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Ion-chromatographic Behavior of Silica Gels Modified by Poly- and Bis(crown ether)s of Benzo-18-crown-6

Masaki NAKAJIMA, Keiichi KIMURA,* and Toshiyuki SHONO*
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565

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Chromatographic behavior of crown ether modified silicas, in which poly- and bis(benzo-18-crown-6)s were attached covalently to silica gel, was investigated on separation of alkali and alkaline earth metal salts, using water or water/methanol as the mobile phase. Poly- and bis(benzo-18-crown-6)-modified silicas have a large affinity for Cs^+, the retention time of alkali metal cations being in the order $Li^+ < Na^+ < Rb^+ < K^+ < Cs^+$. Various anions having a common cation are separable as well as the metal cations on the modified silicas. Also, alkaline earth metal cations were separated on the stationary phases. The temperature effect of retention of alkali metal chlorides was also examined on bis(benzo-18-crown-6)-modified silica.

In the previous papers,[1,2] we have already reported the syntheses of silica gels modified by poly- and bis(benzo-15-crown-5) derivatives as stationary phases of liquid chromatography, and the chromatographic separation of alkali and alkaline earth metal salts on the modified silicas using water or water/methanol as the mobile phase. The following conclusions were attained on the crown ether modified silicas: 1) The stationary phases have a great affinity for K^+ among alkali metal cations, and the retention time increases in the order $Li^+ < Na^+ < Cs^+ < Rb^+ < K^+$; 2) pure solvents such as water or water/methanol can be utilized as the mobile phase without addition of acids, alkalies, and salts unlike the case of conventional ion chromatography; 3) the separation can be controlled by changing the fraction of methanol in the water mobile phase. Thus, poly- and bis(benzo-15-crown-5)-modified silicas have obviously many attractive properties as compared with conventional ion-exchange resins.

On the other hand, poly- and bis(crown ether)s containing benzo-18-crown-6 moiety have exhibited great cation-binding ability for Cs^+ among alkali and alkaline earth metal cations,[3] which has also been verified by the studies of solvent extraction[4] and ion-selective electrodes[5] using them. This specific cation-binding ability of poly- and bis(benzo-18-crown-6) derivatives is expected to be applied to the stationary phase of liquid chromatography.

This paper describes the liquid chromatography of alkali and alkaline earth metal salts on silica gels modified by poly- and bis(benzo-18-crown-6) derivatives. The temperature effect on the chromatographic behavior of the crown ether modified silicas is also discussed.

Experimental

Syntheses of Stationary Phases. Poly(benzo-18-crown-6)-modified silica (I) and bis(benzo-18-crown-6)-modified silica (II) were synthesized in similar ways to the poly- and bis(benzo-15-crown-5)-modified silicas, respectively, as reported in our previous work.[2] The silica gel employed was an irregular type and the average particle diameter was 10 μm. The crown ether contents of poly(benzo-18-crown-6)-modified silica, which were calculated from the weight increase and the carbon elemental analysis, are 0.28 mmol and 0.27 mmol per 1 g of dry modified silica, respectively. The bis(crown ether) contents of bis(benzo-18-crown-6)-modified silica are 0.31 mmol and 0.33 mmol per 1 g of dry modified silica, respectively. The expected structures of them are shown in Fig. 1.

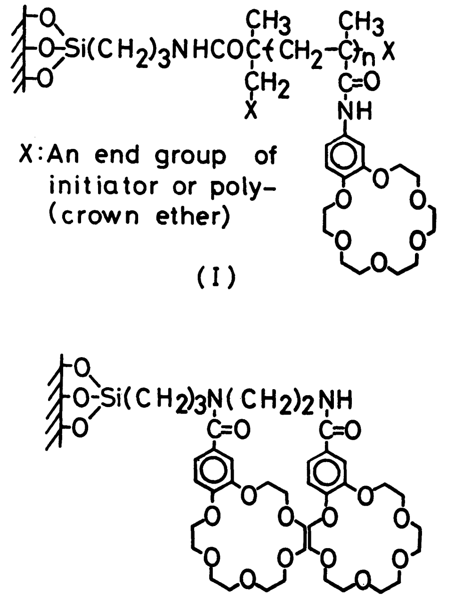

Fig. 1. Expected structures of poly(benzo-18-crown-6)-modified silica and bis(benzo-18-crown-6)-modified silica.

