

Effect of Structural Variation within Lipophilic *N*-(X)sulfonyl Carbamoyl Lariat Ethers on the Selectivity and Efficiency of Competitive Alkali Metal Cation Extraction into Chloroform

Eun Kyung Lee,^{†,‡} Bong Rae Cho,[‡] Hui Hu,[†] and Richard A. Bartsch^{*,†}

Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409-1061, and Department of Chemistry, Korea University, 1-Anamdong, Seoul 136-701, South Korea

Sixteen lipophilic *N*-(X)sulfonyl carbamoyl lariat ethers with polyether ring sizes of 12-crown-4, 14-crown-4, 15-crown-5, and 18-crown-6 are utilized for competitive alkali metal cation extractions from aqueous solutions into chloroform. Variation of the electron-withdrawing properties of X in the series of methyl, phenyl, 4-nitrophenyl, and trifluoromethyl allows the influence of the acidity of the C(O)NHSO₂X group in the side arm upon extraction efficiency and selectivity to be assessed. With X = trifluoromethyl, effective alkali metal cation extractions from acidic, neutral, and basic aqueous solutions are achieved. When the crown ether rings are 14-crown-4, 15-crown-5, and 18-crown-6, selectivities for Li⁺, Na⁺, and K⁺, respectively, are observed. Results are compared with those reported for analogous lariat ether carboxylic acids and phosphonic acid monoethyl esters.

Attachment of a side arm with one or more potential coordination sites to the framework of a macrocyclic polyether (crown ether) produces a lariat ether.^{1,2} The potential of crown ethers as the next generation of specific metal ion-extracting agents was markedly enhanced by the incorporation of a pendant acidic group.^{3–7} Ion exchange of the proton from the acidic function with a metal ion eliminates the need for concomitant transfer of an aqueous-phase anion into the organic phase to preserve electro-neutrality. For potential practical applications that would involve highly hydrophilic chloride, nitrate, or sulfate anions, this factor is of immense importance in terms of extraction efficiency. Applications of proton-ionizable lariat ethers as metal ion-complexing agents have been reviewed.^{8–11}

Although a wide variety of lariat ether carboxylic acids have been reported, only a few proton-ionizable lariat ethers with more acidic pendant groups were described. These include lariat ether phosphonic acid monoalkyl esters,^{12–14} a lariat ether phosphinic acid,¹⁵ and lariat ether phosphoric acid monoalkyl esters.^{16–19} Interpretation of the differences in metal ion complexation behavior of a lariat ether carboxylic acid and a more acidic proton-ionizable lariat ether analogue is hampered by the structural changes that alter both steric and electronic properties of the acidic function.

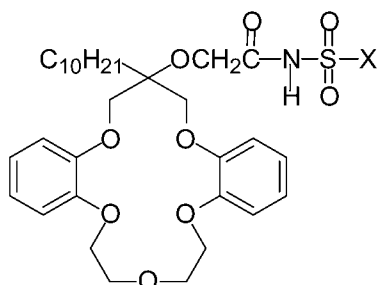
Recently, we described lariat ethers with a novel proton-ionizable group in which the acidity may be “tuned” without inducing significant steric variation.²⁰ For the *N*-(X)sulfonyl carbamoyl lariat ethers **1–4**, only Na⁺ and K⁺ were transferred into the chloroform phase for competitive solvent extractions of aqueous solutions containing Li⁺, Na⁺, K⁺, Rb⁺, and Cs⁺. Although the same Na⁺/K⁺ selectivity was observed for all four extractants, the acidities of the proton-ionizable lariat ethers, as judged from the extraction profiles of chloroform-phase metal loading versus the aqueous-phase pH, decrease in the order **4** > **3** > **1**, **2**. Therefore, it was concluded that variation of X changed the acidity of the proton-ionizable group but had no steric effect at the metal ion coordination site. To provide additional insight into the influence of proton-ionizable group and crown ether ring size

[†] Texas Tech University.

[‡] Korea University.

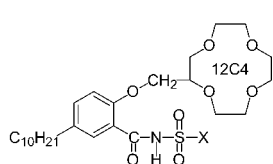
- (1) Gokel, G. W.; Dishong, D. M.; Diamond, C. J. *J. Chem. Soc., Chem. Commun.* **1980**, 1053–1054.
- (2) Gokel, G. W. In *Cation Binding by Macrocycles. Complexation of Cationic Species by Crown Ethers*; Inoue, Y., Gokel, G. W., Eds.; Marcel Dekker: New York, 1990; pp 253–310.
- (3) Helgeson, R. C.; Timko, J. M.; Cram, D. J. *J. Am. Chem. Soc.* **1973**, *95*, 3023–3025.
- (4) Newcomb, M.; Cram, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 1257–1259.
- (5) Nakamura, H.; Takagi, M.; Ueno, T. *Talanta* **1979**, *26*, 921–927.
- (6) Frederick, L. A.; Fyles, T. M.; Gorprasad, M. P.; Whitfield, D. M. *Can. J. Chem.* **1981**, *59*, 1724–1733.
- (7) Bartsch, R. A.; Heo, G. S.; Kang, S. I.; Liu, Y.; Strzelbicki, J. *J. Org. Chem.* **1982**, *47*, 457–460.

