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CATION SEPARATIONS USING A PROTON-IONIZABLE MACROCYCLE IN A DUAL MODULE HOLLOW FIBER MEMBRANE SYSTEM

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ABSTRACT

Separation of metal cations in aqueous solution using a proton-ionizable macrocycle in a dual module hollow fiber membrane system is described. The advantages of this system, such as easy access to all phases, rapid transport rates, and the potential for continuous operation are maintained with the proton-ionizable macrocycles which allow for proton driven transport. Transport is diffusion limited in the organic phase boundary layer near and on the fibers. Hence, the selectivity of the extraction system is maintained. Selective transport of Ag^+ over all other cations tested from neutral source phases and of K^+ over other alkali metal cations from basic source phases using a triazole-18-crown-6 carrier has been demonstrated. Selective K^+ transport from less basic source phases has been demonstrated using the more acidic thiopyridone-18-crown-6 ligand. However, the large aqueous partition of this ligand makes it difficult to maintain it in the organic phase. Design of the separation systems requires a knowledge of extraction equilibrium constants and partition coefficients. These data have been measured in order to understand these membrane systems.

INTRODUCTION

Membranes have received a great deal of attention in the performing of new separations (1). One of the main difficulties

with membranes has been in designing high selectivity into the systems (2). The use of macrocyclic carrier-mediated liquid membranes offers promise for the achievement of high selectivity for particular cations (3).

Despite the promise of selectivity, carrier-mediated liquid membrane stability has been difficult to achieve. Recently (4), we reported the successful use of a dual module hollow fiber (DMHF) membrane contactor using the neutral macrocycle carrier DC18C6 and 2-octanone as solvent. A more detailed description of the DMHF system will be given in the experimental section. This new system exhibits high fluxes, ease in controlling the individual phases of the system, and stability over long periods of time. This system includes the ability to easily replenish membrane solvent and carrier when needed without system downtime. In this work, we report that the system also shows promise in terms of stability when using proton-ionizable macrocycles.

Several macrocycles with one or two ionizable protons have been synthesized (5-8). These ligands can exchange their protons for cations at the source phase-membrane phase interface, and then release the cations in exchange for protons at the membrane-receiving phase interface due to the low pH of the receiving phase. Thus, the gradient-driven transfer of cations through the membrane can be supplemented or completely driven by the proton transfer from low to high pH, in the reverse direction. This method is particularly useful when the source phase cation content must be reduced to a low level. In the present study, the DMHF membrane contactor system has been used to successfully perform alkali metal cation and Ag^+ separations involving proton-ionizable macrocycles. These separation systems were also examined in terms of extraction equilibria and a boundary layer diffusion controlled transport model.

EXPERIMENTAL

The DMHF membrane system (see Figure 1) consisted of a glass 250 ml reservoir containing the source phase, and another of equal volume containing the receiving phase. These aqueous phases were

