Elution delay of fluoride by chromatography of anions on silica gels coated with crown ether dyes

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Abstract

The separation of halide ions by chromatography on silica gel coated with water-insoluble crown ether dyes was investigated. The retention times of fluoride and hydrogencarbonate ions were longer than those of chloride, bromide and iodide ions when distilled water was used as a mobile phase. The order was different from that of traditional anion-exchange selectivity. The elution behaviour is compared with that on silica gel and octadecylsilica gel, and is discussed with regard to the hydrophobicity and the hydrogen-bonding interaction.

Keywords: Coating; Stationary phases, LC; Fluoride; Crown ethers; Inorganic anions

1. Introduction

The separation of several metal ions by physically surfactant-coated columns has been developed [1,2]. It is easy to modify the stationary phase by physical coating and to obtain a variety of selectivities by various coating ligands, compared with chemical modification. Silica gel coated with crown ether derivatives as a packing material has been reported [3]. Although the polyamide crown resin slightly separated some alkali metal ions, it could unexpectedly separate various anions. The order of retention time for halide ions was as follows: $F^- < Cl^- < Br^- < I^-$. Also, ethylvinylbenzene–divinylbenzene copolymer resins physically coated with the cryptand n-decyl-2.2.2 have been reported to separate halide ions, when sodium hydroxide solution is used as an eluent [4–6]. The order of retention time was as follows: $F^- < Cl^- < Br^- < I^- < SCN^-$, although the

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order with a lithium hydroxide eluent was: $F^- = Cl^- = Br^- = I^- < SCN^-$ [6]. These orders were the same as those obtained with a typical elution on anion-exchange resin. The separation was due to the hydrophobicity of these anions and to the anion-exchange interaction with crown ether–alkali metal ion complexes. If the complexation of cryptand with a cation in the eluent was weak, such as the lithium ion, the halides could not be separated.

It has been reported that anions were separated by tetraalkylammonium salt-coated octadecylsilica gel (C_{18}) columns with citrate as the eluent [7]. The elution behaviour of polarisable monovalent anions was greatly influenced by alkyl groups on the quaternary nitrogen atom. The typical order of retention time was as follows: $F^- < Cl^- < Br^- < I^-$. These anions were retained on packings by complicated interactions, such as ion-exchange processes, hydrophobic interactions and ion-pairing effects. Even on a tetraalkylammonium salt-coated C_{18} column which had those complicated interactions, the

fluoride had the shortest retention time among halides.

This work describes the chromatographic separation behaviour of anions, using columns of physically immobilized water-insoluble crown ether dyes on silica gel and C_{18}. The separation behaviour is compared with those obtained on untreated silica gel and C_{18}. The elution order of anions is also discussed.

2. Experimental

2.1. Reagents

Naphthol, naphthylamine and dithizone were purchased from Wako (Osaka, Japan). Alfusone for the chromogenic reagent of fluoride, bathophenanthroline (bphen) and 1-(2-pyridylazo)-2-naphthol (PAN) were purchased from Dojindo (Kumamoto, Japan). Palmitic acid and naphthalene were purchased from Nacalai Tesque (Kyoto, Japan). Dibenzo-18-crown-6, cis-4,4'-dinitrodibenzo-18-crown-6 and cis-4,4'-diaminodibenzo-18-crown-6 were prepared by literature methods [8–10]. Crown ether dyes were prepared according to the diazo-coupling reaction of cis-4,4'-diaminodibenzo-18-crown-6 with 2-naphthol or 2-naphthylamine. The water-insoluble crown ether dyes are illustrated in Fig. 1. The silica particles of 10 μm diameter used
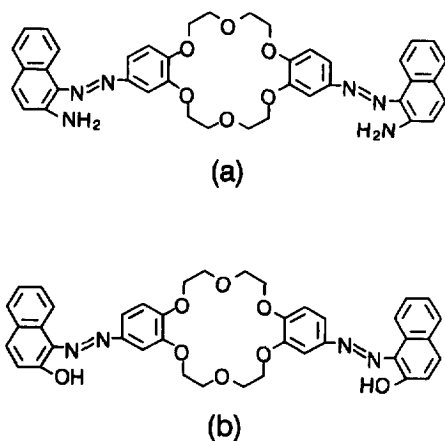

Fig. 1. Structures of two crown ether dyes: (a) cis-bis(1-azo-2-naphthylamino)-dibenzo-18-crown-6 (azo-naphthylamine dye), (b) cis-bis(1-azo-2-naphthol)-dibenzo-18-crown-6 (azo-naphthol dye).

were of Wakogel LC-10H (Wako). The silica gels coated with the crown ether dye were obtained by evaporating the solvent of the N-methyl-2-pyrrolidone solution. The other water-insoluble reagents, such as dithizone, bphen and PAN, were also coated on the silica gel by evaporating the solvent of the chloroform solutions. The coating reagents were used at 0.6 g for 1.5 g of substrate, unless otherwise stated.