- (8) Bartsch, R. A. *Solvent Extr. Ion Exch.* **1989**, *7*, 829–854.
- (9) Brown, P. R.; Bartsch, R. A. In *Inclusion Aspects of Membrane Chemistry*; Atwood, J. L., Ed.; Kluwer Academic Publishers: Boston, 1991; pp 1–57.
- (10) Bartsch, R. A.; Ramesh, V.; Bach, R. O.; Shono, T.; Kimura, K. In *Lithium Chemistry: An Experimental and Theoretical Overview*; Sapsee, A. M., Schleyer, P. v. R., Eds.; Wiley: New York, 1995; pp 393–476.
- (11) Habata, Y.; Akabori, S. *Coord. Chem. Rev.* **1996**, *148*, 97–113.
- (12) Koszuk, J. F.; Czech, B. P.; Walkowiak, W.; Babb, D. A.; Bartsch, R. A. *J. Chem. Soc., Chem. Commun.* **1984**, 1504–1505.
- (13) Pugia, M. J.; Ndip, G.; Lee, H. K.; Yang, I.-W.; Bartsch, R. A. *Anal. Chem.* **1986**, *58*, 2723–2726.
- (14) Walkowiak, W.; Ndip, G.; Bartsch, R. A. *Anal. Chem.* **1999**, *71*, 1021–1026.
- (15) Sachleben, R. A.; Burns, J. H.; Brown, G. M. *Inorg. Chem.* **1988**, *27*, 1787–1790.
- (16) Habata, Y.; Ikeda, M.; Akabori, S. *Tetrahedron Lett.* **1992**, *33*, 3157–3160.
- (17) Habata, Y.; Akabori, S. *Tetrahedron Lett.* **1992**, *33*, 5815–5818.
- (18) Habata, Y.; Ikeda, M.; Akabori, S. *J. Chem. Soc., Perkin Trans. 1* **1992**, 2651–2655.
- (19) Habata, Y.; Ugajin, H.; Akabori, S. *J. Org. Chem.* **1994**, *59*, 676–678.
- (20) Huber, V. J.; Ivy, S. N.; Lu, Jianping; Bartsch, R. A. *J. Chem. Soc., Chem. Commun.* **1997**, 1499–1500.

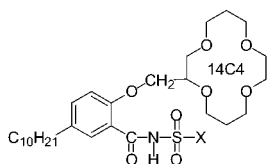


- 1** CH₃
2 C₆H₅
3 C₆H₄-4-NO₂
4 CF₃

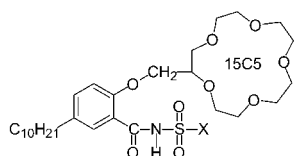
variation upon metal ion complexation, the series of lipophilic *N*-(X)sulfonyl carbamoyl lariat ethers **5–20** was synthesized²¹ in



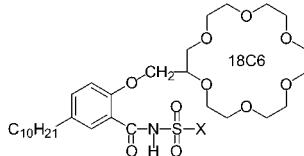
- 5** CH₃
6 C₆H₅
7 C₆H₄-4-NO₂
8 CF₃



- 9** CH₃
10 C₆H₅
11 C₆H₄-4-NO₂
12 CF₃



- 13** CH₃
14 C₆H₅
15 C₆H₄-4-NO₂
16 CF₃



- 17** CH₃
18 C₆H₅
19 C₆H₄-4-NO₂
20 CF₃

which X = methyl, phenyl, 4-nitrophenyl, and trifluoromethyl and the crown ether ring size is systematically varied from 12-crown-4 to 14-crown-4 to 15-crown-5 and 18-crown-6. The metal ion complexation behavior for this series of proton-ionizable lariat ethers was evaluated by competitive solvent extraction of alkali metal cations from aqueous solutions into chloroform. These results are now reported and compared with published alkali metal cation extraction selectivities and efficiencies for analogous lariat ether carboxylic acids and phosphonic acid monoethyl esters.

EXPERIMENTAL SECTION

Reagents. Analytical-grade LiCl (99+%), RbCl (99+%), and CsCl (99.8%) were purchased from Alfa Aesar Chemicals. Analytical-grade NaCl (99.8%) and KCl (99.9%) were obtained from Mallinckrodt. Anhydrous LiOH was purchased from Fisher Scientific. The alkali metal salts were dried at 140 °C for 48 h

prior to their use in solution preparation. Analytical-grade HCl (1.000 ± 0.002 M) and chloroform were EM Science chemicals. Before use, the chloroform was shaken with deionized, distilled water for 15 min to saturate it with water and remove the ethanol stabilizer. Deionized, distilled water was prepared by passing distilled water through three Barnstead model D8922 combination ion-exchange cartridges in series.

