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PROGRESS REPORT

Novel Macrocyclic Carriers for Proton-Coupled Liquid Membrane Transport

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I. ABSTRACT

The objective of our research program is to elucidate the chemical principles which are responsible for the cation selectivity and permeability of liquid membranes containing macrocyclic carriers. Several new macrocyclic carriers were synthesized during the last three year period, including selenium-containing macrocycles, new crown-4 structures, and several new crown structures containing nitrogen based heterocycles as substituents in the principal macrocyclic ring. The cation binding properties of these macrocycles were investigated by potentiometric titration, calorimetric titration, solvent extraction, and NMR techniques. In addition, hydrophobic macrocycles were incorporated into dual hollow fiber membrane systems to investigate their membrane performance, especially in the proton-coupled transport mode. It was found that the dual hollow fiber system maintains the cation selectivity and permeability of supported liquid membranes, while enhancing membrane stability. The diffusion limited transport model was expanded to account for membrane solvent effects. Furthermore, Eu^{2+} transport was found to be similar to that of strontium and much higher than that of the lanthanides, in supported liquid membrane systems.

II. RESEARCH RESULTS FOR PERIOD 1 DEC 1988 - 31 MAY 1991

II.A. SUMMARY OF ACTIVITY

The following table summarizes activities during the reporting period with respect to publication of results, presentation of results, and personnel:

1.	Number of refereed papers published	20
2.	Number of refereed papers in press or submitted	5
3.	Number of oral presentations	34

4.	Number of undergraduate students involved on project	8
5.	Number of graduate students involved on project	5
6.	Number of post-doctoral fellows involved on project	6
7.	Number of faculty involved on project	4

