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# APPLICATION OF MACROCYCLE COMPOUNDS FOR METAL IONS SEPARATION AND REMOVAL – A REVIEW

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## ABSTRACT

A review is presented on macrocyclic compounds novel reagents for metal ions separation and removal in solvent extraction, transport through liquid membranes, and flotation processes. As macrocyclic compounds were used such chemicals as non-ionizable crown ethers, ionizable crown ethers (lariat ethers), calixarenes, and acyclic polyethers. Many literature data as well our own recent research data will be reported on metal ions removal and separation.

Keywords: macrocycles, crown ethers, lariat ethers, metal ions, separation

## INTRODUCTION

Since discovery in 1967 by Pedersen [1] the first crown ether, i.e. dibenzo-18-crown-6 (**1** in Table 1), macrocycle compounds such as non-ionizable crown ethers, ionizable lariat ethers, cryptandes and calixarenes were applied for removal and separation of several metal ions. The recent advances of the crown ethers chemistry were reviewed by few authors [2-3]. Also acyclic polyethers were found as extractants and/or ionic carriers. The macrocycle types tend to form stable complexes with metal ions. Such complexes, which contain species incorporated in the macrocyclic cavity,

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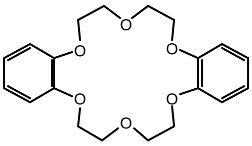
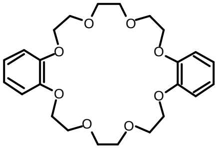
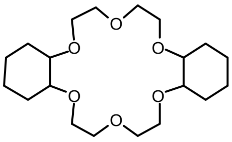
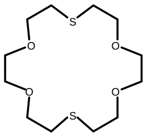
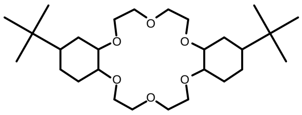
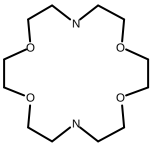
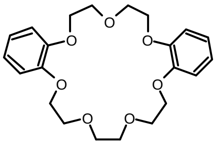
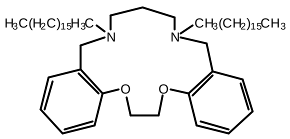
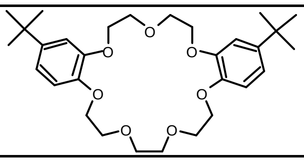
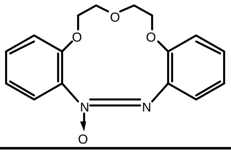
are usually known as inclusion complexes [4]. The general area covering the binding of all types of substrates in molecular cavities often is referred as host-guest chemistry. Structural modifications leads to macrocycle compounds with improved selectivity and efficiency in metal ion separations [5-7].

## NON-IONIZABLE CROWN ETHERS

Most of the macrocycles, which have been used for removal of metal ions, are neutral crown ethers (Table 1). When neutral crown ethers are used to mediate metal cations, anions must accompany the macrocycle complex to maintain electrical neutrality. Research on transport of alkali metal cations through Polymer Inclusion Membranes (PIMs) containing (**1**) shows that fluxes are growing in the order: $Na^+ < Rb^+ < K^+$ [8].

Tab. 1. Non-ionizable crown ethers.

| Compound number | Structural formula | Compound number | Structural formula |
|---|---|---|---|
| **1** |  | **6** |  |
| **2** |  | **7** |  |
| **3** |  | **8** |  |
| **4** |  | **9** |  |
| **5** |  | **10** |  |

A few papers have concerned the selective removal of zinc(II) and cadmium(II) cations with neutral crown ethers. Billah and Hohjo [9] extracted the mixture of cadmium(II) and zinc(II) from aqueous solutions as their thenyltrifluoroacetone complexes with DB18C6 into o-dichlorobenzen. At pH 4.9 only Zn(II) was extracted quantitatively, whereas Cd(II) remained in the aqueous solution. A reverse selectivity in $Zn^{2+}$ and $Cd^{2+}$ separation was obtained in transport across liquid membranes containing other 18-membered crown ether, i.e. **2**. In competitive transport of Zn(II) and Cd(II) through emulsion liquid membrane, near quantitative selectivity for Cd(II) over Zn(II) and Hg(II) has been achieved [9]. This can be explained by the preferential transport of neutral cation-anion moieties of $CdA_2$ from $Zn^{2+}$ and $HgA_2^{2-}$, where A = $SCN^-$, $I^-$, $Br^-$, or $Cl^-$ [10]. Cho et al. [11-13] found out that a single transport of $Cd^{2+}$ across emulsion liquid membranes by **7** from 0.4 M $SCN^-$ aqueous solutions is much more effective in comparison with $Zn^{2+}$.

