Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Effect of Ring-Size Variation within Dibenzocrown Ether Resins upon Ion-Pair Sorption of Alkali-Metal Cations from Aqueous and Aqueous Methanol Solutions

Takashi Hayashita[ab]; John C. White[a]; Jong Chan Lee[a]; Richard A. Bartsch[a]
[a] DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY, TEXAS TECH UNIVERSITY, LUBBOCK, TEXAS [b] Department of Chemistry, Saga University, Saga, Japan

To cite this Article Hayashita, Takashi , White, John C. , Lee, Jong Chan and Bartsch, Richard A.(1993) 'Effect of Ring-Size Variation within Dibenzocrown Ether Resins upon Ion-Pair Sorption of Alkali-Metal Cations from Aqueous and Aqueous Methanol Solutions', Separation Science and Technology, 28: 17, 2607 — 2620
To link to this Article: DOI: 10.1080/01496399308017499
URL: http://dx.doi.org/10.1080/01496399308017499

SEPARATION SCIENCE AND TECHNOLOGY, **28**(17&18), pp. 2607–2620, 1993

Effect of Ring-Size Variation within Dibenzocrown Ether Resins upon Ion-Pair Sorption of Alkali-Metal Cations from Aqueous and Aqueous Methanol Solutions

TAKASHI HAYASHITA,* JOHN C. WHITE, JONG CHAN LEE, and RICHARD A. BARTSCH†
DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY
TEXAS TECH UNIVERSITY
LUBBOCK, TEXAS 79409-1061

ABSTRACT

A batch analysis method has been developed for evaluation of metal salt sorption by crown ether polymers. Selectivity in competitive alkali-metal chloride sorption by a series of formaldehyde condensation polymers of dibenzocrown ethers is influenced by the relationship between the crown ether cavity size and metal ion diameter, as well as the degree of hydration of the metal salt. Effective and selective sorption of KCl from the other alkali-metal chlorides was obtained with a dibenzo-18-crown-6 resin. Excellent sorption selectivity for the monovalent metal chlorides was noted for competitive ion-pair sorption of NaCl, KCl, $MgCl_2$, and $CaCl_2$ by this resin. This resin was examined as a stationary phase for selective column separation of KCl from alkali-metal chlorides and of KCl and NaCl from alkali-metal and alkaline-earth chloride mixtures in 80% methanol–20% water.

INTRODUCTION

Blasius and coworkers synthesized a series of crown ether resins by condensation polymerization reactions of dibenzocrown ethers with formaldehyde (1–4). These resins exhibited selective binding of alkali-metal

* Present address: Department of Chemistry, Saga University, 1 Honjo-machi, Saga 840, Japan.
† To whom correspondence should be addressed.

cations. Compared with conventional ion-exchange resins, however, interactions between the crown ether binding sites and metal cations are weak. To enhance such interactions, we have employed novel chelating resins that possess both ion-exchange and crown ether binding sites in the same matrix (5–10). It was found that sorption selectivity and efficiency were significantly affected by the steric configuration of the binding sites in the resin. Preorganization of the binding site by conformational positioning of a pendant carboxylic acid group over the crown ether cavity provided high sorption selectivity and efficiency. For neutral crown ether resins, such a molecular design of the binding site may also produce specific and effective interactions with metal ion species.

In the present study we report an effective evaluation method for the characterization of metal ion sorption by neutral crown ether resins. The approach is to determine which metal salt species remains on the resin after it is contacted with a concentrated metal salt solution followed by purging of the resin with air or nitrogen. By use of this method, the effect of ring-size variation within dibenzocrown ether resins upon the selectivity and the efficiency of ion-pair sorption for alkali-metal chlorides has been evaluated. In addition, it was found that these neutral crown ether resins exhibit excellent monovalent metal salt selectivity for sorption from solutions of mixed alkali-metal and alkaline earth cations. Column separation of alkali-metal salts from an aqueous–methanol solution containing alkali-metal and alkaline-earth chlorides has been examined.

EXPERIMENTAL

Apparatus

The apparatus was the same as that utilized in previous studies (5–10) with the addition of a gas regulator (Noshok R07-100-RNEA, C. A. Norgren and Co.) for the column separation experiments. To prevent metal contamination, all glassware was soaked in 5% HNO_3 solution for 24 hours and rinsed with distilled deionized water before use.