The salts used were of reagent grade. RP-18 (10 μm) as C_{18} was purchased from Merck (Darmstadt, Germany). The styrene–divinylbenzene copolymer (MCI GEL CHP5C, 10 μm) was purchased from Mitsubishi (Tokyo, Japan). Each of the packing materials was loaded onto a 250 mm×4.0 mm I.D. column. Before the analysis, the distilled water used as the eluent was degassed and the water samples were filtered through a 0.45-μm cellulose acetate filter (Advantec, Tokyo, Japan).

2.2. Instrumentation

The chromatographic system consisted of a Tosoh CCPD pump and CM 8000 conductivity detector and a Rheodyne 7125 injector with 100-μl sample loop. A column was kept in an air-oven (Tosoh CO 8000) thermostated at 35°C. Visible spectra were recorded on a Hitachi Model U-2000 spectrophotometer. The surfaces on reagent-coated silica gels were observed by scanning electron microscopy (SEM) on a JEOL Model JSM-890 instrument.

3. Results and discussion

The separation of potassium halides on the silica gels coated with crown ether dyes, with distilled water as the mobile phase, is illustrated in Fig. 2. We consider that these crown ether–potassium complexes work as the anion exchanger. Neither non-coated silica gel nor non-coated C_{18} could separate the anions under these conditions, although they could be separated by the crown ether dye-coated columns. The halide ions eluted in the sequence $Cl^- < Br^- < I^- < SCN^- < F^-$. This order is the same as that of traditional anion exchange except for the fluoride ion. The long retention time of fluoride was not expected on the anion-exchange chromatography.
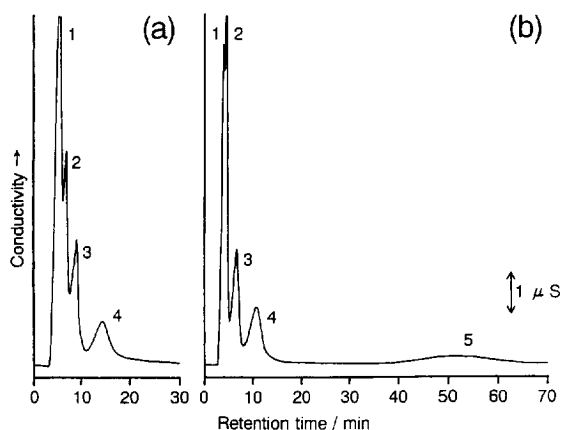
Fig. 2. Typical chromatograms of some $1 \cdot 10^{-4}$ M potassium halides on the crown ether dye-coated silica gels: (a) azo-naphthylamine dye: $1=$ Cl$^-$, Br$^-$; $2=$I$^-$; $3=$ SCN$^-$; $4=$F$^-$; (b) azo-naphthol dye: $1=$Cl$^-$; $2=$Br$^-$; $3=$I$^-$; $4=$SCN$^-$; $5=$F$^-$. Eluent, distilled water; flow-rate, 0.5 ml/min; injection volume, 100 μl.

Therefore, after the effluent fraction of each peak was collected, the fluoride ion in each fraction was spectrophotometrically determined by the lanthanum–alizarin complexone (La–AC) method [11]. Generally, increase of the visible absorption at 620 nm shows the existence of fluoride. The differential absorption spectrum of La–AC is shown in Fig. 3. The absorption at 620 nm increased in the fraction of the last peak, while the increase never appeared in other fractions. Therefore, the last peak was identified as fluoride.

