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Ion-Pair Sorption of Alkali Metal Chlorides by Crown Ether Carboxamide Resins

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ABSTRACT

Ten crown ether carboxamide resins are prepared by condensation polymerization of *N*,*N*-dialkyl *sym*-(*R*)dibenzo-16-crown-5-oxyacetamide monomers with formaldehyde in formic acid. Competitive ion-pair sorption of alkali metal chlorides from aqueous methanol solutions by these novel resins reveals that both sorption selectivity and efficiency are influenced by: 1) the conformational positioning of the pendant carboxamide group with respect to the crown ether cavity; 2) the length of the *N*,*N*-dialkyl chains on the pendant carboxamide group; 3) the methanol content of the aqueous methanol solution; 4) the concentration of alkali metal chlorides in the sample solution; and 5) the temperature of the sample solution. The highest sorption efficiency and Na^+ selectivity are obtained for a resin prepared from *N*,*N*-dibutyl *sym*-(propyl)dibenzo-16-crown-5-oxacetamide monomer in which the geminal propyl group orients the carboxamide-containing side arm over the crown ether cavity. Lengthening the alkyl chains in the carboxamide group is detrimental to both sorption efficiency and selectivity. A very sharp response of alkali metal chloride sorption to the methanol content of the sample solution is noted for the crown ether resins which possess preorganized carboxamide side arms.

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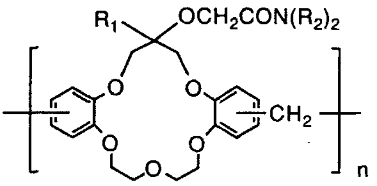
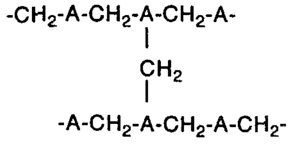
INTRODUCTION

Recently we reported the use of crown ether carboxylic acid resins for selective sorption and separation of alkali metal cations from solution (1–6). For a proper spatial relationship of the carboxylic acid side arm relative to the crown ether binding site, the crown ether carboxylic acid resins exhibit effective and selective sorption of alkali metal cations from aqueous solutions. In such ion-exchange sorption, multivalent metal cation sorption is generally greater than that of monovalent alkali metal cations due to a stronger electrostatic interaction between the ion-exchange group and multivalent metal cations (7). For effective sorption for alkali metal cations, it is necessary to have previously removed the multivalent cations from the sample solution.

In contrast, ion-pair sorption by neutral crown ether resins exhibits a different sorption selectivity. Since multivalent metal cations are heavily hydrated and must be accompanied by equivalent amounts of anions in ion-pair sorption, neutral crown ether resins prefer sorption of alkali metal





$$\begin{array}{c}\text{-}CH_2\text{-}A\text{-}CH_2\text{-}A\text{-}CH_2\text{-}A\text{-}\\ | \\ CH_2 \\ | \\ \text{-}A\text{-}CH_2\text{-}A\text{-}CH_2\text{-}A\text{-}CH_2\text{-}\end{array}$$

11

Resin	R_1	R_2
1	-H	$-C_2H_5$
2	-H	$-C_3H_7$
3	-H	$-C_4H_9$
4	-H	$-C_5H_{11}$
5	-H	$-C_6H_{13}$
6	$-C_3H_7$	$-C_2H_5$
7	$-C_3H_7$	$-C_3H_7$
8	$-C_3H_7$	$-C_4H_9$
9	$-C_3H_7$	$-C_5H_{11}$
10	$-C_3H_7$	$-C_6H_{13}$

FIG. 1 Structures of the dibenzo-16-crown-5 carboxamide resins.

salts over multivalent metal ion salts (8, 9). Compared with conventional ion-exchange resins, the interaction between crown ether binding sites in a neutral crown ether resin and the metal cation is weak. However, the metal salt binding ability and selectivity may be enhanced by introduction of a pendant neutral chelating group near the polyether binding sites in the resin (8).