The *N*-(X)sulfonyl carbamoyl lariat ethers **5–20** were prepared from the corresponding lariat ether carboxylic acids²³ by the procedures reported for the preparation of **1–4**. Details of the synthesis and characterization of **5–20**²¹ will be reported separately.

Apparatus and Instrumentation. The 15-mL, metal-free, conical polypropylene centrifuge tubes with polypropylene caps were purchased from Elkay. Hamilton GasTight syringes were used to transfer samples of the aqueous and organic solutions. A Fisher Vortex Genie 2 mixer and Clay Adams Safety-Head centrifuge were used to agitate samples and separate layers in the water–chloroform mixtures, respectively. The aqueous-phase pH was measured with a Fisher Accumet model AR 25 pH meter and a Corning model X-EI glass body combination electrode. A Dionex model DX-120 ion chromatograph with a self-regenerating cation suppressor and an IonPac CS12A column were used to determine the alkali metal cation concentrations in the strippant.

Solvent Extraction Procedure. Into the centrifuge tube were added 2.00 mL of 5.0 mM proton-ionizable lariat ether solution in chloroform and 1.00 mL of a solution of NaCl, KCl, RbCl, and CsCl (1.00 M in each). Then 1.00 mL of a LiCl–LiOH solution with [Li⁺]_{total} = 1.00 M was added. (In the case of ligands **8**, **12**, **16**, and **20**, 1.00 mL of a LiCl–HCl solution with [Li⁺]_{total} = 1.00 M was utilized in place of the LiCl–LiOH solution to provide the acidic aqueous solutions for the extractions.) The two-phase mixture was vigorously shaken with a vortex mixer for 5 min and then centrifuged for 5 min. A 1.50-mL sample of the organic phase was removed and transferred to a new centrifuge tube. The residual organic phase in the original centrifuge tube was removed, and the equilibrium pH of the aqueous phase was measured. To the organic phase sample, 3.00 mL of 0.10 M HCl solution was added and the mixture was vigorously shaken with a vortex mixer for 5 min and centrifuged for 5 min. A 1.00-mL sample of the aqueous strippant solution was diluted in a 10.0-mL volumetric flask with deionized, distilled water, and the alkali metal cation concentration of the resulting solution was determined by ion chromatography.

RESULTS AND DISCUSSION

Solvent Extraction of Alkali Metal Cations from Aqueous Solutions into Chloroform by Lipophilic *N*-(X)sulfonyl Carbamoyl Lariat Ethers. In earlier studies of alkali metal cation solvent extraction by lariat ether carboxylic acids, it was demonstrated that the efficiencies and selectivity orders for competitive extractions may be quite different from expectations based upon the results of single ion extractions.²² Therefore, competitive alkali metal cation extractions were utilized in this investigation.

Data from competitive solvent extractions of alkali metal cations from aqueous solutions into chloroform by the *N*-methanesulfonyl,

(22) Strzelbicki, J.; Bartsch, R. A. *Anal. Chem.* **1981**, *53*, 1894–1899.

(23) Walkowiak, W.; Kang, S. I.; Stewart, L. E.; Ndip, G.; Bartsch, R. A. *Anal. Chem.* **1990**, *62*, 2022–2026.

(21) Hu, H. M.S. Thesis, Texas Tech University, 2001, pp 76–106.

Table 1. Selectivity and Efficiency of Competitive Alkali Metal Cation Extraction into Chloroform by *N*-(X)sulfonyl Carbamoyl Lariat Ethers and Lariat Ether Carboxylic Acid and Phosphonic Acid Monoethyl Ester Analogues

