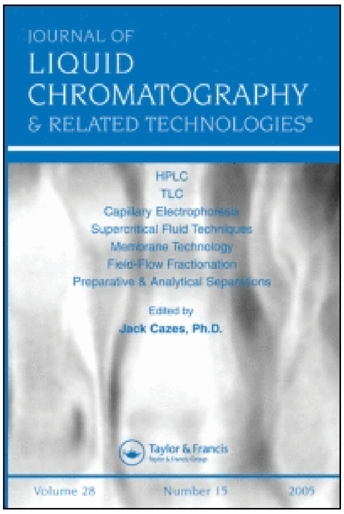

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INVESTIGATION OF CHROMATOGRAPHIC PROPERTIES OF TITANIA. I. ON RETENTION BEHAVIOR OF HYDROXYL AND OTHER SUBSTITUENT ALIPHATIC CARBOXYLIC ACIDS: COMPARISON WITH ZIRCONIA

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ABSTRACT

For demonstrating the presumption that on the hydrous zirconium oxide loaded porous polymer resin (Zr-gel) under alkaline pH the recognition of a position of hydroxyl or carboxyl group was ascribed to formation of a chelate ring, the retention behaviors of hydroxyl and other substituent aliphatic carboxylic acids were evaluated on titania synthesized in this laboratory and compared with those of zirconia provided by the manufacturer. The retention behavior supported the formation of chelate ring and suggested the priority of forming a five-membered ring. On comparison titania and zirconia, the distinct elution order was shown in retention behavior of 2-hydroxycarboxylic acids. It might be ascribed to the difference in the bond angle and distance between metal ion and two oxygen atoms of hydroxyl group and carboxylate anion on formation of chelate ring.

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INTRODUCTION

The search for chromatographic packings with improved physical and chemical properties has recently led to increased attention to transition metal oxides such as titania[1-9] and zirconia.[6-11] Such material has remarkable mechanical, chemical, and thermal stability. Both titania and zirconia are basic oxides and therefore insoluble in alkaline media. Moreover, they are stable in acidic media, down to pH 1. The unique surface of a particular packing is also expected to present a specific separation. Compared with conventional packing materials, titania and zirconia exhibit completely different chemical surfaces. They have both anion- and cation-exchange properties for charged species as well as ligand exchange behavior towards Lewis base, whereas silica behaves only as a cation-exchanger and does not show any ligand exchange behavior. As the interaction of solutes with the surface of the stationary phase determines the chromatographic selectivity, a novel selectivity could be expected when using titania or zirconia as packing material.

The unique surface chemistry, however, may lead to the complexity of retention as well as the expectation based on the novel selectivity. The distinct types of sites on surface can significantly contribute to the retention of a given solute, and can become mutually troublesome ones which cause band-broadening as the case may be. For searching and avoiding the influence of such multi-retentive mechanism, it is necessary to investigate properties of surface. Similarly, it is necessary to have a detailed knowledge of the support when investigating the retention mechanisms in reversed-phase liquid chromatography. However, data on the support cannot be obtained because no manufacturer provides full details. Therefore, we have started an attempt to synthesize supports on a laboratory scale, and have already obtained silica,[5] from hydrolysis and polycondensation reactions of silicon alkoxide by the sol-gel method.[12-14] By the modified method, we have also obtained titania on a laboratory scale.[15]

We have previously reported that there is the possibility of using titania as a selective packing material with high efficiency and stability for ion chromatography.[16] The unique surface chemistry stated above means that it is worth further consideration, from the viewpoint of influence of support on retention, when titania is used as a support.

The objective was to investigate the chromatographic properties of titania by evaluating the retention behaviors of hydroxyl and other substituent aliphatic carboxylic acids as well as inorganic ions by ion chromatography and comparing with zirconia. Inoue et al.[17] have reported that aliphatic carboxylic acids with hydroxyl or carboxyl group at 2-position were specifically retained on the hydrous zirconium oxide loaded porous polymer resin (Zr-gel) under alkaline pH, although hydrous zirconium oxide has cation exchange properties in alkaline pH. This result suggested that hydrous zirconium oxide might recognize a position of hydroxyl and/or carboxyl group of aliphatic carboxylic acids, and that the retention on the Zr-gel might result from the complexation between metal ion and these carboxylic acids.

