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# Selective Sorption and Column Concentration of Alkali-Metal Cations by Carboxylic Acid Resins with Dibenzo-14-crown-4 Subunits and Their Acyclic Polyether Analogues

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Alkali-metal cation sorption from aqueous and aqueous methanolic solutions and column concentration of alkali-metal cations from dilute aqueous solutions by carboxylic acid resins containing dibenzo-14-crown-4 units and their acyclic polyether analogues have been investigated. The crown ether carboxylic acid resins exhibit enhanced sorption selectivity over the acyclic polyether resins. Good sorption selectivity for LI<sup>+</sup> and Na<sup>+</sup> was obtained with a cyclic polyether resin in which the carboxylic acid group is positioned over the crown ether ring. For column concentration of alkali-metal cations from dilute aqueous solutions, gradient elution of the sorbed metal lons from the resin with the carboxylic acid group positioned over the crown ether cavity gave selective column concentration of LI<sup>+</sup> and Na<sup>+</sup>.

# INTRODUCTION

Synthetic macrocyclic multidentate ligands, such as crown ethers, have been utilized extensively for the separation of alkali-metal and alkaline-earth-metal cations, as well as some transition-metal ions from their solutions.<sup>1-3</sup> Of particular importance is the size recognition ability of the cyclic ligands for different metal ions. Efficient complexation of a metal ion by a crown ether is facilitated by a good fit of the cation within the polyether cavity.<sup>2</sup>

Polymerization of such macrocyclic ligands or their immobilization on support materials is important to the development of continuous separation processes and alleviation of the toxicity of some macrocyclic complexing agents.<sup>4,5</sup> In recent studies, the polyether carboxylic acid resins 1-3 (Figure 1), which contain both ion-exchange and cyclic or acyclic polyether binding sites for metal ions, were synthesized<sup>6</sup> and their alkali-metal and alkaline-earth-metal cation sorption behaviors evaluated.<sup>6-8</sup> It was found that both the cyclic or acyclic nature of the polyether unit and the positioning of the pendent carboxylic acid group with respect to the polyether unit played an important role in metal ion recognition. Good sorption selectivity for Na<sup>+</sup> was observed only for dibenzo-16-crown-5 carboxylic acid resin 2 in which the carboxylic acid function is positioned over the polyether cavity. Selective column concentration of Na<sup>+</sup> from a dilute aqueous solution of alkali-metal cations was achieved with resin 2.9

To probe the effect of crown ether ring size and further examine the influence of carboxylic acid group positioning relative to the polyether subunit, new acyclic polyether carboxylic acid resin 4 and crown ether carboxylic acid resins 5 and 6 have now been prepared and their alkali-metal cation sorption and column concentration behaviors investigated. From comparison of the results for previously-examined resins 1 and 2, which have dibenzo-16-crown-5 rings, with those for new resins 5 and 6, which have dibenzo-14-crown-4 rings, the effect of crown ether ring size can be assessed. Similarly, by comparison of the results for resins 3 with 4 and 5 with 6, the influence of positioning of the carboxylic acid group relative to the polyether unit can be examined more completely.

## EXPERIMENTAL SECTION

Apparatus. The apparatus was the same as that reported previously<sup>6-9</sup> with the addition of a Bio-Rad Model 2110 fraction collector for the column concentration study. To prevent metal contamination, all glassware was soaked in 5% HNO<sub>3</sub> solution for 24 h and rinsed with distilled, deionized water before use.

**Reagents.** Sources of inorganic reagents were the same as those reported previously.<sup>6-9</sup> Purified water was prepared by passing distilled water through three Barnstead D8922 combination cartridges in series. *sym*-Hydroxydibenzo-14-crown-4 and *sym*-dibenzo-14-crown-4-oxyacetic acid were prepared by the reported methods.<sup>10-12</sup> *sym*-Ketodibenzo-14-crown-4 (8) was produced by heating *sym-gem*-dihydroxydibenzo-14-crown-4 in a vacuum oven.<sup>13</sup> 1,3-Bis(o-methoxyhenoxy)-2-propanol and resin 3 were synthesized by the reported procedures.<sup>6</sup>