compd	ring size	maximum metals loading, % (pH) ^a	pH _{1/2} ^b	selectivity order and selectivity coefficient ^c
5	12-crown-4	97 (11.6)	9.0	K ~ Na ~ Rb > Cs ~ Li 1.1 1.4 1.8 1.9
6	12-crown-4	97 (12.0)	9.8	Na ~ K ~ Rb > Li ~ Cs 1.1 1.4 1.7 1.8
7	12-crown-4	100 (10.0)	7.8	Na ~ K > Rb ~ Li ~ Cs 1.2 1.7 2.0 2.2
8	12-crown-4	99 (9.6)	5.3	Na ~ K ~ Rb ~ Cs > Li 1.1 1.3 1.4 2.3
21^d	12-crown-4	90 (10.0)	(9.9) ^e	Li > Na > K > Rb, Cs 1.5 2.2 3.0
22^f	12-crown-4	96 (9.0)	(6.0) ^e	Li > Na > K, Rb, Cs 1.9 2.9
9	14-crown-4	98 (10.9)	8.9	Li > Na >> K > Rb, Cs 3.8 60 ND ^g
10	14-crown-4	96 (10.7)	8.6	Li > Na >> K > Rb, Cs 3.3 78 ND ^g
11	14-crown-4	99 (9.1)	7.1	Li > Na >> K > Rb, Cs 3.4 81 ND ^g
12	14-crown-4	100 (10.6)	4.2	Li >> Na >> K, Rb, Cs 18.6 ND ^g
21^d	14-crown-4	90 (10.0)	(9.7) ^e	Li >> Na >> K, Rb, Cs 17 ND ^g
22^f	14-crown-4	97 (9.0)	(6.6) ^e	Li > Na > K, Rb > Cs 6.2 9.6 13
13	15-crown-5	97 (10.5)	8.1	Na > K > Rb > Cs > Li 2.1 7.2 21 91
14	15-crown-5	97 (10.5)	8.0	Na > K > Rb > Cs > Li 3.2 10 26 53
15	15-crown-5	99 (9.9)	6.9	Na > K > Rb > Cs > Li 3.3 10 23 48
16	15-crown-5	94 (10.2)	3.8	Na > K > Rb > Cs > Li 4.2 11 25 62
21^d	15-crown-5	94 (10.0)	(8.3) ^e	Na > K > Rb > Li > Cs 2.1 4.3 5.5 6.7
22^f	15-crown-5	97 (9.0)	(6.7) ^e	Na > K > Rb > Li, Cs 2.3 3.6 9.0
17	18-crown-6	97 (10.5)	6.6	K > Rb >> Cs ~ Na > Li 2.0 10 12 4 ^h
18	18-crown-6	96 (10.5)	6.5	K > Rb >> Na ~ Cs > Li 2.0 12 13 N
19	18-crown-6	99 (9.9)	4.9	K > Rb >> Na > Cs > Li 2.1 11 12 6 ^h
20	18-crown-6	99 (10.0)	1.8	K > Rb >> Na > Cs > Li 2.3 9.2 12 51
21^d	18-crown-6	100 (10.0)	(7.3) ^e	K > Rb > Cs > Na > Li 3.0 4.6 13 64
22^e	18-crown-6	99 (9.0)	(5.0) ^e	K > Rb > Cs > Li, Na 1.7 2.1 ND ^g

^a pH of maximum metal loading in the range of pH 9–12. ^b Aqueous-phase pH at which half of the total metal loading of the organic phase is achieved. ^c Ratio between the organic-phase concentrations of the best extracted alkali metal cation and the indicated second alkali metal cation species at maximum metal loading in the range of pH 9–12. ^d Reference 23. ^e Estimated from graph given in the ref 23. ^f Reference 14. ^g ND, not detected.

N-benzenesulfonyl, *N*-(4-nitrobenzene)sulfonyl, and *N*-trifluoromethanesulfonyl carbamoyl lariat ethers are shown in Figures 1–4, respectively. In Table 1, the selectivity orders, selectivity

coefficients, and maximal metal loadings for this series of extractants are presented. (The selectivity coefficient is defined as the ratio between the organic-phase concentration of the best

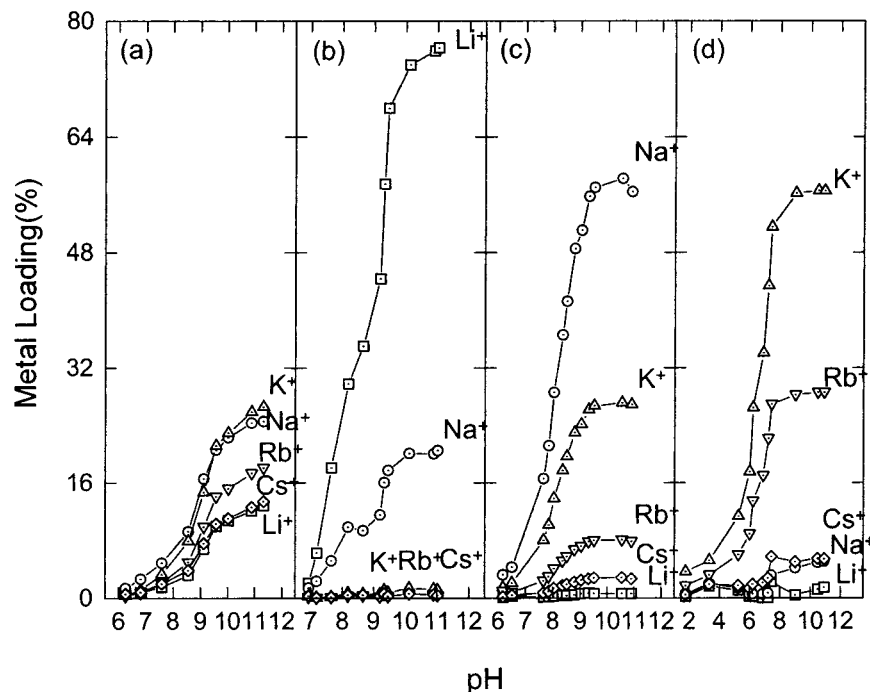
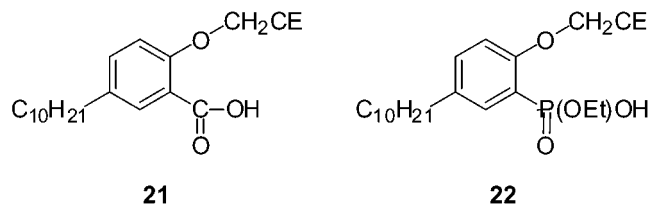


