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Effect of Sidearm Length upon Competitive Alkali Metal Solvent Extraction into Chloroform by Lipophilic Crown Phosphonic Acid Monoalkyl Esters

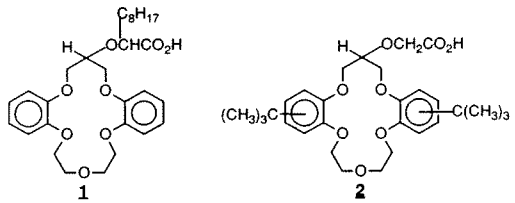
Michael J. Pugia, Grace Ndip, Han Koo Lee,[1] Il-Woo Yang,[2] and Richard A. Bartsch*

Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409-4260

A homologous series of *sym*-bis[4(5)-*tert*-butylbenzo]-16-crown-5-oxyalkylphosphonic acid monoethyl esters has been synthesized and utilized in competitive solvent extraction of alkali metal cations from water into chloroform. The change from Na^+ extraction selectivity for the ionizable crown ethers with short sidearms to Li^+ extraction selectivity for longer armed macrocycles is interpreted as a shift from predominant cation complexation within the polyether cavity for the former to predominant association with the carboxylate group for the latter. Compared with a closely related crown ether carboxylic acid, the extraction of alkali metal cations from acidic aqueous solutions by the crown ether phosphonic acid monoethyl esters exhibits much higher efficiency.

Lipophilic crown ether carboxylic acids, such as **1** and **2**, are novel reagents for the solvent extraction of alkali metal cations from water into chloroform and toluene (*1–3*). For solvent extraction, such ionizable crown ethers possess the distinct advantage over neutral crown ether compounds in that movement of the metal cation from the aqueous phase into the organic medium does not involve concomitant transfer of the aqueous phase anion (*4*). In earlier work, we have established that lipophilic group attachment is required to retain crown ether carboxylic acids in the organic phase during solvent extraction (*1*). Also variation of the lipophilic group attachment site, e.g., in **1** and **2**, has been found to influence the selectivity and efficiency of the solvent extraction process (*3*).

Another potentially important structural parameter is the length of the arm that connects the polyether ring to the ionizable group in these metal–ion complexing agents. Unfortunately, systematic structural variation of the pendant arm length for crown ether carboxylic acids presents certain synthetic difficulties. However, a homologous series of crown ether phosphonic acid monoethyl esters **3–6** which have the same polyether and lipophilic group components as crown ether carboxylic acid **2** is more accessible. We now describe



	n
3	1
4	2
5	3
6	4

the preparation of **3–6** and results for the competitive solvent extraction of alkali metal cations from water into chloroform which establish the appropriate arm length for maximal extraction selectivity and efficiency.

EXPERIMENTAL SECTION

Apparatus. Alkali metal cation concentrations in the aqueous phases were determined with a Dionex Model 10 ion chromatograph. Concentrations of the organic complexing agent in the $CHCl_3$ phases were measured with a Cary Model 17 ultraviolet–visible spectrophotometer. Measurements of pH were performed with a Fisher Accumet Model 620 pH meter using a Corning No. 476193 combination electrode. Melting points were taken with a Fisher Johns melting point apparatus and are uncorrected. ^1H NMR and IR spectra were determined with a Nicolet MS-X infrared spectrophotometer and a Varian EM-360A nuclear magnetic resonance spectrometer, respectively. Mass spectra were obtained with a Hewlett-Packard 5595B GC/MS. Elemental analysis was performed by Galbraith Laboratories (Knoxville, TN).

Reagents. The sources of reagent grade inorganic chemicals and the methods of solvent purification for the extraction experiments were the same as before (*4*). Tetrahydrofuran and pentane were distilled from $LiAlH_4$. Monoethyl iodomethylphosphoric acid (*5*), *sym*-hydroxybis[4(5)-*tert*-butylbenzo]-16-crown-5 (**7**) (*2*), and tetrahydropyranyl-protected ethylene chlorohydrin (*6*) were prepared by published procedures. Allyl

[1] Choongwae Pharma Corp., Seoul, Korea.
[2] Department of Chemistry, Korea Military Academy, Seoul, Korea.

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bromide, 1,4-dibromobutane, PBr_3, and $(EtO)_3P$ were obtained from Aldrich Chemical Co. (Milwaukee, WI).