Preparation of sym-(Hydroxy)(propyl)dibenzo-14-crown-4 (9). To 1.16 g (48 mmol) of magnesium turnings in 40 mL of THF was added 2.96 g (24 mmol) of 1-bromopropane, and the mixture was refluxed until most of the magnesium had been consumed. To the cooled mixture was added 3.78 g (12 mmol) of 8 in 82 mL of THF over a 15-min period, and the mixture was refluxed for 2 h. After cooling, 60 mL of 5% aqueous  $NH_4Cl$  was added and the mixture was stirred for 1.5 h. The THF was evaporated in vacuo, and the residue was extracted with  $Et_2O$  (4 × 30 mL). The combined Et<sub>2</sub>O layers were dried over MgSO<sub>4</sub> and evaporated to give a white solid which was purified by chromatography on alumina with  $Et_2O$  then  $EtOAc/Et_2O$  (1:9) as eluents to afford 1.98 g (46%) of 9 as a white solid with mp 121–122 °C: IR (deposit from CDCl<sub>3</sub> solution on a NaCl plate) 3548 (OH), 1254, 1119 (CO) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.97 (t, 3), 1.40–1.75 (m, 4), 2.10–2.45 (m, 2), 2.73 (br s, 1), 3.95-4.40 (m, 8), 6.80-7.00 (m, 8). Anal. Calcd for C<sub>21</sub>H<sub>26</sub>O<sub>5</sub>: C, 70.37; H, 7.31. Found: C, 70.57; H, 7.44.

Preparation of sym-(Propyl)dibenzo-14-crown-4-oxyacetic Acid (10). To 0.45 g (60% dispersion in mineral oil, 110 mmol) of NaH under nitrogen was added 1.00 g (2.8 mmol) of 9 in 50 mL of THF. After 0.5 h, a solution of 0.91 g (6.5 mmol) of bromoacetic acid in 10 mL of THF was added dropwise. After being stirred for 2 h at room temperature, the mixture was refluxed overnight. The excess NaH was destroyed by careful addition of ice, and the THF was evaporated in vacuo. The residue was acidified to pH 1 with concentrated HCl, and 250 mL of CH<sub>2</sub>Cl<sub>2</sub> was added. After shaking, the  $CH_2Cl_2$  layer was separated and the aqueous layer was extracted with  $CH_2Cl_2$  (3 × 20 mL). The combined CH<sub>2</sub>Cl<sub>2</sub> layers were washed with 5% HCl, dried over  $MgSO_4$ , and evaporated in vacuo to give a gold oil which was passed through a 1-in. bed of alumina using MeOH/EtOAc (1:10) as eluent. The solvents were evaporated from the eluate in vacuo, the pH of the residue was adjusted to 1 with concentrated HCl, and  $CHCl_3$  was added. After shaking, the  $CHCl_3$  layer was separated, washed with water, dried over MgSO<sub>4</sub>, and evaporated in vacuo to give 0.97 g (83%) of 10 as a thick, yellowish oil: IR (deposit from a CDCl<sub>3</sub> solution on a NaCl plate) 3375 (COOH), 1740 (C=O), 1255, 1119 (CO) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.00 (t,

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Figure 1. Structures of the polyether carboxylic acid resins.

3), 1.35–1.65 (m, 2), 1.65–1.90 (m, 2), 2.10–2.60 (m, 2), 4.00–4.40 (m, 8), 4.45 (s, 2), 6.80–7.00 (m, 8), 8.10 (br s, 1). Anal. Calcd for  $C_{23}H_{28}O_7$ -0.3CHCl<sub>3</sub>: C, 61.87; H, 6.31. Found: C, 61.72; H, 6.32.

**Preparation of 1,3-Bis**(*o*-methoxyphenoxy)-2-propanone (11). To 100 mL of  $CH_2Cl_2$  was added 7.43 g (34 mmol) of pyridinium chlorochromate,<sup>14</sup> 1.88 g (23 mmol) of anhydrous NaOAc, 40 g of MgSO<sub>4</sub>, and 7.00 g (23 mmol) of 1,3-bis(*o*-methoxyphenoxy)-2-propanol, and the mixture was stirred for 2 days at room temperature under nitrogen. The mixture was filtered through a bed of Florisil which was subsequently washed with three 30-mL portions of  $CH_2Cl_2$ . The filtrate and washings were evaporated in vacuo to afford a yellow oil which was purified by chromatography on silica gel with hexane/EtOAc (8:1) as eluent to give 3.98 g (57%) of a white solid with mp 69–71 °C: IR (deposit from  $CH_2Cl_2$  solution on a NaCl plate) 1742 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.87 (s, 6), 4.96 (s, 4), 6.84–7.01 (m, 8). Anal. Calcd for  $C_{17}H_{18}O_5$ : C, 67.54; H, 6.00. Found: C, 67.67; H, 6.05.