Materials. Alkali and alkaline earth metal salts employed here were of analytical grade. Water and methanol used as the LC mobile phase were purified by fractional distillation, followed by ultrafiltration, and then were degassed with an ultrasonic cleaner.

Instrumentation. Chromatographic experiments were performed with two chromatograph systems. One was the system assembled with commercially available modules, consisting of a pump (Milton Roy 0369-57), a sample injector (Kyowaseimitsu KHP-UI-130), and a refractometer detector (Waters Associates R-401). The other was also assembled with commercially available modules, consisting of a pump (Waters Associates 6000A), a sample injector (Waters Associates U6K), and a conductivity detector (LDC C-203). In this study, the former and the latter systems were referred to as chromatograph systems 1 and 2, respectively.

A stainless steel column (4 mm i.d., 300 mm length) was

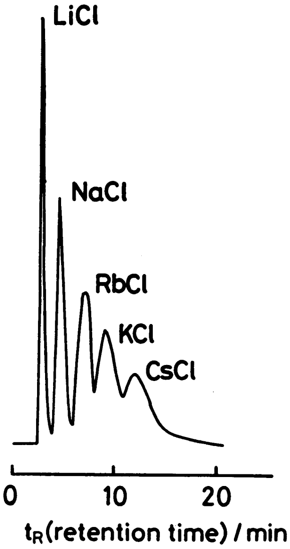

Fig. 2. Separation of alkali metal chlorides on poly(benzo-18-crown-6)-modified silica.
LiCl, 0.08 mg; NaCl, 0.21 mg; KCl, 0.15 mg; RbCl, 0.24 mg; CsCl, 0.34 mg; mobile phase, water/methanol (90/10 vol/vol).

packed with the modified silica (I), by a balanced-density slurry technique, and incorporated to chromatograph system 1. The other stainless steel column (4 mm i.d., 150 mm length) was packed with the modified silica (II), and incorporated to chromatograph system 2.

After the columns were conditioned by elution with a large quantity of water or water/methanol, sample (50 μl (1 l= 1 dm^3)) containing 0.02—0.04 mol l^{-1} salts was injected into systems 1 and 2. Chromatography was performed at a flow rate of 1.0 ml min^{-1} and at room temperature unless otherwise stated. The pressure drops ranged from 40 to 90 kg cm^{-2} on the chromatograph systems. In spite of the longer column length, the pressure drop on system 1 was not so high as that on system 2, of which the double damper system induced extra pressure drop. In some cases, the column temperature on chromatograph system 2 was controlled using a glass column jacket connected to a circulating water bath.

