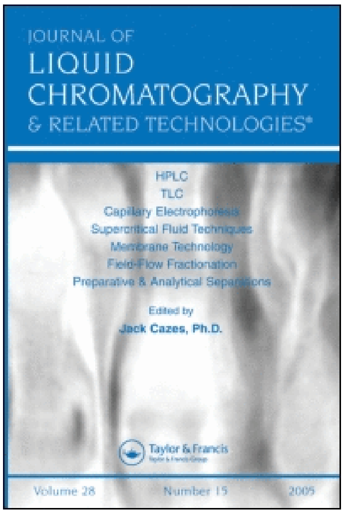


Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Ion Chromatography on Poly(Crown Ether)-Modified Silica Possessing High Affinity For Sodium

M. Nakajima[a]; K. Kimura[a]; E. Hayata[a]; T. Shono[a]
[a] Department of Applied Chemistry, Faculty of Engineering, Osaka University, Osaka, Japan

To cite this Article Nakajima, M. , Kimura, K. , Hayata, E. and Shono, T.(1984) 'Ion Chromatography on Poly(Crown Ether)-Modified Silica Possessing High Affinity For Sodium', Journal of Liquid Chromatography & Related Technologies, 7: 11, 2115 — 2125

To link to this Article: DOI: 10.1080/01483918408068863

URL: http://dx.doi.org/10.1080/01483918408068863

JOURNAL OF LIQUID CHROMATOGRAPHY, 7(11), 2115-2125 (1984)

ION CHROMATOGRAPHY ON POLY(CROWN ETHER)-MODIFIED SILICA POSSESSING HIGH AFFINITY FOR SODIUM

M. Nakajima, K. Kimura*, E. Hayata, and T. Shono*

Department of Applied Chemistry, Faculty of
Engineering, Osaka University, Yamada-oka,
Suita, Osaka 565, Japan

ABSTRACT

Stationary phases which have great affinity for Na^+ were synthesized by incorporating 12-crown-4 polymer on silica gel for liquid chromatography of alkali and alkaline-earth metal ions. The stationary phases interact with Na^+ most strongly of all alkali metal ions as expected, and the retention times on liquid chromatography of alkali metal ions were in the sequence $Li^+ < Cs^+ < Rb^+ < K^+ < Na^+$. On the stationary phase, a mixture of Li^+, Na^+, and K^+ can be separated completely by the elution with water/methanol mixture. By the use of spherical type silica gel instead of irregular type one and by effective end-capping of the residual silanol groups, the peak symmetry was improved significantly.

INTRODUCTION

One of the most important analytical applications of crown ether derivatives is chromatographic separation of ionic species. Several studies have been so far appeared regarding stationary phases containing crown ethers for liquid chromatography. Blasius et al. (1-3) have synthesized numerous crown ether resins and reported their applications to stationary phases for liquid chromatography to separate various ionic and organic compounds. Igawa et al. (4) have described an anion-separable stationary phase obtained by coating polyamide-type crown ether resin on

0148-3919/84/0711-2115$3.50/0

silica gel. We have also reported some applications of crown ether stationary phases in which poly- and bis(crown ether)s are bonded to silica gel covalently (5,6).

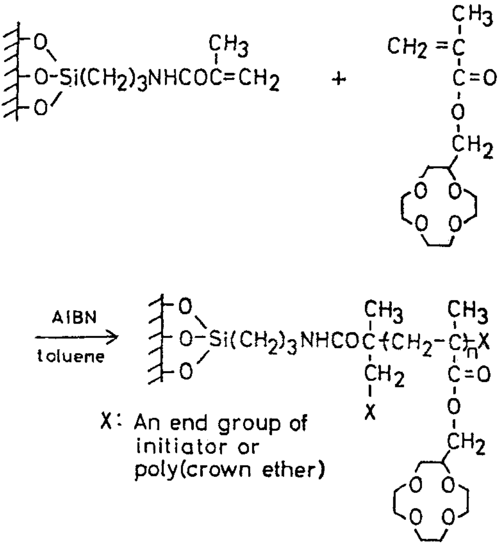
Most of the crown ether stationary phases showed specific chromatographic behaviors which are derived primarily from the ion-complexing abilities of the immobilized crown ethers, possessing great affinity for K^+, Rb^+, or Cs^+. However, very few stationary phase containing a crown ether has specific affinity for Na^+. Therefore, we attempted synthesis of poly(crown ether)-modified silica possessing affinity for Na^+. In this paper we report the synthesis of the stationary phases and the chromatographic separation of alkali and alkaline-earth metal ions on them.

