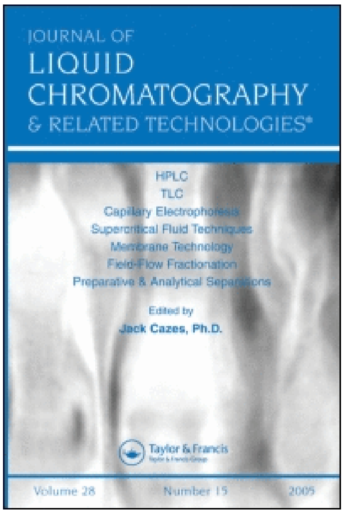

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Effect of Octadecyl-Modification on Retention When Using Titania as a Support

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EFFECT OF OCTADECYL-MODIFICATION ON RETENTION WHEN USING TITANIA AS A SUPPORT

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ABSTRACT

It is important to elucidate the effect of the support on retention when investigating the retention mechanism in reversed phase liquid chromatography. The objective of this research was to examine how octadecyl-modified phase can control the unique nature of Titania. Titania was synthesized in our laboratory by the sol-gel method. Octadecyl-modified Titania was prepared by silylation with a octadecyltriethoxysilane. By using anionic, cationic, acidic and basic solutes, the retention behaviours of the Titania and the octadecyl-modified Titania were determined under reversed phase conditions. In the use of aqueous methanol mobile phases containing acetic acid-sodium acetate or bicine-sodium hydroxide buffer, we observed that the Titania synthesized behaved as an amphoteric ion exchanger, and that the retention behaviours of the octadecyl-modified Titania were significantly influenced by octadecyl-modification. The effect of octadecyl-modification on retention was ascribed not only to octadecyl groups but also silanol groups, which were formed by silylation. The retention behaviour as a whole, however, was

clearly based on behaviour as an amphoteric ion-exchanger. Thus, we concluded that the octadecyl-modified phase, although it really influenced the retention behaviour, could not accomplish controlling the amphoteric ion exchange ability of the Titania in these experiments.

INTRODUCTION

It is generally accepted that the nature of the support can affect the chromatographic properties of bonded stationary phase. It is also necessary to have a detailed knowledge of the support when investigating the retention mechanism in reversed phase liquid chromatography. However, data on the supports cannot be obtained because no manufacturer provides full details. Therefore, we are starting an attempt to synthesize supports on a laboratory scale in order to investigate the effect of the supports on the chromatographic retention behaviour.

Titania has recently attracted interest as a new ceramic packing material, which possesses the desirable mechanical and physical properties of silica, and chemical stability superior to silica.[1-6] Titania is an amphoteric metal oxide and has anion-exchange properties in acidic pH and cation-exchange ones in alkaline pH,[7-8] although silica behaves as an only cation exchanger.[8] This means that the influence of the support on retention is worth further consideration when Titania is used as a support, because this unique nature of Titania would more strongly influence the retention behaviour than that of silica. To elucidate, the influence of the support on retention leads to reveal the function of bonded stationary phase. By octadecyl-modifying Titania, the unique nature, which is the amphoteric ion exchange ability, would be controlled. This degree of controlling the unique nature suggests the effect of octadecyl-modification. Thus, comparison of Titania and octadecyl-modified Titania on the retention behaviour is expected to give information about the function of octadecyl-modified phase.

We have already obtained silica on a laboratory scale,[9] from hydrolysis and polycondensation reactions of silicon alkoxide by the sol-gel method.[10-12] By this modified method, we have also obtained Titania on a laboratory scale.[13] The Titania obtained has been converted to reversed phase packings. To investigate how octadecyl-modified phase can control the unique nature of Titania, the retention behaviours of Titania and the octadecyl-modified Titania obtained, were examined by using aqueous methanol mobile phases containing acetic acid-sodium acetate or bicine-sodium hydroxide buffer as mobile phase.

We found that the Titania obtained behaved as an amphoteric ion exchanger and that the retention behaviours of the octadecyl-modified Titania were significantly influenced by octadecyl-modification. The effect of octadecyl-modification on retention was ascribed not only to octadecyl groups but also silanol groups, which were formed by silylation.

