Note

Adsorption capacity and surface area measurements in high-performance liquid chromatography on dynamically modified silica

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In the course of our studies in liquid chromatography on dynamically modified silica[1–4], numerous observations were made on the relationship between the retention of non-ionic solutes and the amount of quaternary ammonium compound adsorbed on the bare silica.

This paper summarizes these findings and discusses some methods for measuring the adsorption capacity of a liquid chromatographic column. Further, we have previously suggested[2] a linear relationship between the adsorption capacity of a given silica and its specific surface area. Further investigations are described that confirm this suggestion.

EXPERIMENTAL

Adsorption isotherms

Adsorption isotherms were measured using either the breakthrough method or the elution method. The apparatus used for the breakthrough measurements was described in ref. 2 and the adsorption capacities were calculated as reported in ref. 5. In the elution method the quaternary ammonium compound was eluted from the column following equilibration of the chromatographic system[3] and the concentrations in the eluent were determined by either ultraviolet measurements[2] or liquid chromatography[3,4].

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Surface areas

Surface areas were measured by the BET method[6], using a Ströhlein area meter (Ströhlein, Düsseldorf, G.F.R.).

Chromatography

The apparatus and columns used for liquid chromatography have been described previously[2].

Procedures

The adsorption capacities and retentions were measured using various chromatographic systems. The basic system consisted of LiChrosorb Si 60 (5 μm) as the support and 2.5 mM cetyltrimethylammonium (CTMA) bromide in methanol–water–0.2 M potassium phosphate buffer (pH 7.5) (50:45:5) as the eluent. In this system each of the parameters listed in Table I was changed one at a time, over the range of conditions quoted.

Chemicals

All solvents and chemicals were of analytical-reagent grade from E. Merck (Darmstadt, G.F.R.).

RESULTS AND DISCUSSION

The surface area was measured on fourteen different brands of silica and related to the adsorption capacities as determined from the same batch of each individual silica. From Fig. 1a it appears that a linear relationship exists. The areas measured differ from the mean surface areas for each brand of silica specified by the manufacturers. If the mean surface areas are used the linear relationship is still evident, but the variation is much larger (Fig. 1b). The amount of CTMA adsorbed per

TABLE I

PARAMETERS AND RANGE OF CONDITIONS TESTED

| Parameter	Conditions
CTMA concentration	0.5–7.5 mM
pH	4–10
Buffer concentration	2.5–50 mM
Buffer cation	Potassium, ammonium, diethylammonium, triethylammonium, diethanolammonium, triethanolammonium, piperazinium, tetramethylethylenediammonium
Silica packing	Chromosorb LC 6 (1), Hypersil (2), LiChrospher Si 100 (3), LiChrosorb Si 60 (4), LiChrosorb Si 100 (5), Nucleosil 50 (6), Nucleosil 100 (7), Nucleosil 100 V (8), Partisil (9), Polygosil 60 (10), Spherisorb S W (11), Spherosil XOA 600 (12) Spherosil XOA 800 (13), Zorbax SIL (14) (the identification nos. 1–14 are referred to in Fig. 1)
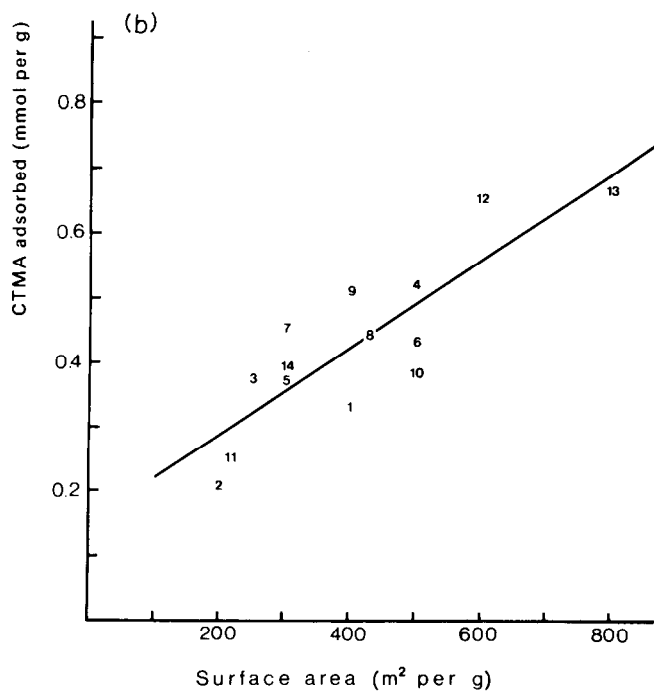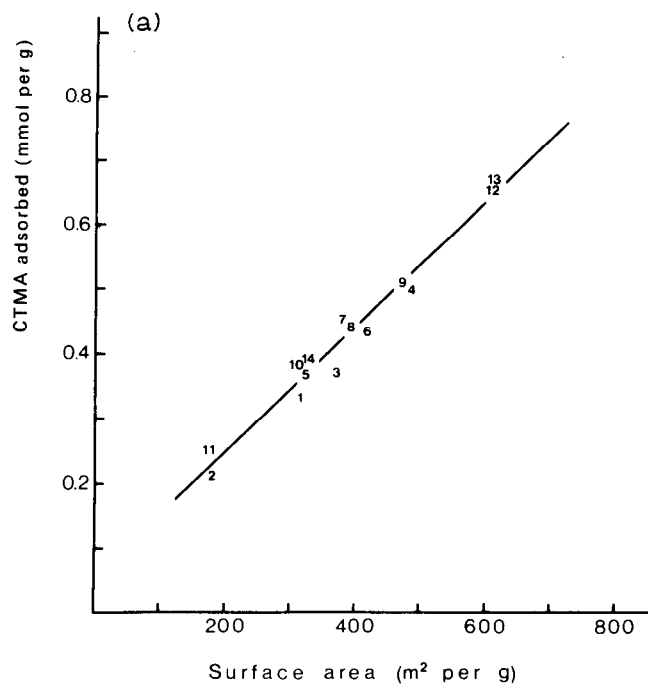
Fig. 1. Adsorption capacity of silica packings as a function of (a) the surface area measured for the given batch of silica or (b) the mean surface area specified by the supplier (ref. 2). The numbers refer to the brand of silica (*cf.*, Table I).