EXPERIMENTAL

Syntheses of stationary phases

The synthetic route and the expected structure of poly(12-crown-4)-modified silica (poly12C4-silica) are illustrated in Fig. 1. In this study both of irregular and spherical type silica gels were employed. The average particle size of the silica gels was 10 µm.

First, the synthesis of poly12C4-silica-I (based on irregular type silica gel) is shown below. To a dry chloroform solution of (3-aminopropyl)triethoxysilane (0.012 mol, 2.66 g) and dry triethylamine (0.012 mol, 1.21 g), a dry chloroform solution of methacryloyl chloride (0.012 mol, 1.1 ml) was added dropwise while stirring and cooling in an ice bath. At room temperature the mixed solution was stirred for 12 h and then refluxed for 2 h in the presence of hydroquinone (6 mg). The solvent was replaced by dry toluene and the triethylamine hydrochloride was filtered off. The toluene solution was placed on 5.90 g of silica gel and the mixture was refluxed while stirring for 4 h. After being filtered off, the resulting vinyl-modified silica-I was washed successively with toluene, chloroform, and methanol, and then dried overnight under vacuum at 80°C. Residual silanol groups of



X: An end group of initiator or poly(crown ether)

Figure 1. Synthesis andexpected structure of poly(12-crown-4)-modified silica.

the vinyl-modified silica-I were capped in the following way. To a suspension of the modified silica (5.74 g) in dry benzene, a benzene solution of trimethylchlorosilane (0.053 mol, 5.8 g) (TMCS) was added dropwise, and the mixture was allowed to stand for 24 h with occasional stirring. A glass tube containing vinyl-modified silica-I and a toluene solution of (12-crown-4)-methyl methacrylate (7) (6.10 mmol, 1.66 g) and α,α'-azobis-(isobutyronitrile) (0.020 mmol, 33 mg) as the initiator was degassed by freeze-and-thaw method and then sealed. Polymerization was carried out by shaking the sealed tube in an incubator at 70°C for 21 h. After the polymerization, the silica gel was washed successively with toluene, chloroform, and methanol.

Poly12C4-silica-S (based on spherical type silica gel) was synthesized in a similar way to poly12C4-silica-I, but the procedure for end-capping of residual silanol groups of the modified silica was different from that for poly12C4-silica-I.

The vinyl-modified silica-S (4.50 g) was suspended in dry hexane and then a hexane solution of hexamethyldisilazane (0.010 mol, 1.64 g) (HMDS) was added dropwise. The suspension was heated at 75°C for 8 h. The resulting modified-silica was washed sufficiently and then dried.

The crown ether contents of poly12C4-silica-I are 0.62 mmol and 0.72 mmol per gram of dry modified silica, which were determined from weight increase and elemental analysis of carbon, respectively. Similarly, the crown ether contents of poly12C4-silica-S were determined as 0.72 mmom and 0.76 mmom per gram.

Other materials

Alkali and alkaline-earth halides employed here are of analytical grade. Water and methanol used as the mobile phase were purified by distillation, followed by ultrafiltration. The water and methanol were degassed by stirring under vacuum, and mixed eluents of water and methanol were further degassed with an ultrasonic cleaner.

Instrumentation

The chromatograph system employed here consists of commercially available modules, consisting of a pump (Waters Associates 6000A), a sample injector (Waters Associates U6K), and a conductivity detector (LDC C-203). The stationary phases were packed into stainless steel columns (4 mm i.d., 300 mm or 150 mm length) by balanced density slurry technique. These packed columns were incorporated to the chromatograph system.

After the columns were conditioned by elution with a large quantity of water or water/methanol, aliquots of sample (50 μl) containing 0.02-0.04 M salts were injected into the system. Chromatography was performed at room temperature at a flow rate of 1.0 ml/min, unless otherwise specified. The pressure drops ranged from 30 to 100 kg/cm^2 when a column of 300 mm length and a flow rate of 1.0 ml/min were adopted.

RESULTS AND DISCUSSION

Polymers containing 12-crown-4 moiety at the side chain, what we call poly(12-crown-4), exhibit high Na^+ selectivity on complexing alkali metal ions, probably because they form stable 2:1 crown ring to ion complexes with the ion by cooperative action of two adjacent crown ether rings in a polymer chain. Attempts were made to immobilize this type of poly(crown ether)s on silica gel in order to obtain stationary phases for ion chromatography which possess high affinity for Na^+.

