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Effect of silver-modified silica on retention and selectivity in normal-phase liquid chromatography

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Abstract

Silica surface modification by silver ions has been studied by high-performance liquid chromatography. After treatment with silver nitrate at pH 4.3 and 7.0, the silver-modified silicas were used in physical and chemical analyses. From measurement with an atomic absorption flame emission spectrophotometer, the amount of silver adsorption was determined to be 420 ppm on silver-modified silica at pH 4.3 and 4500 ppm at pH 7.0. The separation factors, α , of methyl linoleate versus methyl linolenate were measured to be 1.18 on silver-modified silica at pH 7.0, but could not be measured on original non-modified silica, using 1,4-dioxane-*n*-hexane (2.0:98.0, v/v) as the eluent. The experimental results showed that silver-modified silicas gave significant improvement in the separation of the model unsaturated fatty acids.

1. Introduction

The surface of silica and adsorption on that surface has been the subject of many investigations. It has been shown that specific adsorption occurs on the surface silanol groups [1,2]. On the other hand, as the acidic silanol groups are responsible for the cation-exchange properties of silica, the theoretical specific capacity, Q_0 , in aqueous solution was shown to be equivalent to the concentration of surface hydroxyl groups, which is about $8 \mu\text{mol}/\text{m}^2$ for a totally hydroxylated silica [3]. For strongly hydrated multivalent cations, the absorption capacity increases considerably with increasing the pH, as was shown by Vydra and co-workers [4,5].

Depending on pH, metal ions for example may exist in their non-hydrated or their hydrated forms. As a consequence, one can expect a very complex ion-exchange behaviour of silica in electrolyte solution. While water and aqueous solutions reduce the activity and acidity of the surface sites of silica, these properties are considerably enhanced in anhydrous media. In the special case of silica catalysts used for various heterogeneous reactions such as hydration–dehydration and isomerization, the acidity can be measured with the aid of Hammett and arylcarbinol indicators by titration with amines in organic solvents [6]. On the other hand, flash chromatography [7] provides a rapid and inexpensive general method for the preparative separation of mixtures requiring only moderate resolution.

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However, there are few reports, in either physical or chemical research, concerning the effect of silica surface modification by silver ions on the chromatographic properties of the packing [8–12]. Therefore, we have studied the preparation and evaluation of inexpensive silver-modified silica for large-scale preparative separations (e.g. 250 × 20 mm I.D.) and the routine purification of organic compounds. The results were compared with those using expensive high-performance liquid chromatography (HPLC) column gels.

2. Experimental

2.1. Reagent and materials

Benzene, N,N-dimethylaniline, N-methylaniline, 2-ethylpyridine, aniline, dimethylphthalate, di-*n*-butyl phthalate, phenol and calcium hydroxide were obtained from Wako (Osaka, Japan). The other reagents and organic solvents were of analytical reagent grade.

2.2. Porous silicas

Porous silicas were prepared in our laboratories (Table 1, Ag-0) [13]. The particle size was 9.8 μm.

2.3. Silver nitrate solution

Silver nitrate solution (1 g per 100 ml) was prepared by dissolving silver nitrate in desalted and distilled water. After standing for 24 h at

room temperature, the silver nitrate solution was filtered with a membrane filter (0.5 μm).

2.4. Silver-modified silica

A 10-g sample of dried silica (original, Ag-0, Table 1) was immersed in 100 ml of desalted and distilled water. Then the silica suspension was carefully adjusted to pH 4.3 (by adding silver nitrate solution), filtered with a membrane filter (0.5 μm), washed several times with methanol and dried in vacuo at 70°C for one day, finally producing Ag-I-modified silica, whose properties are listed in Table 1.

When this silica suspension had been adjusted to pH 7.0, the Ag-II-modified silica was produced, whose properties are also shown in Table 1.

The silver contents of Ag-0, Ag-I and Ag-II were determined with an SAS-727 Seiko Atomic Absorption Spectrophotometer (Tokyo, Japan) (Table 1). The specific surface areas of Ag-0, Ag-I and Ag-II were determined with an SA-1000 Shibata surface area pore volume analyser (Table 1).

2.5. Apparatus

The HPLC measurements were carried out on a Twinkle instrument (Jasco, Tokyo, Japan), equipped with a Uvidec-100 IV variable-wavelength detector (Jasco, Tokyo, Japan) and a column of 150 × 4.6 mm I.D., packed with Ag-0-, Ag-I- or Ag-II-modified silica.