Preparation of 2-[(o-Methoxyphenoxy)methyl]-1-(omethoxyphenoxy)-2-pentanol (12). To 0.46 g (20 mmol) of magnesium turnings in 100 mL of THF under nitrogen was added 2.44 (20 mmol) of 1-bromopropane, and the mixture was refluxed until the magnesium turnings disappeared. The solution was cooled to 0 °C and 3.00 g (10 mmol) of 11 in 15 mL of THF was added. The reaction mixture was refluxed for 5 h and cooled to 0 °C. After slow addition of 20 mL of 5% aqueous  $NH_4Cl$ , the THF was evaporated in vacuo. To the residue were added EtOAc and water (100 mL of each). After shaking, the EtOAc layer was separated and washed with saturated aqueous NaHCO<sub>3</sub> (30 mL) and then with brine (30 mL). After drying over  $MgSO_4$ , the solvent was evaporated in vacuo to give 3.18 g (93%) of a colorless oil: IR (deposit from CH<sub>2</sub>Cl<sub>2</sub> solution on a NaCl plate) 3474 (OH) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.95 (t, 3), 1.47–1.60 (m, 2), 3.30 (s, 1), 3.80 (s, 6), 3.98-4.17 (AB q, 4), 6.82-6.98 (m, 8). Anal. Calcd for  $C_{20}H_{26}O_5 \cdot 0.25H_2O$ : C, 68.49; H, 7.55. Found: C, 68.72; H, 7.83.

Preparation of 4,4-Bis[(o-methoxyphenoxy)methyl]-3oxaheptanoic Acid (13). After removal of the mineral oil from 3.61 g (60% dispension in mineral oil, 27 mmol) of KH with pentane under nitrogen, 3.20 g (9.2 mmol) of 12 in 50 mL of THF was added. The mixture was stirred for 2 h at room temperature, and 1.93 g (13.8 mmol) of bromoacetic acid in 10 mL of THF was added during 1 h. The mixture was stirred for 3 h and ice-water was carefully added to consume the excess KH. The THF was evaporated in vacuo. The residue was extracted with EtOAc (3  $\times$  30 mL) and then with water (50 mL). The water layer was acidified to pH = 1 with 6 N HCl and extracted with  $CH_2Cl_2$  (3)  $\times$  50 mL). The CH<sub>2</sub>Cl<sub>2</sub> layer was dried over MgSO<sub>4</sub> and evaporated in vacuo to afford 3.55 g (95%) of 13 as a pale yellow oil: IR (deposit from CH<sub>2</sub>Cl<sub>2</sub> solution on a NaCl plate) 2955 (COOH), 1737 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.98 (t, 3), 1.39–1.51 (m, 2), 1.80-1.88 (m, 2), 3.79 (s, 6), 4.09-4.23 (AB q, 4), 4.40 (s, 2), 6.82–7.01 (m, 8). Anal. Calcd for  $C_{22}H_{28}O_7\!\!:$  C, 65.33; H, 6.98. Found: C, 65.04; H, 7.00.



(a) C3H7MgBr, THF. (b) BrCH2CO2H, KH, THF

Figure 2. Synthetic routes to compounds 10 and 13.

**Preparation of Polyether Carboxylic Acid Resins 4–6.** The polyether carboxylic acid resins 4–6 were synthesized by condensation polymerization of the corresponding monomers 13, sym-dibenzo-14-crown-4-oxyacetic acid, and 10, respectively, with formaldehyde in formic acid as described in detail previously.<sup>6</sup> The resins were ground and used in powder form (finer than 100 mesh).