Reagents and Solutions

Sources of reagents and solvents were the same as those reported previously (5–10). Stock aqueous solutions of 0.50 M alkali-metal chlorides (LiCl, NaCl, KCl, RbCl, and CsCl) and of 0.50 M alkali-metal and 0.25 M alkaline-earth chloride mixture (NaCl, KCl, $MgCl_2$ and $CaCl_2$) were stored in polyethylene bottles. Sample solutions were prepared by mixing and diluting these stock solutions. Purified water was prepared by passing distilled water through three Barnstead D8922 combination cartridges in

series. Dibenzocrown ether monomers were prepared by the reported methods (11).

Preparation of Dibenzocrown Ether Resins 1–6

Resins **1–6** were synthesized by condensation polymerization of the corresponding dibenzocrown ether monomers with formaldehyde in formic acid (5). The monomer was dissolved in a solution of formic acid and formaldehyde (37% aqueous solution). The mixture was refluxed for 2 days and allowed to cool to room temperature. The precipitate was collected, washed with formic acid and then water, and dried. For conditioning, the resin was further washed with 0.50 M NaOH, water, 0.30 M HCl, water, acetone, and finally dried at 80°C. In the case of resin **6**, no precipitate was obtained after the reaction. Therefore the reaction mixture was poured into water (500 mL) and the resultant precipitate was collected. A listing of reagent amounts and the yields of dibenzocrown ether resins are presented in Table 1. The resins were ground to a powder form (finer than 100 mesh).

Resin **1**. IR (KBr): 3446 (OH), 1609, 1508 (C=C), 1269, 1053 (CO) cm^{-1}. Analysis calculated for **7**·2.0CH_2OH: C, 72.16; H, 6.18. Found: C, 72.21; H, 6.42.

Resin **2**. IR (KBr): 3448 (OH), 1608, 1508 (C=C), 1277, 1049 (CO) cm^{-1}. Analysis calculated for **7**·3.5CH_2OH: C, 67.80; H, 5.73. Found: C, 68.19; H, 6.13.

Resin **3**. IR (KBr): 3448 (OH), 1608, 1508 (C=C), 1277, 1049 (CO) cm^{-1}. Analysis calculated for **7**·3.3CH_2OH: C, 69.05; H, 6.31. Found: C, 68.95; H, 6.14.

Resin **4**. IR (KBr): 3448 (OH), 1609, 1508 (C=C), 1277, 1051 (CO) cm^{-1}. Analysis calculated for **7**·2.2CH_2OH: C, 67.10; H, 6.47. Found: C, 67.11; H, 6.08.

Resin **5**. IR (KBr): 3442 (OH), 1602, 1508 (C=C), 1301, 1273, 1061 (CO) cm^{-1}. Analysis calculated for **7**: C, 66.49; H, 6.74. Found: C, 64.71; H, 5.75.

Resin **6**. IR (KBr): 3426 (OH), 1597, 1508 (C=C), 1302, 1067 (CO) cm^{-1}. Analysis calculated for **7**: C, 65.35; H, 6.97. Found: C, 63.90; H, 6.18.

Competitive Sorption of Metal Chlorides by Resins 1–6

An aqueous or aqueous methanol solution (5.0 mL) of the five alkali-metal chlorides (0.100 M in each) or of alkali-metal and alkaline-earth chlorides (0.100 M in Na^+ and K^+ and 0.050 M in Mg^{2+} and Ca^{2+}) was shaken with 0.040 g of the dibenzocrown ether resin for 3.0 hours in a 25-

TABLE I
Reagent Amounts and Yields for Polymerizations of Dibenzocrown Ethers

Resin	Monomer	Amount of monomer (mmol)	HCO_2H (mL)	H_2CO (mL)[a]	Yield (%)
1	DB14C4	9.0	200	100	80
2	DB15C5	6.0	95	47	72
3	DB16C5	9.0	200	100	75
4	DB18C6	12.0	200	100	65
5	DB21C7	10.0	165	88	82
6	DB24C8	9.0	200	100	80

[a] 37% aqueous solution.

mL pear-shaped flask with a 14/20 joint and a polypropylene stopper at room temperature (21–23°C) with a Burrel wrist-action shaker. The mixture was filtered with a sintered glass funnel. To remove the sample solution completely, filtration was continued for 20 minutes under aspirator vacuum. (Air was purged through the resin.) The resin was dried at 80°C. Of the dried resin, a 0.020-g sample was shaken with 5.0 mL of pure water for 1.0 hour to strip the metal chlorides from the resin into aqueous solution for analysis by ion chromatography with a Dionex Model 2000i ion chromatograph. For analysis of the alkali-metal and alkaline-earth chloride mixtures, atomic absorption spectrophotometry with a Perkin-Elmer Model 500 atomic absorption spectrophotometer was utilized.