The retention behaviour as a whole, however, was clearly based on behaving as an amphoteric ion-exchanger. Consequently, the octadecyl-modified phase, although really influencing the retention behaviour, could not accomplish controlling the amphoteric ion exchange ability of the Titania in this experiments.

EXPERIMENTAL

Preparation

Titania was prepared and converted to reversed phase packing according to a previously described method,[13] of hydrolysis and polycondensation reaction of titanium isopropylate (Nacalai Tesque Inc., Kyoto, Japan) and by silylation with octadecyltriethoxysilane (Wako Pure Chemical, Osaka, Japan). Octadecyldimethylchlorosilane and octadecyltrichlorosilane were also used as reagents for octadecyl-modification of Titania.

The procedure was as follows: Dry Titania (1g) and silane(1mL) were slurred in 10mL of dry toluene; 5mL of pyridine was added to the reaction mixture to remove the acid generated (this procedure was eliminated in using octadecyltriethoxysilane); and the mixture was refluxed for 6h. The carbon content of modifying ligands was determined by CN-Corder MT-600 (Yanagimoto, Kyoto, Japan). The Titania and octadecyl-modified Titania obtained by silylation with octadecyltriethoxysilane (ODT-1) were slurry-packed in 30 X 4.6 mm I.D. stainless-steel tubes.

Characterization

The particle-size distribution was determined with Coulter Multisizer II (Coulter Electronics Limited, Luton, England). The physical properties of particle were determined by nitrogen adsorption measurement (Fuji-Silysia Chemical(Kasugai, Japan) on a home-made apparatus).

Chromatographic Use

The liquid chromatograph was constructed from a 880 PU pump (Jasco, Tokyo, Japan), a Rheodyne Model 7125 injector and a UVIDEC-100-II detector (254nm)(Jasco). A Model TM108M (Toyo, Tokyo, Japan) was used to maintain the column temperature at 30°C. The chromatograms were recorded on a chromatopac CR1A (Shimadzu, Kyoto, Japan).

Titania has anion-exchange properties in acidic pH and cation-exchange ones in alkaline pH. The objective of our research was to investigate how octadecyl-modified phase can control the unique nature of Titania as described above. In order to evaluate the effect of octadecyl-modification on retention, sodium p-toluenesulfonate(PT) and trimethylphenylammonium chloride(MP) were used as anionic and cationic test solutes. Benzoic acid(B, pKa=4.22) and benzylamine (BA, pKa=9.38) were used as acidic and basic test solutes. Titania and ODT-1 were tested under reversed phase conditions employing 0, 20 and 40 wt% methanol containing acetic acid-sodium acetate (pH4~7) or bicine-sodium hydroxide (pH7~9) buffer as the mobile phases. The buffers used were prepared by dilution with 0.1M acetic acid-0.1M sodium acetate and 0.1M bicine-0.1M sodium hydroxide, respectively, as described elsewhere.[14] The void volume was measured with methanol-d_4 in methanol and D_2O in water.

RESULTS

Preparation

The carbon content of modifying ligands was determined by elemental analysis. The carbon content of ODT-1 was 6.16 %. Attempts at converting Titania to octadecyl-modified Titania by using octadecyldimethylchlorosilane and octadecyltrichlorosilane were unsuccessful because the elemental analysis resulted in their being little carbon.

Characterization

The particle size distribution and the physical properties of Titania were determined with Coulter Multisizer and by nitrogen adsorption measurement. As a result, Titania had a mean particle diameter of 4μm, and the particle size distribution ranged from d_{10} = 5.0 to d_{90} = 3.3μm, and had a surface area of 126 m^2/g, a mean pore diameter of 11.1 nm and a mean pore volume of 0.3 mL/g.