Resin 4, 25% yield: IR (KBr) 3422 (COOH), 1752 (C=O), 1280, 1094 (CO) cm<sup>-1</sup>. Anal. Calcd for 7: C, 66.49; H, 6.74. Found: C, 66.40; H, 6.51.

Resin 5, 60% yield: IR (KBr) 3448 (COOH), 1735 (C=O), 1278, 1094 (CO) cm<sup>-1</sup>. Anal. Calcd for 7.0.5H<sub>2</sub>O: C, 65.20; H, 5.73. Found: C, 65.02; H, 5.52.

Resin 6, 59% yield: IR (KBr) 3448 (COOH), 1735 (C=O), 1278, 1103 (CO) cm<sup>-1</sup>. Anal. Calcd for 7: C, 67.43; H, 6.56. Found: C, 67.80; H, 6.37.

Sorption of Alkali-Metal Cations by Resins 3-6. An aqueous solution of the five alkali-metal chlorides with hydroxides for pH adjustment (5.0 mL, 0.10 M in each) and 0.050 g of the resin were shaken for 3.0 h in a 30-mL, pear-shaped flask with a 14/20 joint and a polypropylene stopper at room temperature (21-23 °C) with a Burrell wrist-action shaker. The aqueous phase was filtered with a sintered glass filter funnel (15 mL, medium porosity), and the equilibrium pH of the aqueous phase was measured. The resin was washed with 100 mL of water and dried. Of the dried resin, a 0.020-g sample was shaken with 5.0 mL of 0.10 M HCl for 1.0 h to strip the alkali-metal cations from the resin into an aqueous solution for analysis by ion chromatography after appropriate dilution.

Column Concentration of Alkali-Metal Cations by Resins 3–6. The column concentration procedure was the same as that reported<sup>9</sup> except that the flow rate was 3.4 mL/min for loading and washing and 0.3 mL/min for stripping. The stripping solutions were collected by 10-drop fractions with a fraction collector and analyzed by ion chromatography after appropriate dilution. After each stripping operation, the volume of the 10-drop fractions (0.25-0.26 mL) was determined with a microsyringe.

#### **RESULTS AND DISCUSSION**

Synthesis of New Dibenzo-Polyether Carboxylic Acid Monomers. By a Grignard reaction, sym-ketodibenzo-14crown-4 (8) was converted into the crown ether tertiary alcohol 9 in 46% yield (Figure 2). Reaction of 9 with KH and the bromoacetic acid gave sym-(propyl)dibenzo-14-crown-4 (10) in 80% yield. Oxidation of 1,3-bis(o-methoxyphenoxy)-2propanol with pyridinium chlorochromate<sup>12</sup> provided the acyclic dibenzopolyether ketone 11 in 57% yield. A Grignard reaction transformed this ketone into tertiary alcohol 12 in 92% yield, and reaction of 12 with KH and then bromoacetic acid gave a 95% yield of acyclic polyether carboxylic acid 13.

Synthesis of New Polyether Carboxylic Acid Resins. The polyether carboxylic acid resins 4-6 were prepared by condensation polymerization of the corresponding dibenzopolyether monomers with formaldehyde in formic acid. As in an earlier study,<sup>6</sup> it was observed that the yield was higher for formation of a cyclic polyether carboxylic acid resin than the corresponding acyclic polyether carboxylic acid resin. New resins 4-6 were characterized by IR spectroscopy and by elemental analysis. The structural representations 1-6 imply polymers with no cross-linking. This is most certainly an



**Figure 3.** Sorption of alkali-metal cations by the polyether carboxylic acid resins vs the equilibrium pH of the aqueous phase for (a) 3, (b) 4, (c) 5, and (d) 6: ( $\Delta$ ) Li<sup>+</sup>, (O) Na<sup>+</sup>, ( $\Box$ ) K<sup>+</sup>, ( $\Delta$ ) Rb<sup>+</sup>, ( $\oplus$ ) Cs<sup>+</sup>.

oversimplification since some level of cross-linking is anticipated.<sup>15</sup> A possible structure for the partially cross-linked resins is given by 7 (Figure 1) in which A is the polyether carboxylic acid unit. In agreement with the results obtained previously for resins 1-3,<sup>6</sup> the elemental analysis data for the new polyether carboxylic acid resins 4-6 are consistent with this formulation.