The next series of experiments dealt with competitive transport of $Sr^{2+}$, $Cs^+$, and $Co^{2+}$ cations from dilute aqueous solutions containing the metal ions species at concentrations of $1.0 \cdot 10^{-6}$ M and 0.10 M sodium nitrate (pH = 4,0) through PIMs with **4**, **5**, and 3,7-dinonyl-naphtalene-1-sulfonic acid (DNNS) as the ionic carriers [14]. We also used mixtures one of studied crown ethers with DNNS as the ionic carriers. The fluxes are shown in Fig. 1.

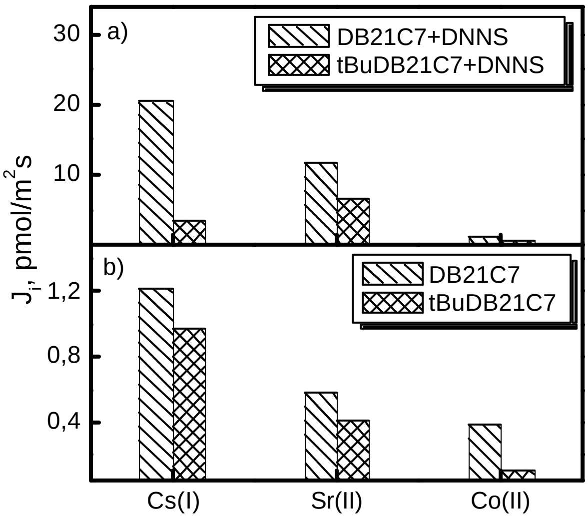


Fig. 1. Cesium(I), strontium(II), and cobalt(II) initial fluxes for competitive transport across PIMs with crown ethers **3**, **4** and DNNS as ionic carriers. Source phase: $1.0 \cdot 10^{-6}$ M of $Cs^+$, $Sr^{2+}$ and $Co^{2+}$, 0.10 M of $NaNO_3$, pH = 4.0; Receiving phase: 0.5 M HCl; Membrane: 0.30 M crown ethers, 0.10 M DNNS.

For both crown ethers with cavity size of 21-crown-7, the initial fluxes for $Cs^+$, $Sr^{2+}$, and $Co^{2+}$ are very low with selectivity order: Cs(I) > Sr(II) > Co(II). Consequently, the removal of all metal cations from the source phase is low and does not exceed 30 % of particular metals. The **4** and DNNS mixture applied as ionic carrier gives the same selectivity order as **4** alone but much higher initial fluxes and recovery factors of cesium(I) are observed. The similar synergetic membrane transport of Sr(II) and Pb(II) through PIMs containing crown ethers and didodecylnaphtalene-sulfonic acid was reported by Nazarenko and Lamb [15]. The **5** and DNNS mixture used as ionic carrier reverse selectivity order in comparison with **5** alone but initial fluxes and recovery factors are not such high as observed for **4** + DNNS mixture. The comparison of two crown ethers with the same, cavity size, shows that attachment of tertbutyl group into two benzo rings as a lipophilic part of crown ether decreases the cesium(I) transport, and increases the strontium(II) transport through PIMs containing the mixture of crown ether (**4** or **5**) and DNNS as an ionic carrier.

Recently, we have studied the competitive transport of Cs$^{+}$, Sr$^{2+}$, and Co$^{2+}$ ($c_{Me} = 1.0\cdot10^{-6}$ M) from 0.1 M aqueous solution of NaNO$_3$ through PIMs containing azoxycrown **10** [16]. The kinetics of this process is shown in Fig. 2.