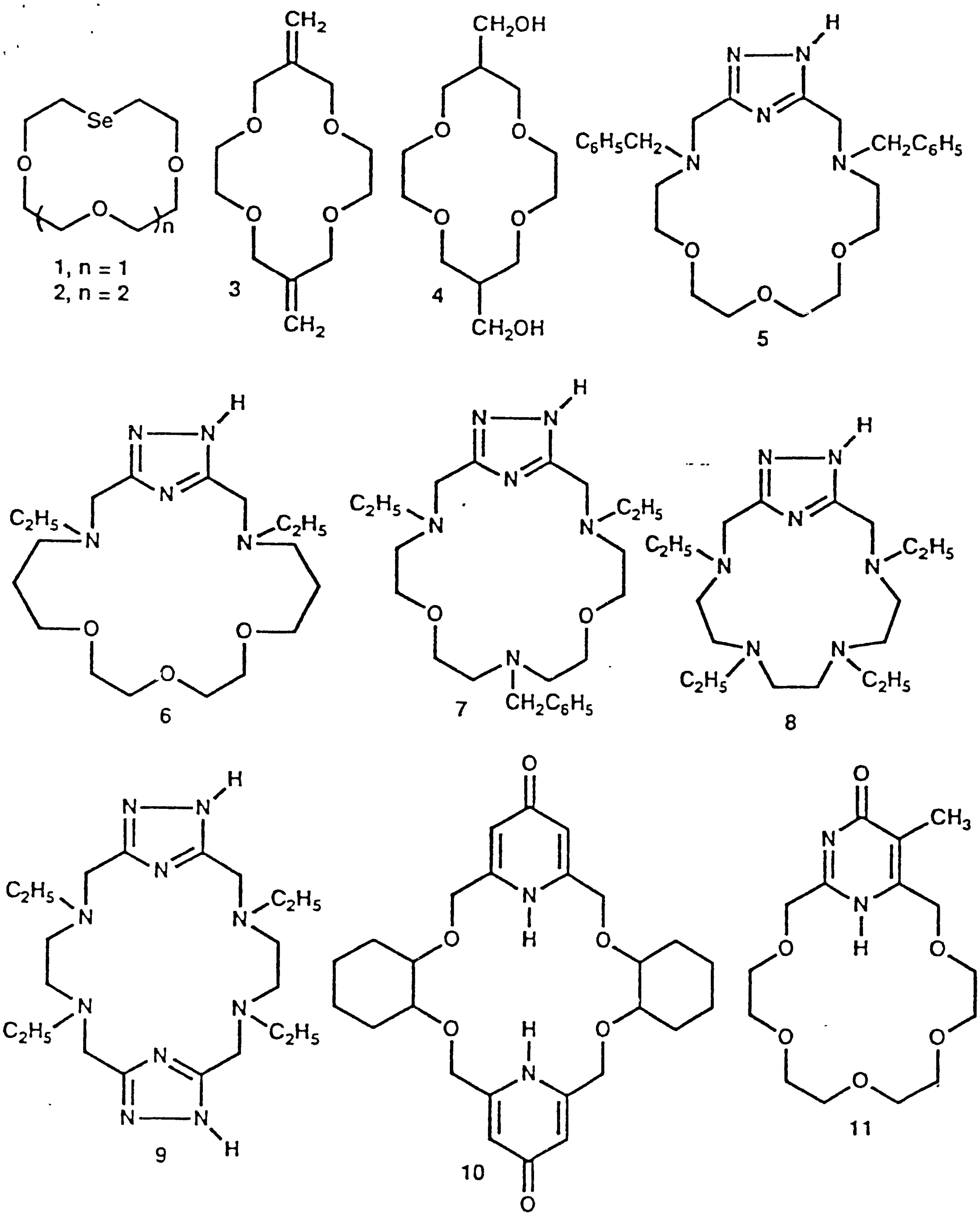
II.B. LIGAND SYNTHESES

New proton-ionizable and other ligands prepared during the past three years are shown in Figure 1. Selenium compounds **1** and **2** were synthesized in an effort to have ligands that would transport silver and lead at a faster rate than comparable sulfur-containing ligands. Transport rates for silver and lead by **2** were not significantly higher and the synthesis was very difficult so that no further work will be done with these selenium-containing compounds. Compound **4** (prepared from 3) was prepared to complex and transport lithium ions. More work will be done on these types of macrocycles. Compounds **5** - **9** have lipophilic groups which enable them to be fully tested in liquid membranes. Compounds **9** and **10** have two proton-ionizable groups and should be able to transport divalent cations without the need for counter anions. Compound **11** is the first member of a new class of proton-ionizable ligands. Other members of this series are being prepared, or are proposed in the accompanying proposal.

II.C. MACROCYCLE CHARACTERIZATION

Several of the new macrocycles were characterized for their pK_a values and cation binding constants. As an example of the results obtained, a study was performed on the effect of substitution of sulfur for oxygen in the macrocyclic ring, including proton-ionizable macrocycles, on selectivity among heavy metal cations. Log K, ΔH, and ΔS values for the

Figure 1. New Macrocyclic Ligands



interactions of Ag^+, Hg^{2+}, and Pb^{2+} with several thiacrown ether ligands were determined in aqueous solution by potentiometry and calorimetry. ^{13}C NMR spin-lattice relaxation times (T_1) and chemical shifts (δ) were determined for pyridonothia-18-crown-6 (PT18C6) in the absence and presence of Ag^+, Hg^{2+}, and Pb^{2+}. A large enhancement of selectivity by PT18C6 for Ag^+ over Hg^{2+} and Pb^{2+} was found. The interactions of thiacrown ether ligands with the metal ions studied were found to be enthalpy-driven. The entropy changes were unfavorable in all cases. The T_1 and δ measurements for PT18C6 interaction with Ag^+ and Hg^{2+} in conjunction with the corresponding thermodynamic data provide a detailed microscopic picture of the macrocycle-metal ion interactions. Both Ag^+ and Hg^{2+} interact strongly with the sulfur portion of PT18C6, but Ag^+ interacts much more strongly than Hg^{2+} with the pyridone portion of the ligand. The influence of preorganization of the binding sites in the macrocycle on binding strength and selectivity was examined. A successful reversal of the common selectivity order of Hg^{2+} over Ag^+ was accomplished by the insertion of a pyridone binding subunit in the thiacrown ether ligand system. The full text of the paper describing this work is in press in the Journal of the American Chemical Society and is appended as an example of work performed on this project.

II.D. MEMBRANE TRANSPORT STUDIES

Studies concerning the separation of metal cations in aqueous solution using proton-ionizable macrocycles were carried out in the Dual Hollow Fiber Membrane System described in the proposal and illustrated in Figure 2. The system involves a double extraction, with membrane solvent flowing thru the fibers of both modules and the source and receiving water phases flowing through the shell side of one of the two modules. The advantages of this system,