Alkali-Metal Cation Sorption by Polyether Carboxylic Acid Resins 3-6. To provide greater relevance to actual metal separation systems, competitive, rather than single species, alkali-metal cation sorption by resins 3-6 was investigated. An aqueous solution (5.0 mL) of the five alkali-metal cations (0.10 M in each) as chlorides and hydroxides was shaken with the resin (0.050 g) for 3 h (even though sorption is probably complete in a matter of minutes<sup>6</sup>). The resin was filtered, washed with water, and dried. Of the dried resin, a weighed portion (0.020 g) was shaken with 5.0 mL of 0.10 M HCl to strip the alkali-metal cations from the resin into an aqueous solution for analysis by ion chromatography. From the ion chromatographic analysis data, the amount of sorbed alkali-metal cations per unit amount of the acid form of the dried resin (millimoles per gram) was calculated. The reproducibility of this alkali-metal cation sorption and stripping procedure for different batches of resin has been demonstrated.<sup>6</sup> For a given resin, the alkali-metal cation sorption at a specified pH was found to be reproducible within 5% of the stated value.

Data for competitive alkali-metal cation sorption as a function of the equilibrium pH of the aqueous phase of acyclic polyether carboxylic acid resin 4 and the dibenzo-14-crown-4 carboxylic acid resins 5 and 6 are presented in Figure 3b-d, respectively. For comparison, data reported earlier<sup>6</sup> for acyclic polyether carboxylic acid resin 3 are given in Figure 3a. As would be anticipated for weak acid resins,<sup>16</sup> alkali-metal cation sorption by resins 3-6 is negligible when the aqueous solution pH is  $\leq 4$  but increases markedly as the pH becomes neutral and then basic.

A commercially available carboxylic acid resin CG-50, a polymethacrylic acid resin, exhibits Li<sup>+</sup> selectivity under basic conditions.<sup>6</sup> This is attributed to a strong ion-association interaction of the carboxylate anion with Li<sup>+</sup>.<sup>17</sup> Thus the Li<sup>+</sup> sorption selectivities found with acyclic polyether carboxylic resins 3 and 4 (Figure 3a,b, respectively) suggest primary interaction of the alkali-metal cations with the ion-exchange sites.

Table I. Sorption of Alkali-Metal Cations from an Aqueous Solution at pH = 12.5 by Polyether Carboxylic Acids 3-6 and Percent Loading

	sorption, mmol/g					
resin	Li <sup>+</sup>	Na <sup>+</sup>	K+	Rb <sup>+</sup>	Cs <sup>+</sup>	% loading
3	0.50	0.47	0.44	0.40	0.41	83
4	0.42	0.41	0.34	0.30	0.31	73
5	0.37	0.57	0.38	0.27	0.30	74
6	0.37	0.44	0.15	0.12	0.16	73

From an examination of the Corey-Pauling-Kortum (CPK) space-filling models, the cavity diameter of a dibenzo-14crown-4 ring is estimated to be 1.2-1.5 Å. The ionic diameters of the alkali-metal cations are as follows: Li<sup>+</sup>, 1.20 Å; Na<sup>+</sup>, 1.90 Å; K<sup>+</sup>, 2.66 Å; Rb<sup>+</sup>, 2.96, Å; Cs<sup>+</sup>, 3.38 Å.<sup>18</sup> On the basis of the relationship between the metal ion and dibenzo-14crown-4 cavity diameters, Li<sup>+</sup> selectivity would be anticipated for crown ether carboxylic acid resins 5 and 6. However resin 5 exhibits Na<sup>+</sup> selectivity and resin 6 shows nearly equal sorption selectivity for Li<sup>+</sup> and Na<sup>+</sup> over the other alkali-metal cations as a group (Figure 3c,d, respectively). The changes in sorption selectivity on going from the acyclic polyether carboxylic acid resins 3 and 4 to the crown ether carboxylic acid resins 5 and 6 are consistent with metal ion-cyclic polyether unit interactions in the latter.