In the present study, crown ether carboxamide resins have been prepared from *N*,*N*-dialkyl *sym*-(*R*)dibenzo-16-crown-5-oxyacetamide monomers. The structural variations within the dibenzo-16-crown-5 carboxamide resins are illustrated in Fig. 1. The length of the linear *N*,*N*-dialkyl groups in the pendant carboxamide function is varied to assess the influence of this structural modification upon the efficiency and selectivity of alkali metal salt sorption. Variation of the R_1 function from hydrogen to a geminal propyl group is anticipated to change the conformational mobility of the carboxamide-containing side arm (1). Thus the influence of the carboxamide group structure and its conformational positioning relative to the polyether binding site upon ion-pair sorption of alkali metal chlorides are evaluated.

EXPERIMENTAL

Apparatus

The apparatus was the same as that utilized in previous studies (1–6). To prevent metal contamination, all glassware was soaked in 5% nitric acid solution for 24 hours and rinsed with deionized water before use.

Reagents

Sources of reagents and solvents were the same as those reported previously (1–6). Deionized water was prepared by passing distilled water through three Barnstead D8922 combination cartridge in series. *sym*-(Hydroxy)dibenzo-16-crown-5 and *sym*-(hydroxy)-(propyl)dibenzo-16-crown-5 were prepared by the reported methods (1, 10). The series of *N*,*N*-dialkyl *sym*-(*R*)dibenzo-16-crown-5-oxyacetamides monomers with R_1 = H and propyl and variation of R_2 alkyl chain length from ethyl to propyl to butyl to pentyl to hexyl were prepared by the reported procedure (11).

Preparation of Crown Ether Carboxamide Resins 1–10

Crown ether resins **1–10** (Fig. 1) were synthesized by condensation polymerization of the corresponding *N*,*N*-dialkyl *sym*-(*R*)dibenzo-16-

crown-5-oxyacetamide monomers with formaldehyde in formic acid as described in detail previously (1–6). To the crown ether monomer dissolved in formic acid, formaldehyde (37% aqueous solution) was added and the mixture was refluxed. The precipitate was collected and washed with deionized water and methanol and dried in an oven at 80°C. The dried resin was coarsely ground, stirred with 0.20 M HCl, filtered, rinsed with deionized water until the pH was that of deionized water, and dried again at 80°C. The resin was ground to a powder form (finer than 60 mesh). The amounts of reagents, reaction conditions and yields are presented in Table 1.

Resin **1**. IR (KBr): 1735, 1719, 1637 (C═O), 1282, 1049 (C—O) cm^{-1}. Analysis calculated for **11** (amide/acid, 45/55): C, 64.70; H, 6.37. Found: C, 64.38; H, 6.57.

Resin **2**. IR (KBr): 1735, 1719, 1637 (C═O), 1282, 1055 (C—O) cm^{-1}. Analysis calculated for **11** (amide/acid, 85/15): C, 66.74; H, 7.22. Found: C, 66.46; H, 6.89.

Resin **3**. IR (KBr): 1735, 1719, 1637 (C═O), 1281, 1049 (C—O) cm^{-1}. Analysis calculated for **11** (amide/acid, 70/30): C, 66.83; H, 7.22. Found: C, 66.65; H, 7.58.

Resin **4**. IR (KBr): 1735, 1719, 1654, 1637 (C═O), 1281, 1055 (C—O) cm^{-1}. Analysis calculated for **11** (amide/acid, 90/10): C, 68.59; H, 7.93. Found: C, 68.44; H, 7.77.