Synthesis of Monoethyl *sym*-Bis[4(5)-*tert*-butylbenzo]-16-crown-5-oxymethylphosphonic Acid (3). Under nitrogen, 0.27 g (6.8 mmol) of NaH (60% dispersion in mineral oil) was washed with dry pentane to remove the mineral oil and was suspended in 50 mL of dry THF. To the stirred mixture, 1.80 g (3.34 mmol) of **7** was added and the mixture was stirred for 1 h. A solution of 1.00 g (3.40 mmol) of monoethyl iodomethylphosphonic acid in 25 mL of dry THF was added dropwise followed by stirring at room temperature for 5 h and refluxing for 48 h. Water (50 mL) was added to the cooled reaction mixture followed by addition of 6 N HCl to pH 1 and refluxing for 20 h. The THF was evaporated in vacuo and the resultant acidic aqueous mixture was extracted with $CHCl_3$ (three 50-mL portions). The combined chloroform extracts were washed with brine and water, dried over $MgSO_4$, and evaporated in vacuo to give the crude product which was chromatographed twice on silica gel columns with CH_2Cl_2–MeOH (10:1) as eluent to give 0.84 g (43%) of **3** as a white crystalline solid with mp 82–83 °C.: IR (deposited film) 3389 (O-H), 1270 (P═O), 1252, 1122 (C—O), 1008, 802 cm^{-1} (P—OEt).; ^1H NMR ($CDCl_3$) δ 1.27 (s, 18), 3.21 (br s, 2), 3.54 (m, 2), 3.70–4.35 (m, 13), 6.85 (br s, 6).; mass spectrum 580.5 (M^+). Anal. Calcd for $C_{30}H_{45}O_9P \cdot 1.1CH_2Cl_2$: C, 55.42; H, 7.06. Found: C, 55.30; H, 7.10.

General Procedure for Synthesis of Crown Ether Phosphonic Acid Monoethyl Esters 4–6. Under nitrogen, 1.42 mmol of the *sym*-bis[4(5)-*tert*-butylbenzo]-16-crown-5-oxyalkyl bromide (**8–10**) and 0.51 g (3.3 mmol) of $(EtO)_3P$ were stirred at 150 °C for 10 h. Excess $(EtO)_3P$ was removed by vacuum distillation and the residue was purified by chromatography on silica gel with CH_2Cl_2–MeOH (20:1) as eluent. The resultant diethyl phosphonate (1.0 mmol) was refluxed under nitrogen for 12 h with 0.25 g of NaOH in 50 mL of EtOH. The solution was cooled to 5 °C and acidified to pH 1 with 6 N HCl. The solvent was removed in vacuo and 30 mL of H_2O was added to the residue. Extraction with CH_2Cl_2, drying over $MgSO_4$, and evaporation in vacuo gave an oil which was purified by chromatography on silica gel with CH_2Cl_2–MeOH (1:1) as eluent.

Diethyl *sym*-bis[4(5)-*tert*-butylbenzo]-16-crown-5-oxyethylphosphonate was obtained as a colorless oil in 87% yield: IR (neat) 1262 (P═O), 1252, 1120 (C—O), 1010, 805 cm^{-1} (P—OEt); ^1H NMR ($CDCl_3$) δ 1.27 (m, 24), 1.92–2.54 (m, 2), 3.70–4.61 (m, 19), 6.85–7.12 (m, 6); mass spectrum 622.4 (M^+). Hydrolysis gave **4** in 94% yield as a colorless oil: IR (neat) 3377 (O—H), 1270 (P═O), 1252, 1122 (C—O), 1010, 805 cm^{-1} (P—OEt); ^1H NMR ($CDCl_3$) δ 1.27 (m, 21), 1.81–2.63 (m, 2), 3.43–4.41 (m, 17), 6.85–7.12 (m, 6). Anal. Calcd for $C_{31}H_{47}O_9P$: C, 62.61; H, 7.97. Found: C, 62.71; H, 8.03.