Since Na<sup>+</sup> is too large to fit within the crown ether cavity, the Na<sup>+</sup> selectivity shown by resin 5 suggests the formation of a complex in which the metal ion perches on the crown ether oxygens while associating with one or more of the oxygen atoms in the sidearm. It should be noted that Na<sup>+</sup> selectivity has also been observed in competitive solvent extraction of alkali-metal cations from water into chloroform by 2-[symdibenzo-14-crown-4-oxy]decanoic acid.<sup>18</sup> On the basis of results of earlier studies conducted with dibenzo-16-crown-5 carboxylic acid resins,<sup>6</sup> attachment of a propyl group to the same polyether ring carbon that bears the oxyacetic acid group is expected to help position the carboxylic acid group over the crown ether cavity.<sup>19</sup> Thus the enhancement of Li<sup>+</sup> sorption relative to the other alkali-metal cations in going from crown ether carboxylic acid resin 5 to 6 may be attributed to preorganization of the binding site in 6 which increases recognition of that metal ion which should be best accommodated within the crown ether cavity.

The alkali-metal cation sorptions and loadings for polyether carboxylic acids 3-6 when the equilibrium pH = 12.5 are presented in Table I. The loading is defined as the total alkali-metal cation sorption, as calculated from the total alkali-metal cation concentration in the stripping solution, divided by the ion-exchange capacity, as calculated from the elemental analysis data. The calculated ion-exchange capacities for resins 3-6 are 2.66, 2.39, 2.57, and 2.32 mmol/g, respectively. The loadings vary from 83% for resin 3 to 53% for resin 6. The diminished loading for resin 6 could result from an increase in the hydrophobicity of the resin or from steric hindrance to metal ion sorption by a more rigid structure. To distinguish between these two possibilites, the effect of medium polarity upon the alkali-metal cation sorption<sup>20</sup> was investigated.

Influence of Medium Polarity upon Alkali-Metal Cation Sorption by Polyether Carboxylic Acid Resins 3-6. The polarity of the medium from which the alkali-metal cations are sorbed might influence the microenvironment of the resin and thereby affect the selectivity and/or efficiency of metal ion sorption. To probe the influence of medium polarity upon metal ion sorption by polyether resins 3-6, each resin was shaken with aqueous methanolic solutions (10, 20, 40, 60, and 80 volume percent of methanol) which were 0.10 M in each of the five alkali-metal cations as the chlorides and



**Figure 4.** Sorption of alkali-metal cations by the polyether carboxylic acid resins vs methanol percentage in the aqueous methanol solvent at pH 12.5–12.9 for (a) 3, (b) 4, (c) 5, and (d) 6: ( $\Delta$ ) Li<sup>+</sup>, (O) Na<sup>+</sup>, ( $\Box$ ) K<sup>+</sup>, ( $\Delta$ ) Rb<sup>+</sup>, ( $\odot$ ) Cs<sup>+</sup>.

Table II. Sorption of Alkali-Metal Cations from 80% Methanol-20% Water at pH = 12.9 by Polyether Carboxylic Acids 3-6 and Percent Loading

resin	Li <sup>+</sup>	Na <sup>+</sup>	K+	Rb+	Cs <sup>+</sup>	% loading
3	0.44	0.58	0.49	0.40	0.36	86
4	0.38	0.53	0.37	0.30	0.30	79
5	0.25	0.73	0.45	0.26	0.23	75
6	0.26	0.74	0.16	0.11	0.12	60

hydroxides, for which the equilibrium pH values were in the range 12.5-12.9. Under such alkaline conditions, maximum alkali-metal cation sorption is anticipated (Figure 3). The resins were filtered, washed, dried, and stripped as before.

Data for the competitive alkali-metal cation sorptions by resins 4-6 as a function of the methanol content of the medium are presented in Figure 4b-d, respectively. For comparison, data reported earlier for acyclic carboxylic acid resin  $3^{20}$  are included as Figure 4a. For all four resins, the influence of the methanol content of the medium is similar. Thus with increasing methanol content, the Na<sup>+</sup> sorption increases, the Li<sup>+</sup> sorption decreases, while the sorptions of K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup> remain nearly the same.