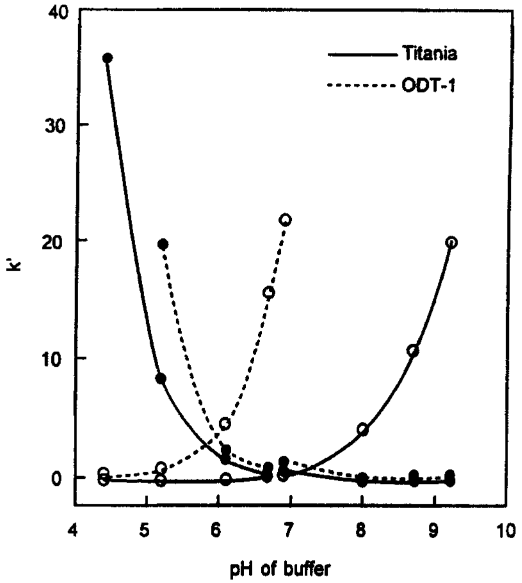

Figure 1. Retention behaviours of PT(●) and MP(○) versus the pH of the mobile phase on Titania and ODT-1. Column, Titania and ODT-1, 30 X 4.6 mmI.D.; mobile phase, acetic acid-sodium acetate and bicine-sodium hydroxide buffers; flow-rate, 1.0 mL/min.

Chromatographic Use

In order to investigate how octadecyl-modified phase can control the amphoteric ion exchange ability of Titania, PT and MP were used as anionic and cationic test solutes. B and BA were used as acidic and basic test solutes.

Use of Buffer as a Mobile Phase

The retention behaviours of the anionic and cationic test solutes on Titania and ODT-1 by using buffer as a mobile phase are shown in Fig. 1. The buffers used were acetic acid-sodium acetate and bicine-sodium hydroxide. As can be seen in Fig. 1, the retention of PT as an anion on Titania decreased steeply as the pH of the mobile phase was increased. On the contrary, that of MP as a cation on Titania increased rapidly as the pH of the mobile phase was increased. The retention behaviours of PT and MP against increasing pH of the mobile phase on ODT-1, were similar to those of PT and MP on Titania.

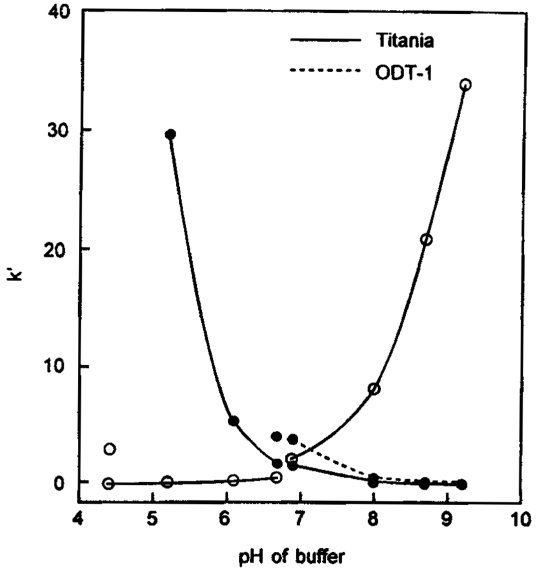

Figure 2. Retention behaviours of B(●) and BA(○) versus the pH of the mobile phase on Titania and ODT-1. Column, Titania and ODT-1, 30 X 4.6 mmI.D.; mobile phase, acetic acid-sodium acetate and bicine-sodium hydroxide buffers; flow-rate, 1.0 mL/min.

However, PT was more strongly retained on ODT-1, and the peak of PT at pH 4.4 was not detectable to be buried in the base line. Furthermore, the retention of MP on ODT-1 began at much lower pH than that of MP on Titania. Figure 2 shows the retention behaviours of the acidic and basic test solutes on Titania and ODT-1 by using buffer as a mobile phase.

As shown in Fig. 2, the retention of B as an acid on Titania decreased steeply as the pH of the mobile phase was increased, and that of BA as a base was reversed. The retention behaviours of B and BA against increasing pH of the mobile phase on ODT-1, could not be displayed entirely because the peaks of B below pH6 and BA above pH 5 were not detectable to be buried in the base line.

In comparison with Fig. 1, B was more strongly retained on Titania and ODT-1 than PT, and BA was also more strongly retained on Titania and ODT-1 than MP.

