{27}Mg reaction. Standards were prepared by spotting an appropriate amount of an atomic adsorption standard (Fisher, BDH or Alpha) on a matrix of silica gel.

RESULTS AND DISCUSSION

The silica used in all experiments is characterized in Table I. The Machery, Nagel & Co. silica purified by extraction with 20% hydrochloric acid seems to be one of the purest materials of this type compared with other silicas analysed for traces of metals by NAA[39]. It contains only calcium at a concentration of ca. 350 ppm, which, as will be shown later, lies in the investigated range of silanol concentrations.

Although, the principle of the gas-phase titration was described previously[4], it is outlined again in Fig. 1, which shows the main feature of the experiment. A known amount of amine is injected into a column. The retention time of amine is very long and, as it moves slowly along the column, it blocks the most active centres on the surface of the adsorbent. During the presence of amine in the column one can inject a rapidly eluting hydrocarbon, e.g., benzene. The period of time elapsed from the injection of amine to the beginning of amine elution permits several injections (their number depends on the amount of amine) of benzene to be made.

The consecutive injections of benzene reveal the decrease in the retention time (or volume) of the solute. The influence of the amine on the retention time of benzene

TABLE I

CHARACTERISTIC OF THE SILICA

Characteristic[a]	Value	
S (m^2 g^{-1})	442	
D (nm)	7.0	
V_p (cm^3 g^{-1})	0.76	
NAA results (ppm):	Al –	Mn –
	Ca 348	Mo –
	Ce –	Na –
	Cr –	Sb 0.133
	Fe –	Sc –
	Hf 0.392	Sm 0.008
	La 16.1	Th –
	Mg 1.25	Ti 16.4

[a] S = specific surface area; D = mean pore diameter; V_p = pore volume.
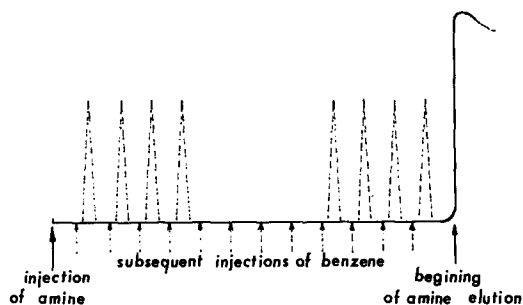
Fig. 1. Principle of the gas phase titration method.

on various adsorbents was shown previously[1-4]. Finally, before the beginning of amine elution, injection of benzene shows the shortest retention time for a given amount of amine, *i.e.*, the benzene retention reaches its final value. For various amounts of amine, various final retention times can be observed[2].

In Fig. 2 the decrease in benzene retention is plotted against the amount of amine injected. An amount of 180 μmol of amine decreases the retention of benzene by 22%. As 1:1 amine–silanol interactions can be assumed, a known amount of amine blocks a corresponding number of silanols, so it can be said that the 22% decrease in benzene retention was caused by blockage of 180 μmol of silanols. One can then further state that these blocked 180 μmol of silanols are responsible for 22% of benzene retention. As the column contained 3.185 g of silica and assuming a silanol concentration of 8 μmol m^{-2} (ref. 8), one can easily calculate the total number of silanols in the column, *viz. ca.* 11 260 μmol; 180 μmol are equal to 1.60% of all available silanols. Silanols are considered to be the main (or the only) adsorption sites on a silica surface[9,10]. Why are 1.60% of the silanols responsible for a 22% decrease in benzene retention? As was shown previously[1-4], a silica surface contains probably a small population of active centres which are much more retentive than the remaining sites. For the detection and
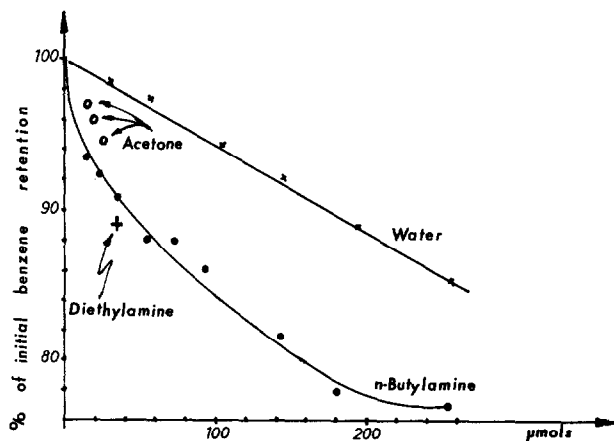

Fig. 2. Effects of various blocking reagents on retention of benzene.

quantification of the sites, blockage with an amine and subsequent examination of retention time of a rapidly eluting hydrocarbon solute can be applied.

