

Metal Ion Separations with Proton-Ionizable Lariat Ethers and Their Polymers

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The preparation of novel and specific organic complexing agents may lead to the development of new separation systems for aqueous metal ions. Thus the introduction of highly lipophilic oximes led to the current utilization of these compounds as commercial extractants for the hydrometallurgy of nonferrous metals.

Crown ethers (macrocyclic polyethers) have been employed in the laboratory-scale solvent extraction of alkali-metal, alkaline-earth, and other metal cations into organic phases (Pedersen 1967; Takeda 1984; McDowell 1988). Attachment of side arms to crown ethers gives lariat ethers (Gokel and Trafton 1990). The presence of one or more potential coordination sites in the side arm of the lariat ether may produce substantial changes in the selectivity and efficiency of metal ion complexation.

The potential of crown ethers as the next generation of specific extracting agents for aqueous metal ions was markedly enhanced by the introduction of lariat ethers which bear pendent proton-ionizable groups (Helgeson, Timko, and Cram 1973; Bartsch et al. 1982). It has been demonstrated that concomitant transfer of an aqueous phase anion into the organic medium is not required for metal ion extraction (Strzelbicki and Bartsch 1981). This factor is of immense importance to potential practical applications of these proton-ionizable crown ethers in which the common, hard, aqueous phase anions (chloride, nitrate, and sulfate) would be involved. The combination of ion binding cavities possessing fixed dimensions with pendent proton-ionizable groups creates novel bifunctional ligands for metal ion complexation. Another advantage of proton-ionizable lariat ethers is the ease with which extracted metal ions may be stripped from the

organic phase by shaking with aqueous mineral acid. Thus both metal ion extraction and stripping are facilitated by the pendent proton-ionizable groups.

Most of the hazardous metal ion species in the Hanford Site tank wastes are members of the alkali-metal, alkaline-earth, lanthanide, and actinide families. These hard metal ion species prefer association with hard donor atoms, such as oxygens. Therefore, crown and lariat ethers are well-suited for complexation with such metal ion species.

The synthesis of several series of proton-ionizable lariat ethers was undertaken to investigate the influence of structural change within the ligand upon the selectivity and efficiency of solvent extractions involving alkali-metal and alkaline-earth cations (Bartsch 1989). Structural variation within the complexing agents includes: 1) the identity of the proton-ionizable group; 2) the ring size and rigidity of the polyether ring; 3) the length of the "arm" which connects the proton-ionizable group to the polyether framework; and 4) the attachment site and nature of the lipophilic group which is necessary to retain the ionized lariat ether in the organic phase during solvent extraction. For solvent extraction of alkali-metal cations, the relationship between the diameters of the metal ion species and the cyclic polyether cavity as well as preorganization of the binding site (Cram 1986) are found to exert a strong influence upon the selectivity and efficiency of competitive extraction processes (Bartsch 1989).

Proton-ionizable lariat ethers are also effective carriers for metal ion transport across liquid membranes (Bartsch et al. 1987). Transport of metal ions from a source aqueous phase through an organic solution of the carrier and into a receiving aqueous phase is coupled with back-transport of

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protons. Thus a pH gradient may be used to drive metal ion transport, even against the metal ion concentration gradient. The influence of structural variation within the carrier upon the selectivity and efficiency of competitive alkali-metal and alkaline-earth cation transport has been evaluated for several liquid membrane configurations. These include bulk chloroform and toluene membranes as well as liquid surfactant (emulsion) membranes and polymer-supported (Bartsch and Strzelbicki 1991; Bartsch, Strzelbicki, and Strzelbicka 1991) liquid membranes. Often, but not in all cases, there is a parallel between the effect of structural change within the ligand in liquid membrane transport and solvent extraction systems.

Very recently we have incorporated proton-ionizable lariat ethers with two benzo group substituents into novel resins by condensation polymerization with formaldehyde in formic acid (Hayashita et al. 1990). These resins differ from customary ion-exchange resins in that they possess cyclic polyether binding sites for metal ions as well as ion exchange sites. The kinetics of both alkali-metal cation sorption by these water-insoluble resins and stripping are markedly improved over those for polymers prepared from neutral crown ethers (Blasius et al. 1974). Furthermore cation complexation does not depend upon the anion identity. The selectivity and efficiency of alkali metal cation sorption by these new resins is strongly influenced by the structure of the proton-ionizable lariat ether monomer from which the resin was synthesized (Hayashita et al. 1990; Hayashita et al. 1991b). These resins have also been utilized in selective column concentration of alkali-metal cations from dilute aqueous solutions (Hayashita et al. 1991a). Due to their robust constitution and high metal ion loading capacities, such resins possess excellent potential for practical application.