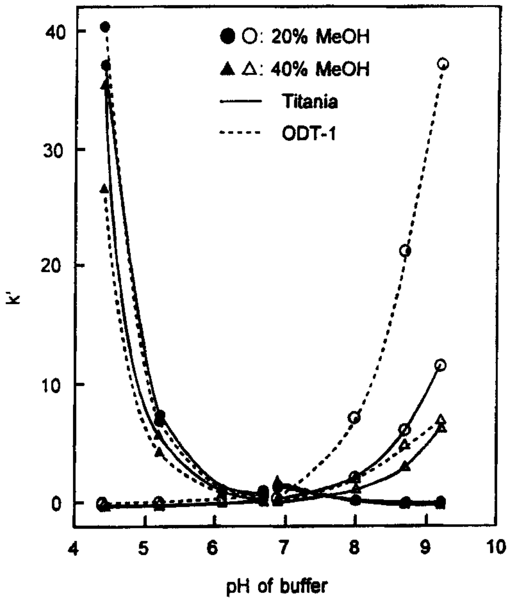

Figure 3. Retention behaviours of PT(●,▲) and MP(O,Δ) versus the pH of the mobile phase on Titania and ODT-1. Columns, Titania and ODT-1, 30 X 4.6 mmI.D.; mobile phase, 20%(●,O) and 40%(▲,Δ) methanol containing acetic acid-sodium acetate or bicine-sodium hydroxide buffer; flow-rate, 1.0 mL/min.

Use of Buffered Methanol as a Mobile Phase

The retention behaviours of PT and MP on Titania and ODT-1 by using 20 (20 % MeOH) and 40 % methanol containing buffer (40 % MeOH) as mobile phases, are shown in Fig. 3. Figure 3 indicates that the retention behaviour of PT against increasing pH of the mobile phase on Titania was similar to that of PT on ODT-1, although PT showed somewhat small retention as the amount of methanol increased.

On the other hand, the retention of MP on Titania, although increased gradually as the pH of the mobile phase was increased, decreased constantly with increasing amount of methanol. Furthermore, the retention of MP on ODT-1 showed remarkable decrease as the amount of methanol increased. Therefore, the retention behaviour of MP against increasing pH of the mobile phase varied from a steep increase in 20 % MeOH to a slight one in 40 % MeOH. On the whole, MP was more strongly retained on ODT-1 than on Titania.

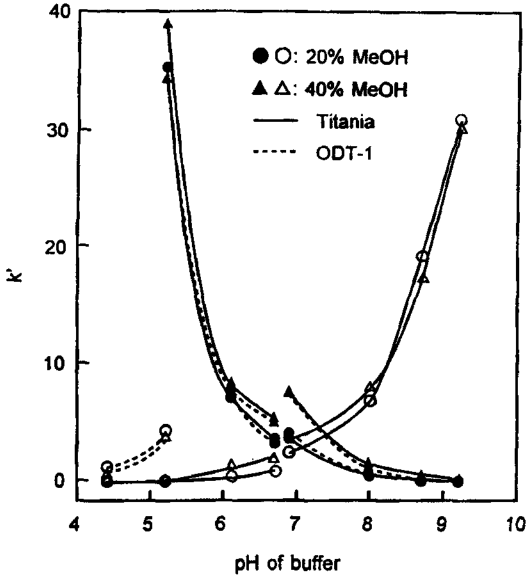

Figure 4. Retention behaviours of B(●,▲) and BA(O,Δ) versus the pH of the mobile phase on Titania and ODT-1. Columns, Titania and ODT-1, 30 X 4.6 mmI.D.; mobile phase, 20%(●,O) and 40%(▲,Δ) methanol containing acetic acid-sodium acetate or bicine-sodium hydroxide buffer; flow-rate, 1.0 mL/min.