Table 1
Characteristics of silver-modified silica

Modified silica	Specific surface area (m ² /g)	Pore volume (ml/g)	pH ^a	Silver adsorption (ppm)
Ag-0 (original)	374	1.21	5.40	–
Ag-I	364	1.21	5.42	420
Ag-II	342	1.20	7.65	4500

^a 5% slurry solution.

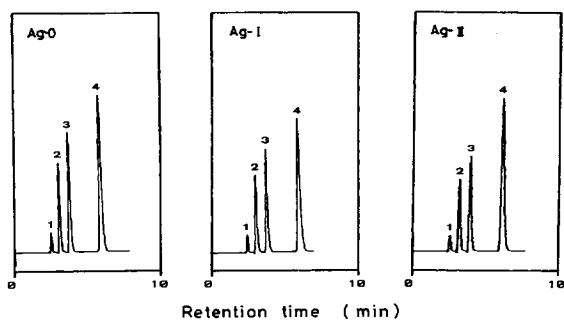


Fig. 1. The chromatographic behaviour of dioctyl phthalate, dibutyl phthalate and dimethyl phthalate (as neutral model compounds) on Ag-0-, Ag-I- and Ag-II-modified silica. HPLC conditions: methanol-*n*-hexane (1:99, v/v); column 150 × 4.6 mm I.D.; flow-rate 1.0 ml/min; detection 254 nm UV. Peaks: 1 = benzene; 2 = dioctyl phthalate; 3 = dibutyl phthalate; 4 = dimethyl phthalate.

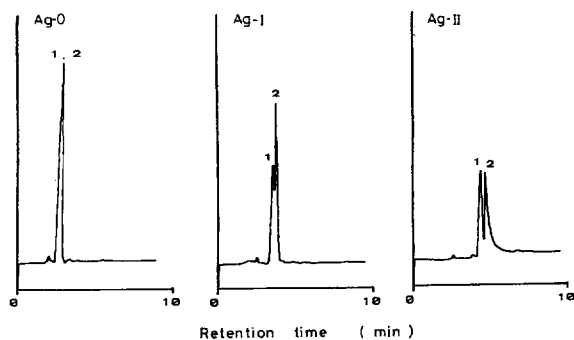


Fig. 2. Chromatographic behaviour of methyl linoleate and methyl linolenate (as model unsaturated fatty acids) on Ag-0-, Ag-I- and Ag-II-modified silica. HPLC conditions: 1,4-dioxane-*n*-hexane (2:98, v/v). Peaks: 1 = methyl linoleate; 2 = methyl linolenate. Other conditions as in Fig. 1.

3. Results and discussion

Fig. 1 shows the separation of the neutral model compounds on Ag-0-, Ag-I- and Ag-II-modified silica using methanol-*n*-hexane (1:99, v/v) as the eluent.

Fig. 2 shows the chromatographic behaviour of model unsaturated fatty acids. Methyl linoleate and methyl linolenate could be separated on Ag-II-modified silica, but not on Ag-0- and Ag-I-modified silica, with 1,4-dioxane-*n*-hexane (2:98, v/v) as the eluent. It was assumed that the effect of ion-exchange absorption on Ag-II affected the separation effect in the presence of silver ions.

The number of theoretical plates (N) and the peak asymmetry factor (As) for model unsaturated fatty acids (methyl linoleate and methyl linolenate) were measured on Ag-0-, Ag-I- or Ag-II-modified silica, with the same eluent (1,4-dioxane-*n*-hexane, 2:98, v/v) (Table 2).

By comparison of Ag-0-, Ag-I- or Ag-II-modified silica, the separation factors, α , were measured for the model unsaturated fatty acid compounds (methyl linoleate and methyl linolenate), under the same HPLC conditions (Table 2).

Table 3 shows that the separation of phenol vs. dimethyl phthalate, due to the influence of silver ions, was worse on NH_2 -modified silica [14,15] than on Ag-0-, Ag-I- and Ag-II-modified silica. The stability of Ag-II-modified silica were determined under the conditions used in this study. The column reproducibility checks were done with methanol-*n*-hexane (1:99, v/v) mixtures for a period of 1000 min at a flow-rate of 1 ml/min.