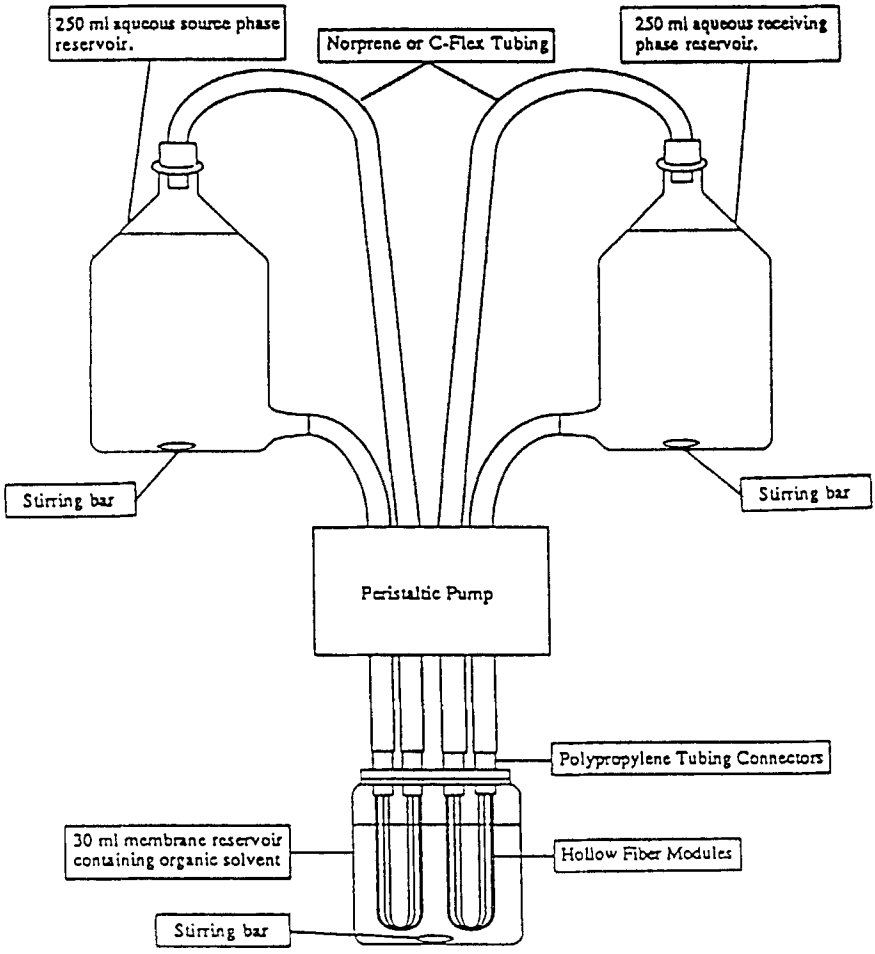


FIGURE 1. Diagram of the DMHF membrane system.

circulated by means of C-Flex or Norprene (Cole-Parmer) tubing and a Masterflex (Cole-Parmer) peristaltic pump through the lumen of a fiber bundle. Each fiber bundle was constructed of 60 lengths of polypropylene microporous hollow fibers. Each bundle was secured using polyethylene tubing connectors and silicone glue (Dow Corning and Mechanics Helper, Inc.). The fibers used, Celgard X20 (Hoechst

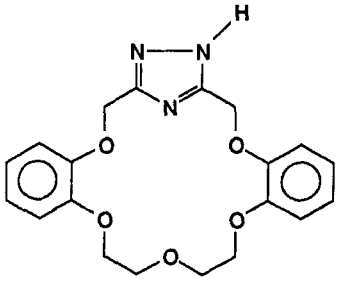
Celanese), have an inside diameter of 400 μm, an outside diameter of 456 μm, an effective pore size of 0.03 μm, and 40% porosity (manufacturer's specifications). Each fiber bundle was 15 cm in length, excluding the polypropylene tubing connectors. Two fiber bundles were held in a U-shape and immersed in a 60 ml membrane reservoir containing 25 ml of the membrane solvent. The average outside surface area of each bundle that was exposed to the solvent was 71 cm^2. Solvent and aqueous reservoirs were continuously stirred with teflon-coated magnetic stirring bars and synchronous stirring motors at 600 rpm (Hurst Manufacturing Co.).

All commercial chemicals were reagent grade and used as supplied from the manufacturer without further purification. The solvent 2-octanone (Aldrich) was used as the organic solvent in all dual module membrane contactor and solvent extraction experiments. The dual module membrane source phases and/or aqueous extraction phases were prepared from $NaNO_3$(Fisher), KNO_3(J.T.Baker), $RbNO_3$(Aldrich), $AgNO_3$(EM), $Pb(NO_3)_2$(Allied), $LiNO_3$(J.T.Baker), LiOH(EM), NaOH(EM), CsOH(Aldrich), KOH(Mallinckrodt), and RbOH(Aldrich) using distilled, deionized water. The receiving phases in the membrane experiments and/or the aqueous phases in the back extractions of the solvent extraction experiments consisted of either distilled deionized water or 1 M HNO_3 prepared from concentrated HNO_3 (Mallinckrodt). The macrocycles used as either membrane carriers or solvent extraction reagents are shown in Figure 2. The concentration of the carrier in the membrane experiments and in the extraction experiments was 1.0 mM. The macrocycles were prepared as reported previously (9,10).