Good reproducibility was observed when an alkali-metal chloride sorption experiment was repeated with another sample of virgin resin from a dibenzocrown ether polymer preparation or with regenerated resin. Alkali-metal chloride sorptions by two different preparations of resin 4 showed good batch-to-batch reproducibility.

Column Sorption of Metal Chlorides by Resin 4

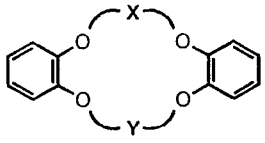
An aqueous methanolic solution (80% methanol–20% water, 5.0 mL) containing five alkali-metal chlorides (0.100 M in each) or an alkali-metal and alkaline-earth chloride mixture (0.100 M in Na^+ and K^+ and 0.050 M in Mg^{2+} and Ca^{2+}) was eluted through a 0.42-cm i.d. column of resin 4 (0.100 g) by regulated nitrogen gas pressure at a flow rate of 0.01–0.08 mL/min. Nitrogen gas was purged through the column for 20 minutes to remove the sample solution completely. The metal chlorides bound to the resin were then stripped with pure water. The stripping solutions were collected by 40-drop fractions and analyzed by ion chromatography or atomic absorption spectrophotometry after appropriate dilution. After

each set of experiments, the volume of the 40-drop fractions (0.72 mL for alkali-metal chloride stripping and 0.86 mL for mixed alkali-metal and alkaline-earth chloride stripping) was calibrated with a microsyringe.

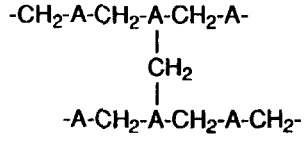
RESULTS AND DISCUSSION

Preparation of Dibenzocrown Ether Resins 1–6

Crown ether resins **1–6** which possess different ring sizes were prepared by condensation polymerization of the corresponding dibenzocrown ether monomers with formaldehyde in formic acid (Table 1). A possible structure for the partially crosslinked resins is given by **7** in which A is the dibenzocrown ether unit in the resin (Fig. 1). The elemental analysis results for resins **1–4** are in agreement with this structure when 2.0–3.5 methylol (—CH_2OH) groups are incorporated into the structural unit of **7**. However, for resins **5** and **6** the addition of methylol groups to **7** did not bring the calculated composition into agreement with the observed elemental analysis results. As expected, the IR spectra for each resin showed very little change from that of the dibenzocrown ether monomer with the exception of an OH stretching vibration due to the methylol groups.



A



7

Resin	Ring Size	X	Y
1	14C4	$-CH_2CH_2CH_2-$	$-CH_2CH_2CH_2-$
2	15C5	$-CH_2CH_2-$	$-CH_2CH_2OCH_2CH_2-$
3	16C5	$-CH_2CH_2CH_2-$	$-CH_2CH_2OCH_2CH_2-$
4	18C6	$-CH_2CH_2OCH_2CH_2-$	$-CH_2CH_2OCH_2CH_2-$
5	21C7	$-CH_2CH_2OCH_2CH_2-$	$-CH_2CH_2(OCH_2CH_2)_2-$
6	24C8	$-CH_2CH_2(OCH_2CH_2)_2-$	$-CH_2CH_2(OCH_2CH_2)_2-$

FIG. 1 Structures of dibenzocrown ether resins.

Ion-Pair Sorption of Alkali-Metal Chlorides by Resin 4

The influence of shaking, purging, and stripping time variation for alkali-metal cation sorption by the dibenzocrown ether resins was assessed with resin **4**. An aqueous solution of the five alkali-metal cations (0.100 M in each) as the chlorides was shaken with resin **4**. Figure 2(a) shows the influence of shaking time upon sorption of alkali-metal chlorides by resin **4**. No significant variation of the sorption was noted for shaking times which ranged from 0.5 to 5.0 hours. Compared with the equilibrium values, more than 95% of the sorption was obtained after shaking for 5 minutes. The resin was filtered and purged by air with an aspirator to remove the sample solution completely. The effect of purging time is shown in Fig. 2(b). Constant sorptions for each metal chloride were noted when the purging times ranged from 10 to 60 minutes. The resin was dried in the oven at 80°C. Of the dried resin, a portion was shaken with pure water to strip the alkali-metal chlorides from the resin into an aqueous solution for analysis by ion chromatography. In Fig. 2(c) the effect of stripping time upon the sorption results is shown. No significant variation was recorded for stripping times which ranged from 1.0 to 5.0 hours. Even with a 5-minute stripping period, most of the metal salts were removed from the resin. These results demonstrate that both alkali-metal chloride