Diethyl *sym*-bis[4(5)-*tert*-butylbenzo]-16-crown-5-oxypropylphosphonate was realized in 61% yield as a colorless oil: IR (neat) 1262 (P═O), 1252, 1120 (C—O), 1010, 805 cm^{-1} (P—OEt); ^1H NMR ($CDCl_3$) δ 1.27–1.42 (m, 24), 1.74–2.21 (m, 4), 3.70–4.61 (m, 19), 6.85–7.12 (m, 6). Hydrolysis produces **5** in 63% yield as a white solid with mp 35–36 °C: IR (KBr) 3377 (O—H), 1270 (P═O), 1252, 1122 (C—O), 1010, 805 cm^{-1} (P-OEt); ^1H NMR ($CDCl_3$) δ 0.88–1.42 (m, 21), 1.72–2.33 (m, 4), 3.70–4.61 (m, 17), 6.85–7.12 (m, 6), 8.23 (br s, 1). Anal. Calcd for $C_{32}H_{49}O_9P$: C, 63.04; H, 8.27. Found: C, 63.19; H, 7.90.

Diethyl *sym*-bis[4(5)-*tert*-butylbenzo]-16-crown-5-oxybutylphosphonate was produced in 77% yield as a colorless oil: IR (neat) 1262 (P═O), 1252, 1122 (C—O), 1008, 805 cm^{-1} (P-OEt); ^1H NMR ($CDCl_3$) δ 1.27–1.42 (m, 24), 1.57–2.11 (m, 6), 3.70–4.61 (m, 19), 6.85–7.12 (m, 6). Hydrolysis gave an 89% yield of **6** as a white solid with mp 32–33 °C; IR (KBr) 3387 (O—H), 1270 (P═O), 1252, 1122 (C—O), 1010, 805 cm^{-1} (P—OEt); ^1H NMR ($CDCl_3$) δ 1.03–2.18 (m, 27), 3.38–4.68 (m, 17), 6.67–7.12 (m, 6). Anal. Calcd for $C_{33}H_{51}O_9P \cdot 0.5H_2O$: C, 62.64; H, 8.44. Found: C, 62.79; H, 8.50.

Synthesis of 1-[*sym*-Bis[4(5)-*tert*-butylbenzo]-16-crown-5-oxy]-2-bromoethane (8). Under nitrogen, 0.40 g (9.8 mmol) of NaH (60% dispersion in mineral oil) was washed with dry pentane to remove the mineral oil and was suspended in 200 mL of dry THF. To the stirred mixture, 3.00 g (6.4 mmol) of **7** was added. After 1 h, a solution of 2.00 g (6.5 mmol) of tetrahydropropanyl-protected ethylene chlorohydrin in 25 mL of THF was added and the mixture was refluxed for 24 h. To the cooled reaction mixture, 100 mL of H_2O was added dropwise and the THF was evaporated in vacuo. Extraction of the residual aqueous layer with CH_2Cl_2 (three 50-mL portions), drying over $MgSO_4$, and evaporation gave an oil which was purified by chromatography on silica gel with Et_2O as eluent to give a 66% yield of the tetrahydropyranyl ether of 2-[*sym*-bis[4(5)-*tert*-butylbenzo]-16-crown-5-oxy]ethanol. The protecting group was removed by stirring with 100 mL of 10% HCl in MeOH for 12 h under nitrogen. Following neutralization by addition of 10% aqueous K_2CO_3, the MeOH was removed in vacuo. Extraction of the resultant aqueous phase with CH_2Cl_2 (two 100-mL portions), drying over $MgSO_4$, and evaporation gave an oil which was purified by chromatography on alumina with CH_2Cl_2 as eluent. A 96% yield of extremely hygroscopic 2-[*sym*-bis[4(5)-*tert*-butylbenzo]-16-crown-5-oxy]ethanol was obtained as a white solid with mp 67–68 °C: IR (deposited film) 3420 (O–H), 1252, 1122 cm^{-1} (C-O); ^1H NMR ($CDCl_3$) δ 0.89–1.37 (m, 18), 3.05 (br s, 1), 3.45–4.23 (m, 17), 6.85–7.12 (m, 6). Anal. Calcd for $C_{29}H_{42}O_7 \cdot 1.15CH_2Cl_2$: C, 60.32; H, 7.43. Found: C, 60.38; H, 7.30. This alcohol (1.50 g, 3.0 mmol) was added to 1.62 (6.0 mmol) of PBr_3 in 15 mL of dry DMF at 5 °C. The mixture was refluxed for 48 h and 100 mL of H_2O was added. Extraction with Et_2O followed by washing of the Et_2O solution with 100 mL of H_2O, drying over $MgSO_4$, and evaporation in vacuo gave an oil which was purified by chromatography on alumina with CH_2Cl_2 as eluent to give **8** as a colorless oil in 83% yield: IR (neat) 1252, 1122 cm^{-1} (C–O); ^1H NMR ($CDCl_3$) δ 0.83–1.39 (m, 18), 3.45–4.44 (m, 17), 6.85–7.12 (m, 6); mass spectrum 565.5 (M^+). Anal. Calcd for $C_{29}H_{41}O_6Br \cdot 0.5H_2O$: C, 60.63; H, 7.37. Found: C, 60.78; H, 7.29.