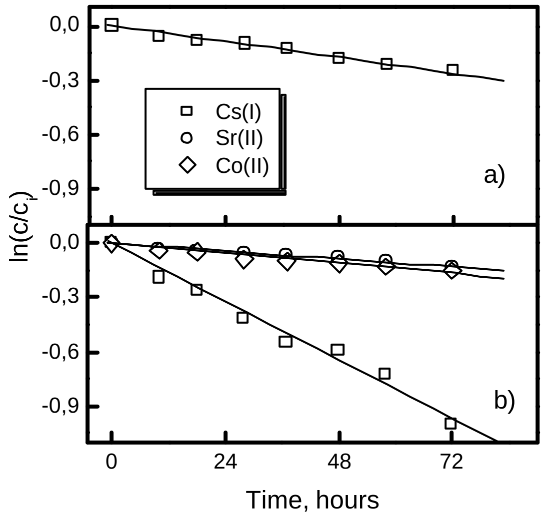


Fig. 2. Kinetics of Cs(I), Sr(II), and Co(II) transport through PIMs containing 0.3 M azacrown (a) and 0.3 M azacrown +0.10 M DNNS.

As can be seen from this figure, azoxycrown **10** applied as an ionic carrier gives very slow transport of Cs(I), with no Sr(II) and Co(II) detected in a receiving phase. The initial flux of Cs(I) was equal to 1.00 pmol/m$^2$s. But applying the mixture of **10** and DNNS as an ionic carrier the higher flux of Cs(I) was observed, i.e. 3.6 pmol/m$^2$s. The initial fluxes of Co(II) and Sr(II) were much smaller and equal to 0.65 and 0.52 pmol/m$^2$s, respectively. Other non-ionizable crown ethers, i.e. **3**, **6**, **8**, and **9** were used for alkali and transition metal cations removal and separation [2].

## LARIAT ETHERS

Crown ethers with pendant acidic functions or acidic groups incorporated into macrocyclic structure are novel ionic carriers in the liquid membranes or collectors in ion flotation process. They are recently called lariat ethers. For such carriers (collectors), the cations are complexed within the cavity of the anionic from of the crown ether during passage through the organic membrane or at aqueous/gas interface and thus eliminating the need for contaminant transport of an aqueous phase anions. The proton ionizable lariat ethers, which were recently studied for metal cations removal and separation are shown in Table 2.

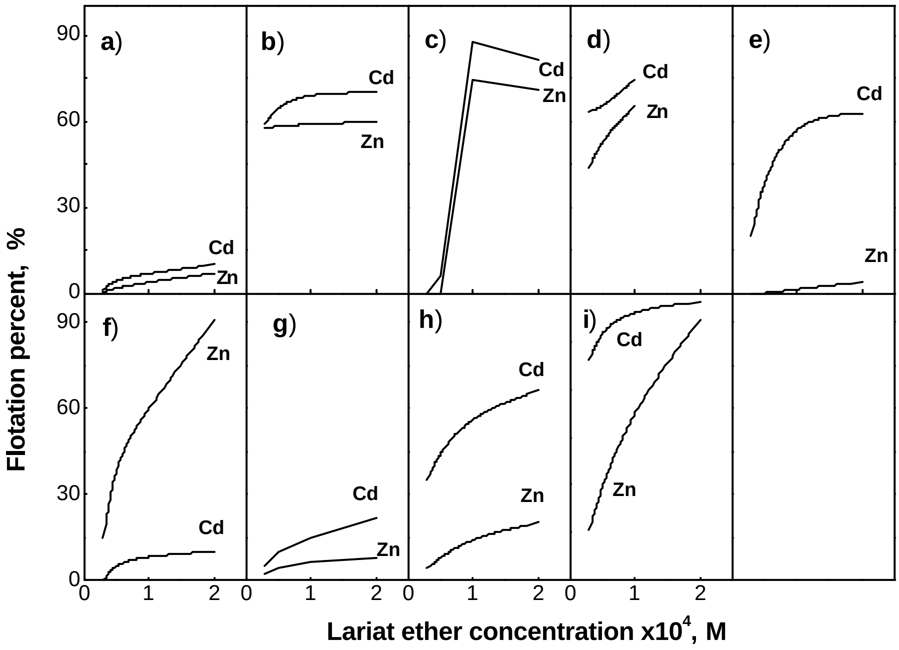
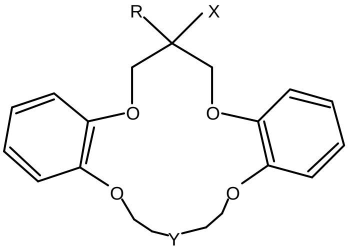