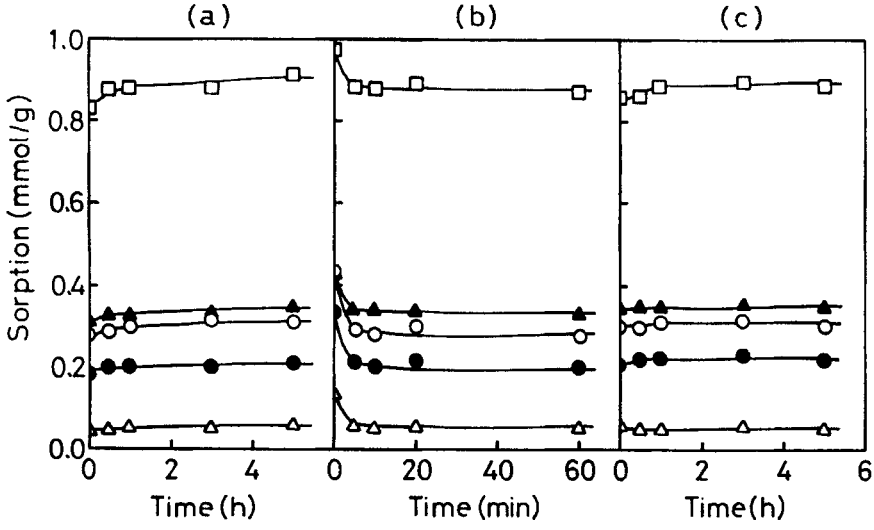


FIG. 2 Influence of experimental variables upon the competitive sorption of alkali-metal chlorides from aqueous solution by dibenzocrown ether resin **4**: (a) shaking time, (b) purging time, (c) stripping time. Li^+ (△), Na^+ (○), K^+ (□), Rb^+ (▲), Cs^+ (●).

sorption and stripping are rapid. Experimental conditions selected for the standard procedure included shaking, purging, and stripping times of 3.0 hours, 20 minutes, and 1.0 hour, respectively.

For resin **4**, data for competitive sorption from a solution of the five alkali-metal chlorides, each at the indicated concentration in 80% methanol–20% water, are compared with those for single species sorptions in Figs. 3(a) and 3(b), respectively. (In Fig. 3b, results from single species sorptions for each of the five alkali-metal chlorides from 80% methanol–20% water are combined in a single plot.) In both the competitive and single species extraction systems, the very low sorption of LiCl is attributable to the high hydration energy of the lithium cation. Clearly the observed sorption selectivity for KCl in the competitive system (Fig. 3a) is much higher than would have been predicted from the single species sorption experiments (Fig. 3b).

Crown ether cavity diameters, as estimated from Corey-Pauling-Kortun (CPK) space-filling models, are compared with diameters of the alkali-metal cations in Table 2. Based upon the preferred relationship between the cavity diameter and size of the alkali-metal cations (13), a sorption selectivity for KCl by the dibenzo-18-crown-6 resin **4** would be predicted.