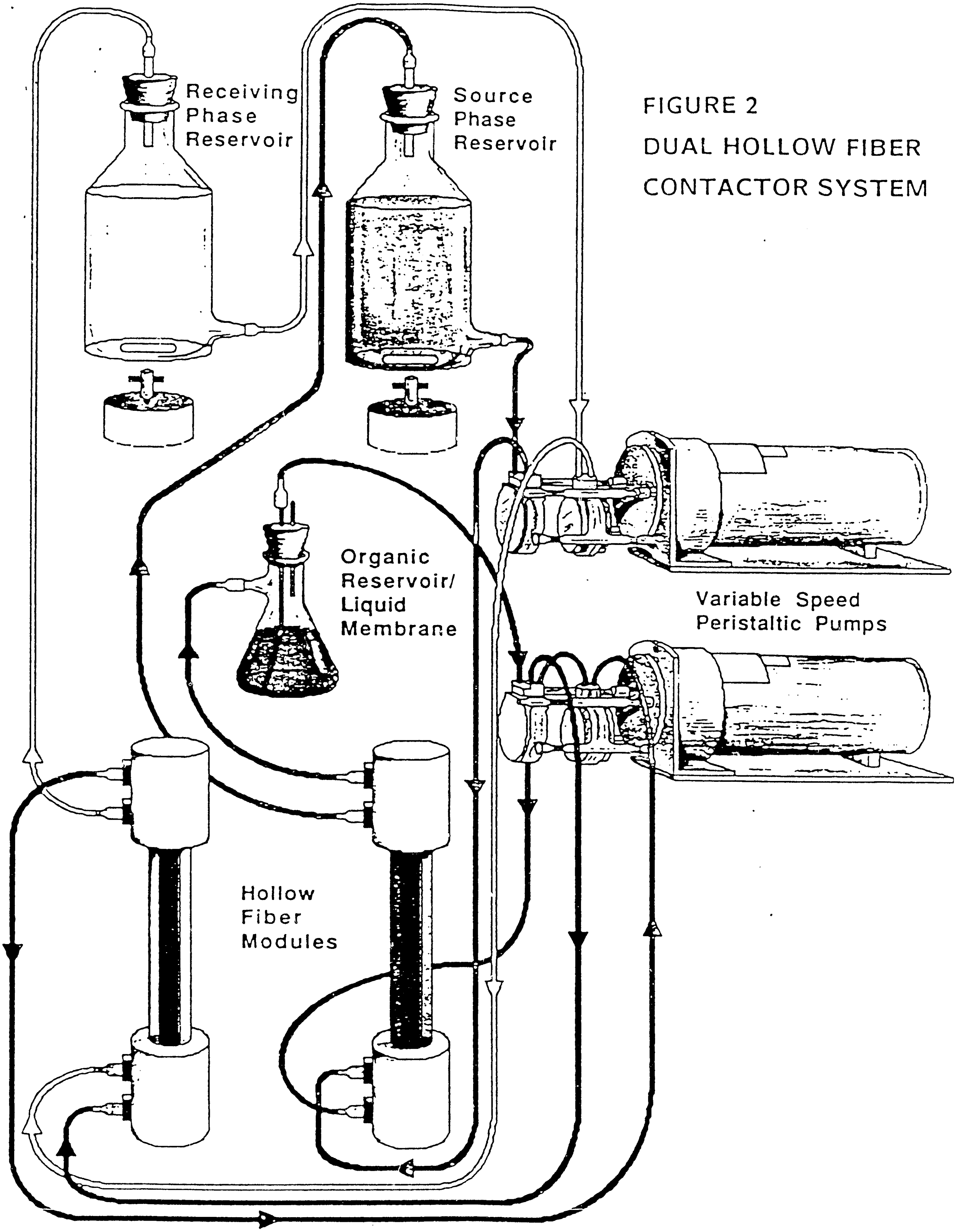


FIGURE 2
DUAL HOLLOW FIBER
CONTACTOR SYSTEM

such as easy access to all phases, rapid transport rates, and the potential for continuous operation, are maintained with the proton-ionizable macrocycles, thus permitting proton driven transport. Transport is diffusion limited in the organic phase boundary layer near and in the fibers. Hence, the selectivity of the extraction system is maintained and is comparable to the hollow-fiber supported membrane configuration.

The dual hollow fiber system was investigated to determine the effect of aqueous solution flow rate and membrane solvent stirring rate on Na^+ and K^+ transport using dicyclohexano-18-crown-6 as the carrier. The results demonstrated that transport increases with increasing stirring speed, but remains constant with increased aqueous flow rate through the fibers within the range of four to twelve ml/min. The membrane solvents hexane, toluene, octane, 1-octanol, 4-methyl-2-pentanone, octanal, and 2-octanone were tested for their ability to preserve membrane integrity in the presence of aqueous solutions of low pH, and to maximize transport. Of these solvents, 2-octanone was found to be most effective in minimizing acid diffusion across the membrane, while giving the highest facilitated K^+ transport rate. Quantitative transport using 18-crown-6 was observed for K^+ over Na^+ (all solvents studied) and Ba^{2+} and Sr^{2+} over Ca^{2+} (only octanol was studied). A description of the dual hollow fiber membrane system and some representative results are described in an article which is in press in Separation Science and Technology.