In comparison with Fig. 1, the retention of PT in buffer and buffered methanol was similar to each other on Titania, and on ODT-1 the retention of PT in buffered methanol was smaller than that of PT in buffer. On the other hand, the retention of MP on Titania decreased constantly in changing from buffer to buffered methanol and that of MP on ODT-1 was shifted to higher pH. Figure 4 shows the retention behaviours of B and BA on Titania and ODT-1 by using 20 and 40 % MeOH containing buffer as mobile phases. As can be seen in Fig. 4, the retention behaviour of B against increasing pH of the mobile phase on Titania was similar to that of B on ODT-1, although B showed somewhat large retention as the amount of methanol increased. The peaks of B on Titania in both mobile phases below pH 5, and on ODT-1 in 20 % MeOH below pH 6 and in 40 % MeOH below pH 5, were not detectable to be buried in the base line. On the other hand, the retention behaviour of BA against increasing pH of the mobile phase on Titania was similar to each other in both mobile phases. The retention of BA on ODT-1 began at much lower pH than that of BA on Titania, and the peaks of BA above pH 6 were not detectable. In comparison with Fig. 3, B was more strongly retained on Titania and ODT-1 than PT, and BA was also more strongly retained on Titania and ODT-1 than

MP. In comparison with Fig. 2, the retention of B in buffered methanol was larger than that of B in buffer on Titania. On the other hand, the retention of BA on Titania was similar to each other in buffer and buffered methanol. The retention of BA on ODT-1 decreased by changing from buffer to buffered methanol, although the retention began at same pH.

DISCUSSION

The focus of our research was to elucidate the effect of the support on retention for investigating the retention mechanism in reversed phase liquid chromatography. To accomplish our objective, we have examined how octadecyl-modified phase could control the nature of the support. Our investigation centered on Titania and octadecyl-modified Titania due to the unique nature of Titania, which shows anion-exchange properties in acidic pH and cation-exchange properties in alkaline pH although silica, which is widely used as a support, behaves only as a cation exchanger. This is because the unique nature of Titania would more strongly influence the retention behaviour than that of silica.

Preparation and Characterization

The first stage of our investigation was to prepare Titania and octadecyl-modified Titania. The Titania obtained had enough particle size distribution and physical properties to be used as a support. The carbon content appeared to be comparable to that of well modified silica packing material, in view of the fact, that Titania had roughly one-third of the surface area of standard silica. However, the evaluation of ODT-1 as a C_{18} silica packing material by the chromatographic characterization method, indicated that the surface coverage was poor, as described previously.[13] Therefore, highly polymerized octadecyl groups seemed to be localized on the Titania surface. The failure of octadecyl-modification by using chlorosilane means that Titania reacted easily with ethoxysilane and scarcely with chlorosilane. We found that alkoxysilane was desirable for silylation of Titania.

Chromatographic Use

Use of Buffer as a Mobile Phase

Titania and ODT-1 were next investigated as the packing materials for evaluating the effect of octadecyl-modification on retention. The retention behaviours of test solutes on Titania and ODT-1 were first examined by using buffer as a mobile phase. As can be seen in Fig. 1, the retention of PT as an anion on Titania decreased steeply as the pH of the mobile phase was increased. On the contrary, that of MP as a cation on Titania increased rapidly as the pH of the mobile phase was increased. This retention data suggest that Titania behaved as an amphoteric ion-exchanger, that is, Titania has anion-exchange properties in acidic pH and cation-exchange ones in alkaline pH. The fact that the retention of MP on ODT-1 began at much lower pH than that of MP on Titania, indicates that ODT-1 had stronger cation-exchange properties than Titania. It is accepted to be caused by the occurrence of cation-exchange with silanol groups because the groups were able to be formed by silylation for octadecyl-modification. Therefore, the retention of PT should be reduced by the ion exclusion effect of silanol groups. However, the retention of PT on ODT-1 actually increased compared to that of PT on Titania. The reason for this increase can be attributed to hydrophobic interaction between octadecyl groups and the hydrophobic residues of PT. Thus, the hydrophobic interaction of octadecyl groups more greatly influenced the retention of PT than the ion exclusion effect of silanol groups. Naturally, the retention of MP on ODT-1 should be influenced by the hydrophobic interaction of octadecyl groups, and this might be one of the causes that retention of MP on ODT-1 began at much lower pH than that of MP on Titania. The evidence for influence of silanol groups would be provided by preparing the octadecyl-modified Titania with octadecyldimethylethoxysilane, because the formation of silanol groups can be eliminated by using monofunctional alkoxysilane. In comparison between Fig. 1 and Fig. 2, B was more strongly retained than PT, and BA was also more strongly retained than MP. These increased retentions can also be ascribed to hydrophobic interaction between hydrophobic sites of Titania and the hydrophobic residues of B and BA, or between the octadecyl groups and the hydrophobic residues of B and BA, because the hydrophobicity of B and BA was higher than that of PT and MP. However, the retention behaviour as a whole, was clearly based on behaviour as an amphoteric ion-exchanger. Finally, the octadecyl-modified phase, although really influenced by the retention behaviour, could not accomplish controlling the amphoteric ion exchange ability of the Titania in this experiments. This may be because the evaluation of ODT-1 as a C_{18} silica packing material is indicated to have low surface coverage, although highly polymerized octadecyl groups seemed to be localized on the Titania surface.