We presumed that the resulting complex was a coordination compound with a ring structure referred to as a chelate ring, therefore, the recognition of a position of hydroxyl or carboxyl group was ascribed to formation of a chelate ring. For demonstrating the presumption by comparing titania with zirconia, the retention behaviors of hydroxycarboxylic acids were evaluated by using bicine-NaOH buffer. In addition, the retention behaviors of some substituted butanoic acids were investigated to estimate the influence of substituent group and position on forming a chelate ring.

We found that the retention behaviors of hydroxycarboxylic acids supported the formation of chelate rings and suggested the priority of forming a five-membered ring. The distinct elution order was shown in retention behavior of 2-hydroxycarboxylic acids by comparison with titania and zirconia. It might be ascribed to the difference in the bond angle and distance between metal ion and two oxygen atoms of hydroxyl group and carboxylate anion on formation of a chelate ring.

EXPERIMENTAL

Preparation and Measurement of Physical Properties of Titania and Zirconia

Titania was synthesized by the method described previously,[15] by hydrolysis and polycondensation of titanium isopropylate (Nacalai Tesque INC, Kyoto, Japan). The titania obtained was slurry packed in 30 mm and 50 mm × 4.6 mm I.D. stainless steal tubes by using 50% (w/w) methanol. The zirconia, which was provided by the Daiichi Kigenso Kagaku Kogyo Co., Ltd. (Osaka, Japan), was slurry packed in 50 mm × 4.6 mm I.D. stainless steal tube by using 2-propanol.

The particle-size distribution was determined with a Coulter Multisizer II (Coulter Electronics, Luton, UK). The surface area, pore volume, and pore diameter were determined by nitrogen absorption measurements (Fuji-Silysia Chemical Ltd., Kasugai, Japan) on a laboratory-made apparatus. The pore diameter of zirconia was further determined by mercury porosimetry.

Evaluation of Ion Exchange Properties of Titania and Zirconia

The ion exchange properties of titania and zirconia were evaluated by the behavior of inorganic ions. Potassium ion as a cationic solute and chloride ion as an anionic solute were prepared by dissolving with potassium chloride, potassium hydroxide, and hydrochloric acid, respectively, in pure water.

Ion chromatography was performed with a Model IC 500P (Yokogawa Analytical Systems Inc., Tokyo, Japan) instrument equipped with sample injector, column oven, suppresser, and conductivity detector. The ion chromatograph was operated under the following conditions: mobile phase: 0.4 mM acetate buffer or 0.4 mM bicine-NaOH buffer; mobile phase flow rate: 1.0 mL min^{-1}; column temperature: 40ºC. In this experiment, suppresser was not used. Columns used were titania (50 mm × 4.6 mm I.D.) and zirconia (50 mm × 4.6 mm I.D.). Data were processed by means of a computer running LC-100 software. The void volume was measured with D_2O in water.

Comparison of Titania and Zirconia on Retention Behavior of Hydroxyl Aliphatic Carboxylic and Substituted Butanoic Acids

Carboxylic acids used as solutes were as follows: glycolic, lactic, 3-hydroxypropanoic, 2- and 3-hydroxybutanoic, glyceric, malic, 2-, 3- and 4-hydroxybutanoic, 2-, 3- and 4-carboxybutanoic, 2- and 3-ketobutanoic acids. Each sample solution was prepared by diluting with water to required concentration.

The ion chromatograph was operated under the following conditions: mobile phase: 0.4 mM bicine-NaOH buffer (pH 7.9, 8.7, 9.2); mobile phase flow rate: 1.0 mL min^{-1}; scavenger: 5 mM sulfuric acid; scavenger flow rate: 1.0 mL min^{-1}; column temperature: 40ºC; and injection volume: 3 µL. Columns used were titania (30 mm × 4.6 mm I.D.) and zirconia (50 mm × 4.6 mm I.D.). Data were processed by means of a computer running LC-100 software.

RESULTS

Measurement of Physical Properties of Titania and Zirconia

The physical properties as packing materials of titania and zirconia are summarized in Table 1. As a result of determination of porosimeter, the pore diameter of zirconia was not more than 7.5 nm.

Table 1

Physical Properties as Packing Materials of Titania and Zirconia

	Titania	**Zirconia**
Mean particle diameter [μm]	3.8	8.2
Particle size distribution		
d_{10} [μm]	10.4	15.0
d_{90} [μm]	2.8	4.6
Surface area [m^2g^{-1}]	177	22
Mean pore diameter [nm]	10.5	---
Mean pore volume [mL g^{-1}]	0.48	0.07

As shown in Table 1, the mean particle diameter of titania was equal to about half of zirconia. Titania and zirconia had a wide range of particle size distribution. The surface area of zirconia was extremely small, zirconia had little pore.