gram of silica may thus be used as a measure of the surface area of a given batch of silica.

The adsorption capacity was measured by either the breakthrough method or the elution method. The breakthrough method has the drawback of requiring a refractive index detector and in some instances it may give erroneous results. This happens under conditions where large amounts of surfactant are adsorbed, because then an initial, partial breakthrough occurs owing to a temporary decrease in pH[3,7]. The breakthrough method does, however, offer information on the adsorption process that cannot be obtained with the elution method[2]. For routine measurements the elution method is the most convenient and accurate.

A third, chromatographic method for the measurement of the adsorption capacity of bare silica is possible. From Fig. 2. it appears that for a given column size and modifier concentration the adsorption capacity for CTMA is proportional to the capacity factor for benzene over a wide range of experimental conditions. The range of conditions underlying Fig. 2 are listed in Table I.

In one instance a limitation to the linear relationship shown in Fig. 2 was found, namely that it holds true only for surfactant concentrations below the critical micellar concentration. Above this concentration the presence of micelles alters the
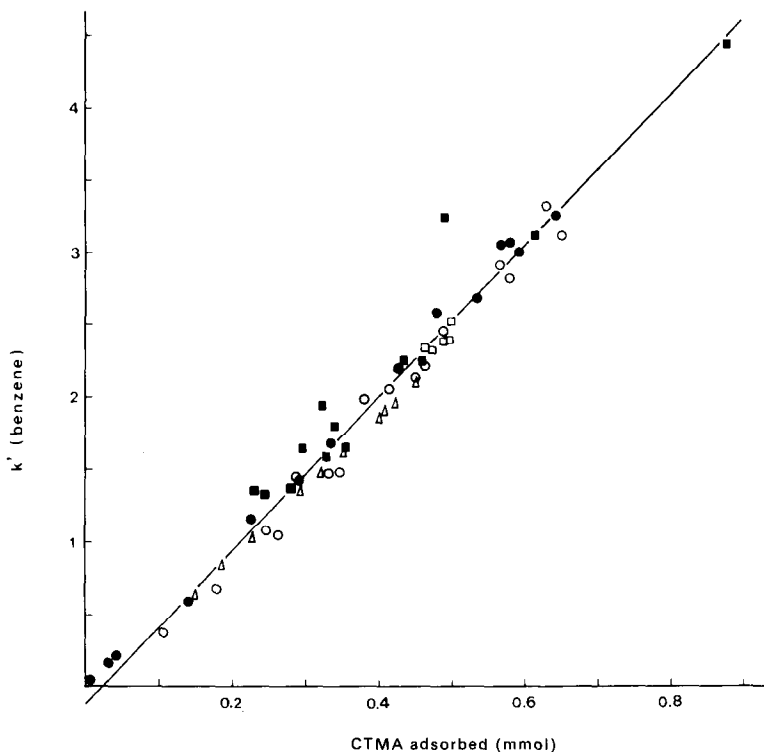

Fig. 2. Relationship between the capacity factor for benzene and the amount of CTMA adsorbed on the silica for ■, different column materials; ○, CTMA concentrations; △, buffer cations; ●, pH values; and □, ionic strengths. Regression line: $y = 5.19 \, x - 0.09$.

eluent to such an extent that the retention of benzene is affected. With this limitation in mind it is possible to use the capacity factor for benzene in a chromatographic system with dynamically modified silica as a measure of the surface area of the silica.

CONCLUSION

The surface area of bare silica was shown to be linearly related to the adsorption capacity for CTMA in a chromatographic system using the dynamically modified silica. The adsorption capacity can be measured using one of the well established methods: the breakthrough method or the elution method. It has been shown that in many instances it is also possible to use the capacity factor of benzene in a dynamically modified system as a measure of the adsorption capacity of the silica.

ACKNOWLEDGEMENT

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