Synthesis of 1-[*sym*-Bis[4(5)-*tert*-butylbenzo]-16-crown-5-oxy]-3-bromopropane (9). Under nitrogen, 0.15 g (3.8 mmol) of NaH (60% dispersion in mineral oil) was washed with dry pentane to remove the mineral oil and was suspended in 22 mL of dry THF. To the stirred mixture, 1.60 g (3.5 mmol) of **7** was added and after 1 h a solution of 0.54 g (7.0 mmol) of allyl bromide in THF (25 mL) was added dropwise. The reaction mixture was stirred at room temperature for 6 h and filtered. Water (8 mL) was added and the solution was evaporated in vacuo to give an oil which was purified by column chromatography on alumina with CH_2Cl_2 as eluent to give 1.31 g (75%) of *sym*-allyloxybis-[4(5)-*tert*-butylbenzo]-16-crown-5 as a colorless oil: IR (neat) 1647 C═C, 1242, 1122 cm^{-1} (C—O); ^1H NMR ($CDCl_3$) δ 0.92–1.54 (m, 18), 3.55–4.49 (m, 15), 5.10–6.15 (m, 3), 6.52–7.14 (m, 6). Anal. Calcd for $C_{30}H_{42}O_6$: C, 72.26; H, 8.49. Found: C, 72.33; H, 8.52. A portion (1.21 g, 2.4 mmol) of this ether was added to a mixture of 0.10 g of $NaBH_4$ in 20 mL of dry THF and 0.3 mL of $BF_3 \cdot Et_2O$ was added at 20–25 °C. The mixture was stirred at room temperature for 2 h and then 0.2 mL of H_2O followed by 1.0 mL of 3 N NaOH was added. During slow addition of 1.2 mL of 30% H_2O_2, the reaction temperature was allowed to rise to 35 °C. After the solution was stirred at 40 °C for 0.5 h, it was evaporated in vacuo and the residue was purified by chromatography on alumina with CH_2Cl_2 as eluent to give 1.22 g (97%) of 3-[*sym*-bis[4(5)-*tert*-butylbenzo]-16-crown-5-oxy]-1-propanol as a colorless oil: IR (neat) 3452 (O–H), 1242, 1122 cm^{-1} (C–O); ^1H NMR ($CDCl_3$) δ 0.92–1.54 (m, 18), 1.72–1.99 (m, 2), 3.33 (br s, 1), 3.55–4.42 (m, 17), 6.72–7.14 (m, 6); mass spectra 516.8 (M^+). Anal. Calcd for $C_{30}H_{44}O_7 \cdot 0.5H_2O$: C, 68.66; H, 8.47. Found: C, 68.55; H, 8.63. Conversion of this alcohol (2.60 g, 5.0 mmol) was accomplished by using the procedure described above for the preparation of **8** to provide 2.80 g (96%) of **9** as a colorless oil: IR (neat) 1252, 1122 cm^{-1} (C–O); ^1H NMR ($CDCl_3$) δ 0.91–1.39 (m, 18), 1.72–2.38 (m, 2), 3.45–4.44 (m, 17), 6.75–7.12 (m, 6). Anal. Calcd for $C_{30}H_{43}O_6Br$: C, 62.17; H, 7.48. Found: C, 62.49; H, 7.77.