Results and Discussion

Separation of Alkali Metal Salts. A typical chromatogram of alkali metal chlorides on poly(benzo-18-crown-6)-modified silica is depicted in Fig. 2. A mixture of alkali metal (Li^+, Na^+, K^+, Rb^+, and Cs^+) chlorides was separated successfully on the crown ether modified silica, their retention time increasing in the sequence $Li^+ < Na^+ < Rb^+ < K^+ < Cs^+$. The crown ether modified silica showed a large affinity for Cs^+, which is presumably attributed to the cation-binding ability of the crown ether. Since poly- and bis(crown ether)s possessing neighboring crown ether moieties are favorable for forming sandwich-type 2 : 1 crown ether ring to cation complexes with particular metal cations which are slightly larger than the crown ether cavity, they often exhibit excellent selectivities and great cation-binding abilities for Cs^+ compared to the corresponding monocyclic crown ethers.[3-5] This cooperative effect of poly(benzo-18-crown-6) on binding metal cations is reflected on the chromatographic behavior of the modified silica. As a result, Cs^+ was retained longer than other alkali metal cations. K^+, which can fit into the cavity of benzo-18-crown-6, forms stable 1 : 1 crown ether ring to cation complexes. Rb^+, which is between Cs^+ and K^+ in cation size, is thought to form both 1 : 1 and 2 : 1 crown ether ring to cation complexes, but they may not be very stable. Na^+, which has a smaller cation size than K^+, is not bound very strongly by the crown ether. Conceivably, there is no appreciable interaction between the crown ether and Li^+, which has the smallest size among alkali metal cations. Obviously, the complexing ability of poly(benzo-18-crown-6) derivatives is reflected on the elution sequence of alkali metal salts.

Table 1. Retention time of alkali metal chlorides on poly(benzo-18-crown-6)-modified silica

	Retention time/min		
		H_2O/MeOH	
	H_2O	90/10	75/25
Li^+	2.8	2.7	2.9
Na^+	4.3	4.5	5.8
K^+	7.7	9.0	12.5
Rb^+	6.2	7.0	9.5
Cs^+	8.7	12.0	20.7

Table 2. Separation factor of alkali metal chlorides on poly(benzo-18-crown-6)-modified silica

	Separation factor[a)]		
		H_2O/MeOH	
	H_2O	90/10	75/25
Na^+	3.8	5.2	5.8
K^+	1.2	1.5	1.8
Rb^+	1.7	2.2	2.6

a) Separation factor of Na^+, K^+, and Rb^+ over Cs^+.

The retention time of alkali metal chlorides and the separation factors of NaCl, KCl, and RbCl over CsCl on poly(benzo-18-crown-6)-modified silica with water and water/methanol elution systems are given in Tables 1 and 2, respectively. Although the difference of retention time between K^+ and Cs^+ was observed by elution of pure water, the Cs^+ peak was too broad to be separated completely from the neighboring K^+ one. When a mixture of metal chlorides was eluted by water, the chromatogram gave four apparent peaks, which can be assigned to Li^+, Na^+, Rb^+, and K^+/Cs^+. If a water/methanol mixture is utilized instead of pure water as the mobile phase, the retention time of alkali metal cations increases with the rise of methanol fraction in the mobile phase except for Li^+ which is scarcely complexed by the crown ether. Consequently, the differences of retention time among their cations also increased. This is mainly due to the increased complexing abilities of the crown ether in water/methanol compared with that in water. The separation factor

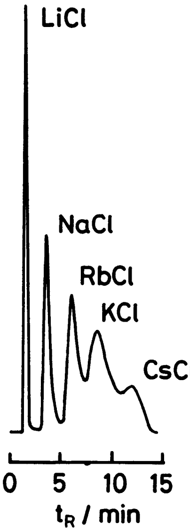

Fig. 3. Separation of alkali metal chlorides on bis(benzo-18-crown-6)-modified silica.
LiCl, 0.08 mg; NaCl, 0.12 mg; KCl, 0.15 mg; RbCl, 0.25 mg; CsCl, 0.34 mg; mobile phase, water/methanol (75/25 vol/vol).

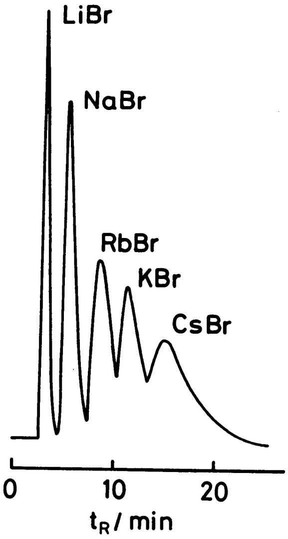

Fig. 4. Separation of alkali metal bromides on poly(benzo-18-crown-6)-modified silica.
LiBr, 0.17 mg; NaBr, 0.24 mg; KBr, 0.24 mg; RbBr, 0.34 mg; CsBr, 0.53 mg; mobile phase, water/methanol (90/10 vol/vol).