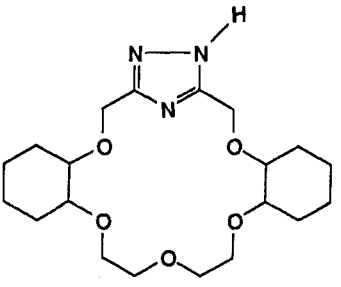
Solvent extraction experiments were performed to determine the equilibrium constant (K_{ex}) for the reaction

$$M^+_{aq} + HL_{org} = ML_{org} + H^+_{aq} \quad (1)$$

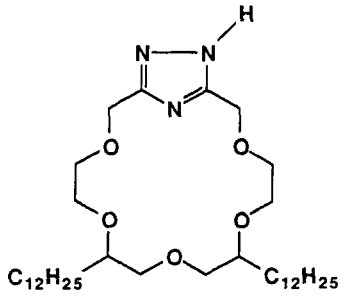
for each metal ion, where M^+ = Li^+, Na^+, K^+, Rb^+, Cs^+, or Ag^+; L was any of the four triazolo-18-crown-6 macrocycles (first four structures in Figure 2) examined in this study. The organic diluent was always 2-octanone. Equal volumes (5 ml) of the aqueous and organic phases were stirred at 600 rpm until equilibrium of the phases (no changes in phase composition) was achieved. When the



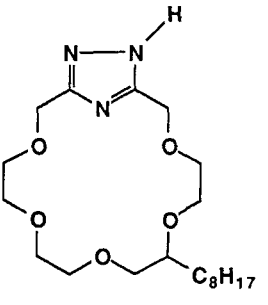
Dibenzotriazolo-18-Crown-6
$B_2Tr18C6$



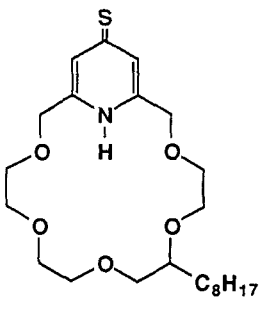
Dicyclohexanotriazolo-18-Crown-6
$Cy_2Tr18C6$



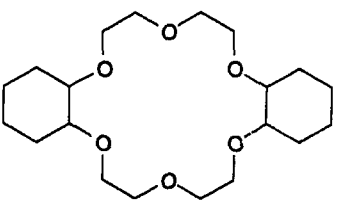
DiC_{12}-Triazolo-18-Crown-6
$(C_{12})_2Tr18C6$



Octyltriazolo-18-Crown-6
$C_8Tr18C6$



Octylthiopyridono-18-Crown-6
$C_8TPy18C6$



Dicyclohexano-18-Crown-6
Cy_218C6

FIGURE 2. Structural formulas of macrocycles studied

amount of a metal cation extracted was small, the metal ion was back extracted from the organic phase into an equal volume of 1 M HNO_3 for greater accuracy in analysis. The measured changes in species concentration (M^+_{aq} and H^+_{aq}) were used to determine K_{ex} values in a method similar to that of Ouchi et al. (11), which has been used for the extraction of cations plus co-anions by neutral macrocycles. In the case of the ligand, the partition coefficient (K_p) value (see Eq. 2)

$$L^-_{aq} + H_2O = HL_{org} + OH^-_{aq} \quad (2)$$

was estimated using the measured macrocycle concentrations in both aqueous and organic phases, and the pH value of the aqueous phase at equilibrium. Since the triazolo-18-crown-6 does not complex with Li^+, a LiOH aqueous solution was chosen as the aqueous phase.

Each membrane experiment was run for at least 8 hours. Samples for analysis were taken periodically (usually hourly) from the receiving phase. New hollow fiber bundles were made for each experiment. The samples were analyzed for metal cation content using either AA spectrophotometry (Perkin Elmer Model 603) or ICP spectrophotometry (Perkin Elmer Model Plasma II). The concentration of the ligand in the organic phase was measured with a Cary Model 17 ultraviolet-visible spectrophotometer. The experiments were performed in triplicate. Membrane and solvent extraction blank experiments, run under identical system conditions minus the presence of the macrocycle, were performed in each case to show that no transport or extraction occurred that was not mediated by the macrocycle.