In work to model membrane transport in general, the diffusion-limited transport model for neutral macrocycle-mediated cation transport in membranes was used to quantify the membrane solvent effects on the fundamental parameters in the model and to evaluate their relative importance. The fundamental parameters involved are the extraction equilibrium constant, macrocycle partition coefficient, and diffusion coefficient. Experimental measurements and predictive correlation calculations were made to quantify these fundamental parameters. Membrane stability was also quantified by examining relative solvent solubilities and solvent compatibility with various membrane types. It was found, in general, that membrane stability must be balanced against rapid transport in choosing a membrane solvent. Retention of the macrocycle in the membrane and diffusion coefficients are greatest with small carbon chain solvents containing few chlorine atoms. On the other hand, high boiling points and low water solubility are obtained with long carbon chain solvents containing increasing numbers of chlorine atoms. Extraction equilibrium constants also decrease with increasing carbon chain lengths and increasing numbers of chlorine atoms, but the decrease is not uniform like the changes in the other parameters. Little effect of solvent type on membrane selectivity was observed. The transport model and quantification of these fundamental parameters permit accurate predictions in the choice of solvent in designing stable membranes with optimal transport properties.

Selective transport of Ag^+ over virtually all other cations from neutral source phases and of K^+ over other soluble cations from basic source phases using a triazolo-18-crown-6 carrier was demonstrated. Selective K^+ transport from less basic source phases was demonstrated using the more acidic thiopyridono-18-crown-6 ligand. However, this ligand is difficult to maintain in the organic phase. Design of the separation systems requires a knowledge of extraction equilibrium constants and partition coefficients. These data were determined in order to understand these membrane systems. This work is currently being prepared for publication.

Macrocycle-mediated transport of Eu^{3+} and Eu^{2+} from an aqueous solution through a modified thin-sheet-supported liquid membrane was studied and compared with that of Sr^{2+},

Gd^{3+}, and Nd^{3+}. Transport of Eu^{2+} was found to be more effective than that of trivalent lanthanide cations using bis (1-hydroxylheptyl) DC18C6 as the membrane carrier. The flux of Eu^{2+} was similar to that of Sr^{2+} while those of Eu^{3+}, Gd^{3+}, and Nd^{3+} were almost identical and much less than that of Sr^{2+}. A paper reporting these results has been published in the Journal of Membrane Science.

A review of crystal structures of Li^+-macrocycle complexes has been published in Chemical Reviews. In addition, crystal structures of complexes formed between Li^+ and several novel macrocyclic ligands have been determined and papers describing the work is in preparation. A primary objective of this part of the program is to identify the papameters which govern Li^+ coordination in order to be able to design and prepare macrocycles with superior Li^+ complexing ability.

III. COMPLIANCE WITH AGREEMENT REQUIREMENTS

The research effort is proceeding in compliance with the objectives and procedures set forth in the original proposal.

IV. INTERACTION WITH OTHER DOE CONTRACTORS

During the contact period we have exchanged information and insights with several other DOE contractors such as B. Moyer at Oak Ridge National Laboratory, C. Babcock at Bend Research, R. Bartsch at Texas Tech U.,S. Alexandratos at U. of Tennessee, and P. Horwitz at Argonne National Laboratory.

V. EDUCATIONAL BENEFITS

The concept of applying membrane technology and macrocycles of novel design to making inorganic separations is being developed in this work. The success of the project requires involvement from many disciplines--inorganic chemistry, coordination chemistry, membrane science, organic chemistry, physical chemistry, macrocycle chemistry and chemical engineering. This project has stimulated the intellectual involvement of professors, post-doctoral students, graduate students, and undergraduate students participating in the project from widely separated fields. A sizeable number of individuals have contributed to the research effort, as indicated in Section II.A.

VI. PUBLICATION AND PRESENTATION OF RESULTS

VI.A. Papers Published 1988 - 1991

The following publications reporting results obtained under this contract were published during the last three year funding period. Those published in the last year are marked with a *. Copies of the latter papers are included in the appendix for DOE internal use. Copies of the other papers were submitted previously.

1. J.D. Lamb, R.L. Bruening, R.M. Izatt, Y. Hirashima, P.K. Tse, and J.J. Christensen, "Characterization of a Supported Liquid Membrane for Macrocycle-Mediated Selective Cation Transport", J. Membr. Sci., 37, 13-26 (1988).

2. R.M. Izatt, J.D. Lamb, and R.L Bruening, "Comparison of Bulk, Emulsion, Thin Sheet Supported, and Hollow Fiber Supported Liquid Membranes in Macrocycle-Mediated Cation Separations," Sep. Sci. and Tech., 23, 1645-1658 (1988).