Resin **5**. IR (KBr): 1735, 1719, 1654, 1637 (C═O), 1282, 1055 (C—O)

TABLE 1
Reaction Conditions and Yields

Resin	Monomer grams	Monomer millimoles	HCO_2H (mL)	H_2CO[a] (mL)	Reaction time (days)	Yield (%)
1	1.0	2.2	25	60	6	10
2	3.0	6.2	69	69	3	20
3	1.0	1.9	11	11	3	42
4	2.8	5.2	54	54	3	50
5	4.0	7.0	108	72	6	33
6	1.0	2.0	23	53	4	10
7	3.1	5.9	64	64	3	40
8	3.0	5.4	64	64	3	35
9	3.0	2.2	62	62	3	39
10	4.1	6.8	114	74	5	39

[a] 37% aqueous solution.

cm^{-1}. Analysis calculated for **11** (amide/acid, 85/15): C, 69.89; H, 7.55. Found: C, 69.26; H, 7.84.

Resin **6**. IR (KBr): 1735, 1719, 1654, 1637 (C═O), 1282, 1049 (C—O) cm^{-1}. Analysis calculated for **11** (amide/acid, 50/50): C, 68.63; H, 6.73. Found: C, 68.34; H, 6.70.

Resin **7**. IR (KBr): 1735, 1718, 1637 (C═O), 1282, 1052 (C—O) cm^{-1}. Analysis calculated for **11** (amide/acid, 65/35): C, 66.89; H, 7.23. Found: C, 66.59; H, 7.14.

Resin **8**. IR (KBr): 1735, 1720, 1637 (C═O), 1281, 1055 (C—O) cm^{-1}. Analysis calculated for **11** (amide/acid, 65/35): C, 67.43; H, 7.44. Found: C, 67.04; H, 7.58.

Resin **9**. IR (KBr): 1735, 1720, 1637 (C═O), 1275, 1054 (C—O) cm^{-1}. Analysis calculated for **11** (amide/acid, 60/40): C, 67.57; H, 7.48. Found: C, 67.37; H, 7.31.

Resin **10**. IR (KBr): 1735, 1720, 1637 (C═O), 1275, 1054 (C—O) cm^{-1}. Analysis calculated for **11** (amide/acid, 60/40): C, 67.99; H, 7.64. Found: C, 68.01; H, 7.33.

Ion-Pair Sorption of Alkali Metal Chlorides by Resins 1–10

An aqueous or aqueous methanol solution (5.0 mL) of the five alkali metal chlorides (0.10 M in each) was shaken with 0.040 g of the resin in a 25-mL, pear-shaped flask with a 14/20 joint and a polypropylene stopper for 3.0 hours at room temperature (21–23°C) with a Burrell wrist-action shaker. The mixture was filtered with a sintered glass funnel. To remove any residual sample solution, filtration was continued for 20 minutes under aspirator vacuum with air passing through the resin. The resin was dried in an oven at 80°C for 12 hours. Of the dried resin, a 0.20-g sample was shaken with 5.0 mL of deionized water for 1.0 hour to strip the alkali metal chlorides from the resin into an aqueous solution for analysis by ion chromatography with a Dionex Model 2000i chromatograph.

RESULTS AND DISCUSSION

Preparation of Crown Ether Carboxamide Resins

Two series of crown ether carboxamide resins were prepared from *N*,*N*-dialky *sym*-dibenzo-16-crown-5-oxyacetamide and *sym*-(propyl)dibenzo-16-crown-5-oxyacetamide monomers by condensation polymerization with formaldehyde in formic acid. For each series, the *N*,*N*-dialkyl groups were varied from ethyl to propyl to butyl to pentyl to hexyl. The structural representations **1–10** (Fig. 1) imply polymers with no crosslinking. This is most certainly an oversimplification, since some level of crosslinking is anticipated. A possible structure for the partially crosslinked resins is given by **11** (Fig. 1) in which A is the dibenzocrown ether carboxamide unit.