RESULTS AND DISCUSSION

Ag^+ Separation Using Octyltriazolo-18-Crown-6

Triazolo-18-crown-6 molecules containing a variety of hydrophobic sidearms have been synthesized (9). It has been shown in other laboratory membrane systems that selective transport of Ag^+ by these macrocycles occurs over virtually all other metal cations from a source phase of neutral pH (12). In the present study, it

TABLE 1. COMPETITIVE TRANSPORT OF METAL CATIONS ACROSS A 2-OCTANONE MEMBRANE FROM NEUTRAL SOURCE PHASE[a]

Carrier	Average cation flux and standard deviation ($mol \cdot s^{-1} \cdot m^{-2}$)	Total cation flux ($mol \cdot s^{-1} \cdot m^{-2}$)	Transport selectivity order
C_8Tr18C6	Ag^+ $(1.3 \pm 0.1) \times 10^{-6}$ Pb^{2+} $(1.5 \pm 0.2) \times 10^{-7}$ K^+ $(6.2 \pm 3.5) \times 10^{-8}$	1.5×10^{-6}	$Ag^+ > Pb^{2+} > K^+$

[a]Transport in a 0.5 M $AgNO_3$, 0.5 M $Pb(NO_3)_2$, 0.5 M KNO_3/1.0 mM C_8Tr18C6 in 2-octanone/1.0 M HNO_3 liquid membrane.

was desired to show that these selectivities can be maintained with the stable and easily engineered DMHF system.

Table 1 shows the selective transport of Ag^+ over Pb^{2+} and K^+ from a neutral solution containing equal molar quantities of these cations. Figure 3 was chosen as the example of the transport curve. These results demonstrate that the cation selectivities determined previously using C_8Tr18C6 in bulk and emulsion membranes (12) also apply to the DMHF membrane system. The DMHF system maintains the selectivities of macrocycles observed with other membrane systems, and has the advantages of easy access to source, receiving, and membrane phases, transport rates competitive with those of other types of membranes, and the potential for continuous operation.

Selectivity for K^+ Over Na^+, Rb^+ and Cs^+ Using Triazolo-18-crown-6

Previous results have shown that when the source phase pH is raised to 12 or greater, a pyridono-18-crown-6 type macrocycle can be used to selectively transport K^+ over the other alkali and the alkaline earth metal cations (13). Because the triazolo-18-crown-6 macrocycle is similar in structure to pyridono-18-crown-6, we expected that triazolo-18-crown-6 could be used for alkali matal cation separations.

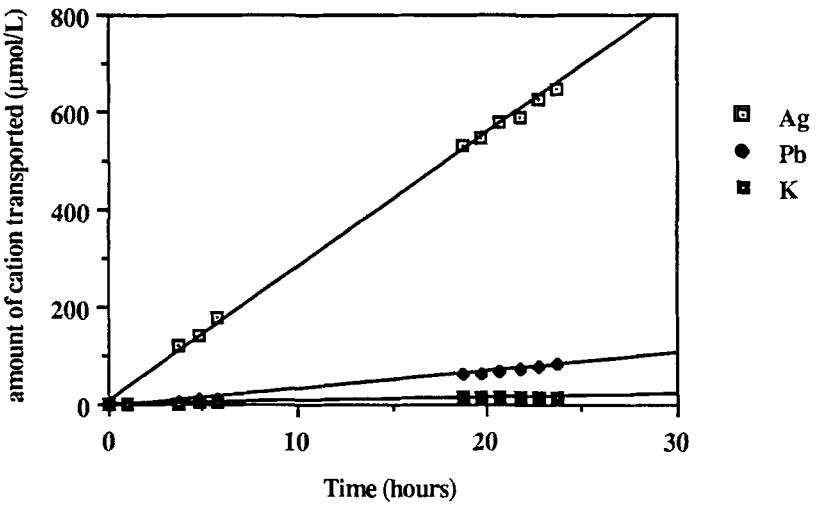


FIGURE 3. Plot of Ag^+, Pb^{+2}, and K^+ octyltriazolo-18-crown-6-mediated transport vs. time.