Evaluation of Ion Exchange Properties of Titania and Zirconia

Figure 1 indicates the retention behaviors of potassium ion as cationic solute and chloride ion as anionic solute on titania and zirconia. As shown in Figure 1, the retention behavior of chloride ion on titania decreased steeply as the pH of the mobile phase was increased. The retention behavior of potassium ion on titania increased rapidly as the pH of the mobile phase was increased. On the other hand, the retention behavior of chloride ion on zirconia decreased gradually as the pH of the mobile phase was increased. The retention behavior of potassium ion on zirconia increased slightly as the pH of the mobile phase was increased.

Comparison of Titania and Zirconia on Retention Behavior of Hydroxyl Aliphatic Carboxylic Acids

The retention behaviors of hydroxycarboxylic acids on titania and zirconia were evaluated by using glycolic, lactic, 3-hydroxypropanoic, 2- and 3-hydroxybutanoic, glyceric, malic acids. Figure 2 shows the retention behaviors of glycolic, lactic, 2-hydroxybutanoic and 3-hydroxypropanoic acids on titania and zirconia by using 0.4 mM bicine-NaOH buffer (pH 8.7). As can be seen in Figure 2(A), 2-hydroxycarboxylic acids such as glycolic, lactic and 2-hydroxybutanoic acids were retained on titania, and 3-hydroxypropanoic acid

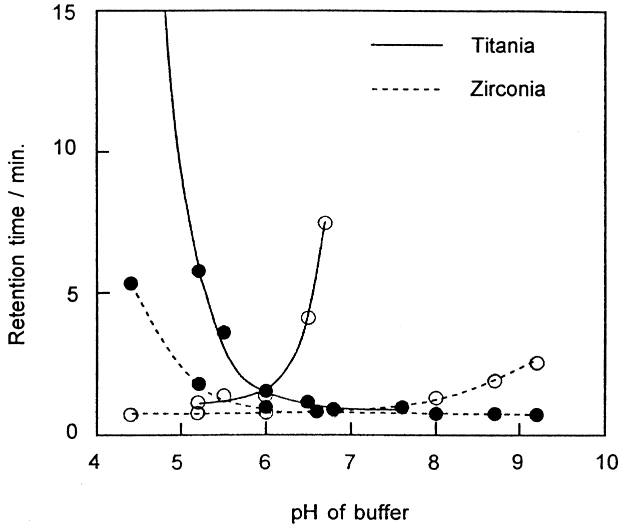


Figure 1. Retention behavior of potassium ion (ξ) and chloride ion (Ļ) versus the pH of buffer on titania (solid line) and zirconia (dotted line). Mobile phase: 0.4 mM acetic acid-sodium acetate buffer, 0.4 mM bicine-NaOH buffer; flow rate: 1.0 mL min^{-1}; column temperature: 40°C; detector: conductivity detector.

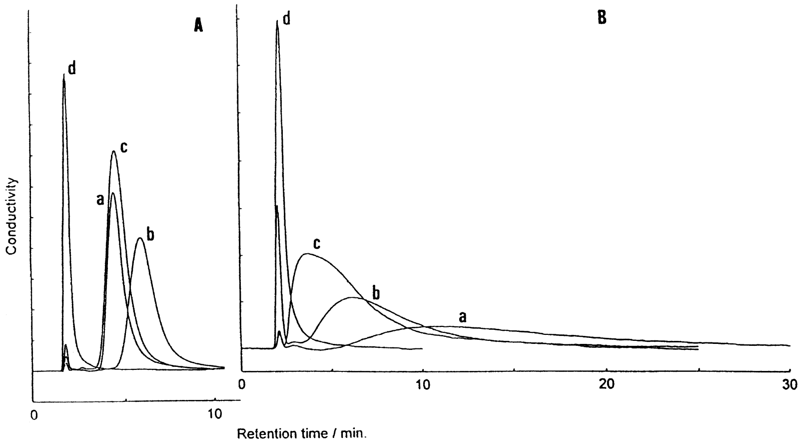


Figure 2. Chromatograms of glycolic (a), lactic (b), 2-hydroxybutanoic (c) and 3-hydroxypropanoic acids (d) on titania (A) and zirconia (B). Mobile phase: 0.4 mM bicine-NaOH buffer (pH 8.7); flow rate: 1.0 mL min^{-1}; scavenger: 5 mM sulfuric acid; scavenger flow rate: 1.0 mL min^{-1}; column temperature: 40°C; detector: conductivity detector.