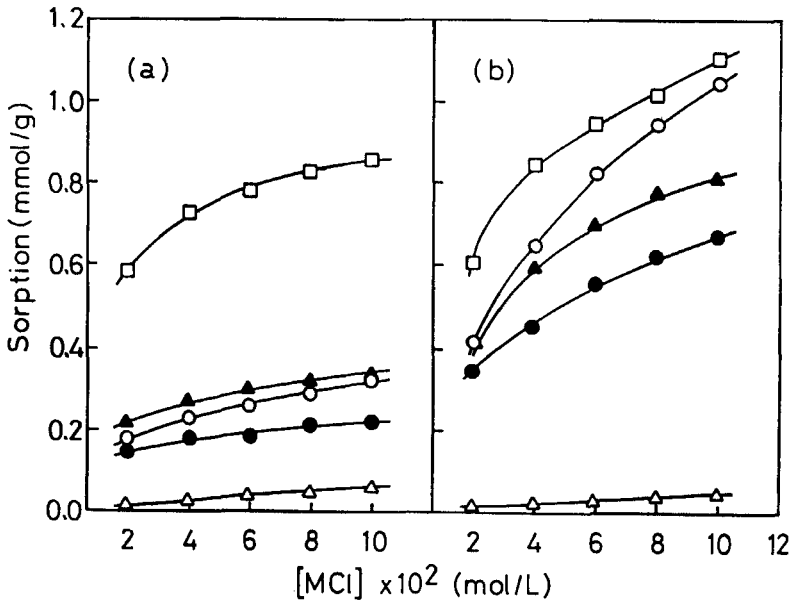


FIG. 3 Effect of alkali-metal chloride concentrations in 80% methanol–20% water upon sorption by dibenzocrown ether resin **4**: (a) competitive sorption, (b) single species sorption. Li^+ (△), Na^+ (○), K^+ (□), Rb^+ (▲), Cs^+ (●).

TABLE 2
Diameters of Crown Ether Cavities[a] and Alkali-Metal Cations[b] in Angstroms

Crown ether	Cavity diameter	Alkali-metal cation	Diameter
14-Crown-4	1.2–1.5	Li^+	1.20
15-Crown-5	1.7–2.2	Na^+	1.90
16-Crown-5	2.0–2.4	K^+	2.66
18-Crown-6	2.6–3.2	Rb^+	2.96
21-Crown-7	3.4–4.3	Cs^+	3.38
24-Crown-8	4.5		

[a] Estimated from CPK models, Reference 12.
[b] Reference 11.

Effect of Ring Size Variation within Dibenzocrown Ether Resins upon Competitive Sorption of Alkali-Metal Chlorides

Data for the competitive sorption of alkali-metal chlorides (0.100 M in each) by resins **1–6** as a function of the methanol content in the aqueous methanol sample solution are shown in Fig. 4. Except for LiCl, sorption of each alkali-metal chloride increased as the methanol content in the sample solution was enhanced. Such sorption increases are reasonable in view of the two-to-three log unit increase in stability constants for metal ion-crown ether interactions when the solvent is changed from water to methanol (13). Since the resins should be more compatible with methanol than with water, enhanced alkali-metal chloride sorption may also result from increased accessibility into the polymer matrix as the water content decreases.

Resin **1**, which has a small 14-crown-4 ring, exhibits very poor sorption for all five alkali-metal chlorides. This demonstrates that interaction between the polyether ring and the metal cation plays an important role in ion-pair sorption. Observed sorption selectivities for resins **2–6** are: $K^+ > Rb^+ > Na^+$, $Cs^+ > Li^+$ for **2**; $Na^+ > K^+$, Rb^+, $Cs^+ > Li^+$ for **3**; $K^+ \gg Na^+$, Rb^+, $Cs^+ > Li^+$ for **4**; $Rb^+ > K^+ > Cs^+ \gg Na^+$, Li^+ for **5**; and K^+, Rb^+, $Cs^+ > Na^+ > Li^+$ for **6**. Since resin **6** dissolved in the 80% methanol–20% water solution of five alkali-metal chlorides (0.10 M in each), sorption results from a 80% methanol–20% water solution could not obtained with this resin.

Figure 5 compares the influence of ring size variation within dibenzocrown ether resins **1–5** upon the competitive sorption of alkali-metal chlorides from 80% methanol–20% water solutions. KCl sorption is enhanced as the ring size of the crown ether is increased and reaches a