Resin **5** was prepared first. The monomer (4.0 g) was dissolved in 108 mL of formic acid, and 72 mL of formaldehyde (37% aqueous solution) was added. The mixture was refluxed at 110–115°C for 6 days to give a 33% yield of resin. Synthesis of resin **10** under very similar conditions gave a 39% resin yield. To shorten the reaction time, the relative proportions of formic acid and formaldehyde were changed from 3:2 to 1:1 for the preparation of resins **1–4** and **6–9**. After reaction for 3 days, resins **3**, **4**, and **7–9** were obtained in 35–50% yields. Under these conditions, resin **2** was isolated in low yield (20%) and no precipitation of the resin was noted for **1** and **6**. By changing the relative proportions of formic acid and formaldehyde from 1:1 to 1:2, resins **1** and **6** were obtained in 10% yields after refluxing for 6 and 4 days, respectively.

The polymerization was found to cause some degree of hydrolysis of the carboxamide groups in the resin to carboxylic acid functions. This was confirmed in the IR spectra of the resins in which separate carbonyl absorptions for tertiary amide (1630–1670 cm^{-1}) and carboxylic acid (1700–1725 cm^{-1}) groups were observed for each resin (see the Experimental Section). In agreement, the elemental analysis results were inconsistent with calculated values based upon unhydrolyzed crown ether carboxamide resins. However, calculated values for resins with a mixture of carboxamide and carboxylic acid pendant groups agreed with the observed elemental analysis values. The calculated compositions and elemental analysis data are given in the Experimental Section.

Effect of *N,N*-Dialkylcarboxamide and Geminal Group Variation for Ion-Pair Sorption of Alkali Metal Chlorides by Crown Ether Carboxamide Resins 1–10

Results for competitive sorption of alkali metal chlorides from aqueous and aqueous methanol solutions by resins **1–3** and **6–8** as a function of the methanol content in the sample solutions are presented in Figs. 2(a–f), respectively. Aqueous methanol solutions were utilized to vary the polarity of the sample solution. It is known that metal ion–crown ether interactions are enhanced as the polarity of the liquid medium is lowered (12). Reproducibility of the alkali metal chloride sorption and stripping procedure has been demonstrated previously (1, 9). In this study for a given resin, the reproducibility of alkali metal chloride sorption from 80% methanol–20% water was found to be within ±0.07 times the stated value for

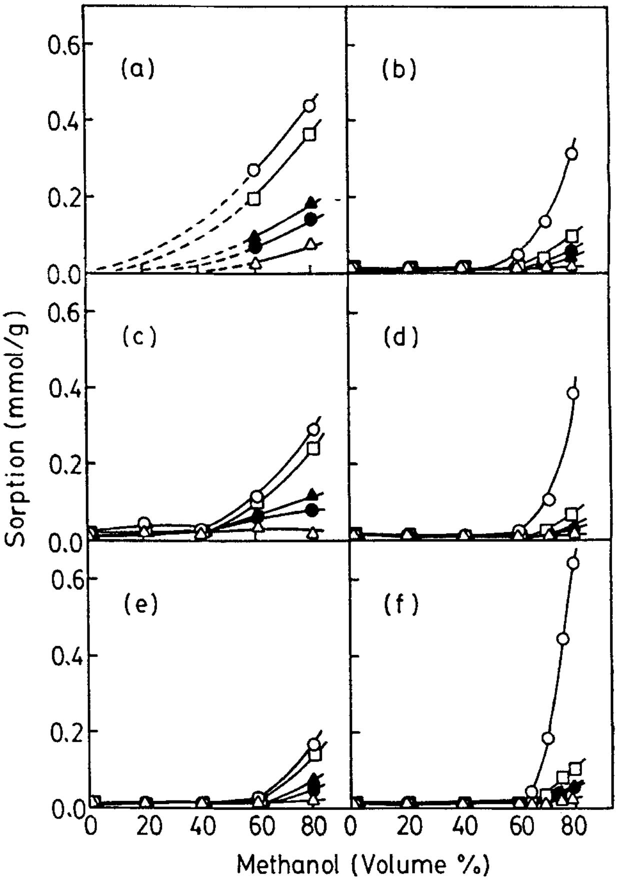


FIG. 2 Sorption of alkali metal chlorides by dibenzo-16-crown-5 carboxamide resins vs the methanol content of the aqueous methanol sample solution for resins (a) **1**, (b) **6**, (c) **2**, (d) **7**, (e) **3**, and (f) **8**: (△) Li^+, (○) Na^+, (□) K^+, (▲) Rb^+, (●) Cs^+.

lithium chloride and ±0.05 times the stated values for other alkali metal chlorides.