Table 2
Number of theoretical plates (N) and peak asymmetry factor (As) on Ag-0-, Ag-I- and Ag-II-modified silica

Modified silica	Methyl linoleate ^a		Methyl linolenate ^a		Dioctyl phthalate ^b		Dibutyl phthalate ^b		Dimethyl phthalate ^b	
	N	As	N	As	N	As	N	As	N	As
Ag-0	—	—	—	—	2776	1.1	3542	1.1	5079	0.9
Ag-I	—	—	—	—	3325	0.9	3500	0.9	3673	0.8
Ag-II	1494	—	2009	—	2952	1.2	3248	1.2	5385	1.2

N : per 15 cm.

^a Conditions as in Fig. 2.

^b Conditions as in Fig. 1.

Table 3
Chromatographic data of phenol (as acidic model compound) on Ag-0-, Ag-I-, Ag-II- and NH₂-modified silica

Modified silica	Separation factor, $\alpha = k'_A/k'_B$; phenol vs. DMP
Ag-0	3.06
Ag-I	4.50
Ag-II	4.37
NH ₂	–

DMP = dimethyl phthalate. Conditions as in Fig. 1.

It was suggested that the separation mechanism was affected mainly by the Ag–Si bond on the silica surface and that the silanol groups on the silica surface have an ion-adsorption interaction effect on the retention of some unsaturated fatty acid compounds; and on also unpaired selections [16].

Fig. 3 shows the relationship between the amount of silver adsorption on Ag-0 and a 5% slurry solution of each pH-treated silica; the latter elevates the amount of silver adsorption.

From studies with liquid chromatography with

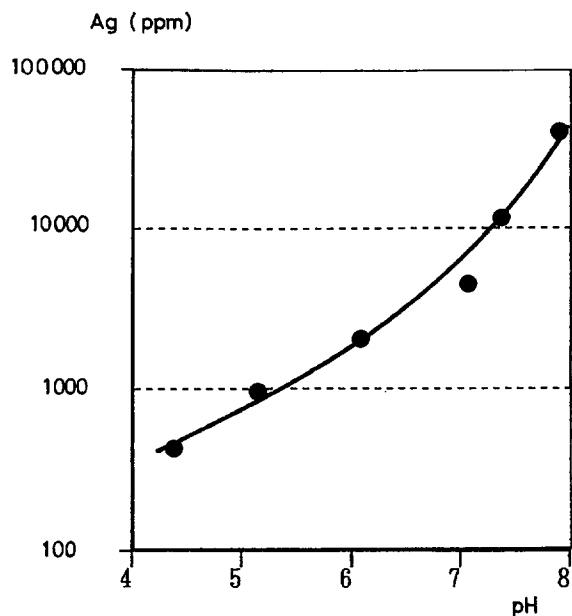


Fig. 3. Relationship between the amount of silver adsorption from a 5% slurry solution for silica treated at different pH values.

silica as sorbent, it is generally known that the interaction of the silica surface with the solute depends on the silanol groups. In previous papers [17,18], it was assumed that the hydrogen-bonded silanol groups on the silica surface have an inhibitory effect on the retention of the solute and that the retention effect was mainly due to free silanol groups on the silica surface. Moreover, the authors assumed that the silanol groups which reacted with the chemical reagent hexamethyldisilazane (HMDS) or octadecyldimethylchlorosilane (ODS) were mainly the free ones on the silica surface. It was also shown that the silanol group concentration, $\alpha_{OH(s)}$, of the reactive silanol is almost constant at about 2 groups per 100 Å² (1 nm², mean pore diameter 116 Å, specific surface area 298 m²/g, pore volume 1.22 ml/g, mean particle size 5.0 μm). According to our methods [14,15], the amount of silver on the silver-modified silica was 0.147 groups per 100 Å² (1 nm²) at pH 7.0.

From these experimental results, it was shown that silver-modified silicas were associated with a significant improvement in the separation of basic compounds, and that a relatively small amount of silver was needed to improve the separation of some unsaturated fatty acids.

In conclusion, it was indicated in the above discussions that Ag-II-modified silica is more suitable for the selective separation of some basic model compounds and can be prepared less expensively than purchased columns.

It is concluded from the present investigation that it is not sufficient to evaluate silica gels solely by the amount of silver on the silver-modified silica. The relation between the amount of silver adsorption and the specific surface of the silica supports must also be considered.

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