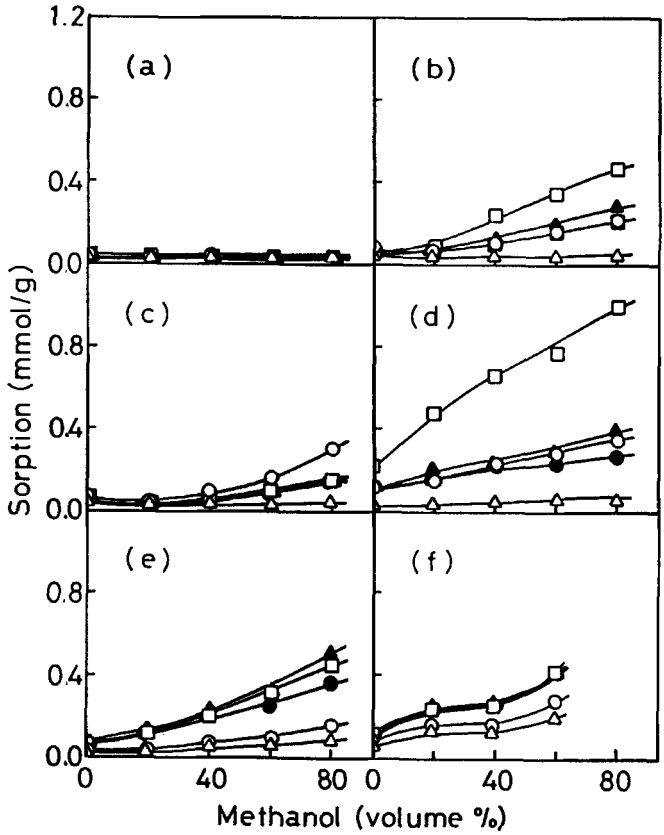


FIG. 4 Effect of methanol content for competitive sorption of alkali-metal chlorides from aqueous methanol solutions by dibenzocrown ether resins: (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **5**, (f) **6**. Li^+ (△), Na^+ (○), K^+ (□), Rb^+ (▲), Cs^+ (●).

maximum for the 18-crown-6 ring. Further expansion of the ring size causes a diminution in the KCl sorption. Although the sorption efficiency was much lower, a similar sorption profile is noted for NaCl. The sorption profiles for LiCl, RbCl, and CsCl show continuous enhancement as the crown ether ring size is increased. As can be seen from Fig. 5, the sorption behavior for the 16-crown-5 resin **3**, which has a three-carbon bridge in the crown ether unit, does not fit the pattern established by resins **1**, **2**, **4**, and **5**, which have only two-carbon bridges in their crown ether rings.

Total alkali-metal chloride sorptions from 80% methanol–20% water and loadings for resins **1–6** are presented in Table 3. The loading is defined as the total alkali-metal chloride sorption by the resin divided by the ion-

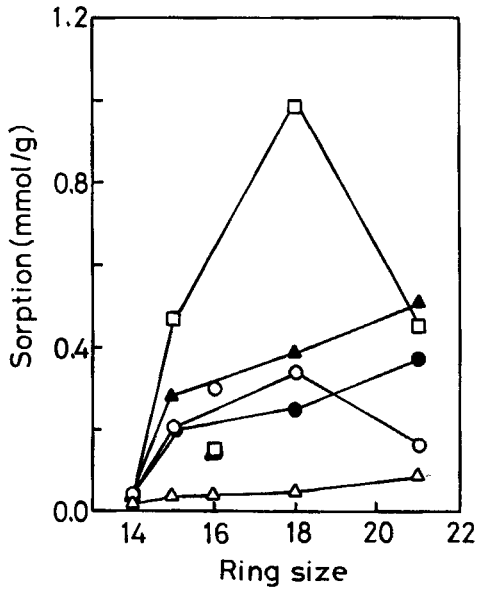


FIG. 5 Influence of ring-size variation within dibenzocrown ether resins **1–5** upon competitive alkali-metal cation sorption from 80% methanol–20% water. Li^+ (△), Na^+ (○), K^+ (□), Rb^+ (▲), Cs^+ (●).

TABLE 3
Ion-Exchange Capacities and Total Sorptions of Alkali-Metal Cations by Dibenzocrown Ether Resins

Resin	Ring size	Ion-exchange capacity (mmol/g)[a]	Total sorption (mmol/g)[b]	Loading (%)
1	14-Crown-4	3.20	0.19	6
2	15-Crown-5	3.05	1.20	39
3	16-Crown-5	2.92	0.76	26
4	18-Crown-6	2.69	1.80	67
5	21-Crown-7	2.40	1.58	66
6	24-Crown-8	2.17	(1.79)[c]	82

[a] Calculated from elemental analysis data.
[b] Data from 80% methanol–20% water.
[c] Data from 60% methanol–40% water.

exchange capacity as calculated from elemental analysis data. An increase in the number of donor oxygens generally enhances the dipole interaction with metal cations as well as accessibility by the sample solution into the resin matrix. Thus loadings are enhanced as the crown ether ring size is increased, with the exception of resin **3**. Apparently the three-carbon bridge in the crown ether units of resin **3** produces a lower sorption efficiency. For resin **6**, the loading is 82% even though the data were obtained in a 60% methanol–40% water system. This is attributed to the large number of ethyleneoxy linkages in the crown ether units of this resin which enhance accessibility by the sample solution.

Competitive Ion-Pair Sorption of NaCl, KCl, $MgCl_2$, and $CaCl_2$ by Resin 4

To evaluate the competitive ion-pair sorption of alkali-metal and alkaline-earth chlorides by resin **4**, a mixture of NaCl, KCl, $MgCl_2$ and $CaCl_2$, which includes the most frequently encountered alkali-metal and alkaline-earth cations, was investigated.