Figure 1. Metal loading of the organic phase vs the pH of the aqueous phase for competitive alkali metal cation extraction into chloroform by *N*-methanesulfonyl carbamoyl lariat ethers with ring sizes of (a) 12-crown-4, **5**; (b) 14-crown-4, **9**; (c) 15-crown-5, **13**; and (d) 18-crown-6, **17**.

extracted alkali metal cation and the indicated second alkali metal species at the pH of maximum metals loading between 9 and 12.) For comparison, reported data for analogous lariat ether carboxylic acids²³ and phosphonic acid monoethyl esters¹⁴ (**21** and **22**, respectively, with CE = crown ether) are included.



Effect of Proton-Ionizable Group on Extraction Efficiency.

From the data presented in Table 1, high extraction efficiencies are noted for *N*(X)sulfonyl carbamoyl lariat ethers **5–20** with maximal metal loadings of 94–100% calculated on the basis of 1:1 complex formation.

Also listed in Table 1 are values for $pH_{1/2}$, the aqueous-phase pH at which half of the maximum metal loading of the organic phase is achieved. The $pH_{1/2}$ values allow the functional acidities of proton-ionizable groups in the ligands to be compared. Although the $pH_{1/2}$ value for a proton-ionizable lariat ether is controlled by both the acidity of the pendant group and the strength of metal ion binding by the crown ether ring, the former can be compared for ligands with the same ring size. As can be seen from the data in Table 1, acidity of the C(O)NHSO₂X group increases in the order X = methyl < phenyl < 4-nitrophenyl < trifluoromethyl as is expected from their electron-withdrawing abilities.²⁴ Comparison with data from the literature for analogous lariat ether carboxylic

acids²³ and phosphonic acid monoethyl esters¹⁴ gives an expanded acidity ordering of CO₂H < C(O)NHSO₂CH₃ ~ C(O)NHS(C₆H₅) < C(O)NHSO₂C₆H₄-4-NO₂ < P(O)(OC₂H₅)OH < C(O)NHSO₂CF₃.

Variation of the X group in the lipophilic *N*(X)sulfonyl carbamoyl lariat ether strongly influences the effective pH range for the extractant. Thus with X = methyl, phenyl, and 4-nitrophenyl and crown ether ring sizes of 12-crown-4, 14-crown-4, and 15-crown-5, effective alkali metal cation extraction takes place only from basic aqueous solutions (Figures 1–3). With the same X groups and a crown ether ring size of 18-crown-6, extraction takes place from weakly acidic and neutral aqueous solutions as well (Figures 1–3). On the other hand, with X = trifluoromethyl, effective alkali metal cation extraction is achieved from acidic, neutral, and basic aqueous solutions for all crown ether ring sized (Figure 4).

The crown ether ring size also influences the effective pH range for a given X group in the *N*(X)sulfonyl carbamoyl lariat ether extractants. In Figure 5 is shown the combined metal loading of the chloroform phase as a function of the aqueous-phase pH for competitive solvent extraction of alkali metal cations by lipophilic *N*-benzenesulfonyl carbamoyl lariat ethers **6**, **10**, **14**, and **18**. As can be seen, for the same pendant acidic function, the efficiency with which the ligand extracts metal ions from more acidic solutions increases as the crown ether ring size is enlarged: 12-crown-4 < 14-crown-4 < 15-crown-5 < 18-crown-6. Presumably, this results from stronger metal ion binding as the size of the crown ether and the number of oxygens in the crown ether ring are increased.

Effect of Ring Size Variation on Extraction Selectivity. The lipophilic *N*-methanesulfonyl carbamoyl lariat ethers **5**, **9**, **13**, and **17** provide a series of ionophores in which the crown ether rings are 12-crown-4, 14-crown-4, 15-crown-5, and 18-crown-6, respectively. The selectivity orders for **9**, **13**, and **17** are as follows:

(24) March, J. *Advanced Organic Chemistry. Reactions, Mechanisms, and Structure*, 3rd ed.; Wiley: New York, 1985; pp 237–250.