Fig. 3. Competitive ion flotation of Zn(II) and Cd(II) in presence of lariat ethers: **15** (a), **14** (b), **13** (c), **12** (d), **16** (e), **26** (f), **27**, (g) **28**, (h) and **29** (i). $[Zn^{2+}] = [Cd^{2+}] = 1.0 \cdot 10^{-5}$ M, pH = 4.0, [Foaming agent] = $2.0 \cdot 10^{-4}$ M.

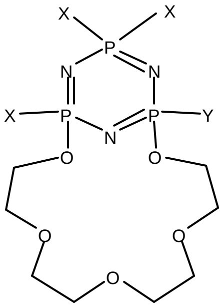
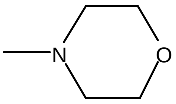
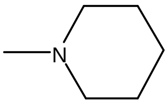
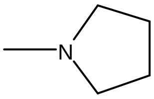
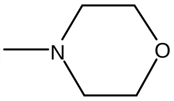
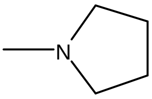
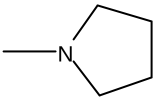
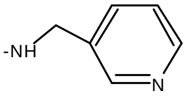
Tab. 2. Proton-ionizable lariat ethers.

<table>
<tr><td colspan="5">General formula<br> </td></tr>
<tr><th>No.</th><th>R</th><th>X</th><th>Y</th><th>n</th></tr>
<tr><td>**11**</td><td>$C_nH_{2n+1}$</td><td>$OCH_2COOH$</td><td>$(CH_2)_2O(CH_2)_2$</td><td>2÷16</td></tr>
<tr><td>**12**</td><td>$C_{10}H_{21}$</td><td>$OCH_2COOH$</td><td>$(CH_2)_2O(CH_2)_2$</td><td></td></tr>
<tr><td>**13**</td><td>$C_{10}H_{21}$</td><td>$O(CH_2)_3SO_3Na$</td><td>$(CH_2)_2O(CH_2)_2$</td><td></td></tr>
<tr><td>**14**</td><td>$C_3H_7$</td><td>$O(CH_2)_3SO_3Na$</td><td>$(CH_2)_2O(CH_2)_2$</td><td></td></tr>
<tr><td>**15**</td><td>H</td><td>$O(CH_2)_3SO_3Na$</td><td>$(CH_2)_2O(CH_2)_2$</td><td></td></tr>
<tr><td>**16**</td><td>$C_4H_9$</td><td>$OCH_2PO(OH)(C_2H_5)$</td><td>$(CH_2)_2O(CH_2)_2$</td><td></td></tr>
<tr><td>**17**</td><td>$C_6H_5$</td><td>$OCH_2COOH$</td><td>$(CH_2)_2\text{-}O(CH_2)_2$</td><td></td></tr>
<tr><td>**18**</td><td>$2\text{-}(CH_3)C_6H_4$</td><td>$OCH_2COOH$</td><td>$(CH_2)_2\text{-}O(CH_2)_2$</td><td></td></tr>
<tr><td>**19**</td><td>$3\text{-}(CH_3)C_6H_4$</td><td>$OCH_2COOH$</td><td>$(CH_2)_2\text{-}O(CH_2)_2$</td><td></td></tr>
<tr><td>**20**</td><td>$4\text{-}(CH_3)C_6H_4$</td><td>$OCH_2COOH$</td><td>$(CH_2)_2\text{-}O(CH_2)_2$</td><td></td></tr>
<tr><td>**21**</td><td>$3,5\text{-}(CH_3)C_6H_4$</td><td>$OCH_2COOH$</td><td>$(CH_2)_2\text{-}O(CH_2)_2$</td><td></td></tr>
<tr><td>**22**</td><td>$C_6H_5\text{-}(CH_2)_n$</td><td>$OCH_2\text{-}CO\text{-}NH\text{-}(SO_2)\text{-}CH_3$</td><td>$(CH_2)_2\text{-}O(CH_2)_2$</td><td>0÷5</td></tr>
<tr><td>**23**</td><td>$C_6H_4\text{-}(CH_2)_4$</td><td>$OCH_2\text{-}CO\text{-}NH\text{-}(SO_2)\text{-}C_6H_5$</td><td>$(CH_2)_2\text{-}O(CH_2)_2$</td><td></td></tr>
<tr><td>**24**</td><td>$C_6H_4\text{-}(CH_2)_4$</td><td>$OCH_2\text{-}CO\text{-}NH\text{-}(SO_2)\text{-}C_6H_4NO_2$</td><td>$(CH_2)_2\text{-}O(CH_2)_2$</td><td></td></tr>
<tr><td>**25**</td><td>$C_6H_4\text{-}(CH_2)_4$</td><td>$OCH_2\text{-}CO\text{-}NH\text{-}(SO_2)\text{-}CF_3$</td><td>$(CH_2)_2\text{-}O(CH_2)_2$</td><td></td></tr>
<tr><td>**26**</td><td>H</td><td>$OCH_2COOH$</td><td>$(CH_2)_2$</td><td></td></tr>
<tr><td>**27**</td><td>$CH_3$</td><td>$OCH_2COOH$</td><td>$(CH_2)_2O(CH_2)_2O$ $(CH_2)_2$</td><td></td></tr>
<tr><td>**28**</td><td>$C_2H_5$</td><td>$OCH_2COOH$</td><td>$(CH_2)_2O(CH_2)_2O$ $(CH_2)_2$</td><td></td></tr>
<tr><td>**29**</td><td>$C_3H_7$</td><td>$OCH_2COOH$</td><td>$(CH_2)_2O(CH_2)_2O$ $(CH_2)_2$</td><td></td></tr>
</table>