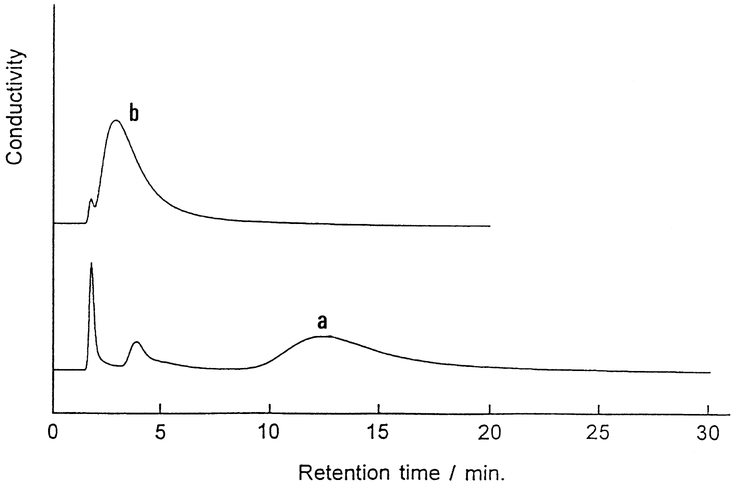


Figure 3. Chromatograms of glyceric (a) and malic acids (b) on titania. The analytical conditions are as in Figure 2.

was eluted rapidly. Figure 2(B) shows that the retention behavior on zirconia was similar to that on titania described above, except for the peak shape and elution order of 2-hydroxycarboxylic acid. That is to say, the peak shapes of 2-hydroxycarboxylic acids were symmetrical in Figure 2(A) and broad in Figure 2(B). The retention of those increased in the order glycolic < 2-hydroxybutanoic < lactic acid in Figure 2(A), and 2-hydroxybutanoic < lactic < glycolic acid in Figure 2(B). On titania and zirconia, 3-hydroxybutanoic acid was eluted rapidly, as well as 3-hydroxypropanoic acid. At pH 9.2, the retention of those as a whole, decreased rapidly on titania and zirconia, respectively. Figure 3 shows the retention behaviors of glyceric and malic acids on titania by using 0.4 mM bicine-NaOH buffer (pH 8.7). On zirconia, glyceric and malic acids were strongly retained and the peaks of those were not detectable to be buried in the base line. As shown in Figure 3, glyceric acid was most strongly retained on titania and the peak shape was symmetrical. The peak shape of malic acid was broad in spite of small retention.

Comparison of Titania and Zirconia on Retention Behavior of Substituted Butanoic Acids

Retention behaviors of some substituted butanoic acids were investigated to estimate the influence of substituent group and position on forming chelate rings. Figure 4 shows retention behaviors of 2-, 3- and 4-hydroxybutanoic acids on titania and zirconia by using 0.4 mM bicine-NaOH buffer (pH 7.9).

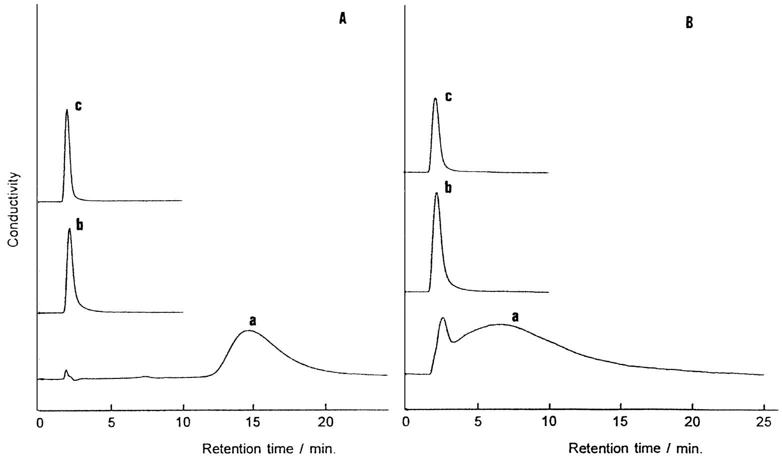


Figure 4. Chromatograms of 2- (a), 3- (b) and 4-hydroxybutanoic acids (c) on titania (A) and zirconia (B). Mobile phase: 0.4 mM bicine-NaOH buffer(pH 7.9); flow rate: 1.0 mL min^{-1}; scavenger: 5 mM sulfuric acid; scavenger flow rate: 1.0 mL min^{-1}; column temperature: 40ºC; detector: conductivity detector.

