Separation Behavior of Anions on ODS Modified with Phthalocyanine Cobalt (III) Complex

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A stationary phase was prepared by modification of octadecyl silanized silica gels (ODS) with phthalocyanine cobalt (III) for separation of anions. The elution sequence of anions on the column packed with the modified ODS is in the order of Cl\(^-\) < NO\(_3\)\(^-\) < CIO\(_4\)\(^-\) < I\(^-\) < SCN\(^-\) < NO\(_2\)\(^-\), which was quite different from the elution sequence observed on a conventional anion exchange column. The strong retention of NO\(_2\)\(^-\) on the column was explained by a result of adsorption experiment of NO\(_2\)\(^-\) and NO\(_3\)\(^-\) on the modified ODS.

Keywords Phthalocyanine cobalt complex, anion separation, ion chromatography

Anion exchange resin is commonly used for packing of a separation column for anion chromatography. The elution sequence of anions from the column is generally the same sequence of increase in hydrophobicity of anions. For example, the sequence of Cl\(^-\) < NO\(_3\)\(^-\) < NO\(_2\)\(^-\) < I\(^-\) < SCN\(^-\) < CIO\(_4\)\(^-\) is often observed. Hydrophobic anion such as CIO\(_4\)\(^-\) is strongly retained on the anion exchange column and sometimes is difficult to elute from the column. The elution sequence of anions is almost the same as the anion selectivity of a liquid anion exchange membrane electrode based on a classical anion exchanger such as quaternary ammonium ion, which sequence is called the Hofmeister anion series. Since the selectivity sequence of the liquid anion exchange membrane electrode is governed by the partition coefficient of anions between the aqueous and membrane phases, it is also dependent on the hydrophobicity of anions.

Simon et al. have reported a novel anion-selective electrode based on organometallic compounds such as vitamin B\(_{12}\) and trioctyltin chloride. These electrodes exhibit a quite different selectivity pattern from the Hofmeister anion series observed for the classical anion-exchanger based membrane electrode. Especially, the electrode shows high selectivity to NO\(_2\)\(^-\) or SCN\(^-\), whereas it shows low selectivity to CIO\(_4\)\(^-\). They concluded that there exists a strong interaction between the center metal atom of the compounds, Co(III) and Sn(IV), and NO\(_2\) or SCN\(^-\) and the organometallic compounds act as an anion carrier. We found out that a liquid membrane containing tetra tert-butylphthalocyanine cobalt (III) (TBPcCo(III)) also showed the similar selectivity pattern to that observed for the vitamin B\(_{12}\) based electrode. Since TBPcCo(III) is insoluble to water and has a tendency to adsorb on solid surface, if a stationary phase can be prepared by modification of a supporting material with TBPcCo(III), a quite different elution sequence of anions from the stationary phase of a conventional anion chromatography is expected to be achieved by using the prepared stationary phase. Meyerhoff et al. have prepared metal porphyrin-immobilized silica gel and applied it to separation of aromatic sulfonates and aromatic carboxylates. However, they have not examined the separation of common inorganic anions systematically.

In this paper, we prepared the stationary phase by modification of octadecylsilanized silica gel (ODS) with TBPcCo(III) and studied the separation behavior of anions on the prepared stationary phase. The another stationary phase was also prepared by modification of the ODS with phthalocyanine cobalt(III) (PcCo(III)) for comparison. The elution sequence was discussed with the experimental result of adsorptivity of NO\(_2\)\(^-\) and NO\(_3\)\(^-\) on the TBPcCo(III) modified ODS.