The elution delay of fluoride was considered to be due to complexation of the fluoride with metal ions

originating from impurity in the silica gels and reaction of the fluoride with silanol groups on the surface of the silica gels. The elution delay of fluoride was also observed on the non-coated silica-gel column, although the elution delay was slight. The silanol on the surface of the silica gel dissociates the proton at pK_a 7.1 [12]. The silanol groups interacted as a weak cation-exchanger [13] and could separate some metal ions [14–17]. In our case, since the pH of the eluent is 5.5, the proton dissociation of silanol groups is small. Therefore, if the silanol groups were left on the crown ether dye-coated silica gels, the silanol groups might mainly react with the fluoride ion, but not with cations. Fig. 4 shows the dependence of capacity factor (k') on the quantity of coating crown ether dye. The chloride gave the shortest retention time among many salts (e.g. nitrates, sulphates, halides and carboxylates). The k' values were calculated, using the retention time of chloride as a reference. The k' values increased with increasing quantity of coating reagent. Therefore, the elution delay of fluoride is due to the coating crown ether dyes. Although the elution delay was not observed on the C_{18} column, it was observed on the crown ether dye-coated C_{18} column. Furthermore, the elution delay of fluoride was observed on the crown ether dye-coated stylene–divinylbenzene co-polymer, although separation of halides could not be accomplished. The best separation was achieved using silica gel as a substrate.

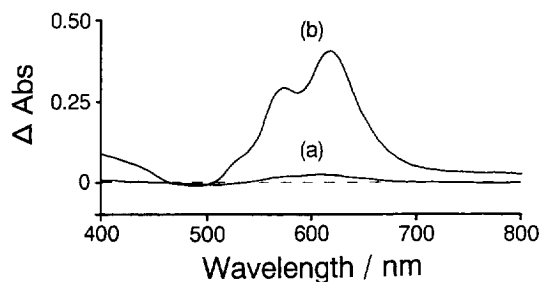The surfaces of these crown ether dye-coated

Fig. 3. Differential absorption spectra of La–AC in the fractions of each anion with an Alfusone (0.5%, w/v)–acetone (20%, v/v) solution: (a) the fractions supposed to contain the chloride, bromide, iodide and thiocyanate ions, (b) the fraction supposed to contain the fluoride ion.
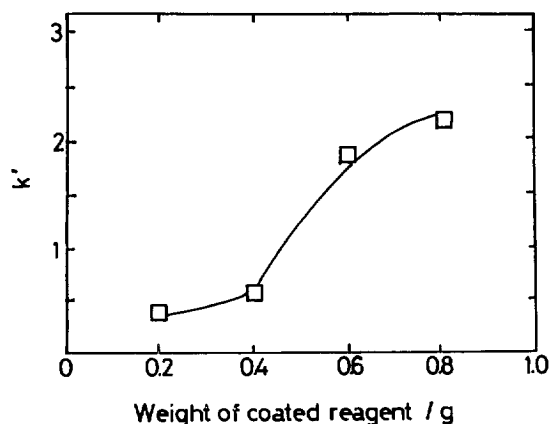

Fig. 4. The dependence of k' for fluoride on the quantity of coating azo-naphthylamine dye for 1.5 g of silica gel.

silica gels were observed by optical microscopy and
SEM. There were no observations of the naked silica
gels by optical microscopy. On the other hand, the
observation by SEM could not distinguish the crown
ether dye-coated silica gels from non-coated silica
gels because of colourless views. The silica gels
coated with the water-insoluble reagent at the same
quantity as crown ether dyes were observed by SEM.
In the case of palmitic acid-coated silica gels and C_{18}
needle crystals of the excess palmitic acid were
found on these surfaces. Therefore, the crown ether
dye-coated silica gels would be completely covered
with the coating reagents. Accordingly, there should
be no influence on metal ions from impurity and
silanol groups.

Furthermore, the k' values of halides on the crown
ether dye-coated silica gels are compared with silica
gels coated with some water-insoluble reagents, such
as bphen, dithizone and PAN, in Table 1. All the k'
values for fluoride are larger than those for the other
halides. The order of the delay time is as follows:
1-naphthylamine < dithizone < azo-naphthylamine
dye < 1-naphthol < PAN < dibenzo-18-crown-6 <
bphen < azo-naphthol dye. All the coating reagents
have hydrogen-bond acceptor sites. In other words,
when the coating reagents have a strong hydrogen-
bond acceptor, the fluoride showed a long retention
time. In the case of the crown ether dyes, after the
potassium ion coordination, the halide ions could
interact with the crown ether complex electrostatical-
ly. Generally, this would give separation of the
halide ions. However, potassium halides on the
dibenzo-18-crown-6-coated silica gels could not be
separated using distilled water as the eluent, except