3. M. Bochenska, J.F. Biernat, J.S. Bradshaw, H. Koyama, and R.M. Izatt, "Sulfonamides as Ionophores for Ion-Selective Electrodes. II. Macrocyclic Ligands Containing Two Sulfonamide Groups as Ionophores," J. Incl. Phenom., **6**, 593-597 (1988).

4. R.M. Izatt, G.C. LindH, J.S. Bradshaw, C.W. McDaniel, and R.L. Bruening, "Proton-Ionizable Crown Compounds: Transport of Alkali and Alkaline Earth Cations Using Proton-Ionizable Triazolo Macrocycles," Sep. Sci. and Tech., **23(12&13)**, 1813-1823 (1988).

5. J.S. Bradshaw, J.M. Guynn, S.G. Wood, K.E. Krakowiak, R.M. Izatt, C.W. McDaniel, B.E. Wilson, N.K. Dalley, and G.C. LindH, "Proton-Ionizable Crown Compounds. 16. Synthesis, Structural Features and Cation Transport Studies of Crown Ethers Containing the 4-Pyridone N-Hydroxide Subcyclic Group," J. Org. Chem., **53**, 2811-2816 (1988).

6. R.M. Izatt, G.C. LindH, R.L. Bruening, P. Huszthy, C.W. McDaniel, J.S. Bradshaw, and J.J. Christensen, "Separation of Silver from Other Metal Cations Using Pyridone and Triazole Macrocycles in Liquid Membrane Systems", Anal. Chem., **60**, 1694-1699 (1988).

7. R.M. Izatt, R.L. Bruening, M.L. Bruening, G.C. LindH, and J.J. Christensen, "Modeling Diffusion-Limited, Neutral-Macrocycle-Mediated Cation Transport in Supported Liquid Membranes," Anal. Chem., **61**, 1140-1148 (1989).

8. R.M. Izatt, D.K. Roper, R.L. Bruening, and J.D. Lamb, "Macrocycle-Mediated Cation Transport Using Hollow Fiber Supported Liquid Membranes", J. Membrane Sci., **45**, 73-84 (1989).

9. M. Bochenska, J.F. Biernat, Masek Topolski, J.S. Bradshaw, R.L. Bruening, R.M. Izatt, and N.K. Dalley, "Solvent Extraction Studies of New bis- Sulfonamide Group-Containing Podands," J. Incl. Phenom., 7, 599-611, (1989).

10. C.W. McDaniel, J.S. Bradshaw, K.H. Tarbet, G.C. LindH and R.M. Izatt, "Synthesis of Two New Crown Ethers Containing Selenium and the Complexation of One of Them with Silver and Lead," J. Incl. Phenom., 7, 545-548 (1989).

11. C.W. McDaniel, J.S. Bradshaw, K.E. Krakowiak, R.M. Izatt, P.B. Savage, B.J. Tarbet, and R.L. Bruening, "Preparation of Crown Compounds Containing Allyloxymethyl or Butenyl Groups for Attachment to Silica Gel or Containing Long Chain Lipophilic Groups for Use in Liquid Membrane Systems," J. Heterocyclic Chem., 26, 413-419 (1989).

12. R.M. Izatt, G.C. LindH, J.F. Biernat, M. Bochenska, R.L. Bruening, J.S. Bradshaw, and J.J. Christensen, "Proton-Ionizable Crown Compounds. 17. Transport Studies of Alkali Metal Ions in a H_2O-CH_2Cl_2-H_2O Liquid Membrane System by Macrocycles Containing Two Sulfonamide Groups Derived from o- and m- Phenylene Diamine", J. Incl. Phenom., 7, 487-499, (1989).

13. R.M. Izatt, G.C. LindH, and P. Huszthy, G.A. Clark, R.L. Bruening, J.S. Bradshaw, and J.J. Christensen, "Proton-Ionizable Crown Compounds. 18. Comparison of Alkali Metal Transport in a H_2O-CH_2Cl_2-H_2O Liquid Membrane System by Four Proton-Ionizable Macrocycles Containing the Dialkylhydrogenphosphate Moiety", J. Incl. Phenom., 7, 501-509, (1989).

14. R.L. Bruening, R.M. Izatt, and J.S. Bradshaw, "Understanding Cation-Macrocycle Binding Selectivity in Single Solvent, Extraction, and Liquid Membrane Systems by Quantifying Thermodynamic Interactions", in Cation Binding by Macrocycles, Y. Inoue and G.W. Gokel (Eds), Marcel Dekker, New York, 1990, pp. 111-132.