Bartsch et al. has widely studied the competitive solvent extraction and transport across liquid membranes of alkali metal cations from aqueous solutions using ionizable lariat ethers (**11**, **17** ÷ **25**) [17-20]. On the other hand, the competitive ion flotation of $Zn^{2+}$ and $Cd^{2+}$ cations with proton – ionizable lariat ethers **12** ÷ **16** and **26** ÷ **29** is shown in Fig. 3 [21]. The following selectivity sequences for studied lariat ethers were observed: for dibenzo-13-crown-4 $Cd^{2+} < Zn^{2+}$, for dibenzo-16-crown-5 $Zn^{2+} \leq Cd^{2+}$, and for dibenzo-19-crown-6 $Zn^{2+} < Cd^{2+}$.

One of the most developing aspects of new ligands is the design and synthesis of lariat ethers which are side-armed crown ethers with pendant groups attached to the so called pivot atoms [22]. These macrocycles are known as PNP – lariat ethers. Examples of new type lariat ether with cyclophosphazene subunits are given in Table 3. The results of competitive ion flotation for $Zn^{2+}$ and $Cd^{2+}$ cations using diphosphaza-crown ethers with PNP-16-crown-6 cavity size (**30** ÷ **36**) are shown in Fig. 4. For all substituents better floatability of Cd(II) than Zn(II) cations was received [23].

Tab. 3. Cyclophosphazene PNP-crown derivatives.

| Structure | Compound number | Substituent |
|---|---|---|
|  | **30** | X = Y:  |
| | **31** | X = Y:  |
| | **32** | X = Y:  |
| | **33** | X = Y: $O(CH_2CH_2O)_3CH_3$ |
| | **34** | X :  Y: $NH(CH_2)_3OH$ |
| | **35** | X :  Y: $-NH(CH_2)_3OH$ |
| | **36** | X :  Y:  |