Use of Buffered Methanol as a Mobile Phase

The retention behaviours of test solutes on Titania and ODT-1 were next examined by using buffered methanol as a mobile phase to enhance a function of the octadecyl group. The retention behaviour of MP was most sensitive to the addition of methanol and showed reversed phase chromatographic retention behaviour not only on ODT-1 but on Titania, as can be seen in Fig. 3. With an increasing amount of methanol, the retention of MP decreased constantly on

Titania. and showed remarkable decrease on ODT-1. The expected results were that MP was hardly retained in further increase in methanol because the retention of MP was hindered by the addition of methanol. Actually, MP showed only slight retention in 80 % buffered methanol as described previously.[13] The addition of methanol may contribute to either suppressing the ion exchange ability of Titania and ODT-1 or weakening that of MP. In the previous paper,[13] we predicted that the slight retention of MP was inhibited by the strong adsorption of buffer components on Titania. This prediction, however, resulted from the use of only 80 % methanol containing 0.1M acetic acid-0.1M sodium acetate. In the present paper, by using diluted buffer and low methanol content, two causes may offer a reasonable explanation for weakening the ion exchange ability of MP. One of the causes is that in changing from buffer to buffered methanol, the retention of MP on ODT-1 was shifted to higher pH for decreasing in cation-exchange interaction with silanol groups, whereas that of BA, which was cation-like in this experimental range, did not. Another, is that the retention behaviour of BA was not very sensitive to the addition of methanol and those of PT and B not either, compared with that of MP. Weakening of the ion exchange ability of MP seems to be caused by solvation of methanol. The unambiguous evidence for the weakening of the ion exchange ability of MP should be necessary to examine other cations. By the addition of methanol, however, the evidence for enhancing a function of octadecyl group was not given. The retention behaviours of PT between Titania and ODT-1 were similar to each other, although some difference was shown between 20 % and 40 % MeOH for hydrophobic interaction. The retention behaviours of B between Titania and ODT-1 were also similar to each other, although the retention of B was larger in 40 % MeOH than that of B in 20 % MeOH. The reason for the somewhat large retention of B as the amount of methanol increased was not clear, but it seemed to be attributed to Titania. Therefore, we concluded that the effect of octadecyl-modification on retention could not be clearly observed in buffered methanol.

The retention behaviour as a whole, was clearly based on behaviour as an amphoteric ion-exchanger. In conclusion, the octadecyl-modified phase, although really influencing the retention behaviour, could not accomplish controlling the amphoteric ion exchange ability of the Titania in this experiment. However, further examination for controlling the amphoteric ion exchange ability of Titania, can be made by the preparation of the octadecyl-modified Titania with various surface coverages because the evaluation of ODT-1 as a C_{18} silica packing material indicated that the surface coverage was poor, and the formation of silanol groups can be eliminated in using monofunctional alkoxysilane. The next stage of our investigation will be under way to improve the above, and to present the reason for the unambiguous evidence of weakening the ion exchange ability of MP.

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