Due to low yield of resin **1**, only two compositions of aqueous methanol solution were examined (Fig. 1a). In light of the results obtained in earlier studies (1–6), the pendant carboxamide group is expected to be flexible when R_1 = H. In contrast, attachment of a propyl group to the same ring carbon that bears the carboxamide side arm should position the carboxamide group over the crown ether cavity. Resins **1–3**, which possess flexible carboxamide groups, exhibit poor sorption selectivity, and the sorption efficiency diminishes as the length of alkyl chain in the carboxamide group is increased (Figs. 2a, 2c, and 2e). In contrast, selective Na^+ sorption is noted for resins **6–8** (Figs. 2b, 2d, and 2f), which possess preorganized carboxamide groups. For resins **6–8**, no alkali metal chloride sorption is detected from aqueous sample solutions or those containing up to 60% methanol. However, above 60% methanol content, NaCl sorption increases sharply and highly selective sorption for Na^+ is evident. Thus, with a preorganized side arm, the carboxamide group behaves as a sorption gate that responds sharply to the polarity of the sample solution. To determine if swelling of the *N*,*N*-dialkyl portion of the carboxamide group might be the causative factor, the swelling properties of resin **8** were examined. It was found that there was no significant change in resin volume in 60 and 80% methanolic solutions.

In Figs. 3(a–d) are shown the results for alkali metal chloride sorption by resins **4**, **5**, **9**, and **10**, respectively. Resins **4** and **9**, for which the *N*,*N*-

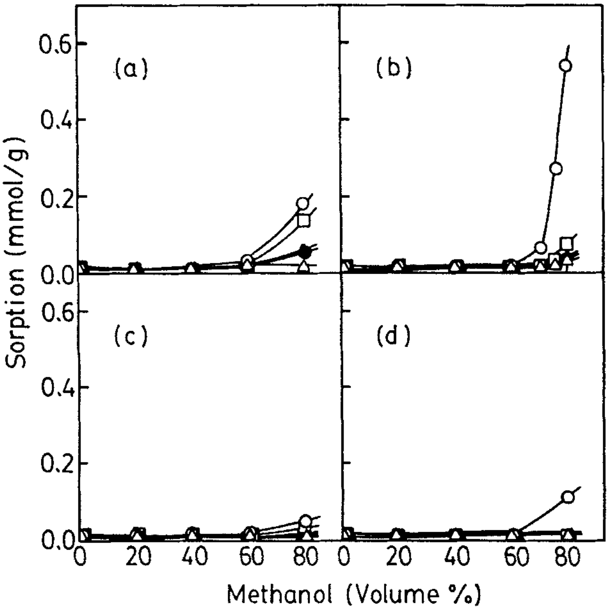


FIG. 3 Sorption of alkali metal chlorides by dibenzo-16-crown-5 carboxamide resins vs the methanol content of the aqueous methanol sample solution for resins (a) **4**, (b) **9**, (c) **5**, and (d) **10**: (△) Li^+, (○) Na^+, (□) K^+, (▲) Rb^+, (●) Cs^+.

dialkyl groups are pentyl, show similar sorption profiles to those observed for resins **3** and **8**, for which the groups are butyl. Thus resin **4** exhibits poor selectivity for alkali metal chloride sorption. Addition of a geminal propyl group (resin **9**) gives a sharp increase in NaCl sorption when the methanol content of the sample solution is above 60%. However, elongation of the *N*,*N*-dialkyl groups from pentyl to hexyl causes a diminution of alkali metal chloride sorption for both resins **5** and **10** in comparison with resins **4** and **9**, respectively.