However, the application of an amine appeared to be troublesome, particularly on bare silica surfaces because the very long retention time made the experiments very time consuming. Moreover, on some silica surfaces, the amine was chemisorbed irreversibly and even prolonged conditioning at elevated temperatures did not restore the column to its initial properties (we have to state here that for silylated surfaces an amine still seems to be the best choice). For this reason, other compounds were examined as possible blocking reagents, viz., water, methanol, acetone and diethyl ketone (DEK).

Molecules of water are able to block the strongest adsorption sites on the silica surface. However, we observed a much smaller effect of water than of an amine on the retention of benzene. Some results are shown in Fig. 2. As can be seen, 180 μmol of n-butylamine cause a 22% decrease in the retention of benzene whereas the same amount of water decreases the retention by only 10.5%. The observed effect of a lower retentivity of benzene (or more generally of hydrocarbons) on a wet than on a dry silica surface can be considered as contradictory to the results of Hair and Hertl[10], but we think the contradiction arises because the effect seems to be the sum of two opposing phenomena: a decrease in retention as a result of blockage of the strongest adsorption sites and an increase in retention as a result of the presence of water[10]. It is likely that the former effect prevails and overall we observe a decrease in the retention of benzene.

There are two disadvantages of water as the blocking reagent. First, the retention time of water at 150°C was very short, allowing one to three injections of benzene to be made before the beginning of water elution. After 10–15 min from the injection of water the adsorbent (silica) regained its initial properties. Second, the low molecular weight of water means that 1 μl contains as much as 55 μmol (whereas with n-butylamine 1 μl = 10.14 μmol), which makes it difficult to investigate the smallest populations of the strongest adsorption sites.

Methanol and acetone were also tested. However, the relatively short retention times of the compounds and their high volatility make their application as blocking reagents difficult, at least at 150°C, i.e., the temperature used in these experiments. Some results obtained with acetone are included in Fig. 2. Generally, neither water, methanol nor acetone should be used to replace an amine as a blocking reagent.

However, the attempt to employ DEK instead of the amine seemed to be successful. DEK is relatively non-volatile and its density and molecular weight mean that 1 μl = 9.47 μmol, which is suitable for the titration of small populations of adsorption sites.

The problem of comparing the effects of the various blocking reagents was overcome by plotting

$$\Delta V_r = \frac{\Delta V(\text{cm}^3)}{A(\mu\text{mol})} = f(c_A) \ (\mu\text{mol m}^{-2})$$

where ΔV is the decrease in the retention volume of benzene (or other solute), A the amount of blocking reagent, ΔV_r the relative decrease in retention volume, or in other words, the decrease in the retention of benzene caused by 1 μmol of the blocking

reagent at a given surface concentration of the reagent, and c_A the surface concentration of the blocking reagent.

In Fig. 3 the effects of n-butylamine and DEK on the retention of benzene are compared. The two curves lies close each other, which indicates blockage of the same adsorption sites on the silica surface. The amine curve bends at values of $c_A = 0.02$ and $0.05 \ \mu$mol m^{-2} whereas the DEK curve bends at $c_A = 0.03 \ \mu$mol m^{-2}. Hence the surface concentration of the strongest adsorption sites can be determined to be 0.02–$0.03 \ \mu$mol m^{-2}. The linear decrease in the ΔV_r values over the range 0–0.02 (0.03) μmol m^{-2} indicates the existence of a broad range of strongly retentive silanols with decreasing strength of interaction. Assuming the total number of silanols to be $8 \ \mu$mol m^{-2}, the strongly interacting population constitutes only 0.25–0.38% of the total number of the hydroxyls. Such a population can considerably influence the retention of hydrocarbon solutes. It should be emphasized that the surface concentration of the population has to be considered to be a characteristic peculiarity of the given silica and not a general property.

The dependence of the relative decrease in the retention volume of n-hexane on the amount of amine injected is shown in Fig. 4. The adsorption of n-hexane (*i.e.*, an n-alkane molecule belonging to the first group of the Kiselev classification[47]) is stronger on the small population of strongly interacting adsorption sites than on other sites on the surface; this was observed for both n-butylamine and DEK as the blocking reagent. The respective values of ΔV_r for benzene and n-hexane indicate that the interactions of the sites are about ten times stronger with benzene than with n-hexane.