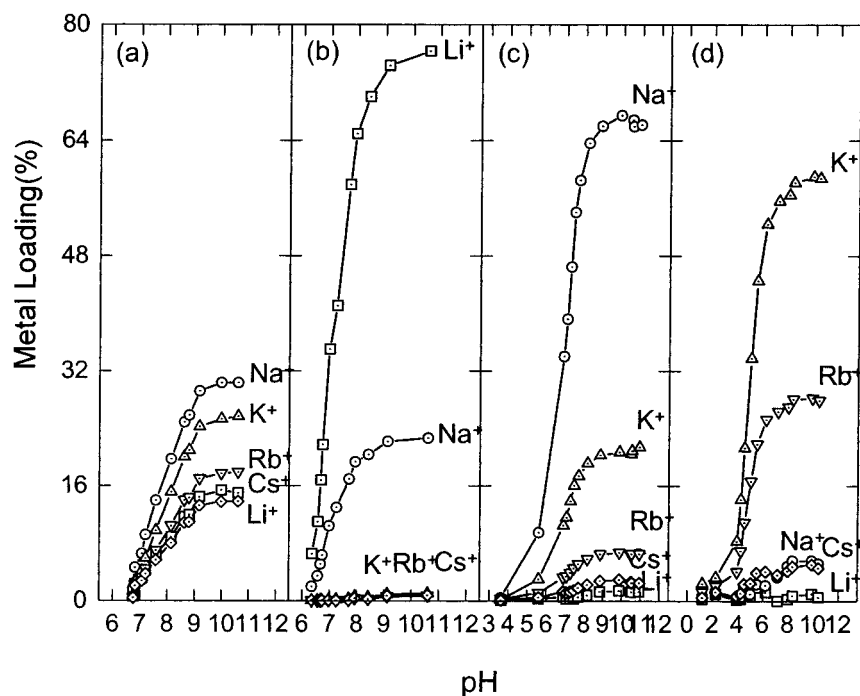


Figure 2. Metal loading of the organic phase vs the pH of the aqueous phase for competitive alkali metal cation extraction into chloroform by *N*-benzenesulfonyl carbamoyl lariat ethers with ring sizes of (a) 12-crown-4, **6**; (b) 14-crown-4, **10**; (c) 15-crown-5, **14**; and (d) 18-crown-6, **18**.

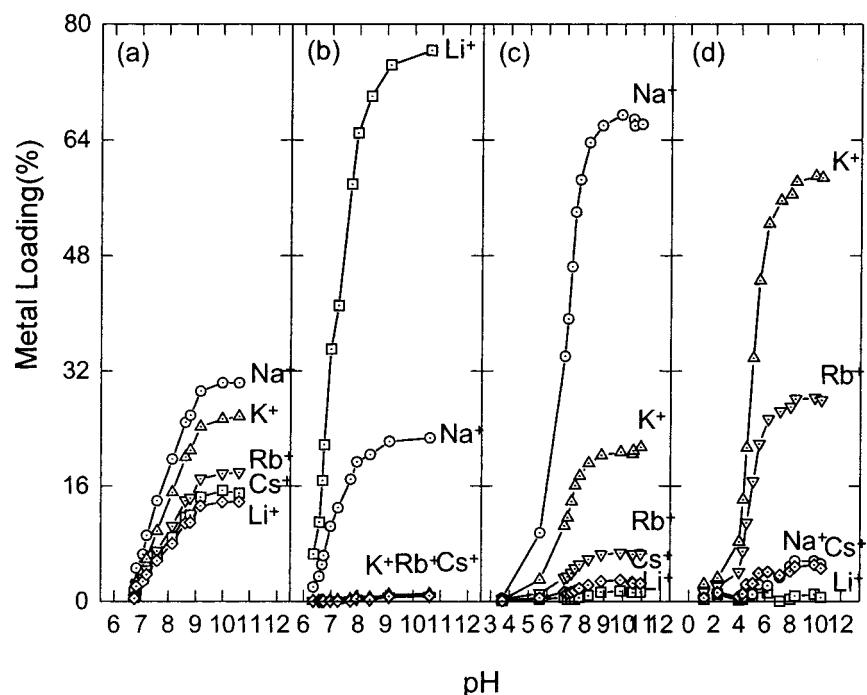


Figure 3. Metal loading of the organic phase vs the pH of the aqueous phase for competitive alkali metal cation extraction into chloroform by *N*-(4-nitrobenzene)sulfonyl carbamoyl lariat ethers with ring sizes of (a) 12-crown-4, **7**; (b) 14-crown-4, **11**; (c) 15-crown-5, **15**; and (d) 18-crown-6, **19**.