Figures 4(a) and 4(b) compare the influence of *N*,*N*-dialkyl group variation upon the sorption of each alkali metal chloride from 80% methanol–20% water by resins **1–10**. For resins **1–5** which have flexible carboxamide groups, the sorption efficiency decreases monotonously as the alkyl chains in the carboxamide group are lengthened (Fig. 4a). For resins **6–9** (Fig. 4b), the sorption levels for Li^+, K^+, Rb^+, and Cs^+ show little change as the *N*,*N*-dialkyl groups are lengthened from ethyl to propyl to butyl to pentyl before declining with hexyl (resin **10**). On the other hand,

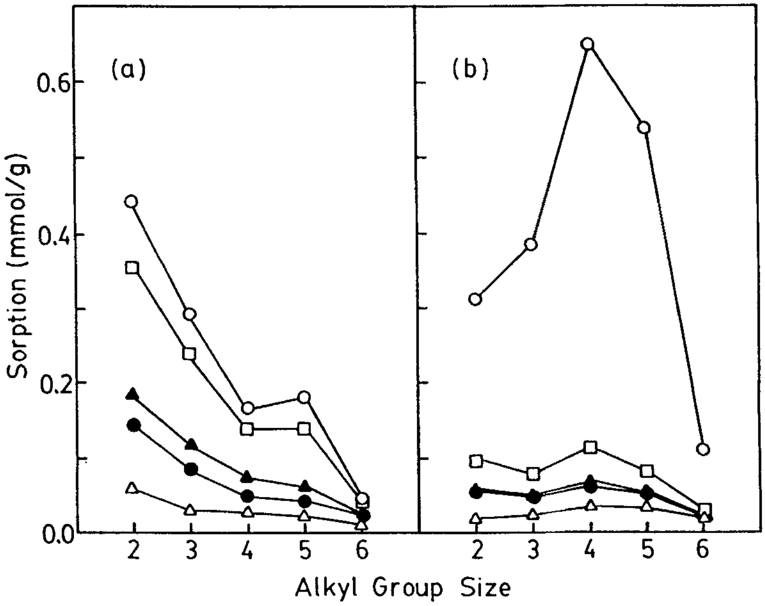


FIG. 4 Effect of alkyl chain length in the *N*,*N*-dialkyl carboxamide group upon alkali metal chloride sorption from 80% methanol–20% water by (a) *N*,*N*-dialkyl *sym*-dibenzo-16-crown-5-oxyamide resins **1–5** and (b) *N*,*N*-dialkyl *sym*-(propyl)dibenzo-16-crown-5-oxyamide resins **6–10**: (△) Li^+, (○) Na^+, (□) K^+, (▲) Rb^+, (●) Cs^+.

Na^+ sorption increases as the *N*,*N*-dialkyl group is varied from ethyl to propyl to butyl in resins **6–8**, respectively, and is more than twice as high for resin **8** than resin **6**. When the *N*,*N*-dialkyl groups are changed from butyl to pentyl (resin **9**), the Na^+ sorption decreases somewhat and then plummets for the *N*,*N*-di(hexyl) carboxamide resin **10**. It is proposed that the influence of the *N*,*N*-dialkyl group on Na^+ sorption by resins **6–8** may be rationalized by a combination of inductive and hydrophobic effects. Thus complexation-enhancing electron release by the alkyl group increases in the order ethyl < propyl < butyl < pentyl, hexyl (13). On the other hand, the lipophilicity of the resin increases as the *N*,*N*-dialkyl groups are lengthened. Apparently the best balance between the counteracting inductive and hydrophobic effects of the *N*,*N*-dialkyl groups is achieved in the *N*,*N*-di(butyl) carboxamide resin **8**.