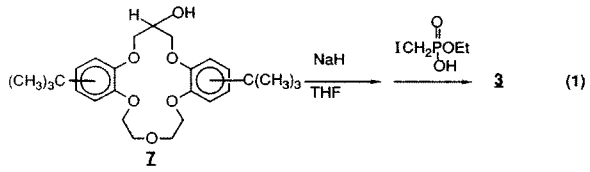
Synthesis of 1-[*sym*-Bis[4(5)-*tert*-butylbenzo]-16-crown-5-oxy]-4-bromobutane (10). A solution of 1,4-dibromobutane (2.59 g, 12.0 mmol) and **7** (1.83 g, 4.0 mmol) in CH_2Cl_2 (9 mL) was stirred vigorously with 68 mg (0.20 mmol) of tetrabutylammonium hydrogen sulfate in 3 mL of 50% aqueous NaOH. After 6 h, H_2O (10 mL) and CH_2Cl_2 (50 mL) were added. The CH_2Cl_2 layer was separated, washed with H_2O (three 100-mL portions), dried over $MgSO_4$, and evaporated in vacuo to give an oil which was purified by chromatography on alumina with EtOAc as eluent to provide 1.66 g (70%) of **10** as a colorless oil: IR (neat) 1252, 1122 cm^{-1} (C–O); ^1H NMR ($CDCl_3$) δ 0.86–1.42 (m, 18),

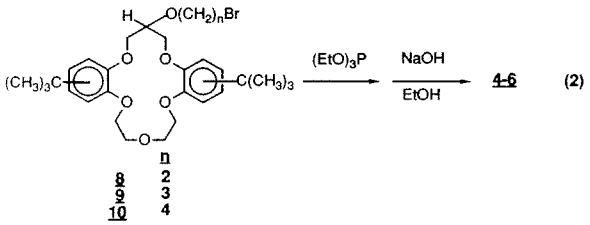
1.72–2.10 (m, 4), 3.43–4.49 (m, 17), 6.70–7.12 (m, 6). Anal. Calcd for $C_{31}H_{45}O_6Br$: C, 62.73; H, 7.64. Found: C, 62.39; H, 7.41.

Extraction Procedure. An aqueous solution of the alkali metal chlorides with hydroxides for pH adjustment (5.0 mL, 0.25 M in each) and a $CHCl_3$ solution (5.0 mL of the complexing agent (0.050 M)) were shaken for 30 min in a 30-mL separatory funnel at room temperature. The 5.0-mL phases were separated and the equilibrium pH of the aqueous phase was measured. Of the organic phase, 4.0 mL was removed and shaken with 5.0 mL of 0.1 N HCl for 30 min to strip the metal cations from the organic phase into aqueous solution for analysis by ion chromatography. A small sample of the stripped organic phase was removed and diluted with $CHCl_3$ in a 10-mL volumetric flask and the absorption was measured at 273–274 nm to determine the concentration of the complexing agent in the $CHCl_3$ layer.

RESULTS AND DISCUSSION

Synthesis of Lipophilic Crown Ether Phosphonic Acid Monoethyl Esters. The lipophilic ionizable crown ether **3** was prepared in 42% yield by reaction of the alkoxide from crown ether alcohol **7** with monoethyl iodomethylphosphonic acid (eq 1). The multistep syntheses of lipophilic crown ether phosphonic acid monoethyl esters **4–6** involved the initial preparation of the crown ether substituted alkyl bromides **8–10** from **7** by an independent route for each bromide (see Experimental Section). Subsequently **8–10** were reacted with triethyl phosphite to form lipophilic crown ether phosphonic acid diethyl esters in 63–87% yields which produced monoethyl esters **4–6** upon basic hydrolysis (eq 2). Attempts to prepare **4** by a one-step reaction of the alkoxide from **7** and diethyl 2-bromethylphosphonate (*7*) were unsuccessful as was an attempt to induce conjugate addition of the same alkoxide with diethyl vinylphosphonate (*7*).





Competitive Solvent Extraction of Alkali Metal Cations into Chloroform by Lipophilic Crown Ether Phosphonic Acid Monoethyl Esters. Potential metal ion complexing agents **3–6** are a homologous series in which the number of methylene groups between the polyether unit and ionizable group is varied from one to four. Such systematic structural variation allows the effect of the pendant arm length on the selectivity and efficiency of metal ion complexation to be probed.

In our studies of alkali metal cation solvent extraction by crown ether carboxylic acids, it was demonstrated that the efficiencies and selectivity orders for competive extractions are often quite different from expectations based upon the results of single ion extractions (*1*, *4*). Therefore, competitive extractions were utilized in this investigation.