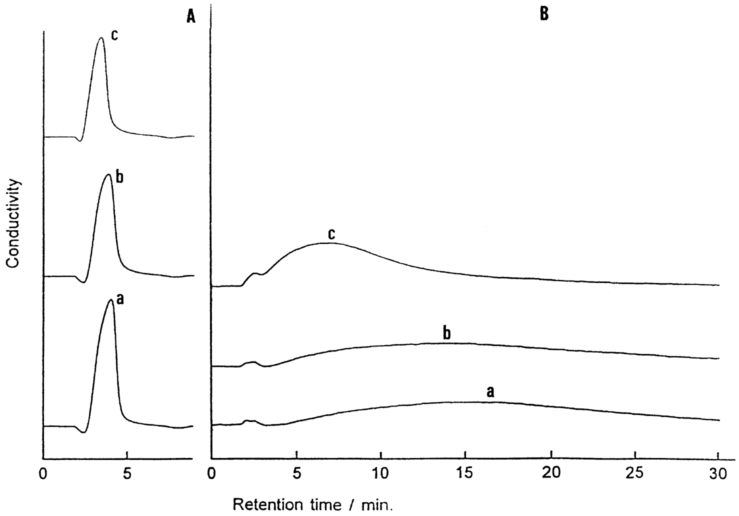


Figure 5. Chromatograms of 2- (a), 3- (b) and 4-carboxybutanoic acids (c) on titania (A) and zirconia (B). The analytical conditions are as in Figure 4.

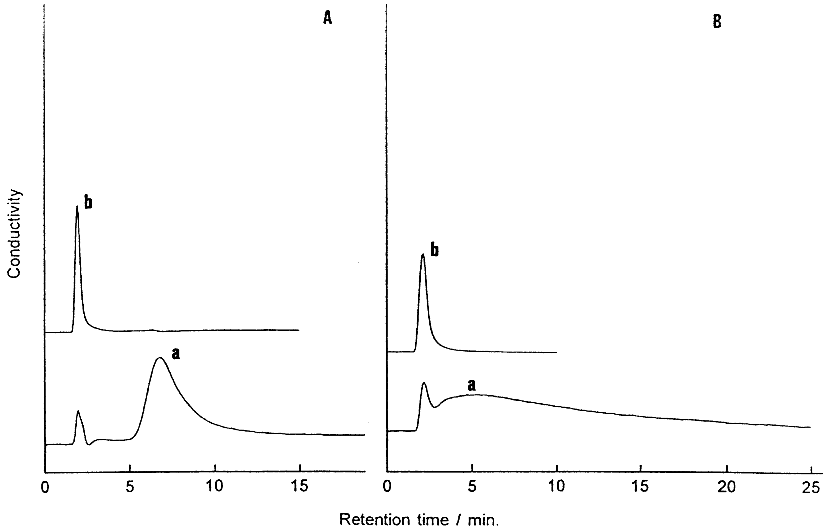


Figure 6. Chromatograms of 2- (a) and 3-ketobutanoic acids (b) on titania (A) and zirconia (B). The analytical conditions are as in Figure 4.

As can be seen in Figure 4, 2-hydroxybutanoic acid was strongly retained on titania and zirconia, and the others were eluted rapidly. The peak shape of 2-hydroxybutanoic acid on zirconia was broad in spite of smaller retention than on titania.

The retention behaviors of 2-, 3- and 4-carboxybutanoic acids on titania and zirconia are shown in Figure 5. The serious differences were observed. As can be seen from Figure 5(A), three carboxybutanoic acids were slightly retained and those peak shapes were distorted. On the other hand, the retention of those was large and increased in the order 4-carboxy < 3-carboxy < 2-carboxybutanoic acid, and those peak shapes were broad on zirconia as shown in Figure 5(B).