Although some degree of hydrolysis of the carboxamide side arms in the resins to carboxylic acid functions occurs during the polymerization, the profile for sorption of alkali metal chlorides from neutral aqueous methanolic solutions by *sym*-(propyl)dibenzo-16-crown-5-oxacetic acid resin reported earlier (8) is quite different from that found in this study for the corresponding *N*,*N*-dialkyl carboxamide resins **6–8**. The former exhibited a monotonous increase in alkali metal chloride sorption when the methanol content of the sample solution was increased, whereas the latter exhibited a sharp response of NaCl sorption to the polarity of the sample solution. This difference verifies predominant alkali metal chloride sorption by the crown ether carboxamide units in the present resins.

TABLE 2
Ion-Exchange Capacity and Total Sorption of Alkali Metal Chlorides by Dibenzo-16-crown-5 Carboxamide Resins

Resin	Ion-exchange capacity (mmol/g)[a]	Total sorption (mmol/g)[b]	Percent loading
1	2.26	1.20	53
2	2.04	0.76	37
3	2.01	0.46	23
4	1.84	0.46	25
5	1.78	0.15	8
6	2.05	0.56	27
7	1.94	0.60	31
8	1.88	0.94	50
9	1.84	0.76	41
10	1.78	0.21	12

[a] Calculated from elemental analysis data.

[b] Data from the 80% methanol–20% water system.

The total alkali metal chloride sorption from 80% methanol–20% water and percent loading values for crown ether carboxamide resins **1–10** are listed in Table 2. The loading is defined as the total alkali metal chloride sorption by the resin divided by the ion-exchange capacity as calculated from the elemental analysis data. Since hydrolysis of the carboxamide group occurs to some extent during the resin synthesis, calculation of the ion-exchange capacity was based upon the number of crown ether units in the resin. For resins **1–5** which have flexible carboxamide side arms, the total alkali metal chloride loading decreases from 53% for **1** to 37% for **2** to 23% for **3**. The efficiency remains constant for **4** (25%) before exhibiting a marked decrease in loading (8%) with **5**. For resins **6–10**, which possess preorganized carboxamide side arms, the total alkali metal chloride loading increases from 27% for **6** to 31% for **7** to 50% for **8** before dropping to 41% for **9** and 12% for **10**. Thus the maximal loading is observed for resin **8** which has preorganized *N*,*N*-di(butyl) carboxamide side arms.

Effect of Salt Concentration and Solution Temperature upon Ion-Pair Sorption of Alkali Metal Chlorides by Resin 8

Data for competitive ion-pair sorption of alkali metal chlorides by resin **8** from 80% methanol–20% water as a function of alkali metal chloride concentration are shown in Fig. 5. Ion-pair sorption by the neutral crown ether resin is described by

$$[\mathrm{M^+}]_a + [\mathrm{Cl^-}]_a + [\mathrm{CE}]_r \rightleftharpoons [\mathrm{CE{-}M^+Cl^-}]_r \qquad (1)$$

where the subscripts "a" and "r" denote the aqueous and the resin phases, respectively. As would be predicted from Eq. (1), sorption efficiencies for the alkali metal chlorides increase as their concentrations in the sample solution are enhanced (Fig. 5). The $\mathrm{Na^+/K^+}$ sorption selectivities remain high and constant at 5.3–5.6 as the concentration of each alkali metal chloride in the sample solution is varied from 0.06 to 0.10 M.