$\text{Li}^+ > \text{Na}^+$, with undetectable K^+ , Rb^+ , and Cs^+ ; $\text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+ > \text{Li}^+$; and, $\text{K}^+ > \text{Rb}^+ > \text{Na}^+, \text{Cs}^+ > \text{Li}^+$, respectively (Figure 1). Thus, each ligand exhibits an extraction selectivity for the alkali metal cation that provides the best fit with the crown ether ring,²³ which suggests formation of nesting complexes²⁵ in which the metal ion is included within the polyether ring. On the

other hand, for ionophore **5**, in which the 12-crown-4 ring is too small to accommodate even Li^+ , the extraction selectivity order is $\text{Na}^+, \text{K}^+ > \text{Rb}^+ > \text{Cs}^+ > \text{Li}^+$, which suggests formation of perching complexes.²⁵

Very similar effects of the crown ether ring size on the extraction selectivity order are noted for the series of lipophilic *N*-benzenesulfonyl carbamoyl lariat ethers **6**, **10**, **14**, and **18** (Figure 2), *N*-(4-nitrobenzene)sulfonyl carbamoyl lariat ethers **7**,

(25) Cram, D. J.; Trueblood, K. N. In *Host–Guest Complex Chemistry*; Vögtle, F., Weber, E., Eds.; Springer: New York, 1985; pp 125–128.

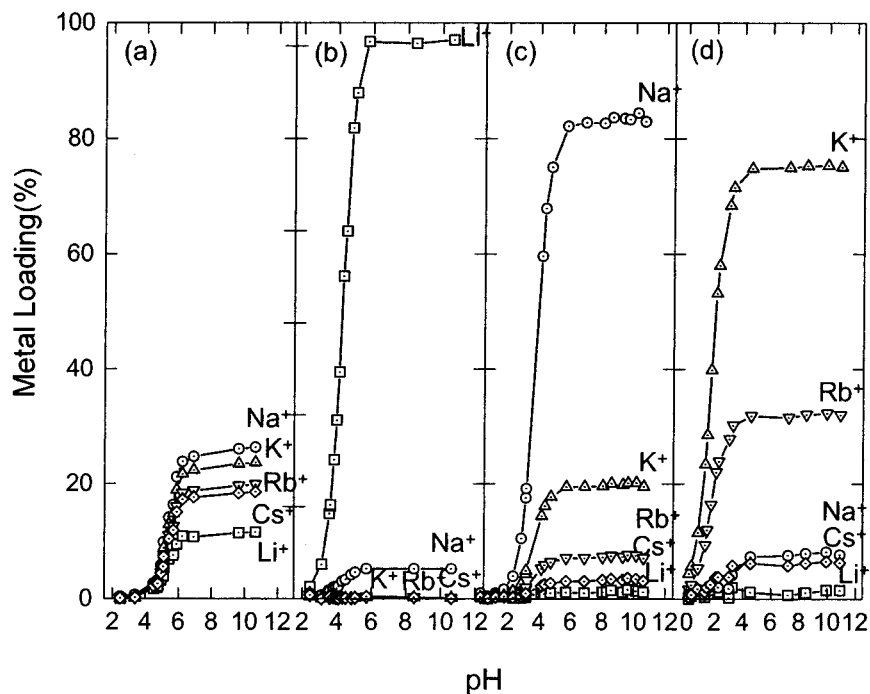


Figure 4. Metal loading of the organic phase vs the pH of the aqueous phase for competitive alkali metal cation extraction from aqueous solutions into chloroform by *N*-trifluoromethanesulfonyl carbamoyl lariat ethers with ring sizes of (a) 12-crown-4, **8**; (b) 14-crown-4, **12**; (c) 15-crown-5, **16**; and (d) 18-crown-6, **20**.

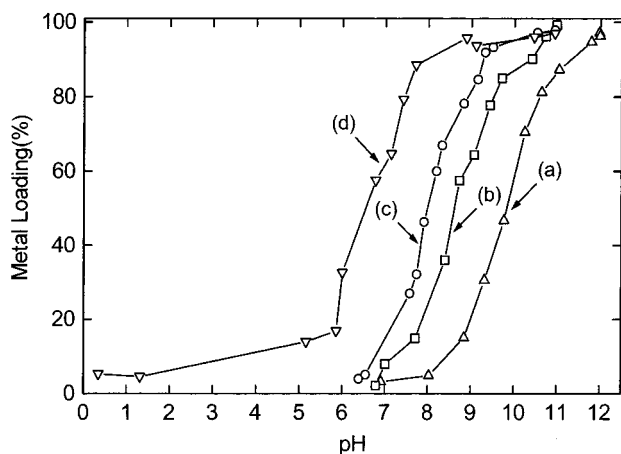


Figure 5. Combined metal loading of the organic phase vs the pH of the aqueous phase for competitive alkali metal cation extraction into chloroform by *N*-benzenesulfonyl carbamoyl lariat ethers with ring sizes of (a) 12-crown-4, **6**; (b) 14-crown-4, **10**; (c) 15-crown-5, **14**; and (d) 18-crown-6, **18**.