Acknowledgment

This research has been supported primarily by the Division of Chemical Sciences of the Office of Basic Energy Sciences of the U.S. Department of Energy. Support from the Advanced Technology Program of the State of Texas is also acknowledged.

References

- Bartsch, R. A. 1989. "Effects of Structural Variation Within Proton-Ionizable Crown Ethers upon the Selectivity and Efficiency of Solvent Extraction of Alkali Metal and Alkaline Earth Cations." *Solv. Ext. Ion Exch.* 7:829-854.
- Bartsch, R. A., W. A. Charewicz, S. I. Kang, and W. Walkowiak. 1987. "Proton-Coupled Transport of Alkali Metal Cations Across Liquid Membranes by Ionizable Crown Ethers." In *Liquid Membranes. Theory and Applications*, ACS Symposium Series 347, eds. R. D. Noble and J. D. Way, pp. 86-97. American Chemical Society, Washington, D.C.
- Bartsch, R. A., G. S. Heo, S. I. Kang, Y. Liu, and J. Strzelbicki. 1982. "Synthesis and Acidity of Crown Ethers with Pendant Carboxylic Acid Groups." *J. Org. Chem.* 47:457-460.
- Bartsch, R. A., and J. Strzelbicki. 1991. "Proton-Coupled Transport of Alkali Metal Cations Across Polymer-Supported Liquid Membranes by a Lipophilic Crown Ether Carboxylic Acid." Abstract I&EC 11, 201st National Meeting of the American Chemical Society, Atlanta, Georgia, April 1991.
- Bartsch, R. A., J. Strzelbicki, and B. Strzelbicka. 1991. "Influence of Structural Variation Within Lipophilic, Proton-Ionizable Crown Ether Carriers upon Proton-Coupled Transport of Alkali Metal Cations Across Polymer-Supported Liquid Membranes." Abstract I&EC 75, 201st National Meeting of the American Chemical Society, Atlanta, Georgia, April 1991.
- Blasius, E., W. Adrian, K.-P. Janzen, and G. Klautke. 1974. "Darstellung und Eigenschaften von Austauschern auf Basis von Kronenverbindungen." *J. Chromatogr.* 96:89-97.
- Cram, D. J. 1986. "Preorganization-From Solvents to Spherands." *Angew. Chem., Int. Ed. Engl.* 25:1039-1057.
- Gokel, G. W., and J. E. Trafton. 1990. "Cation Binding by Lariat Ethers." In *Cation Binding by Macrocycles*, eds. Y. Inoue, G. W. Gokel, pp. 253-310. Dekker, New York.

Hayashita, T., M.-J. Goo, J. C. Lee, J. S. Kim, J. Krzykawski, and R. A. Bartsch. 1990. "Selective Sorption of Alkali-Metal Cations by Carboxylic Acid Resins Containing Acyclic or Cyclic Polyether Units." *Anal. Chem.* 62:2283-2287.

Hayashita, T., J. H. Lee, S. Chen, and R. A. Bartsch. 1991a. "Selective Column Concentration of Alkali-Metal Cations with a Crown Ether Carboxylic Acid Resin." *Anal. Chem.*, 63:1844-1847.

Hayashita, T., M.-J. Goo, J. S. Kim, and R. A. Bartsch. 1991b. "Effect of Structural Variation Within *Sym*-(R)Dibenzo-16-crown-5-oxyacetic Acid Resins upon the Selectivity and Efficiency of Alkali Metal Cation Sorption." *Talanta*, in press.

Helgeson, R. C., J. M. Timko, and D. J. Cram. 1973. "Structural Requirements for Cyclic Ethers to Complex and Lipophilize Metal Cations or α -Amino Acids." *J. Am. Chem. Soc.* 95:3023-3025.

McDowell, W. J. 1988. "Crown Ether as Solvent Extraction Reagents: Where Do We Stand?" *Sep. Sci. Technol.* 23:1251-1268.

Pedersen, C. J. 1967. "Cyclic Polyethers and Their Complexes with Metal Salts." *J. Am. Chem. Soc.* 89:7017-7026.

Strzelbicki, J., and R. A. Bartsch. 1981. "Extraction of Alkali Metal Cations from Aqueous Solutions by a Crown Ether Carboxylic Acid." *Anal. Chem.* 53:1894-1899.

Takeda, Y. 1984. "The Solvent Extraction of Metal Ions by Crown Compounds." *Top. Curr. Chem.* 121:1-38.



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