In Figure 1 results for competitive extractions of aqueous solutions in which the concentrations of each alkali metal chloride were 0.25 M with 0.050 M chloroform solutions of **3–6** are compared. For **3–6** no loss of complexing agents from the organic phase was observed even when the aqueous phase

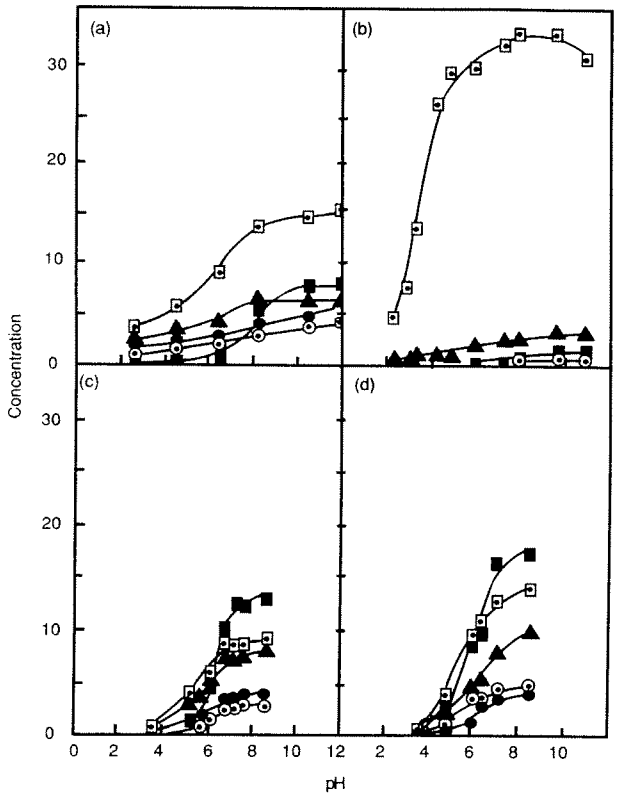


Figure 1. Concentrations of alkali metal cations ($\times 10^3$) in the chloroform phase vs. the pH of the aqueous phase for competitive solvent extractions of 0.25 M alkali metal cations by 0.050 M (a) **3**, (b) **4**, (c) **5**, and (d) **6**: (■) Li, (□) Na, (▲) K, (●) Rb, (○) Cs.

became highly basic. With regards to extraction efficiencies, complexing agents **3–5** behave similarly with organic phase metal ion loadings of 65–75% at pH 9, whereas for **6** the loading at this pH was 90%.

The differences in alkali metal cation extraction selectivities found for **3–6** are striking. Thus the observed selectivity orders are $Na^+ > Li^+ > K^+ > Rb^+, Cs^+$ for **3**, $Na^+ \gg K^+ > Li > Cs^+ > Rb^+$ for **4**, and $Li^+ > Na^+ > K^+ > Rb^+, Cs^+$ for **5** and **6**. To interpret these data it should be recalled that the cavity size in a dibenzo-16-crown-5 compound is most appropriate for complexation of Na^+ (*2*). Also in recent studies we have noted that lipophilic phosphonic acid monoethyl esters which do not have polyether units exhibit modest Li^+ selectivity in competitive solvent extractions of alkali metal cations into chloroform (*8*). Thus the extraction selectivity orders observed for **3–6** indicate that the metal cation is complexed within the crown ether rings of **3** and **4**, but coordinates primarily with the monoethyl phosphonate center in **5** and **6**.

Examination of Corey–Pauling–Kortum (CPK) space-filling models reveals that in **5** and **6** the arms are too long to produce readily accessible conformations in which a metal ion complexed within the polyether unit could simultaneously coordinate with the pendant ionized group. On the other hand, the CPK models indicate that in **4** the ionizable group may be easily oriented directly over the crown ether cavity. However, in **3** the arm is too short to allow the ionized group to be easily situated over the crown ether cavity. In support of the last contention is the X-ray crystal structure of lithium crown ether carboxylate **11** in which Li^+ is coordinated within the polyether cavity and a water molecule bridges the gap between Li^+ and the ionized group (*9*).

Combination of the solvent extraction results with the structural information gained from examination of the CPK models establishes that the highest extraction selectivity can be anticipated when the arm length is appropriate to position a pendant ionized group directly over the polyether cavity.