Experimental

Reagents

TBPcCo(II) and PcCo(II) were obtained from Wako Pure Chemical Co. ODSs of FineSIL C18-5 (particle size: 5 µm) and TSK-gel ODS 80Tm (10 µm) were obtained from J&asco, and Tosoh, respectively. The oxidation of the Co(II) complexes of PcCo(II) and TBPcCo(II) to Co(III) was carried out by treating 0.2 g of the complex with 2.5 mL of SOCl\(_2\) in 100 mL of o-nitrotoluene.
Voltammograms were obtained by using a rotating disk electrode. Pyridine solutions of 5 x 10^{-4} \text{M} (M = \text{mol dm}^{-3}) cobalt complex containing 1 mM tetaethylammonium perchlorate as a supporting electrolyte were used. Voltammograms were obtained by using an electrochemical analyzer (Bioanalytical Systems, BAS 100B) and a rotating disk electrode unit (BAS, RDE-1) on an X-Y recorder (Fujitsu, FP-300). The electrochemical cell was constructed from a Pt auxiliary electrode, an Ag/AgCl (3 M KCl) reference electrode and a glassy carbon electrode (3 mm diameter).

**Preparation of stationary phase**

0.5 g of ODS was suspended in 20 mL of 5 x 10^{-4} \text{M} \text{PcCo(III)} pyridine solution or in 50 mL of 2 x 10^{-4} \text{M} \text{TBPcCo(III)} DMF solution in a flask, and pyridine or DMF was slowly evaporated by using an evaporator under reduced pressure. During evaporation of the solvent, the cobalt complex was adsorbed on the surface of ODS. The ODSs modified with \text{PcCo(III)} and \text{TBPcCo(III)} were washed with aqueous ethanol (1:1 \text{v/v}) and dried in vacuum. The resulting ODS was packed in a stainless steel column (4.6 mm \Phi \times 15 \text{cm}) by the slurry packing method using an acetate buffer solution (pH 3.4 containing 20\% ethanol).

**Determination of amount of modified cobalt complex on ODS**

To determine the amount of modified phthalocyanine cobalt complex on the surface of ODS, 0.03 g \text{TBPcCo(III)-modified ODS} was weighed and taken in an Erlenmeyer flask. Then, DMF was added to the flask to dissolve the complex from the modified ODS and the dissolved solution was collected in a 100 mL volumetric flask. This procedure was repeated several times until the complex was completely dissolved. After filling up the flask to 100 mL, absorbance of the collected solution was measured and the concentration of the complex was calculated from the calibration curve obtained from the standard DMF solution of \text{TBPcCo(III)}.

**Apparatus and procedure of chromatography**

The chromatographic system was constructed from a pump (Yanagimoto, L4000W), an injector (Rheodyne, 7125), the column packed with \text{TBPcCo(III)}-ODS (TSK-gel), a conductometric detector (Toso, CM-8) and a UV spectrophotometric detector (JASCO, UVISPEC 100-VI) and a two-pen recorder (Yokogawa, 3066). A 100 \mu L of a sample solution was injected into an eluent stream of acetate buffer solution and lead to the column. The separated anions on the column were detected by the UV detector (at the wavelength 225 nm) and the conductometric detector connected in series. The detector signals were fed to the recorder and a chromatogram was obtained on the recorder.

**Adsorptivity of NO\textsubscript{2} and NO\textsubscript{3} on modified ODS**

0.20 g of \text{PcCo(III)}-ODS or \text{TBCo(III)}-ODS was taken into a test tube. A 20 mL of a mixed solution of 1.0 x 10^{-4} \text{M} \text{NaNO}_2 and 1.0 x 10^{-4} \text{M} \text{NaNO}_3 containing 4.2 x 10^{-3} \text{M} acetate buffer was added to the test tube. The pH of the solution was adjusted by changing the concentration ratio of acetate to acetic acid. The test tube was shaken for 1 hr and centrifuged for 10 min. The concentration of \text{NO}_2^- and \text{NO}_3^- in the equilibrated solution was determined by ion chromatography using the same chromatographic system as described above except for the commercial anion exchange column (Toso, TSK-ICAnion-PW) and the eluent specified for the column.