Figure 6 shows the retention behaviors of 2- and 3-ketobutanoic acids on titania and zirconia. As can be seen in Figure 6, 2-ketobutanoic acid was strongly retained, and the other eluted rapidly on titania and zirconia. The peak shape of 2-ketobutanoic acid on zirconia was broad in spite of smaller retention than on titania. In comparison of Figure 4 and Figure 6, the retention behaviors of hydroxybutanoic acids were similar to those of ketobutanoic acids. At pH 8.7, the retention of those as a whole, decreased rapidly on titania and zirconia, respectively.

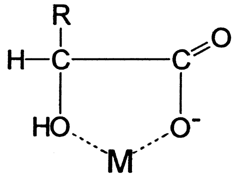
DISCUSSION

From determining physical properties as packing materials, it was found that titania was a reasonable packing material and zirconia was a nonporous material with low surface areas in spite of the twice mean particle diameter of titania. The properties as packing materials of zirconia might provide low chromatographic efficiency. Actually the peak shape on evaluating ion exchange properties by ion chromatography was asymmetrical, and the peak shapes of hydroxycarboxylic acids and others were asymmetrical or broad. However, it is not clear whether poor peak shape is attributed to physical properties as packing materials or chromatographic properties on zirconia. We considered it to be attributed primarily to chromatographic properties of zirconia, and discussed retention behavior of zirconia.

The anion- and cation-exchange behavior is thought to arise from the protonation of surface hydroxyl groups in acidic pH and deprotonation of surface hydroxyl groups in alkaline pH. The amphoteric ion exchange properties of titania and zirconia were demonstrated by the retention behaviors of inorganic ions. The ion exchange properties of titania and zirconia differed significantly from one another in acidic and alkaline pH. It seemed to result from the difference of the number of surface hydroxyl group mostly, and the difference of the nature of the group which might be based on distinction of bonded metal ion. Titania showed the point of intersection in the vicinity of pH6, which has been observed as the pH at which the amounts of adsorbed potassium ion and chloride ion are equal,[18] zirconia did it between pH 6 and 7. The ion exchange properties of titania were much stronger than those of zirconia. Titania behaved as an amphoteric ion exchanger and retention on titania would have a great effect of ion exchange. Zirconia behaved only as an anion-exchanger in acetate buffer and only as a cation-exchanger in bicine buffer, and retention on zirconia might have slight influence of ion exchange.

Our main research was to demonstrate the presumption concerning the ability of recognizing position of hydrous zirconium oxide toward hydroxyl and carboxyl groups of aliphatic carboxylic acids by comparing of titania and zirconia. Our presumption was that the recognition of a position of hydroxyl or carboxyl group was ascribed to formation of a chelate ring. To accomplish this objective we evaluated the retention behaviors of hydroxycarboxylic acids on titania and zirconia. In addition, the retention behaviors of some substituted butanoic acids were investigated to estimate the influence of substituent group and position on forming a chelate ring.

The first stage of our investigation evaluated the retention behaviors and the effect of alkyl substituent of 2-hydroxycarboxylic acid on titania and zirconia. From the results, 2-hydroxycarboxylic acids with alkyl substituent



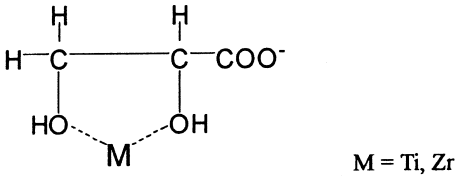
$R=H$:Glycolic acid
$R=CH_3$:Lactic acid
$R=CH_2CH_3$:2-hydroxybutanoic acid
M = Ti, Zr

Scheme 1

used as solutes were clearly recognized on titania and zirconia. The recognition suggested that 2-hydroxycarboxylic acid formed five-membered ring between metal ion (titanium or zirconium ion) and two oxygen atoms of hydroxyl group and carboxylate anion as shown in Scheme 1.