It has been proposed that the strong ion associative interaction of Li<sup>+</sup> with carboxylate anions in ion-exchange resins takes place through the dipole of a water molecule.<sup>17</sup> Also relevant is the X-ray crystal structure of the lithium carboxylate salt of the monomer of resin 5 which has a bridging water molecule between the crown ether-bound Li<sup>+</sup> and the pendent carboxylate anion.<sup>21</sup> Thus dimunition of such water-mediated sorption of Li<sup>+</sup> by polyether carboxylic acid resins 3-6 as the methanol content of the medium is enhanced may be rationalized. Such decreases in Li<sup>+</sup> sorption are coupled with enhanced adsorption of the best sorbed cation Na<sup>+</sup>. It is interesting to note the similarities in Li<sup>+</sup> and Na<sup>+</sup> sorption profiles for resins 4 and 6 versus 3 and 5 which suggest that the propyl group also helps to preorganize the binding site in acyclic polyether resin 4, albeit to a lesser degree than in the cyclic polyether resin 6.

In Table II are recorded the alkali-metal cation sorption and loading data for resins 3-6 in 80% methanol-20% water at an equilibrium pH of 12.9. Comparison with the data contained in Table I reveals that the efficiency of alkali-metal



**Figure 5**. Concentration factors (CF) for alkali-metal cations from a sample solution (1.0 L, pH = 10.4,  $6.0 \times 10^{-5}$  M in each alkali-metal cation) vs the elution volume of 0.10 M HCl for columns of resins (a) **3**, (b) **4**, (c) **5**, and (d) **6**: ( $\Delta$ ) Li<sup>+</sup>, (O) Na<sup>+</sup>, ( $\Box$ ) K<sup>+</sup>, ( $\Delta$ ) Rb<sup>+</sup>, ( $\odot$ ) Cs<sup>+</sup>.

cation sorption exhibits only a very modest increase in loading (1-7%) as the polarity of the medium is decreased by a change from water to 80% methanol-20% water. Thus the lower loading for resin 6 than the other three polyether carboxylic acid resins 3-5 appears to arise from steric hindrance to metal ion sorption by a more rigid structure rather than a more hydrophobic nature of the resin.

Selective Column Concentration of Alkali-Metal Cations by Polyether Carboxylic Acid Resins 3–6. Polyether carboxylic acid resins are potential candidates as stationary phases for selective column concentration of alkali-metal cations from dilute aqueous solution.<sup>9</sup> Selective column concentration of Na<sup>+</sup> was achieved with dibenzo-16crown-5 carboxylic acid resin 2 in which the pendent carboxylic acid group is positioned over the crown ether cavity. The column concentration behavior of polyether carboxylic acid resins 3–6 has now been examined.

An aqueous solution (1.00 L, pH = 10.2) of the five alkali-metal cations  $(6.00 \times 10^{-5} \text{ M} \text{ each})$  as the chlorides and hydroxides was eluted through a 0.42-cm-i.d. column of resin (0.10 g) at a flow rate of 3.4 mL/min, and the column was washed with 100 mL of water at the same flow rate. The sorbed alkali-metal cations were then stripped with 0.10 M HCl at a flow rate of 0.3 mL/min, fractions were collected, and the fractions were analyzed by ion chromatography. Profiles for elution of sorbed alkali-metal cations from polyether carboxylic acid resin 3–6 are shown in Figure 5a–d, respectively, in which the concentration factor (CF) is defined as

$$CF = \frac{\text{conc of } M^+ \text{ in the stripping solution}}{\text{initial conc of } M^+ \text{ in the sample solution}}$$
(1)

For acyclic polyether carboxylic acid resins 3 and 4, most of the resin-bound alkali-metal cations were eluted in the first 3.0 mL of stripping solution and the maximum CF values are in the range 300-400. No separation of alkali-metal cations during elution was noted for resin 3 (Figure 5a). However for resin 4, the elution of both Li<sup>+</sup> and Na<sup>+</sup> is slightly retarded compared with that for the other alkali-metal cations (Figure

Table III. Total Alkali-Metal Cation Sorption and Percent **Recovery in Column Concentration by Polyether Carboxylic Acid Resins 3-6** 

sorption, mmol/g (recovery, %)							
resin	Li <sup>+</sup>	Na <sup>+</sup>	K+	Rb <sup>+</sup>	Cs <sup>+</sup>		
3	0.24 (40)	0.22 (37)	0.24 (40)	0.22 (37)	0.23 (39)		
4	0.28 (46)	0.26 (43)	0.21 (35)	0.18 (30)	0.19 (32)		
5	0.25 (42)	0.37 (62)	0.27 (45)	0.18 (30)	0.18 (30)		
6	0.24 (40)	0.26 (43)	0.10 (17)	0.07 (11)	0.08 (14)		