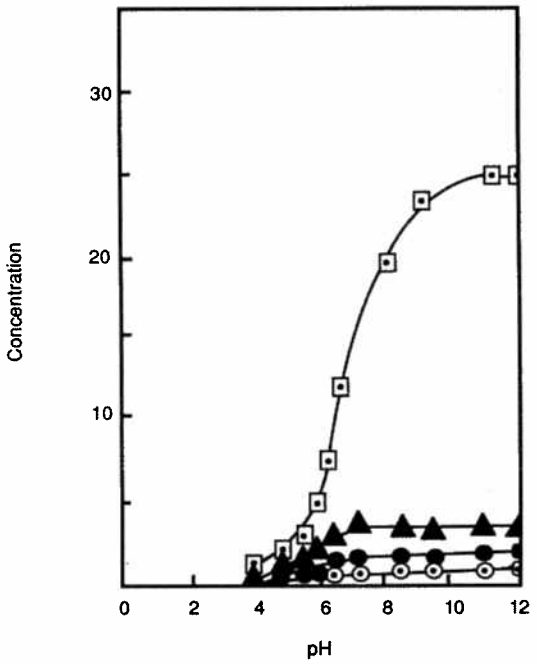


Figure 2. Concentrations of alkali metal cations ($\times 10^3$) in the chloroform phase vs. the pH of the aqueous phase for competitive solvent extraction of 0.25 M alkali metal cations by 0.05 M **2**: (■) Li, (□) Na, (▲) K, (●) Rb, (○) Cs. Data were taken from ref 2.

Effect of Ionizable Group Variation. Compound **3** and the previously investigated **2** are structurally identical except for the ionizable groups. For the former, the ionizable group is a phosphonic acid monoethyl ester; whereas for the latter, it is a carboxylic acid.

Data from competitive solvent extraction of alkali metal cations from water into chloroform by **2** (*2*) are reproduced in Figure 2. Comparison of the solvent extraction results in Figures 1a and 2 reveals a broader effective pH range for **3** than for **2**. Thus alkali metal cations are extracted into the organic phase by **3** even when the aqueous phase is quite acidic. On the other hand, extraction of alkali metal cations with **2** is appreciable only from neutral and basic aqueous phases. Since the ionized form is required for extraction, this difference is readily interpretable in terms of an anticipated greater acidity of a phosphonic acid monoalkyl ester than an analogous carboxylic acid. Maximal metal ion loading of the organic phase is somewhat greater for **3** than **2**.

Although Na^+ is the dominant alkali metal cation extracted by both **2** and **3**, the extraction selectivity changes from $Na^+ \gg K^+ > Rb^+ > Cs^+$ with no detectable Li^+ for **2** to $Na^+ > Li^+$, $K^+ > Rb^+ > Cs^+$ for **3**. The marked increase in facility with which Li^+ is transferred into the organic phase by **3** may be attributed to an innate preference for Li^+ extraction by the phosphonic acid monoalkyl ester unit itself (*8*).

These results demonstrate that even within a common framework of crown ether unit, lipophilic group, and pendant arm length, the identity of the ionizable group does influence both the selectivity and efficiency of alkali metal cation solvent extraction.

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Registry No. **3**, 103958-95-8; **4**, 103958-96-9; **5**, 103958-97-0; **6**, 103958-98-1; **7**, 103958-99-2; **8**, 103959-00-8; **9**, 103959-01-9; **10**, 103959-02-0; Li, 7439-93-2; Na, 7440-23-5; K, 7440-09-7; Rb, 7440-17-7; Cs, 7440-46-2; diethyl *sym*-bis[4(5)-*tert*-butylbenzo]-16-crown-5-oxyethylphosphonate, 103959-03-1; diethyl *sym*-bis[4(5)-*tert*-butylbenzo]-16-crown-5-oxypropylphosphonate, 103959-04-2; diethyl *sym*-bis[4(5)-*tert*-butylbenzo]-16-crown-5-oxybutylphosphonate, 103959-05-3; 2-[*sym*-bis[4(5)-*tert*-butylbenzo]-16-crown-5-oxy]ethanol tetrahydropyranyl ether, 103959-06-4; 2-[*sym*-bis[4(5)-*tert*-butylbenzo]-6-crown-5-oxy]-ethanol, 103959-07-5; *sym*-allyloxybis[4(5)-*tert*-butylbenzo]-16-crown-5, 103959-08-6; 3-[*sym*-bis[4(5)-*tert*-butylbenzo]-16-crown-5-oxy]-1-propanol, 103959-09-7.

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