15. R.M. Izatt, J.S. Bradshaw, J.D. Lamb, and R.L. Bruening, "Emulsion and Supported Liquid Membranes", in Liquid Membranes: Chemical Applications, T. Araki and H. Tsukube (Eds.), CRC Press, Inc. Boca Raton, FL, 1990.

16. R.M. Izatt, R.L. Bruening, M.L. Bruening, and J.D. Lamb, "Quantitating the Effect of Solvent Type on Neutral Macrocycle-Mediated Cation Transport in Liquid Membranes", Isr. J. Chem., **30**, 239-245 (1990).

17. K.E. Krakowiak, J.S. Bradshaw, and R.M. Izatt, "One-Step Methods to Prepare Cryptands and Crowns Containing Reactive Functional Groups", J. Heterocyclic Chem., 27, 1011-1014 (1990).

*18. C.Y. Zhu and R.M. Izatt, "Macrocycle-Mediated Separation of Eu^{2+} from Trivalent Lanthanide Cations in a Modified Thin-Sheet-Supported Liquid Membrane System," J. Membrane Sci., **50**, 319-324 (1990).

*19. U. Olsher, R.M. Izatt, J.S. Bradshaw, and N.K. Dalley, "Coordination Chemistry of Lithium Ion: A Crystal and Molecular Structure Review," Chem. Rev., **91**, 137-164 (1991).

*20. U. Olsher, K.E. Krakowiak, N.K. Dalley, and J.S. Bradshaw, "Syn-Bishydroxymethyl-14-Crown-4: A Possible Preorganized Molecule for Simultaneous Lithium Complexation and Anion Solvation," Tetrahedron, **47**, 2947-2956 (1991).

VI.B. Papers in Press or Submitted

1. J.D. Lamb, R.L. Bruening, D.A. Linsley, C. Smith and R.M. Izatt, "Characterization of a Macrocycle-mediated Dual Module Hollow Fiber Membrane Contactor for Making Cation Separations," Sep. Sci. Technol., in press.

2. J.S. Bradshaw, K.E. Krakowiak, P. Huszthy, and R.M. Izatt, "Proton-Imizable Crown Compounds. 20. The Synthesis of Polyazatriazolo- Polyazabistriazolo- and Bispyridino-Crown Ligands Containing Lipophilic Hydrocarbon Substituents," J. Heterocyclic Chem., in press.

3. G. Wu, W. Jiang, J.D. Lamb, J.S. Bradshaw, and R.M. Izatt, "High Specificity Thiacrown Ether Reagents for Silver (I) over Bivalent Mercury and Lead. Thermodynamic and ^{13}C NMR Relaxation Time Studies," J. Am. Chem. Soc., in press.

4. U. Olsher, N.K. Dalley, and J. Weiming, "Dibenzo-14-Crown-4: Preorganized Basis of Square Pyramid Coordination for Lithium Ions," J. Incl. Phenom., in press.

5. N.K. Dalley, W. Jiang, and U. Olsher, "The Crystal Structure of Dibenzo-14-Crown-4, a Preorganized Basis of Square Pyramid Coordination for Lithium Ions," J. Incl. Phenom., in press.

6. U. Olsher, F. Frolow, N.K. Dalley, J. Weiming, Z.Y. Yu, J.M. Knobeloch, and R.A. Bartsch, "Crown Ether Alcohols as Bifunctional Ligands for Simultaneous Cation Complexation and Anion Solvation", J. Am. Chem. Soc., in press.

7. R.M. Izatt, K. Pawlak, J.S. Bradshaw and R.L. Bruening, "Thermodynamic and Kinetic Data for Macrocycle Interactions with Cations and Anions," Chem. Rev., in press.

VI.C. Presentation of Results

1. J.D. Lamb, R.L. Bruening, D.K. Roper, and R.M. Izatt, "Macrocycle-Mediated Cation Separations in Hollow Fiber Supported Liquid Membranes", Second Annual National Meeting of the North American Membrane Society, Syracuse, NY, June 1-2, 1988.

2. R.M. Izatt, R.L. Bruening, J.D. Lamb, and J.S. Bradshaw, "Design of Macrocycles to Perform Cation Separations in Liquid Membrane Systems", Invited Lecture, Second Annual National Meeting of the North American Membrane Society, Syracuse, NY, June 1-3, 1988.