**Results and Discussion**

**Oxidation state of the cobalt complex**

Fig. 1 shows the linear sweep voltammograms of the pyridine solution of (a) \text{PcCo(II)} obtained commercially and (b) \text{PcCo(III)} obtained by treating with \text{SOCl}_2 at the rotating disk electrode. A anodic limiting current is observed at higher potential range than 0.4 \text{V} for the \text{PcCo(II)} pyridine solution as shown in Fig. 1 (a). The half wave potential is +0.2 \text{V}. This wave indicates the oxidation of cobalt complex from Co(II) to Co(III). This means that the oxidation state of cobalt of the original phthalocyanine cobalt complex is +2. For the phthalocyanine cobalt complex treated with \text{SOCl}_2, the cathodic limiting current is observed in lower potential range than 0.0 \text{V}, as shown in Fig. 1 (b). The half wave potential is +0.2 \text{V}. No anodic current is observed. This means that oxidation state of cobalt of the phthalocyanine cobalt complex treated with \text{SOCl}_2 is +3 and there is no \text{PcCo(II)} species. The similar voltammograms were obtained for \text{TBPcCo} complexes in DMF. Oxidation of \text{PcCo(II)} and \text{TBPcCo(II)} by \text{SOCl}_2 was verified to be completed to Co(III) by the voltammetric measurement.

**Determination of amount of modified cobalt complexes on ODS**

The amounts of modified \text{TBPcCo(III)} on the Fine SIL ODS and TSK-gel ODS were 14.0 and 14.7 \mu mol / g-ODS, respectively from the calibration curve of \text{TBPcCo(III)} in DMF (log\text{E}=5.1 at 664 nm). The amount of the cobalt complex is almost the same irrespective of the difference of kind of ODS. This may be due to only the surface of the supporting material (ODS) is modified with phthalocyanine complex and the
surface area of the supporting material is not so different each other. The amount of the complex is almost the same or smaller than ion-exchange capacity of a conventional pellicular-type anion exchange resin used for ion chromatography, which resin has anion exchange group only on the surface of the supporting material.

**Effect of pH of eluent on the retention of anions**

Fig. 2 shows a chromatogram of an anion mixture of NO$_3^-$, SCN$^-$ and NO$_2^-$ obtained by the column packed with ODS (TSK-gel) modified with TBPcCo(III). In this case the acetate buffer solution of pH 6.0 was used for the eluent. Each peaks was identified from the peak obtained by chromatographying a single anion. As can be seen from Fig. 2, the elution sequence of anion is quite different from that observed for a conventional ion chromatography. The elution sequence of the conventional anion exchange column is NO$_2^-$< NO$_3^-$< SCN$^-$. The elution order of the present column between NO$_3^-$ (SCN$^-$) and NO$_2^-$ is reversed. Judging from the tailed-shape chromatogram of NO$_2^-$, NO$_2^-$ is strongly adsorbed on the column. This indicates that NO$_2^-$ strongly coordinates to the center atom of the complex, Co(III). Though the other anions such as Cl$^-$, ClO$_4^-$ and I$^-$ could not be separated by the same eluent of Fig. 2 the separation of such anion was achieved by using an acetate buffer solution adjusted to pH 3.5, as shown in Fig. 3. The elution sequence is in the order of Cl$^-<$ NO$_3^-$< ClO$_4^-$< I$^-<$ SCN$^-$. It should be noted that the peak of ClO$_4^-$ is appeared earlier than that of I$^-$ and SCN$^-$ in retention time. For a conventional anion exchange column, ClO$_4^-$ is strongly retained in the column because this ion is very hydrophobic and has strong affinity to the anion exchange resin. In this case, NO$_2^-$ was strongly adsorbed on the modified ODS and was not eluted by the acetate buffer of pH 3.5.

The retention time of anions on the TBPcCo(III) modified ODS column is listed in Table 1 for the eluents of different pH. As increasing in pH of the eluent, retention time is remarkably decreased. Especially, NO$_2^-$ could not be eluted by the eluent of pH 3.5, but it was eluted by the eluent of pH 6.0 in short retention time. This indicates that elution ability of OH$^-$ is larger than that of CH$_3$COO$^-$. In other word, OH$^-$ has larger dendency to coordinate to Co(III) than CH$_3$COO$^-$. 