Chromatographic behavior of alkali metal salts on poly12C4-silica-I

Chromatography was performed using a column of 300 mm length packed with poly12C4-silica-I. When alkali metal chlorides were chromatographed by the elution with pure water, the retention times of them were not remarkably different. That is to say, Na^+ was slightly retained longer than the other alkali metal ions, which were hardly retained on the modified silica. Generally, in water, which is highly polar solvent, the complexation of crown ether with the ions is weak. When water/methanol (50/50 v/v) was used as the mobile phase, the retention times of the metal ions were increased and marked differences were also observed among them. This stationary phase retained Na^+ most strongly of all alkali metal ions as expected from the complexing ability of the poly(crown ether)s, their retention times being in the sequence $Li^+<Cs^+<Rb^+<K^+<Na^+$. On the chromatography of mixtures of Li^+, Na^+, and K^+ under this elution condition, Na^+ are completely separated from Li^+ and K^+, although baseline separation of Li^+ and K^+ was not attained. Change in the retention time of alkali metal ions were followed with increasing methanol fraction in the eluent (Fig. 2). The retention time of Li^+ was scarecely altered by increasing methanol fraction in the mobile phase, whereas those of Na^+ and K^+ were increased. In the retention times Rb^+ and Cs^+ are close to K^+, even if pure methanol was used as the mobile phase. The elution sequence of them was not changed with any methanol

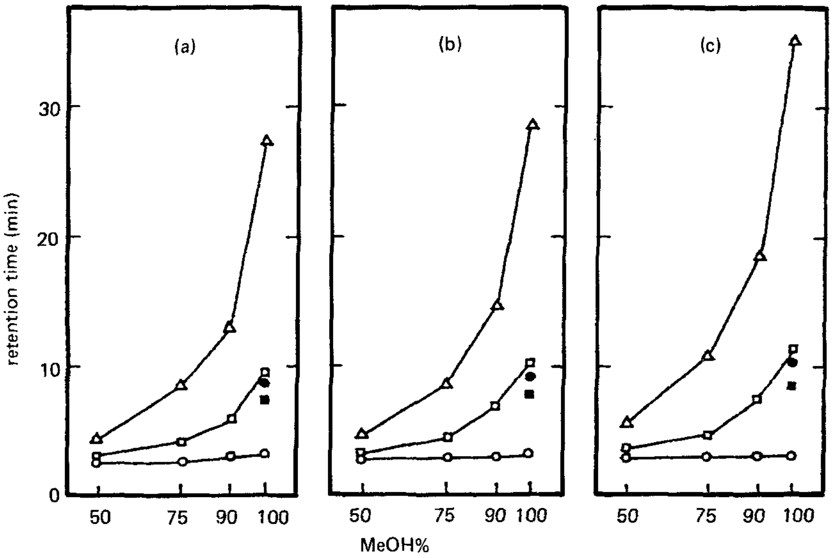


Figure 2. Dependence of the retention time of alkali metal halides upon methanol fraction in eluent. (a) chloride, (b) bromide, (c) iodide; (○) Li, (△) Na, (□) K, (●) Rb, (■) Cs.

fraction in the mobile phase. On the elution with pure methanol, the retention times of chlorides of Li^+, K^+, and Na^+ were 2.7, 9.4, and 27 min, respectively. The retention time difference of them is large enough for their baseline separation, but it takes very long to separate them under this elution condition. In Fig. 3 the separation of Li^+, K^+, and Na^+ is shown under the best elution condition, this is, using water/methanol (25/75 v/v), together with that using water/methanol (50/50 v/v) for comparison. In Fig. 3(a) the separation of Li^+, K^+, and Na^+ was complete, whereas that between Li^+ and K^+ is still insufficient in Fig. 3(b).

It is well known that the ion-complexing abilities of crown ethers were governed by the kind of counter anions as well as of cations. On this stationary phase the retention of metal salts was dependent upon their counter anions, especially, at high