The elution order of 2-hydroxycarboxylic acids on titania and zirconia was distinct from each other, that is, glycolic (R=H in scheme 1) < 2-hydroxybutanoic ($R=CH_2CH_3$) < lactic acid ($R=CH_3$) on titania, and 2-hydroxybutanoic ($R=CH_2CH_3$) < lactic ($R=CH_3$) < glycolic acid (R=H) on zirconia. The difference was ascribed to the effect of alkyl group. The introduction of substituent led to two effects, one of which was change in basicity of donor atom, and the other was steric hindrance in formation a chelate ring. The elution order on zirconia was inversely proportional to the increase in the alkyl chain of substituent, and hence was regarded to be predominantly influenced by steric hindrance. On the other hand, the elution order on titania was influenced by both basicity of donor atom and steric hindrance. In view of only the effect of basicity of donor atom, the retention of those was presumed to increase in the order glycolic (R=H) < lactic ($R=CH_3$) < 2-hydroxybutanoic acid ($R=CH_2CH_3$). But, 2-hydroxybutanoic acid was less retained than lactic acid, and this fact suggested the effect of steric hindrance. Such difference of substituent effects in retention on titania and zirconia might be ascribed to the difference in the bond angle and distance between metal ion and two oxygen atoms of hydroxyl group and carboxylate anion.

By using the acids which hydroxyl or carboxyl group was substituted for methyl group of 2-hydroxybutanoic acid, namely glyceric and malic acids, as solutes, the retention behavior of those provided significant information. The five-membered ring between metal ion and glyceric acid was depicted by $R=CH_2OH$ in scheme 1. The malic acid ring was $R=CH_2COO^-$ in a similar manner as above. However, these schemes predicted rapid elution of two acids by considering substituent effects described above, and could not account for large retention of glyceric acid and broad peak shape of malic acid in spite of small retention on titania, and the strong retention of glyceric and malic acids on zirconia.



Scheme 2

The problem was solved by drawing other chelate rings as shown in scheme 2. Glyceric acid formed a rigid chelate ring between titanium ion and two oxygen atoms of two hydroxyl groups and was strongly retained on titania. On the other hand, the retention of malic acid seemed reasonable to be influenced by the electrostatic force of attraction or the ligand exchange between other neighboring metal ions and CH_2COO^- group. The small retention and broad peak were attributed to the influence of bivalent anion exclusion by deprotonation of surface hydroxyl groups on titania in alkaline pH as well as the substituent effect described above. The strong retention of malic acid on zirconia might be ascribed to weakness of anion exclusion because the ion exchange properties of titania were much stronger than those of zirconia.

The second stage of our investigation estimated the influence of substituent group and position on forming a chelate ring by the retention behaviors of some substituted butanoic acids. The retention behaviors of hydroxybutanoic acids supported the five-membered ring between metal ion and acid as shown in scheme 1. Further, the retention behaviors of ketobutanoic acids suggested the priority of forming five-membered ring between metal ion and acid because 3-ketobutanoic acid that might form a six-membered ring, was eluted rapidly on titania and zirconia. The interesting result was provided by the retention behaviors of carboxybutanoic acids. The retention behavior that might result from carboxybutanoic acid was bivalent anion. The small retention and distorted peak on titania were attributed to the influence of bivalent anion exclusion by deprotonation of surface hydroxyl groups in alkaline pH.

The broad peak on zirconia might be attributed to the electrostatic force of attraction between metal ion and bivalent anion or the ligand exchange of neighboring metal ions for two oxygen atoms of two carboxylate anions because of the failure to form a five-membered ring. Therefore, it is necessary to consider, in detail, the retention behavior of bivalent anion.

In conclusion, we were able to investigate the chromatographic property of the titania synthesized on our laboratory and the zirconia provided by the manufacturer. The comparison of titania and zirconia on our research indicated that the ion exchange properties of titania were much stronger than those of zirconia. Therefore, it should be noted that the stronger cation exchange properties appeared occasionally as the effect of anion exclusion when the ligand exchange separation on titania was carried out in alkaline pH. This complexity is undesirable for excellent separation, but it is interesting from the viewpoint of investigating the retention mechanisms of titania. On the other hand, the retention mechanism on zirconia was found to be dominated by ligand exchange.

Our presumption that the recognition of a position of hydroxyl or carboxyl group was ascribed to formation of a chelate ring was supported by retention behavior of hydroxycarboxylic acids, which suggested the priority of forming a five-membered ring. The reason for the distinct elution order of 2-hydroxycarboxylic acids on titania and zirconia might be ascribed to the difference in the bond angle and distance between metal ion and two oxygen atoms of hydroxyl group and carboxylate anion on formation of a chelate ring. This is because titania differed from zirconia in the bond angles and distances between a metal ion and oxygen atoms and in the distances between two oxygen atoms in crystal structure. It should be emphasized that it is important to take into account the crystal structures of metal oxides for the purpose of ligand exchange separation accompanying formation of a chelate ring.

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