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**Fig. 1** Voltammograms of cobalt complexes. (a) PcCo(II), (b) PcCo(III), solvent: pyridine, rotating speed: 300 rpm, scan speed: 20 mV s$^{-1}$.

**Fig. 2** Chromatogram of anions on the phthalocyanine cobalt(III)-modified ODS. Eluent: 4.2 mM acetate buffer, pH 6.0, Column: phthalocyanine cobalt(III) modified ODS (4.6 mm i.d. x 15 cm), Sample: sodium salts of anion depicted in the Figure (NO$_2^-$: 1.0 mM, NO$_3^-$: 0.1 mM, SCN$^-$: 0.2 mM, 100 µL).

**Fig. 3** Chromatogram of anions on the phthalocyanine cobalt(III)-modified ODS. Eluent: 1.0 mM acetate buffer, pH 3.5, Sample: 0.1 mM sodium salts of Cl$^-$, NO$_3^-$, ClO$_4^-$, I$^-$, 0.5 mM NaSCN, 100 µL. The other conditions are the same as in Fig. 2.
Adsoptivity of NO$_2^-$ and NO$_3^-$ on TBPcCo(III) modified ODS

In order to clarify the cause of the inverse of retention time of NO$_2^-$ and NO$_3^-$ adsorptivity of two anions on the ODS modified with TBPcCo(III) was evaluated by batch experiment. Table 2 shows the amount of NO$_2^-$ and NO$_3^-$ adsorbed on the untreated ODS (TSK-gel) and the ODS (TSK-gel) modified with TBPcCo(III). The untreated ODS shows a little adsorptivity to NO$_2^-$ at pH 3.5, but no adsorptivity to NO$_3^-$ at pH 4.9 and to NO$_3^-$ at both pH 3.5 and 4.9. On the other hand, the TBPcCo(III)-ODS shows adsorption selectivity between NO$_2^-$ and NO$_3^-$, namely, TBPcCo(III)-ODS adsorbs NO$_2^-$ preferentially. This selective adsorption of the TBPcCo(III)-ODS to NO$_2^-$ is the cause of the long retention on the column packed with the TBPcCo(III)-ODS. The amount of NO$_3^-$ adsorbed on the TBPcCo(III)-ODS at pH 3.5 is larger than that at pH 4.9.

As described in the previous section, since the amount of modified TBPcCo(III) on the ODS is 14.7 μmol / g-ODS, total ion exchange capacity is estimated to be the same value of modified TBPcCo(III), if NO$_2^-$ forms the 1:1 complex with TBPcCo(III). The amount of NO$_2^-$ adsorbed on the TBPcCo(III)-ODS is 6% and 24% of the estimated capacity at pH 4.9 and pH 3.5 respectively. This may be due to that OH$^-$ or CH$_3$COO$^-$ ion competitively coordinates to the TBPcCo(III) complex because the concentration of CH$_3$COO$^-$ was higher than that of NO$_3^-$ in the solution. The result of the lower adsorptivity of NO$_3^-$ in higher pH may be due to that the OH$^-$ ion strongly coordinates to TBPcCo(III). This is consistent to the short retention time of NO$_2^-$ on the column packed with TBPcCo(III)-ODS for the eluent of higher pH.

In conclusion, we have demonstrated that the column packed with the ODS modified with and TBPcCo(III) has a quite different elution sequence of anions from the conventional anion exchange column. This unique separation behavior is verified to come from the different coordination tendency of anions to the center metal of the complex, Co(III). The separation mechanism of anions is estimated to be ligand exchange mechanism, as shown in Fig. 4. Since the coordination of anions to the center metal of the complex is dependent on the kinds of metal, a different type of anion separation column can be expected by modification of different metal complexes. According to the Simon's report, trioctyltin chloride acts as an anion carrier. This type of carrier is one of candidates for modification of ODS for anion separation column. We have started studies on the separation behavior of anions on the ODS modified with organotin compounds.

![Fig. 4 Estimated separation mechanism of anion on TBPcCo(III)-ODS](image)

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References