for fluoride. In the work of Lamb et al. [4–6], as the
crown ether ring is flexible, because of the alkyl
chain between crown ether ring and substrate, the
potassium ion is easily coordinated. The potassium
ion complex works as an anion exchanger. In our
case, as the crown ether ring of crown ether dyes is
adsorbed on silica gels, interaction of the potassium
ion with the crown ether ring is weak. Therefore,
functioning of the crown ether dyes as an anion
exchanger is small and separation of halides is poor.
The elution delay of fluoride would be attributed to
the fact that the crown ether oxides hydrogen-bonded
with water molecules work as hydrogen-bond accep-
tors. The 1-naphthol-coated silica gels gave a longer
retention time for fluoride than the 1-naphthylamine-
coated silica gels. Similarly, the azo-naphthol dye
gave a longer retention time for fluoride than the
azo-naphthylamine dye. This is due to the difference
in the strength of the hydrogen-bond between fluo-
ride and –OH or –NH_2 group. Fig. 5 shows the
dependence of k' on temperature. Although the k'
values on the azo-naphthol dye decreased with
increasing temperature, the values on the azo-naph-
thylamine dye decreased only slightly. The azo-
naphthol dye would give a stronger interaction with
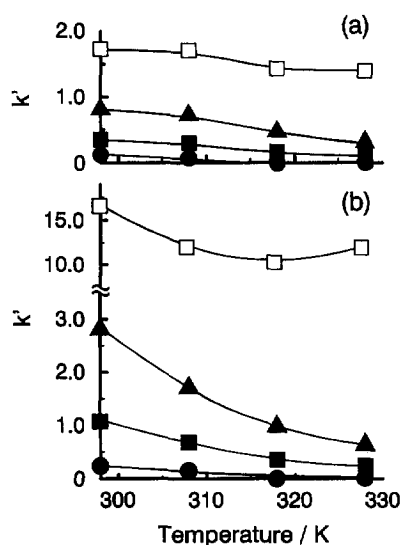the fluoride ion than the azo-naphthylamine dye. The

Table 1
The k' values of anions with coating reagents

Reagent	k'				
	F⁻	Cl	Br	I	SCN
1-Naphthylamine	1.62	1	1.02	1.13	1.36
PAN	1.83	1	1.00	1.13	1.23
Dithizone	1.98	1	1.02	1.07	1.13
Azo-naphthylamine dye	2.06	1	1.08	1.32	1.60
1-Naphthol	2.54	1	1.00	1.03	1.03
Dibenzo-18-crown-6	3.51	1	1.00	1.03	1.03
Bphen	5.87	1	1.04	1.20	1.41
Azo-naphthol dye	11.75	1	1.10	1.63	2.68

Fig. 5. The dependences of k' on temperature for (a) azo-naph-
thylamine dye- and (b) azo-naphthol dye-coated silica gels. (□)
F⁻; (●) Br⁻; (■) I⁻; (▲) SCN⁻.

phenolic –OH group has both properties of hydrogen-bonding donor and acceptor and this was reflected in the dependence of the k' values on temperature for the azo-naphthol dye. This is the reason why the phenolic –OH gives a longer retention time than the $-NH_2$ group. Also, the crown ether ring of crown ether dyes needs to keep the azo-naphthol and the azo-naphthylamine in an effective hydrogen-bonding place.

The fluoride ion is the strongest hydrogen-bond acceptor among halide ions, because the fluoride ion is the conjugated base of a weak acid. In fact, the hydrogencarbonate ion, which is also the conjugated base of a weak acid, gave a long retention time like the fluoride ion, as shown in Fig. 6. Although the fluoride ion almost exists as F^- at pH 5.5, because of $pK_a=3.6$ of hydrofluoric acid, the form of the fluoride ion kept on the coated columns is not obvious. The equilibrium via hydrogen ion between the conjugated bases of weak acids such as the fluoride ion and the coated packings would exist. The fluoride ion would behave as $HF(H_2O)_x$ with hydrogen ion on the coated packings with distilled water as the eluent. The $HF(H_2O)_x$ species are apparently hydrogen-bonded with hydrogen-bond acceptors of the packings.

The fluoride gave the same retention time as other halides on the crown ether dye-coated column with 50 mM Na_2SO_4 solution of pH 5.6 as the eluent. Since the salt, sodium sulphate, in the eluent interacts with the coating reagents, it interrupts the

hydrogen-bond of $HF(H_2O)_x$ with the coating reagents. Therefore, fluoride is not eluted as $HF(H_2O)_x$ but as F^-. The fluoride ion gives the short retention time. The short retention time of fluoride using NaOH solution as an eluent by Lamb et al. [4–6] also corresponds with this result.

