Journal of Chromatography, 391 (1987) 266–268
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 19 308

Note

Influence of silica surface heterogeneity on the retention of hydrocarbons in gas chromatography

JACEK NAWROCKI
Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznań (Poland)
(Received September 26th, 1986)

Silica surfaces are heterogeneous, which has often been explained by the presence of various kinds of silanols (single, geminal and vicinal) and siloxane bonds on the surface. Recently, it has been shown that the extremely small number of active sites on the silanized surface of silica can be responsible for a high retention of benzene[1]. Such a small number of sites cannot be explained by the different kinds of silanols mentioned above. The previous results[1] led to this investigation of the surface of bare silica.

EXPERIMENTAL

A GCHF 18.3 gas chromatograph (Chromatron, Berlin, G.D.R.) equipped with a flame ionization detector was used with argon as the carrier gas. A stainless-steel column (0.5 m × 0.4 cm I.D.) packed with Kieselgel 60 silica gel (Macherey, Nagel & Co., Düren, F.R.G.) previously extracted with 20% hydrochloric acid in a Soxhlet apparatus for several days and then washed with doubly distilled water until neutral was used.

Hamilton syringes (10 and 50 μl) were employed for the injection of *n*-butylamine (Hopkin and Williams, Chadwell Heath, U.K.). The amine was distilled before use. A 1 μl Hamilton syringe was used for the injection of benzene; 0.5 μl of benzene vapour was injected. The column temperature was kept at 150°C.

The specific surface area of the silica was measured by means of a Gravimat vacuum microbalance (Sartorius, Göttingen, F.R.G.) and was found to be 330 m^2/g.

RESULTS AND DISCUSSION

The injection of an amine on to a bare silica results in blockage of the active sites on the silica surface. As a 1:1 mechanism can be assumed, a known amount of the amine blocks a corresponding number of the sites. At the column temperature amine moves slowly along the column and blocks the strongest sites on the surface. The retention time of the amine is very long (it takes several hours for elution of the amine to start) and this permits the retention time of much faster eluting hydrocarbons to be measured during the presence of the amine in the column. In other words, it is possible to check how the blockage of silanols influences the retention of a hydrocarbon solute.

0021-9673/87/$03.50

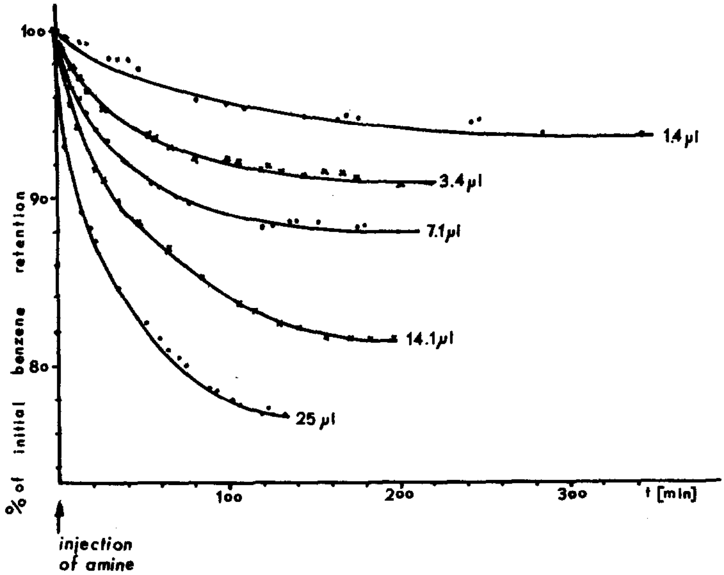

Fig. 1. Dependence of benzene retention on the amount of amine injected.

Fig. 1 shows the curves of the retention volume of benzene *vs.* time after injection of *n*-butylamine for various amounts of the amine. The retention time of the amine obviously depends on the amount injected. The more amine is present in the column, the larger and faster are the changes in the retention volume of benzene. The amounts of the amine used were in the range 1.4–25 µl, which is equal 14.2–253.5 µmol. The columns contained 3.185 g of silica and assuming an average of 8 µmol of hydroxy groups per square metre, it therefore contained over 8400 µmol of silanols. This means that the amine could block 0.15–3% of the total silanols. The blockage resulted in a 6.5–23% reduction in the retention of benzene. This indicates that the very small number of sites is responsible for the high retention.

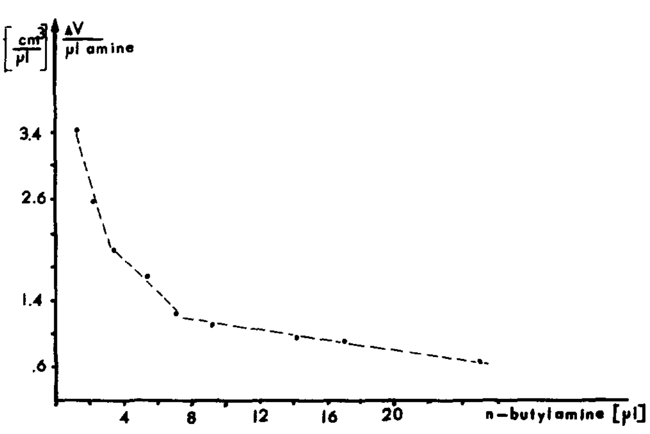

Fig. 2. Relative change in benzene retention in relation to the amount of the amine. ΔV = Decrease in benzene retention volume caused by a given amount of the amine.

Fig. 2 shows the relative changes in the retention of benzene in relation to the amount of amine injected. It can be clearly seen that the silanols differ among themselves in their strength of interaction with the aromatic hydrocarbon solute. First hydroxy groups blocked with the first small amounts of the amine have the strongest influence on the retention of benzene, then the strength of the interaction decreases.

The varying accesibility of silanols, micropores or small amounts of impurities in the silica gel can be considered to be potential reasons for the observed activity. It has been found that Al, B and Fe can considerably enhance the acidity of silanols in their vicinity, but some intrinsic activity of the pure gel was suspected[2].

The high reactivity of a small number of silanols can possibly explain the considerable differences between liquid chromatographic packings despite their similar carbon coverages when one considers that at least 50% of silanols on the silica surface cannot react with the silanizing reagent for steric reasons.

REFERENCES

1 J. Nawrocki, *J. Chromatogr.*, 362 (1986) 117.
2 P. B. West, G. L. Haller and R. L. Burwell, Jr., *J. Catal.*, 29 (1973) 486.