11, **15**, and **19** (Figure 3), and *N*-trifluoromethanesulfonyl carbamoyl lariat ethers **8**, **12**, **16**, and **20** (Figure 4). However, the Li^+/Na^+ selectivity of 18.6 obtained with the *N*-trifluoromethanesulfonyl carbamoyl 14-crown-4 **12** is much higher than the ratios of 3.3–3.8 observed with analogues in which X = methyl, phenyl, and 4-nitrophenyl. The high Li^+/Na^+ selectivity for **12** was reproducible and is even higher than that reported for the lipophilic lariat ether carboxylic acid **21** with the same 14-crown-4 ring.²³ For these two extractants with high Li^+/Na^+ selectivity, the *N*-trifluoromethanesulfonyl carbamoyl 14-crown-4 ligand **12** is more versatile since it effectively extracts alkali metal cations from acidic and neutral, as well as basic, aqueous solutions.

Effect of the Proton-Ionizable Group on Extraction Selectivity. Comparison of the selectivity order and selectivity coefficient data for the *N*-(X)sulfonyl carbamoyl lariat ethers **5–20** with those published for analogous lariat ether carboxylic acids **21**²³ and lariat ether phosphonic acids **22**¹⁴ with CE = 12-crown-4, 14-crown-4, 15-crown-5, and 18-crown-6 is instructive. For polyether ring size of 18-crown-6, 15-crown-5, and 14-crown-4, the best and second-best extracted alkali metal ions remain the same as the identity of the proton-ionizable group in the side arm is varied (Table 1). With CE = 18-crown-6, these metal ions are K^+ and Rb^+ and there is only a very modest influence of the proton-ionizable group identity on the K^+/Rb^+ selectivity, which varies in the range of 1.7–3.0. A similar situation is noted when CE = 15-crown-5 for which the metal ions are Na^+ and K^+ with Na^+/K^+ selectivities of 2.1–4.2.

The slight influence of the pendant proton-ionizable group identity on metal ion extraction selectivity observed for extractants with 18-crown-6 and 15-crown-5 rings changes markedly for ligands with smaller crown ether rings. With CE = 14-crown-4, the relative amounts Li^+ and Na^+ extracted are found to be strongly affected by variation of the proton-ionizable group. Thus, high Li^+/Na^+ selectivities of 17 and 18.6 are observed with the lariat ether carboxylic acid **21** and *N*-trifluoromethanesulfonyl carbamoyl lariat ether **12**, respectively. The Li^+/Na^+ selectivity decreases to 6.2 for lariat ether phosphonic acid monoethyl ester **22** and then diminishes further to 3.3–3.8 for the *N*-(X)sulfonyl carbamoyl lariat ethers **9–11**. Comparison of the extraction profiles for the *N*-(X)sulfonyl carbamoyl compounds **9**, **10**, and **12** shown in Figures 1, 2, and 4 with those reported for the corresponding carboxylic acid and phosphonic acid monoethyl ester (**21** and **22**, respectively, with CE = 14-crown-4) indicates an increasing acidity order of **9** ~ **10** ~ **21** < **22** < **12**. Thus, factors

other than the acidity of the pendant proton-ionizable group appear to control the Li^+/Na^+ selectivity.

The relatively low extraction selectivities noted for ligands **5–8** and **21** and **22** with CE = 12-crown-4 are attributed to a polyether ring size that is too small to accommodate even Li^+ . Although both the lariat ether carboxylic and phosphonic acid monoethyl ester exhibit weak Li^+ extraction selectivity, the *N*-(X)sulfonyl carbamoyl lariat ethers **5–8** show weak extraction selectivity for Na^+ and K^+ . This indicates an appreciable influence of the nature of the pendant proton-ionizable group on both the extraction selectivity and the selectivity order when perching complexes are formed.

CONCLUSIONS

Lipophilic *N*-(X)sulfonyl carbamoyl lariat ethers **5–20** effectively extract alkali metal cations from aqueous solutions into chloroform. The effective pH range of the extractant is a function

of the X group and the size of the macrocyclic ring. The extraction selectivity order is controlled by the size of the polyether ring with Li^+ , Na^+ , and K^+ as the best extracted cations with 14-crown-4, 15-crown-5, and 18-crown-6 rings, respectively. Within this series of ionophores, the 14-crown-4 compound **12** has the highest Li^+ selectivity yet reported for a proton-ionizable lariat ether.

ACKNOWLEDGMENT

The research conducted at Texas Tech University was supported by the Division of Chemical Sciences, Biosciences, and Geosciences of the Office of Basic Energy Sciences of the U.S. Department of Energy (Grant DE-FG03-94-ER14416).

Received for review December 13, 2001. Accepted February 26, 2002.

AC015734O