Results for competitive ion-pair sorption for resin **4** as a function of the methanol content of the sample solution is shown in Fig. 6. The sorptions of both NaCl and KCl increase as the methanol content of sample solution is enhanced. This sorption profile is similar to that observed for NaCl and KCl in competitive alkali-metal chloride sorption (Fig. 3d). The difference in sorption efficiencies for the alkali-metal and alkaline-earth chlorides is marked. The divalent metal cations are heavily hydrated and must be accompanied by two hydrated anions for ion-pair sorption. Thus, as with LiCl, the alkaline-earth chlorides are very poorly sorbed by this crown ether resin. It is interesting to note that the sorption selectivity found for crown ether resin **4** is quite different from that observed with conventional ion-exchange resins. Cation-exchange resins prefer sorption of more highly charged metal cations from solution due to the stronger electrostatic interaction between the ion-exchange groups and metal ions. Therefore, cation-exchange resins usually shown selectivity for sorption of alkaline-earth cations over alkali-metal cations (14). On the other hand, the crown ether resin **4** shows sorption selectivity for alkali-metal chlorides over alkaline-earth chlorides. Thus fundamentally different separation processes by crown ether resins can be expected.

Selective Column Sorption and Separation of Metal Chlorides by Resin 4

Column sorption behavior of metal chlorides was investigated with resin **4**. An 80% methanol–20% water solution (5.0 mL) containing the five

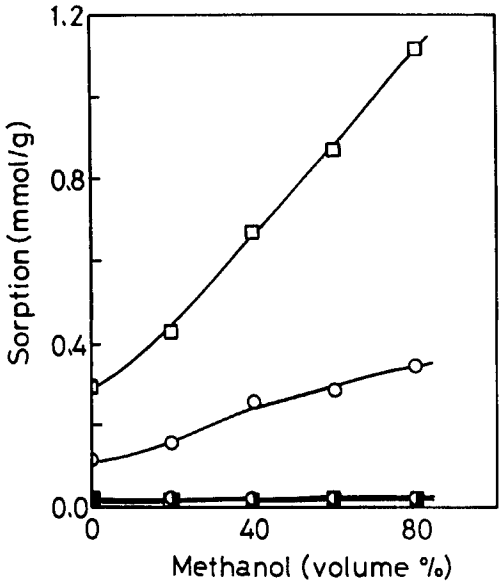


FIG. 6 Effect of methanol content for competitive sorption of NaCl, KCl, $MgCl_2$, and $CaCl_2$ from aqueous methanol solutions by dibenzocrown ether resin **4**. Na^+ (○), K^+ (□), Mg^{2+} (◑), Ca^{2+} (◨).

alkali-metal chlorides or an alkali-metal and alkaline-earth chloride mixture (NaCl, KCl, $MgCl_2$, $CaCl_2$) was passed through a column of resin **4** and the column was purged with a nitrogen gas for 20 minutes to remove the sample solution completely. The sorbed metal chlorides were then stripped from the resin by elution with pure water.

Figure 7(a) shows the stripping behavior of the five alkali-metal chlorides after column sorption by resin **4** as a function of the elution volume of water. The elution order is LiCl > CsCl > RbCl, NaCl > KCl, with significant retardation of elution for KCl. This elution ordering is the reverse of the sorption selectivities observed in the batch analysis experiments (Fig. 3d). The maximum concentration for KCl in the eluent was observed in the second fraction and reached 0.20 mol/L, which is approximately twice as high as those for NaCl and RbCl.

In Figure 7(b) the elution of mixed alkali-metal and alkaline-earth chlorides which had been sorbed by a column of resin **4** is shown. Only KCl and NaCl were eluted in significant amounts. Although the recovery of these metal chlorides from the sample solution was low (recoveries were 26% for KCl and 8% for NaCl), it is evident that the monovalent metal