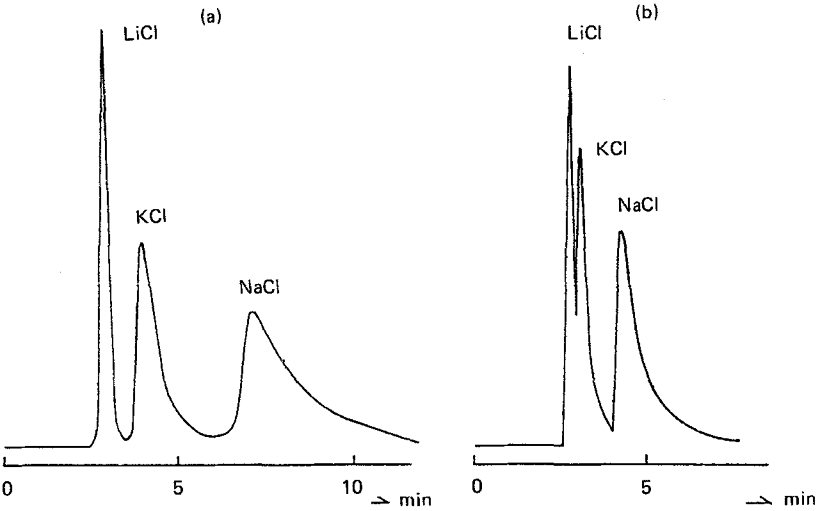


Figure 3. Chromatographic separation of alkali metal chlorides on poly(12-crown-4)-modified silica-I. Column length: 300 mm; mobile phase: (a) water/methanol (25/75 v/v); (b) water/methanol (50/50 v/v); sample: LiCl, 0.08 mg; NaCl, 0.12 mg; KCl, 0.15 mg.

methanol fraction in the mobile phase (Fig. 2). The retention of anions accompanying a common cation is increased in the sequence $Cl^- < Br^- < I^-$ except Li^+ which is scarecely retained on the stationary phase even by the elution with pure methanol. However, the differences of retention times among the anions with a common cation were so small that they could not be separated to each other in this chromatography.

Chromatographic behavior of alkali metal salts on poly12C4-silica-S

In order to improve the column efficiency and the peak shapes, spherical type of silica gel was employed instead of irregular type one, and end-capping of residual silanol groups by HMDS was attempted instead of by TMCS.

As described in the experimental section, the stationary phases based on irregular- and spherical-type silica gels are almost the same in the crown ether content. Fig. 4 demonstrates

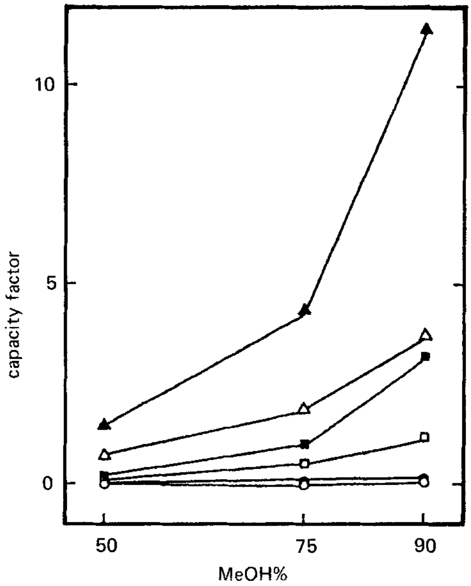


Figure 4. Dependence of capacity factors of alkali metal chlorides upon elution composition on chromatography using the different type of poly(12-crown-4)-modified silicas. (○) LiCl, (△) NaCl, (□) KCl on poly(12-crown-4)-modified silica-I; (●) LiCl, (▲) NaCl, (■) KCl on poly(12-crown-4)-modified silica-S.

the dependence of the capacity factors on the eluent composition of metal ions with respect to both stationary phases. Since Li^+ was hardly retained on either stationary phase, the capacity factors of Li^+ was not changed practically. However, Na^+ and K^+ have larger capacity factors on poly12C4-silica-S than poly12C4-silica-I. One of the reason is that the spherical type silica gel can be packed into a column more densely than irregular one. In other words, the former stationary phase is larger in the contents of crown ether per a column than the latter one, which in turn results in the strong retention of metal ions in a column packed with poly12C4-silica-S column compared with poly12C4-silica-I. By the elution with water/methanol (40/60 v/v), baseline separation of three alkali metal chlorides was attained on poly12C4-silica-S