As shown in Fig. 2(f), resin **8** exhibits a marked change in sorption ability when the methanol content of the sample solution is changed from 60 and 80%. In view of such sensitivity of sorption efficiency to the polarity of the sample solution, it was surmised that sorption might also be thermally responsive (14). To examine this possibility, the temperature effect upon ion-pair sorption of alkali metal chlorides by resin **8** was investigated for samples solutions containing 60 and 80% methanol. The aqueous methanol solutions of the five alkali metal chlorides (0.10 M in each) were stirred with resin **8** in a thermostated water bath at 0–4, 25, 50, and 75°C. The resin was filtered and purged with air by an aspirator to remove

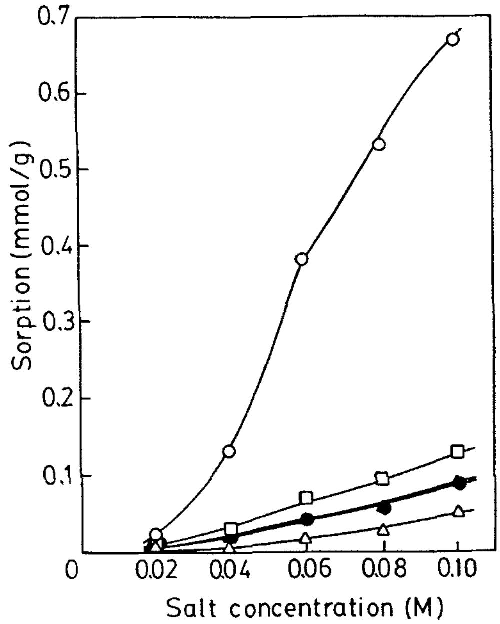


FIG. 5 Effect of alkali metal chloride concentration upon ion-pair sorption from 80% methanol–20% water by resin **8**: (△) Li^+, (○) Na^+, (□) K^+, (▲) Rb^+, (●) Cs^+.

TABLE 3
Effect of Temperature upon Ion-Pair Sorption by Resin **8**

Temperature (°C)	Methanol (%)	Sorption (mmol/g)				
		Li^+	Na^+	K^+	Cs^+	Rb^+
0–4	60	0.02	0.04	0.02	0.02	0.01
25	60	0.02	0.03	0.01	0.02	0.01
50	60	0.02	0.03	0.02	0.02	0.02
75	60	0.02	0.04	0.02	0.02	0.01
0–4	80	0.05	0.71	P[a]	P	P
25	80	0.05	0.66	0.11	0.07	0.06
50	80	0.06	0.44	0.10	0.07	0.06
75	80	0.07	0.26	0.09	0.08	0.07

[a] Precipitation.

the sample solution completely. The resin was dried in an oven at 80°C. Of the dried resin, a weighed portion was shaken with deionized water to strip the alkali metal chlorides from the resin into an aqueous solution for analysis by ion chromatography. Results for the sorption of alkali metal chlorides by resin **8** at various temperatures are presented in Table 3. For 60% methanol, no discernible change in sorption is observed when the temperature is varied from 0 to 75°C. In 80% methanol, precipitation of some alkali metal salts was noted at 0–4°C. On the other hand, for 80% methanol sample solutions at 25, 50, and 75°C, the NaCl sorption decreases markedly as the temperature of the sample solution is enhanced. Thus the temperature of the sample solution is also demonstrated to be an important factor for regulating the selectivity and efficiency of ion-pair sorption by this crown ether carboxamide resin.

CONCLUSION

Dibenzo-16-crown-5 resins which possess a preorganized *N*,*N*-dialkyl carboxamide side arm exhibit pronounced selectivity for Na^+ in alkali metal chloride sorption and a sharp response to the polarity of the sample solution. The highest sorption efficiency and Na^+ selectivity are obtained for resin **8** which was prepared by condensation polymerization of *N*,*N*-di(butyl) *sym*-(propyl)dibenzo-16-crown-5-oxyacetamide with formaldehyde in formic acid. Longer alkyl chains in the carboxamide group are found to be detrimental to both sorption efficiency and selectivity. Both the salt concentration and temperature in the sample solution affect ion-pair sorption of alkali metal chlorides by resin **8** from 80% methanol–20% water. The sorption efficiency increases as the concentration of alkali metal chlorides in the sample solution is enhanced. On the other hand, NaCl sorption diminishes significantly as the temperature of the sample solution is increased from 25 to 50 to 75°C.

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