TABLE 2. COMPETTITIVE TRANSPORT OF METAL CATIONS ACROSS A 2-OCTANONE MEMBRANE FROM BASIC SOURCE PHASE

Carrier	Average cation flux and standard deviation ($mol \cdot s^{-1} \cdot m^{-2}$)	Total cation flux ($mol \cdot s^{-1} \cdot m^{-2}$)	Transport selectivity order
$C_8Tr18C6$[a]	K^+ (2.5 ± 0.2) x 10^{-7} Na^+ (3.9 ± 0.5) x 10^{-8}	2.9 x 10^{-7}	$K^+ > Na^+$
$C_8Tr18C6$[b]	K^+ (6.1 ± 0.5) x 10^{-7} Rb^+ (3.4 ± 0.7) x 10^{-8} Cs^+ (2.2 ± 1.0) x 10^{-8}	6.7 x 10^{-7}	$K^+ > Rb^+ > Cs^+$
$(C_{12})_2Tr18C6$[c]	K^+ (1.0 ± 0.4) x 10^{-7} Na^+(2.2 ± 0.7) x 10^{-8} Rb^+ (1.8 ± < 0.4) x 10^{-8} Cs^+ (1.1 ±<0.4) x 10^{-8}	1.5 x 10^{-7}	$K^+ > Na^+ > Rb^+ > Cs^+$

[a]Transport in a 0.5 M NaOH, 0.5 M KOH/ 1.0 mM $C_8Tr18C6$ in 2-octanone/1.0 M HNO_3 liquid membrane.
[b]Transport in a 0.1 M KOH, 0.1 M RbOH, 0.1 M CsOH/1.0 mM $C_8Tr18C6$ in 2-octanone/1.0 M HNO_3 liquid membrane.
[c]Transport in a 0.1 M NaOH, 0.1 M KOH, 0.1 M RbOH, 0.1 M CsOH/1.0 mM $DC_{12}Tr18C6$ in 2-octanone/1.0 M HNO_3 liquid membrane.

TABLE 3. COMPETITIVE TRANSPORT OF METAL CATIONS ACROSS A 2-OCTANONE MEMBRANE FROM NEUTRAL SOURCE PHASE[a]

Carrier	Average cation flux and standard deviation ($mol \cdot s^{-1} \cdot m^{-2}$)	Total cation flux ($mol \cdot s^{-1} \cdot m^{-2}$)	Transport selectivity order
C_8TPyl8C6	$K^+(1.7 \pm 0.1) \times 10^{-7}$ $Rb^+ (4.8 \pm 1.7) \times 10^{-8}$ $Na^+(2.1 \pm 0.4) \times 10^{-8}$	2.4×10^{-7}	$K^+ > Rb^+ > Na^+$

[a]Transport in a 0.1 M $NaNO_3$, 0.1 M KNO_3, and 0.1 M $RbNO_3$/1.0 mM C_8TPyl8C6 in 2-octanone/1.0 M HNO_3 liquid membrane system

Competitive experiments were performed in which the source phase contained K^+ and Na^+; K^+, Rb^+ and Cs^+; or K^+, Na^+, Rb^+ and Cs^+. The results are summarized in Table 2. In all cases, K^+ was transported selectively over the remaining cations.

K^+, Na^+, Rb^+ and Cs^+ Transport by Octylthiopyridono-18-crown-6

Previous experimental results have demonstrated that for the liquid membrane systems in which the carrier contains pyridono moieties, alkali metal cations are extracted into the membrane and transported in these systems only when the source phase pH is greater than the pK_a values (14) of the macrocycles. The pK_a value for removal of a proton from pyridono-18-crown-6 is 10.98 (15). This value is much higher than the pK_a value of 8.3 (16) for the corresponding thiopyridone compound. It would seem that the more acidic C_8TPyl8C6 could be used for alkali metal cation separation from less basic source phases than those required in the case of octyl-pyridone-18-crown-6. The results in Table 3 show that this is the case, i.e., K^+ is selectively transported over other alkali metal cations from a neutral source phase. Due to the greater solubility of this ligand in water (soon after the experiment began, the aqueous solution became yellowish), the efficiency for cation transport is not high.