NAA showed only four trace metals in ppm range: Ca, 348; La, 16.1; Ti, 16.4; and Mg, 1.25 ppm. No traces of Al, Fe and Na were detected. The latter are usually present in chromatographic-grade silica at relatively high concentrations[39]. We should emphasize the unique purity of the silica gel used here; all of the known (ref. 39 and our
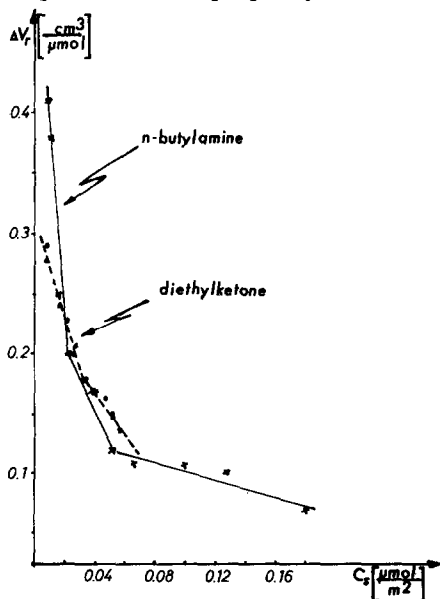

Fig. 3. Gas phase titration curves of silica gel MN. Blocking reagents: *n*-butylamine and DEK. Solute: benzene. Column temperature: 150°C.
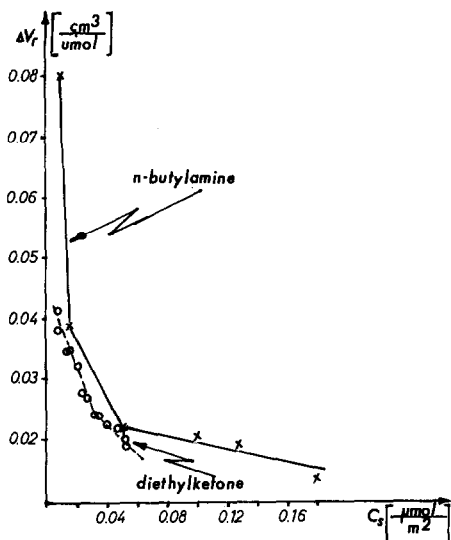
Fig. 4. Gas phase titration curves of silica gel MN. Blocking reagents: *n*-butylamine and DEK. Solute: *n*-hexane. Column temperature: 150°C.

work) silicas analysed for trace metals always contained much more impurities at higher concentrations. This unique character of the silica led us to correlate the observed Ca concentration with the "end-point" of gas-phase titration. It would be interesting to consider the results of the gas-phase titration taking into account the NAA values. Three problems can be discussed at this point: can Ca cations influence the acidity of the surface silanols?; how can the bulk concentration of Ca be recalculated as surface concentration?; and how can one compare the surface Ca concentration and the "end-points" in gas-phase titration?

The presence of Mg in the silica structure was shown[32] to produce so-called structural Lewis sites, which increased the acidity of the neighbouring silanols. The similarity of Mg and Ca allows a similar influence of Ca on the silanol acidity to be assumed. Mg inserted in the silica network can exist there in octa- or tetra-coordinated form.

The silica gel used in this work had a specific surface area of $442 \ m^2 \ g^{-1}$. Taking into account the specific gravity of the amorphous silica $(2.2 \ g \ cm^{-3})[8]$, we can easily calculate the average thickness of the silica skeleton, *i.e.*, *ca.* 2 nm. As the average length of Si–O bonds and the average Si–O–Si angle are well known (0.1604 nm and 130°, respectively), most of the silica walls should contain about four silicon atoms in their thickness. Other sources[48–50] report the specific gravity of the silica to be 1.9 $g \ cm^{-3}$, which would give a slightly thicker wall. We can conclude that each of the Ca atoms present in the silica network will have a surface Si atom in its vicinity. This simply means that each of the trace metal atoms can influence the acidity of the surface silanol.

Recently, Sadek *et al.*[51] also confirmed that metal impurities do not directly participate deleteriously in the chromatography of many classes of compounds, but they indirectly influence adjacent silanol groups, which causes the effect seen chromatographically.

A 348 ppm amount of Ca corresponds to 8.7 μmol of Ca per gram of SiO_2, which leads to a Ca surface concentration of 0.02 μmol m^{-2} (for La and Ti the respective values are 0.0003 and 0.0008 μmol m^{-2}). This Ca surface concentration corresponds very well with the first gas-phase titration end-point for amine titration, but for DEK the first titration end-point is observed at 0.03 μmol m^{-2}.

As one can see in Figs. 3 and 4, the strongly interacting silanols are not identical. It can be speculated that traces of metals influence the acidity of the silanols, depending on the distance between the metal and the silanol. The situation is comparable to the IR band for hydrogen-bonded silanols, the broadness of which is caused by different mutual distances between the silanols[10]. It is likely also that one trace metal atom influences the acidity of two or more silanols.

The above discussion does not prove that the existence of strongly interacting silanols is caused by the metal impurities, but the agreement between the Ca concentration and the titration end-point seems to be striking and worth further research.

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