The effects of counter cations on separation of anions on the azo-naphthylamine dye-coated silica gels are summarized in Table 2. A couple of crown ether dye-coated columns could not separate the cations. The elution order of anions was independent of cation type. The potassium ion, which has a large complex formation constant with dibenzo-18-crown-6 [18], did not influence separation of anions on these crown ether dye-coated columns. If the hydrophobicity of silica gels only increased by the crown ether dye-coated silica gels, the anion elutions for hydrophobic tetraalkylammonium salts would be slower than that for hydrophilic alkali metal salts. However, tetraalkylammonium ions such as $(CH_3)_4N^-$ and $(n\text{-}C_4H_9)_4N^+$, which are hydrophobic cations, did not change the elution of anions. Therefore, the crown ether dyes would have few interactions with these cations. Difficulties in separation arose on the polyamide crown ether resin, that is, if more than one kind of cation was present, the one anion gave multiple peaks [3]. However, the cation independence on the crown ether dyes could simplify the identification of the anion peaks, even if more than one kind of cation was present in the sample. The peak height of $1 \cdot 10^{-3}$ M on the azo-naphthol dye coated silica gels decreased in the following order: $(n\text{-}C_4H_9)_4NF > RbF > CsF > NH_4F > (CH_3)_4NF > NaF > LiF > KF$. However, the limiting
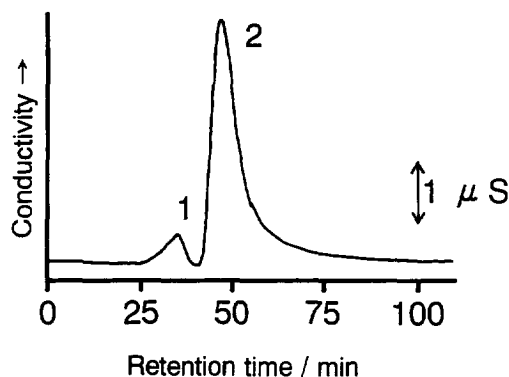

Fig. 6. Chromatogram of mixture of $2 \cdot 10^{-4}$ M sodium fluoride and $1 \cdot 10^{-3}$ sodium hydrogencarbonate on the azo-naphthylamine dye-coated silica gels: $1=F^-$; $2=HCO_3^-$. Eluent, distilled water; flow-rate, 0.1 ml/min; injection volume, 100 μl.

Table 2
The k' values of anions with several cations on the azo-naphthylamine dye-coated silica gels

Cation	k'				
	F^-	Cl^-	Br^-	I^-	SCN^-
Li^+	1.44	1	1.16	1.44	–
Na^-	1.83	1	1.06	1.25	1.50
K^+	2.06	1	1.08	1.32	1.60
Rb^+	1.69	1	1.04	1.24	–
Cs^-	1.84	1	1.10	1.33	–
NH_4^+	1.76	1	1.00	1.18	1.43
$(CH_3)_4N^+$	1.80	1	1.04	1.26	–
$(n\text{-}C_4H_9)_4N^+$	2.00	1	1.08	1.36	–

molar conductivity of Rb^+ is the largest among the others [Rb^+ (77.8 S cm^2 mol^{-1})>Cs^+ (77.3)>NH_4^+ (73.6)>K^+ (73.50)>Na^+ (50.10)>$(CH_3)_4N^+$ (44.9)>Li^+ (38.7)>$(n\text{-}C_4H_9)_4N^+$ (19.5) at 25°C] [19]. This is due to impurities of the salts and weakness of elution by the distilled water. The flow-rates did not improve the anion separations, although a slow flow-rate gave slightly better separation. Also, the azo-naphthol dye showed the same effect of flow-rate as the azo-naphthylamine dye.

4. Conclusions

Chromatography with distilled water as the eluent, is valuable, because its background conductivity is lower than that of eluents such as salt solutions and little baseline drift occurs. The very low background conductivity increases sensitivity. Distilled water as the eluent gave rise to large capacity factors of conjugated bases of weak acids on the crown ether dye-coated columns. The large capacity factor is thought to be caused by the hydrogen-bonding interaction of $HF(H_2O)_x$. In the case of KF sample, a linear relationship from 0.1 to 4.0 μg F^-/ml was obtained at the correlation coefficient 0.999. Also, the columns of the silica gel coated with the crown ether dyes are stable for more than 6 months.

Acknowledgments

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