TABLE 4. EXTRACTION EQUILIBRIUM CONSTANT (2-OCTANONE), AND PARTITION COEFFICIENT (2-OCTANONE) FOR INTERACTION OF SOME TRIAZOLO-18-CROWN-6 LIGANDS WITH ALKALI CATIONS

Macrocycle	K_p[a]	K_{ex}[b] $[M^{-1}]$			
		Na	K	Rb	Cs
$Cy_2Tr18C6$	1.04	0.27	0.29	0.15	0.14
$C_8Tr18C6$	1.28	0.94	1.22	0.83	0.57
$B_2Tr18C6$	>33.33[c]	0.85	d	0.75	0.50
$(C_{12})_2Tr18C6$	>33.33[c]	9.10	21.96	7.60	4.80

[a]Partition coefficient, $L^-_{aq} + H_2O = HL_{org} + OH^-_{aq}$
[b]Extraction equilibrium constant, $OH^-_{aq} + M^+_{aq} + HL_{org} = ML_{org} + H_2O$
[c]The macrocycle stayed in the organic phase, virtually quantitatively; detection limit of the macrocycle in the aqueous phase is less than 0.01 mMole
[d]The complex precipated.

Kp Variation with Substituents

Accurate measurement of facilitated cation transport in the membrane systems requires that loss of the macrocyclic carrier to the aqueous phases adjacent to the membrane be minimized. This may be accomplished by adding lipophilic substituent groups to the parent macrocycles in order to increase the ligand hydrophobicity. Because the different substituent groups affect ligand hydrophobicity in different ways, the K_p values for the different ligands were determined.

Triazolo-18-crown-6 type ligands exhibit ultraviolet absorption at 194-196 nm. None of the substituent groups studied here caused any significant variation in the position or the intensity of the absorption maximum. A control experiment also illustrated that the triazolo-18-crown-6 does not complex with Li^+. Therefore, the concentration of the ligand was determined by solvent

extraction using 0.3 M LiOH as source phase and 1 mM ligand in 2-octanone solution as the receiving phase and measuring the receiving phase ultraviolet absorption.

The K_p results are summarized in Table 4. It is seen that the Kp value for $(C_{12})_2$Tr18C6 is greater than that for C_8Tr18C6. The reason for the increased Kp value is that DC_{12}Tr18C6 has an additional chain and 12 rather than 8 carbon atoms in each chain. The Kp value for B_2Tr18C6 is greater than that of Cy_2Tr18C6. This is consistent with reported partitioning results for $Cy_2$18C6 and $B_2$18C6 (14).

K_{ex} Values: Comparision for Different Triazolo-18-crown-6 Ligands and Different Alkali Metal Cations

The K_{ex} values have been determined by solvent extraction experiments for different triazolo-18-crown-6 ligands and different alkali metal cations. The results are summarized in Table 4.

For each alkali metal cation, the extraction sequence for different ligands is $(C_{12})_2$Tr18C6> C_8Tr18C6> B_2Tr18C6> Cy_2Tr18C6. Since the Kp value for Cy_2Tr18C6 is very large, its extraction ability should be low. Due to the electron withdrawing effect of the benzo group and its effect for decreasing the ring flexibility, B_2Tr18C6 is not a good extraction agent. Comparing $(C_{12})_2$Tr18C6 with C_8Tr18C6, the Kp value for $(C_{12})_2$Tr18C6 is lower and its extraction ability is greater.

For each ligand, the extraction sequence is $K^+ > Na^+ > Rb^+ > Cs^+$. Since the ionic crystal radius of K^+ best matches the 18-crown-6 cavity radius, K^+ is bound most strongly by 18-crown-6 macrocycles. The ionic crystal radius of Na^+ is less than the 18-crown-6 cavity radius, but the ionic crystal radii of Rb^+ and Cs^+ are both larger than the 18-crown-6 cavity radius. Na^+ and Rb^+ are similar in their extraction behavior, with Na^+ being slightly preferred. In the complex process, the size matching appears to be the controlling factor. The extraction sequence data correspond well with the sequence results from the membrane experiment (Table 2). The reason for the sequence agreement is that transport is essentially diffusion limited in the organic phase boundary layer

near and on the membrane fibers (4,7,17,18). Since the $\underline{K}_{ex}$ values are derived from single cation solvent extraction experiments, these values qualitatively correspond to the membrane separation results. In previous work, we have shown that $\underline{K}_{ex}$ and flux values are quantitatively related when single cations are used in both experiments (17).