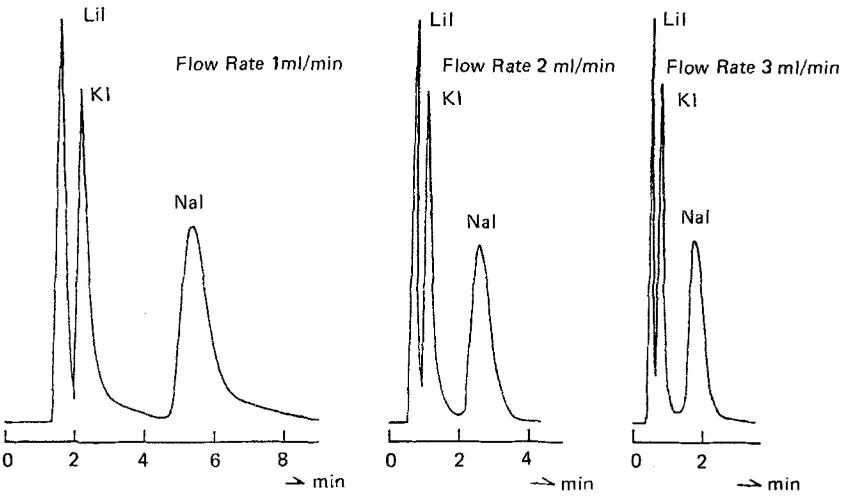


Figure 5. Effect of flow rate upon chromatographic separation of alkali metal iodides on poly(12-crown-4)-modified silica-S. column length: 150 mm; mobile phase: water/methanol (50/50 v/v); sample: LiI, 0.27 mg; NaI, 0.30 mg; KI, 0.33 mg.

whereas this was not the case in poly12C4-silica-I. Also, intensive tailing of the Na^+ peak which was obseved in poly12C4-silica-I has disappeared in this case, although slightly taining of K^+ peak still remained. This is thought to be due mainly to the effective end-capping of residual silanol groups on the surface of silica gel by HMDS compared to by TMCS, which was confirmed by the elemental analysis of carbon and the weight increase of the modified silicas on the syntheses.

Although Li^+, Na^+, and K^+ are completely separated on poly12C4-silica-S under the above-mentioned elution condition, it still takes 9 min to separate them. Some attempts were made to implove the separation time. Generally, separation times are dependent on capacity factor, column length, and flow rate. A column of 150 mm length and flow rates higher than 1 ml/min are tried to attain more speedy chromatographic separation of them. Fig. 5 depicts chromatograms of alkali metal iodides by the elution with water/methanol (50/50 v/v) at a flow rate of 1, 2,

TABLE I

Retention Times of Alkaline-earth Metal Chlorides on Poly-(12-crown-4)-modified Silica-S

	water/methanol (v/v)			
	50/50	40/60	25/75	10/90
$MgCl_2$	2.7	3.0	3.1	5.4
$CaCl_2$	2.8	3.0	3.6	6.9
$SrCl_2$	2.8	3.0	3.9	8.7
$BaCl_2$	3.3	4.9	5.7	10.4

retention time in min.; column length: 300 mm

and 3 ml/min. Even at a high flow rate of 3 ml/min, these metal ions are separated successfully within 2.5 min.

Chromatographic behavior of alkaline-earth metal salts

Crown ethers complex alkaline-earth metal ions as well as alkali metal ions. The poly12C4-silica was tested for its usefulness on chromatographic separation of alkaline-earth metal ions. Alkaline-earth metal ions were eluted in the sequence $Mg^{2+}<Ca^{2+}<Sr^{2+}<Ba^{2+}$, the retention times of them being listed in Table I. The stationary phase in which poly(12-crown-4) is immobilized on silica gel shows large affinity for Ba^{2+}. This retention behavior is very similar to those of the crown ether resins (2,3) and the other poly(crown ether)s-modified silicas reported previously (5,6). When water/methanol (50/50 v/v) was used as the mobile phase, the retention times of Mg^{2+}, Ca^{2+}, and Sr^{2+} are close to each other. Increasing methanol fraction of mobile phase enhanced their retention on the stationary phase, but broadened their peaks concurrently.

ACKNOWLEDGMENTS

The author (K.K.) expresses his grateful thanks to the Foundation Hattori-Hokokai for financial assistance.

REFERENCES

1. Blasius, E., Janzen, K.-P., Keller, M., Lander, H., Nguyen-Tien, T., and Scholten, G., Talanta, 27, 107, 1980.

2. Blasius, E., Janzen, K.-P., Adrian, W., Klein, W., Klotz, H., Luxenburger, H., Mernke, E., Nguyen, V.B., Nguyen-Tien, T., Rausch, R., Stockemer, J., and Toussaint, A., Talanta, 27, 127, 1980.

3. Blasius, E., Janzen, K.-P., Klein, W., Klotz, H., Nguyen, V.B., Nguyen-Tien, T., Pfeiffer, R., Scholten, G., Simon, H., Stockemer, H., and Toussaint, A., J.Chromatogr., 201, 147, 1980.

4. Igawa, M., Saito, K., Tsukamoto, J., and Tanaka, M., Anal.Chem., 53, 1942, 1891.

5. Nakajima, M., Kimura, K., and Shono, T., Anal.Chem., 55, 463, 1983.

6. Nakajima, M., Kimura, K., and Shono, T., Bull.Chem.Soc.Jpn., 56, 3052, 1983.

7. Maeda, T., Ouchi, M., Kimura, K., and Shono, T., Chem.Lett., 1981, 1573.