of K^+ over Cs^+ changed from 1.2 with water to 1.8 with water/methanol (75/25 vol/vol). In practice, the elution with water/methanol led to the base-line separation of K^+ and Cs^+, while their peaks overlapped each other on elution with water. However, the chromatography of alkali metal halides by elution with water/methanol (75/25 vol/vol) is rather time-consuming, and the separation of Rb^+ and K^+ is slightly inferior to that with water/methanol (90/10 vol/vol). Thus, the best chromatographic separation of alkali metal chlorides on poly(benzo-18-crown-6)-modified silica was attained using water/methanol (90/10 vol/vol) as the mobile phase, as can be seen in Fig. 2. Chromatographic retention of alkali metal chlorides on bis(crown ether)-modified silica containing benzo-18-crown-6 moiety is similar to that on the poly(crown ether)-modified silica. The alkali metal cation affinity to the modified silica increased again in the sequence $Li^+ < Na^+ < Rb^+ < K^+ < Cs^+$, and thus the modified silica retained Cs^+ longer. In this case, some cooperative effect of bis(crown ether)s on binding alkali metal cations also seems to contribute to the Cs^+ selectivity. On this stationary phase, K^+ and Cs^+ were not separated at all when pure water was used as the mobile phase, but addition of methanol to the mobile phase allowed them to separate each other. A typical chromatogram of alkali metal chlorides on bis(benzo-18-crown-6)-modified silica is demonstrated in Fig. 3. Each peak of Rb^+, K^+, and Cs^+ was so broad that their separations were not base-line ones. The retention time of alkali metal chlorides is summarized in Table 3. Naturally, they were eluted faster on bis(benzo-18-crown-6)-modified silica because of the difference in the column length.

With the stationary phase consisting of poly(benzo-18-crown-6)-modified silica, alkali metal bromides and iodides were also separated (Fig. 4). The elution orders of alkali metal bromides and iodides were the same as that of alkali metal chlorides. Generally, the complexing abilities of crown ethers for metal cations are also governed by the kind of counter anions, and cations possessing a large anion tend to be complexed easily by crown ether. Capacity factors of alkali metal chlorides, bromides, and iodides in chromatographic separation on the modified silica by elution with water/methanol (90/10 vol/vol) are shown in Fig. 5. The capacity factor of anions having a common cation increased in the sequence $Cl^- < Br^- < I^-$. Salts containing a much larger anion such as thiocyanate had greater capacity factors than the metal halides. Chromatographic retention of alkali metal bromides and iodides also depended on the fraction of water and methanol. Similar anion-dependence was observed for bis(benzo-18-crown-6)-modified silica as well. There is a remarkable difference in capacity factors among alkali metal chlorides, bromides, and iodides, as shown in Fig. 5. This means that separation of anions possessing a common cation can be attained, as demonstrated in Fig. 6.

TABLE 3. RETENTION TIME OF ALKALI METAL CHLORIDES ON BIS(BENZO-18-CROWN-6)-MODIFIED SILICA

	Retention time/min			
	H_2O	H_2O/MeOH		
		90/10	75/25	50/50
Li^+	1.4	1.4	1.4	1.5
Na^+	2.1	2.6	2.8	5.9
K^+	4.2	5.6	7.5	18.0
Rb^+	3.1	3.9	5.3	13.4
Cs^+	4.8	6.5	11.6	25.4

Separation of Alkaline Earth Metal Salts. Crown ethers have an ability to form complexes with alkaline