CONCLUSIONS

The DMHF system can be used to perform proton-ionizable macrocycle-mediated separations. The order of $\underline{K}_{ex}$ corresponds well to that found in membrane transport. Using this system, Ag^+ can be separated from virtually all other cations from neutral source phases using C_8Tr18C6, while K^+ separation over other soluble cations can be accomplished using the same macrocycle and a highly basic source phase. The K^+ separation can be performed from less basic source phases using C_8Tpy18C6 due to the lower pK_a value for this ligand. However, potential problems with macrocycle loss to the aqueous phases must still be considered with the system as it must be with other liquid membrane systems.

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REFERENCES

1. R.D. Noble and J.D. Way, Eds., Liquid Membranes: Theory and Applications, American Chemical Society, Washington, DC (1987).

2. C.J. King, Ed., Separation and Purification: Critical Needs and Opportunities, National Academy Press, Washington, DC, (1987).

3. J.D. Lamb, R.M. Izatt, and J.J. Christensen in Progress in Macrocyclic Chemistry, Vol. 2, R.M. Izatt and J.J. Christensen, Eds., John Wiley & Sons, New York, 1981.

4. J.D.Lamb, R.L. Bruening, D.A. Linsley, C. Smith, and R.M. Izatt, Sep. Sci. Technol., 25, 1407 (1990).

5. R.M. Izatt, G.C. Lindh, G.A. Clark, J.S. Bradshaw, Y.Nakatsuji, J.D. Lamb, and J.J. Christensen, J. Chem. Soc., Chem. Commun., 23, 1676 (1985).

6. R.M. Izatt, G.C. LindH, G.A. CLark, Y. Nakatsuji, J.S. Bradshaw, J.D. Lamb and J.J. Christensen, J. Membr. Sci., 31, 1 (1987).

7. R.M. Izatt, G.C. LindH, R.L. Bruening, P. Huszthy, C.W. McDaniel, J.S. Bradshaw, and J.J. Christensen, Anal. Chem., 60, 1694 (1988).

8. R.A. Bartsch, W.A. Charewicz, S.I. Kang, and W. Walkowiak in Liquid Membranes: Theory and Applications, R.D. Noble and J.D. Way, Eds., American Chemical Society, Washington, DC., 1987.

9. J.S. Bradshaw, C.W. McDaniel, B.D. Skidmore, R.B. Nielsen, B.E. Wilson, N.K. Dalley, and R.M. Izatt, J. Heterocyclic Chem., 24, 1085 (1987).

10. C.W. McDaniel, J.S. Bradshaw, K.E. Krakowiak, R.M. Izatt, P.B. Savage, B.J. Tarbet, and R.L. Bruening, J. Heterocyclic Chem., 26, 413 (1989).

11. M. Ouchi, Y. Inoue, K. Wada, S. Iketani, T. Hakushi, and E. Weber, J. Org. Chem., 52, 2420 (1987).

12. R.M. Izatt, G.C. LindH, R.L. Bruening, P. Huszthy, C.W. McDaniel, J.S. Bradshaw, and J.J. Christensen, Anal. Chem., 60, 1694 (1988).

13. R.M. Izatt, G.C. LindH, G.A. Clark, Y. Nakatsuji, J.S. Bradshaw, J.D. Lamb, J.J. Christensen, J. Membr. Sci., 31, 1 (1987).

14. C.J. Pedersen, J. Am. Chem. Soc., 89, 7017 (1967).

15. Y. Nakatsuji, J.S. Bradshaw, P-K. Tse, G. Arena, B.E. Wilson, N.K. Dalley and R.M. Izatt, J. Chem. Soc., 749 (1985).

16. A. Albert and G. B. Barlin, J. Chem. Soc., 2384 (1959).

17. R.M. Izatt, R.L. Bruening, M.L. Bruening, G.C. LindH, and J.J. Christensen, Anal. Chem., 61, 1140 (1989).

18. R.M. Izatt, D.K. Roper, R.L. Bruening, and J.D. Lamb, J. Membrane Sci., 45, 73 (1989).