3. R.M. Izatt, "Macrocycle-Mediated Separations of Metal Ions", the University of Tel Aviv, Israel, June 16, 1988.

4. R.M. Izatt, "Macrocycle-Mediated Separations of Metal Ions", Weizmann Institute, Rehovot, Israel, June 22, 1988.

5. Geng Wu, R.M. Izatt and R.B. Davidson, "Complexation of Cryptand-222 and 18-Crown-6 with some Alkali Metal Ions in Several Dioxane-Water Solvent Mixtures", Calorimetry Conference, Bartlesville, Oklahoma, August 8-12, 1988.

6. R.M. Izatt, "Design of Selectivity into Macrocycle-Mediated Cation Separation Systems", Oakland University, Rochester Hills, Michigan, September 20-21, 1988.

7. R.M. Izatt, "Design of Selectivity into Macrocycle-Mediated Cation Separation Systems", Michigan State University, East Lansing, Michigan, September 22, 1988.

8. C. Smith, J.D. Lamb, D.A. Lindsley, R.L. Bruening, and R.M. Izatt, "Selective Metal Cation Transport in Novel Dual Module Hollow Fiber Liquid Membranes," Spring Research Conference, Brigham Young University, Provo, Utah, Sponsored by the College of Physical and Mathematical Sciences and Central Utah Section of the American Chemical Society, March 11, 1989.

9. G. Wu, and R.M. Izatt, " Thermodynamic and Spectral Studies of Interactions of the 1,4 and 1,10 Dithia Derivatives of 18-Crown-6 with Pd(II) and Hg(II) Ions in Aqueous Solution at 25°C", Spring Research Conference, Brigham Young University, Provo, Utah, Sponsored by the College of Physical and Mathematical Sciences and Central Utah Section of the American Chemical Society, March 11, 1989.

10. R.M. Izatt, "Design of Selectivity into Cation Separation Systems Using Macrocycles," Chemistry Department Seminar, Northern Illinois University, Dekalb, Illinois, March 28, 1989.

11. J.S. Bradshaw, K.E. Krakowiak, B.J. Tarbet, C.W. McDaniel, P. Huszthy, R.L. Bruening, and R.M. Izatt, "New Nitrogen-Containing Macrocyclic Ligands for Cation Separation Processes," Invited Lecture, 197th National Meeting of the American Chemical Society, Dallas, TX, April 9-14, 1989.

12. R.M. Izatt, "Design of Selectivity Into Cation Separation Systems Using Macrocycles," University of Florence, Florence, Italy, May 19, 1989.

13. R.M. Izatt, "Design of Macrocycle Selectivity into Permanent Solid Supported Separation Systems" Invited Plenary Lecture, XIV International Symposium on Macrocyclic Chemistry, Townsville, Australia, June 25-28, 1989.

14. R.M. Izatt, R.L. Bruening, J.S. Bradshaw, L.D. Griffin, and M.L. Bruening, "Macrocycle-Mediated Separations Using Ligand-Bonded Silica Gel and Dual Module Hollow Fiber Membranes", Invited Section Lecture, XXVII International Conference on Coordination Chemistry (ICCC), Broadbeach, Queensland, Australia, July 2-7, 1989.

15. R.M. Izatt, "Design of Selectivity into Separation Systems Involving Multidentate Ligands", XXVII International Conference on Coordination Chemistry, Marysville, Australia, July 10-19, 1989.

16. R.M. Izatt, "Design of Selectivity into Separation Systems Involving Multidentate Ligands", University of Oslo, Oslo, Norway, July 27, 1989.

17. G. Wu, and R.M. Izatt, " Thermodynamic and Spectral Studies of Interactions at 25°C of the 1,4 and 1,10 Dithia Derivatives of 18-Crown-6 with Pd(II) and Hg(II) Ions in Aqueous Solution", 44th Annual Calorimetry Conference, Oak Ridge, Tennessee, July 30 - August 4, 1989.

18. R.M. Izatt, R.L. Bruening, J.S. Bradshaw, J.D. Lamb, "Characterization of a Macrocycle-Mediated Dual Module Hollow Fiber Membrane Contactor for Making Cation Separations", Conference on Separation Science and Technology for Energy Applications, Gatlinberg, Tennessee, October 1989.

19. R.M. Izatt, R.L. Bruening, J.S. Bradshaw, J.D. Lamb, "Judicious Use of Macrocycles to Achieve High Separation Efficiency in Liquid Membrane and Column Systems", American Institute of Chemical Engineers (AIChE), San Francisco, California, November 5-10, 1989.

20. R.M. Izatt, "Principles Governing Design of Cation Selectivity into Separation Systems", University of Madrid, Madrid, Spain, April 4, 1990.

21. J.S. Bradshaw, "Macrocycles-Important New Materials for Removing Metal Ions From Water," 1989 Utah Award Lecture, April 14, 1990.