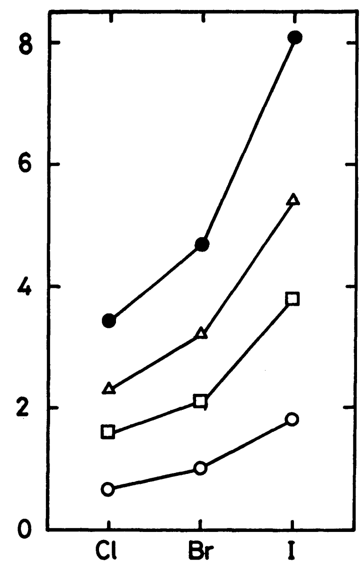

Fig. 5. Capacity factor on poly(benzo-18-crown-6)-modified silica.
Mobile phase, water/methanol (90/10 vol/vol); (○), NaCl; (△), KCl; (□), RbCl; (●), CsCl.

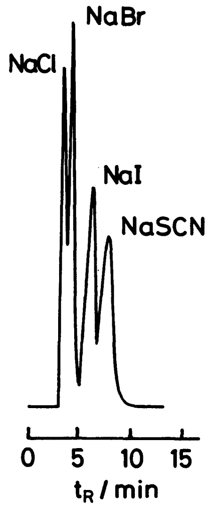

Fig. 6. Separation of a mixture of sodium salt on bis(benzo-18-crown-6)-modified silica.
NaCl, 0.12 mg; NaBr, 0.24 mg; NaI, 0.30 mg; NaSCN, 0.16 mg; mobile phase, water/methanol (75/25 vol/vol).

Table 4. Retention time of alkaline earth metal chlorides on poly(benzo-18-crown-6) modified silica

	Retention time/min		
	H_2O	H_2O/MeOH	
		90/10	75/25
Mg^{2+}	2.9	2.8	3.0
Ca^{2+}	3.1	3.3	3.8
Sr^{2+}	5.1	6.3	7.9
Ba^{2+}	8.4	9.0	12.6

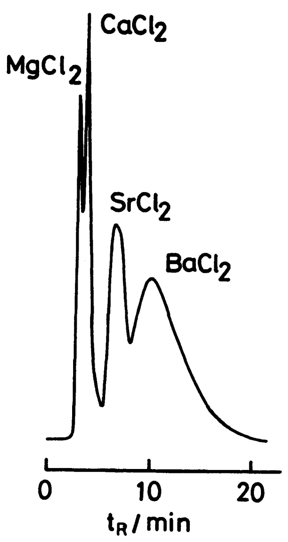

Fig. 7. Separation of alkaline earth metal chlorides on poly(benzo-18-crown-6)-modified silica.
$MgCl_2$, 0.10 mg; $CaCl_2$, 0.15 mg; $SrCl_2$, 0.27 mg; $BaCl_2$, 0.63 mg; mobile phase, water/methanol (90/10 vol/vol).

earth metal cations as well. However, not only the relative size of alkaline earth metal cation and crown ether ring, but also their strong hydration affects the complexing ability of the crown ethers. When alkaline earth metal chlorides were chromatographed on poly(benzo-18-crown-6)-modified silica, the retention time increased in the sequence $Mg^{2+}<Ca^{2+}<Sr^{2+}<Ba^{2+}$. That is to say, this modified silica has a large affinity for Ba^{2+} among alkaline earth metal cations. Mg^{2+} and Ca^{2+} were slightly separated using pure water as the mobile phase, but their separation was improved with addition of methanol, successful separation being observed with water/methanol (75/25 vol/vol). However, since the peak of Ba^{2+} is broadened on this elution condition, the peaks of Sr^{2+} and Ba^{2+} overlapped with each other. A typical chromatogram of alkaline earth metal salts on poly(benzo-18-crown-6)-modified silica is given in Fig. 7, the retention time being listed in Table 4. Bis(benzo-18-crown-6)-modified silica exhibited chromatographic behavior analogous to poly(benzo-18-crown-6)-modified silica. Also, in the chromatographic separation of alkaline earth metal salts on the crown ether modified silica, the anion dependence was the same as that for alkali metal salts.