5b). The elution order for crown ether carboxylic acid resin 5 is  $Rb^+$ ,  $Cs^+ > Li^+$ ,  $K^+ > Na^+$  with significant retardation of Na<sup>+</sup> elution and a maximal CF value near 500 (Figure 5c). For crown ether carboxylic acid resin 6 (Figure 5d), the elution order is  $K^+$ ,  $Rb^+$ ,  $Cs^+ > Li^+$ ,  $Na^+$  with significant retardation of Li<sup>+</sup> and Na<sup>+</sup> elution and maximum CF values approaching 600. The elution retardation orderings are in agreement with the sorption selectivities observed in the batch analysis experiments (see Table I). Thus the same structural features of the resin which produce enhanced sorption through stronger complexation also retard elution of the more tightly bound cations.

The total alkali-metal cation sorptions and percent recoveries are presented in Table III. For resin 6, the recoveries of Li<sup>+</sup> and Na<sup>+</sup> were 40 and 43%, respectively, while those for the other alkali-metal cations were in the range 11-17%. Although the sorption levels observed in the column concentration system are lower than those found in the batch sorption system (Table I) due to different pH and sample conditions, the alkali-metal cation sorption selectivities are quite similar. This indicates that the viability of a given column concentration system can be predicted by a batch sorption analysis experiment.

To accentuate the differences between weakly bound and more strongly bound alkali-metal cations, the use of gradient elution was investigated for crown ether carboxylic acid resin 6. The sample solution (1.0 L, pH = 10.4) of five alkali-metal cations ( $6.00 \times 10^{-5}$  M in each) was passed through the column of resin 6 and unbound metal ions were removed by washing with water as before. Elution was performed with 1.06 mL of 0.050 M HCl, then 3.2 mL of water, and then 1.0 M HCl. The elution profile is presented in Figure 6. Of the second peak, 84% was comprised of Li<sup>+</sup> and Na<sup>+</sup> and the maximum CF values for Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup> were 605, 712, 104, 35, and 70, respectively. Of the recovered Li<sup>+</sup> and Na<sup>+</sup>, 46 and 54%, respectively, were in the second peak. Thus selective concentration and separation of both Li<sup>+</sup> and Na<sup>+</sup> from the other alkali-metal cations was achieved by gradient elution of sorbed metal ions from crown ether carboxylic acid 6 in which the carboxylic acid group is positioned over the polyether cavity.

#### CONCLUSIONS

Both the crown ether ring size and positioning of the carboxylic acid group over the polyether ring are important factors for metal ion recognition. Compared with the results for dibenzo-16-crown-5 carboxylic acid resin 2, a substantial difference in alkali-metal cation sorption by the analogous dibenzo-14-crown-4 carboxylic acid resin 6 was observed. The sorption selectivity was found to be considerably better for cyclic polyether resins 5 and 6 than with the corresponding acyclic polyether resins 3 and 4. The sorption selectivity was found to increase in the order resin 3 < resin 4 < resin 5 <resin 6 which demonstrates that structural rigidity improves sorption selectivity of the binding site. Good sorption selectivity for both Li<sup>+</sup> and Na<sup>+</sup> was obtained for resin 6 in which the pendent carboxylic acid group is positioned over the crown



Elution volume (mL)

Figure 6. Concentration factors (CF) for alkali-metal cations from a sample solution (1.0 L, pH = 10.4, 6.0  $\times$  10<sup>-5</sup> M in each aikali-metal cation) with a column of resin 6 vs the elution volume of (I) 0.05 M HCl, (II) H<sub>2</sub>O, and (III) 1.0 M HCl: (Δ) Li<sup>+</sup>, (Ο) Na<sup>+</sup>, (□) K<sup>+</sup>, (Δ) Rb<sup>+</sup>, (•) Cs<sup>+</sup>.

ether cavity. Use of resin 6 as a stationary phase was shown to provide selective concentration of both Li<sup>+</sup> and Na<sup>+</sup> from a dilute aqueous solution of five alkali-metal cations.

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