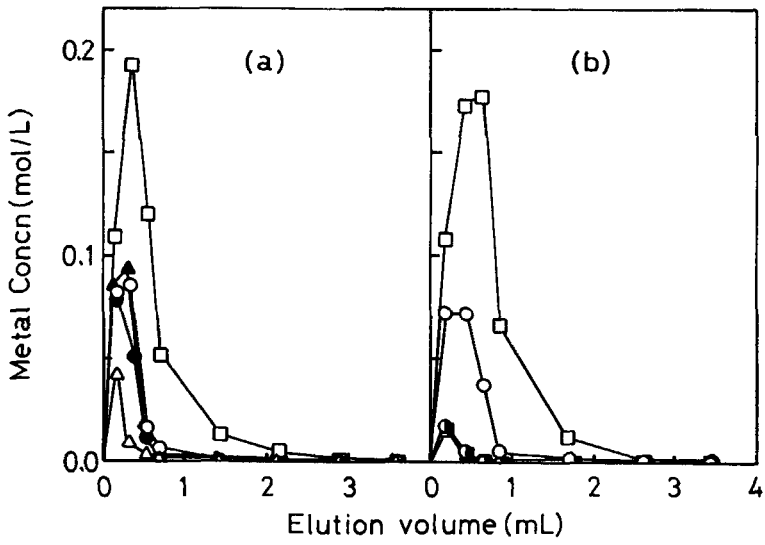


FIG. 7 Elution of sorbed metal chlorides from a column of dibenzocrown ether resin 4 with water; (a) competitive system of five alkali-metal chlorides; (b) competitive system of NaCl, KCl, $MgCl_2$, and $CaCl_2$. Li^+ (△), Na^+ (○), K^+ (□), Rb^+ (▲), Cs^+ (●), Mg^{2+} (◑), Ca^{2+} (◨).

chlorides were effectively separated from the mixture of monovalent and divalent metal ion chlorides. To enhance the efficiency of this system, the binding ability of the crown ether units in the resin must be improved. The introduction of neutral side arm groups, such as amide functions, might improve the efficiency and selectivity of ion-pair sorption.

ACKNOWLEDGMENTS

This research was supported by the Division of Chemical Sciences of the Office of Basic Energy Sciences of the U.S. Department of Energy (Grant DE-FG05-88ER13832) and the Advanced Technology Program of the Texas Higher Education Coordinating Board.

REFERENCES

1. E. Blasius, W. Adrian, K.-P. Janzen, and C. J. Klautke, *J. Chromatogr.*, *96*, 89 (1974).
2. E. Blasius and P.-G. Mauer, *Ibid.*, *125*, 511 (1976).
3. E. Blasius, K.-P. Janzen, W. Adrian, G. Klautke, R. Lorscheider, P.-G. Maurer, V. B. Nguyen, T. Nguyen-Tien, G. Scholten, and J. Stockemer, *Z. Anal. Chem.*, *284*, 337 (1977).

4. E. Blasius, K.-P. Janzen, W. Adrian, W. Klein, H. Klotz, H. Luxenburger, E. Mernke, V. B. Nguyen, T. Nguyen-Tien, R. Raush, J. Stockemer, and A. Toussaint, *Talanta*, *27*, 127 (1980).
5. T. Hayashita, M.-J. Goo, J. C. Lee, J. S. Kim, J. Krzykawski, and R. A. Bartsch, *Anal. Chem.*, *62*, 2283 (1990).
6. T. Hayashita and R. A. Bartsch, *Ibid.*, *63*, 1847 (1991).
7. T. Hayashita, J. H. Lee, S. Chen, and R. A. Bartsch, *Ibid.*, *63*, 1844 (1991).
8. T. Hayashita, M.-J. Goo, J. S. Kim, and R. A. Bartsch, *Talanta*, *38*, 1453 (1991).
9. T. Hayashita, J. H. Lee, J. C. Lee, J. Krzykawski, and R. A. Bartsch, *Ibid.*, *39*, 857 (1992).
10. T. Hayashita, J. H. Lee, M. G. Hankins, J. C. Lee, J. S. Kim, J. M. Knobeloch, and R. A. Bartsch, *Anal. Chem.*, *64*, 815 (1992).
11. C. J. Pedersen, *J. Am. Chem. Soc.*, *89*, 7017 (1967).
12. W. Walkowiak, W. A. Charewicz, S. I. Kang, I.-W. Yang, M. J. Pugia, and R. A. Bartsch, *Anal. Chem.*, *62*, 2018 (1990).
13. R. M. Izatt, J. M. Bradshaw, S. A. Nielsen, J. D. Lamb, J. J. Christensen, and D. Sen, *Chem. Rev.*, *85*, 271 (1985).
14. K. Porfner, *Ion Exchangers*, Ann Arbor Science Publishers, Ann Arbor, Michigan, 1972, pp. 44–48.

Received by editor October 1, 1992
Revised May 10, 1993