Temperature Effect of Retention of Alkali Metal Chlorides on Bis(benzo-18-crown-6)-modified Silica. Generally, the column temperature plays an important role in the sample solubility, the retention time, the viscosity of the mobile phase, and the column efficiency. Therefore, the temperature dependence of the retention time for alkali metal chlorides was examined using bis(benzo-18-crown-6)-modified silica. The retention time decreased with increasing column temperature except that of Li^+ which scarcely changed at any temperature. Plots of ln k (capacity factor) *vs.* $1/T$ for the alkali metal cations gave straight lines with positive slopes (Fig. 8). It is known that the complexation of crown ethers with cation is an exothermic reaction, which is reflected in

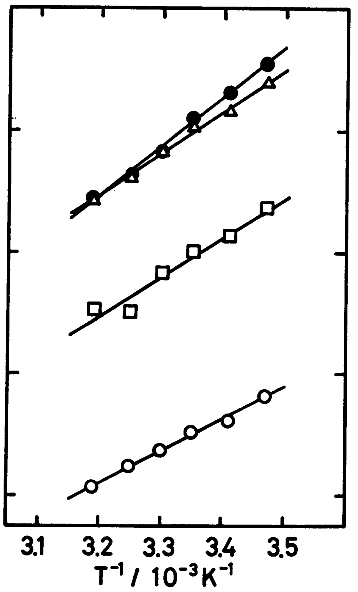

Fig. 8. Plots of ln *k* *vs.* $1/T$ on bis(benzo-18-crown-6)-modified silica.
(○), NaCl; (△), KCl; (□), RbCl; (●), CsCl.

the negative enthalpy changes (the positive slopes of the straight lines). Although the retention time approached to each other with the rise of temperature, separation of a mixture of Li^+, Na^+, and K^+ was rather excellent at elevated temperatures (Fig. 9). This is mainly due to the high column efficiency derived from a large diffusion coefficient of the mobile phase. Furthermore, the separation time was shorter at 40 °C (within 4 min) than at 15 °C (within 5.5 min). Thus the separation time can be easily adjusted to the best one by varying the column temperature.

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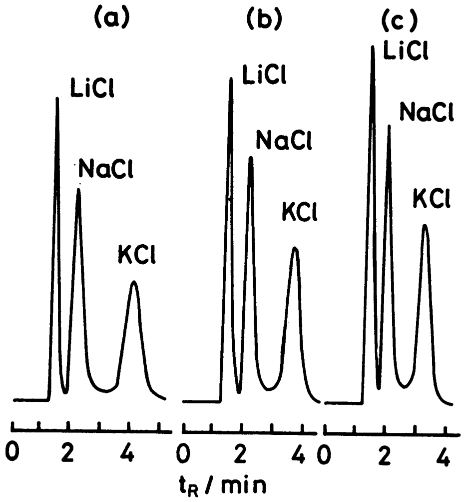

Fig. 9. Temperature dependence of chromatographic behavior of alkali metal chlorides on bis(benzo-18-crown-6)-modified silica.
LiCl, 0.09 mg; NaCl, 0.12 mg; KCl, 0.15 mg; mobile phase, water; (a), 20 °C; (b), 30 °C; (c), 40 °C.

References

1) K. Kimura, M. Nakajima, and T. Shono, *Anal. Lett.*, **13** 741 (1980).

2) M. Nakajima, K. Kimura, and T. Shono, *Anal. Chem.*, **55**, 463 (1983).

3) S. Kopolow, T. E. Hogen Esch, and J. Smid, *Macromolecules*, **6**, 133 (1973).

4) K. Kimura, T. Maeda, and T. Shono, *Talanta*, **26**, 945 (1979).

5) K. Kimura, H. Tamura, and T. Shono, *J. Electroanal. Chem. Interfacial Electrochem.*, **105**, 335 (1979).