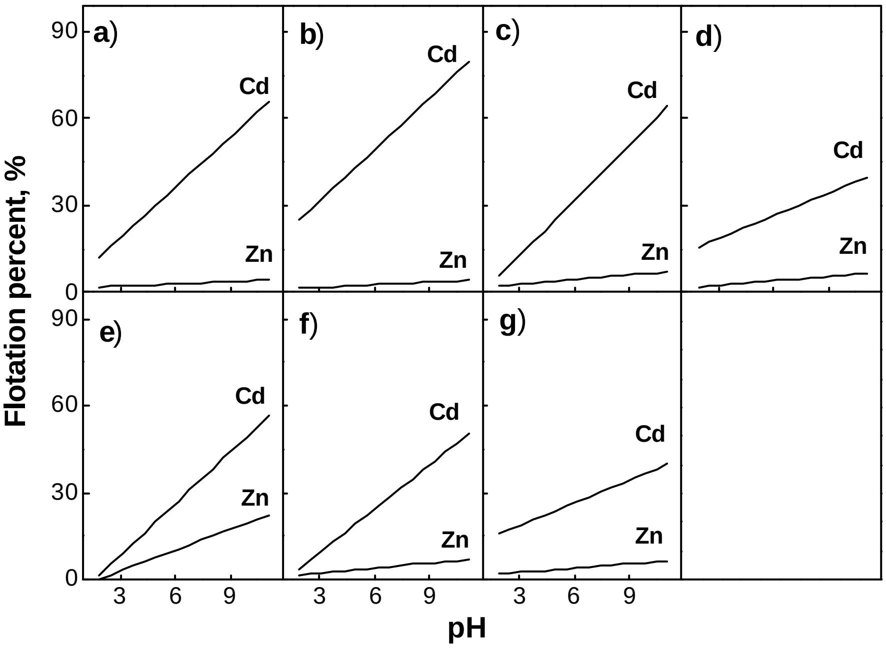
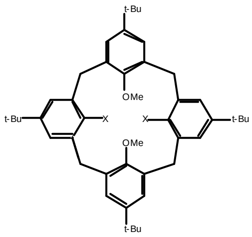
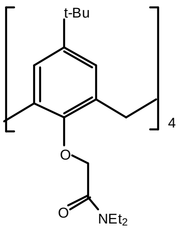
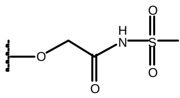
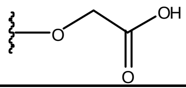
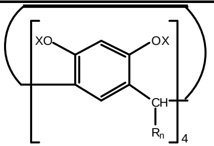
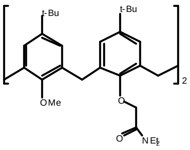
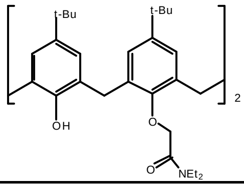


Fig. 4. Competitive ion flotation of Zn(II) and Cd(II) in presence of lariat ethers: **30** (a), **31** (b), **32** (c), **33** (d), **34** (e), **35** (f), and **36** (g). $[Zn^{2+}] = [Cd^{2+}] = 1.0 \cdot 10^{-5}$ M, pH = 4.0, [Foaming agent]= $2.0 \cdot 10^{-4}$ M.

## CALIXARENES

Another important class of macrocyclic host molecules, which efficiently and selectively bind a variety of ionic and neutral guest species are calixarenes [24]. Calix[4]arenes **37** ÷ **41** were used by Talanova et al. for selective $Pb^{2+}$ solvent extraction [25]. These new calixarenes with two N-(X)sulfonyl carboxamide groups of tuneable acidity were found to exhibit good to excellent extraction selectivity for $Pb^{2+}$ over most alkali, alkaline earth, and transition metal ions. Also calix[4]arenes were used as collectors of ion flotation process. Koide et al. [26] investigated compound **42** as collector in competitive flotation of alkali metal cations - $Cs^+$ cations were floated selectively. Other calixarene, i.e. phosphate esters of C-undecylcalix[4]resorcinarene (**43**), was used as the collector for uranium(VI) ion flotation from very dilute aqueous solutions [27]. The flotability of $UO_2^{2+}$ cations was nearly 100 % at pH = 7.0. Lower rim amide-substituted calix[4]arenes **44** ÷ **46** were found as extractants for Cr(VI), Mo(VI), W(VI), Re(VII), Se(VI), and U(VI) from aqueous solutions into an organic phase [28].

Tab. 4. Calixarenes.