22. K.E. Krakowiak, J.S. Bradshaw, and R.M. Izatt, "Preparation of Polyaza-Crowns Using a Crab-Like Cyclization Procedure," 199th Am. Chem. Soc. National Meeting, Boston, MA, April 22-27, 1990.

23. R.M. Izatt, "Principles Governing Design of Cation Selectivity into Separation Systems", University of Messina, Messina, Italy, May 18, 1990.

24. R.M. Izatt, "Principles Governing Design of Cation Selectivity into Separation Systems", University of Catania, Catania, Italy, May 19, 1990.

25. H. An, J.S. Bradshaw, K.E. Krakowiak, G. Wu, and R.M. Izatt, "Synthesis of Macrobicyclic Polyethers with Nitrogen Atom Bridgeheads", 45th Northwest/10th Rocky Mountain American Chemical Society Regional Meeting, Salt Lake City, Utah, June 13-15, 1990.

26. K.E. Krakowiak, J.S. Bradshaw, N.K. Dalley, and R.M. Izatt, "The Preparation of Peraza-Crowns Containing the Piperazine Moiety by the Crab-Like Cyclization Reaction", 45th Northwest/10th Rocky Mountain American Chemical Society Regional Meeting, Salt Lake City, Utah, June 13-15, 1990.

27. G. Wu, N.K. Dalley, W. Jiang, and R.M. Izatt, "Validity of the Size Selectivity Rule in Thiophilic Metal Ion-Thiocrown Ether Interactions," 45th Northwest/10th Rocky Mountain American Chemical Society Regional Meeting, Salt Lake City, Utah, June 13-15, 1990.

28. J.S. Bradshaw, "Proton-Ionizable Macrocyclic Ligands and Their Use to Transport Cations in Liquid Membrane Systems," Invited Lecture, Polish School of Supramolecular Chemistry, Gdansk, Poland, August 20-31, 1990.

29. G. Wu and R.M. Izatt, "Effect of Macrocyclic Donor Atom Type on the Thermodynamic Properties (Log $\underline{K}$, $\Delta\underline{H}$, and $\Delta\underline{S}$) of Silver (I)-Thiocrown Ether Interactions" 200th ACS National Meeting, Washington, D.C., August 26-31, 1990

30. R.M. Izatt, "Design of Cation Selectivity into Chemical Systems," Institute of Physical Chemistry, Ukranian Academy of Sciences, Kiev, USSR, August 31, 1990.

31. G. Wu, R.M. Izatt, and J.S. Bradshaw, "High-Specificity Chelating Reagents for Silver Ion," 201st ACS National Meeting, Atlanta, GA April 14-19, 1991.

32. R.M. Izatt, J.S. Bradshaw, G. Wu, K.E. Karakowiak, R.L. Bruening, and B.J. Tarbet, "Design of Metal-Ion Specificity into Macrocyclic Ligands," 201st ACS National Meeting, Atlanta, GA, April 14-19, 1991.

33. J.D. Lamb, "Macrocyclic Ligands as Cation-Selective Carriers in Liquid Membrane", Institute of Nuclear Science and Technology, Sichuan University, PRC, May, 1991.

34. R.M. Izatt, R.L. Bruening, C. Wang, N. Edge, J.S. Bradshaw, and J.D. Lamb, "Cation Separations Using a Proton-Ionizable Macrocycle in a Dual Module Hollow Fiber Membrane," Seventh Symposium on Separation Science and Technology for Energy Applications, Knoxville, TN, October 20-24, 1991.

VII. APPENDIX

VII.A. Copies of Three Representative Papers

1. G. Wu, W. Jiang, J.D. Lamb, J.S. Bradshaw, and R.M. Izatt, "High Specificity Thiacrown Ether Reagents for Silver (I) over Bivalent Mercury and Lead. Thermodynamic and ^{13}C NMR Relaxation Time Studies," J. Am. Chem. Soc., in press.

2. J.S. Bradshaw, K.E. Krakowiak, P. Huszthy, and R.M. Izatt, "Proton-Ionizable Crown Compounds. 20. The Synthesis of Polyazatriazolo-, Polyazabistriazolo- and Bispyridono-Crown Ligands Containing Lipophilic Hydrocarbon Substituents," J. Heterocyclic Chem., **28**, 773-775 (1991).

3. R.M. Izatt, R.L. Bruening, M.L. Bruening, G.C. LindH, and J.J. Christensen, "Modeling Diffusion-Limited, Neutral-Macrocycle-Mediated Cation Transport in Supported Liquid Membranes," Anal. Chem., **61**, 1140-1148 (1989).

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