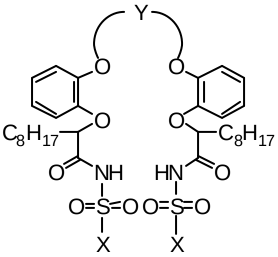
| Structural formula | | | No. | Structural formula | No. |
|---|---|---|---|---|---|
|  | X: | Y: | |  | **45** |
| |  | $CF_3$ | **37** | | |
| | | $CH_3$ | **38** | | |
| | | $C_6H_5$ | **39** | | |
| | | 4-$NO_2$-<br>$C_6H_4$ | **40** | | |
| | X:<br> | | **41** | | |
|  | X: H<br>n = 8, 12, 16 | | **42** |  | **46** |
| | X: POOH + PO(OH)$_2$<br>n = 12 | | **43** | | |
|  | | | **44** | | |

## ACYCLIC POLYETHERS

Acyclic polyethers have been also used for separation of alkali metal, alkaline earth metal and transition metal cations [29-31]. Previously Walkowiak et al. [32,33] has studied the competitive solvent extraction of metal cations using proton-ionizable polyethers with two carboxylic groups. The removal of alkali metal cations from aqueous solutions was investigated. On the other hand, Lee et al. [34] using a lipophilic acyclic polyether dicarboxylic acid has studied the transport of $Pb^{2+}$ in through polymer inclusion and bulk liquid membranes. Structures of acyclic polyethers used to transport $Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$, and $Ba^{2+}$ cations through PIMs are shown in Table 5. Competitive transport of alkaline earth metal cations across plasticized cellulose triacetate membranes by acyclic di-ionizable polyethers **47** ÷ **58** was investigated by Eliasi [35].

The structural variations, which were investigated, include varying length of the "bridge" that connects two identical halves of the carrier. Also, the acidity of the ligands was tuned by varying the terminal groups; this acidity is increasing in the order: $CH_3 < C_6H_5 < 4\text{-}NO_2\text{-}C_6H_4 < CF_3$. For polyethers with phenyl groups, i.e. **48**, **52**, and **56** the total transport rate was very small (i.e. below 0.025 $\mu$mol/m$^2$s). The highest values of fluxes were observed for polyethers with trifluoromethyl groups. The total fluxes for **50**, **54**, and **58** were equal to 4.61, 2.22, and 1.92 μmol/m$^2$s, respectively. For all studied acyclic poyethers, with increasing of the bridge length, i.e. Y (Table 5), the total flux of alkaline earth metal cations decreases. The best transported metal cation was barium, and for **49**, **50**, and **54** the values of molar Ba$^{2+}$/total metal ratio were equal to 0.96.

Tab. 5. Acyclic di-ionizable polyethers.

| General structure | Compound number | Y | X |
|---|---|---|---|
|  | **47** | $(CH_2)_2$ | $CH_3$ |
| | **48** | $(CH_2)_2$ | $C_6H_5$ |
| | **49** | $(CH_2)_2$ | 4-$NO_2$-$C_6H_4$ |
| | **50** | $(CH_2)_2$ | $CF_3$ |
| | **51** | $(CH_2)_3$ | $CH_3$ |
| | **52** | $(CH_2)_3$ | $C_6H_5$ |
| | **53** | $(CH_2)_3$ | 4-$NO_2$-$C_6H_4$ |
| | **54** | $(CH_2)_3$ | $CF_3$ |
| | **55** | $(CH_2CH_2)_2O$ | $CH_3$ |
| | **56** | $(CH_2CH_2)_2O$ | $C_6H_5$ |
| | **57** | $(CH_2CH_2)_2O$ | 4-$NO_2$-$C_6H_4$ |
| | **58** | $(CH_2CH_2)_2O$ | $CF_3$ |

The single and competitive transport of alkaline earth metal cations through bulk and supported liquid membranes using a proton dicarboxylic acyclic polyethers was reported by Kim et al. [36,37] For the compounds having the same n-buthyl side chain as a lipophilic tail and the number of ethylene glycol units increasing from one to three, the flux of transport for single alkaline earth cations increased. In most cases, during competitive transport, the selectivity of calcium cations over the other alkaline earth metal cations was found to be enhanced.

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