Selective Removal of Barium and Hardness Ions from Brackish Water with Chemically Enhanced Electrodialysis

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Abstract

The use of nonconventional water resource for energy and industrial applications often requires extraction of low-level undesirable ions from benign dominant ions. In this study, selective extraction of Ba^{2+} and Mg^{2+} from synthetic brine solutions was evaluated using strong-acid cation exchange membranes modified with surface deposition of macrocyclic molecules including crown-ethers and calixarenes. Compared to the bare membrane, vinylbenzo-18-crown-6 (VB18C6) and calix[4]arene-amended membranes showed increased selectivity for Ba^{2+} and Mg^{2+} with respect to the dominant ion (Na^{+}) by up to four folds, with calix[4]arene-modified membrane achieving more selective separation than VB18C6. Optimal selectivity was achieved at a moderate to high current density (3.1 to 6.3 mA/cm^2), which was attributed to the alleviation of transport limitation in the boundary layer by the surface modification. Amendment of a calix[4]arene derivative with a crown-6 “boot strap” and two carboxylic groups resulted in reduced selectivity due to formation of strong complexes with divalent ions. These results show that surface deposition of ion sequestrants can be a versatile approach to improve membrane’s selectivity, however, the performance is also sensitive to feed water salinity, current loading, and the macrocycle-ion chemistry, where there is a trade-off between ion affinity and mobility.

Keywords: electrodialysis, crown ether, calixarenes, barium, magnesium, divalent selectivity

Synopsis

Surface amendment of a cation exchange membrane with crown ether or calixarene-based ion sequestrants increases the selectivity of electrodialysis process for divalent ions.

Introduction

The interdependence of energy and water has generated significant interest in tapping into nonconventional water sources for industrial and energy exploration applications.[1] Among various ion separation technologies, pressure-driven membrane separation such as reverse osmosis (RO)[2] and thermally enabled separation processes such as membrane distillation[3] have found increasing use in treating water for total dissolved solids (TDS) removal for domestic use. However, in many industrial applications, the major ionic constituents are innocuous for water's intended functions, while the ions of concerns are minority species. For instance, the efficiency of water as cooling medium is affected by elevated presence of hardness ions, and the applications of brackish water from deep underground formation in energy exploration are constrained by high levels of Ba^{2+}, Sr^{2+}, and naturally occurring radioactive minerals.[4-6] To this end, using conventional desalination technologies to remove low-concentration problematic ions from saline water matrices will incur an excessive energy input. There is a pressing need for technologies that can preferentially remove ions of choice without going through general desalination processes.

Electrodialysis (ED) is an established technology for treating brackish water of moderate to high TDS.[7-9] Compared to RO and nanofiltration (NF), ED is able to withstand a broader range of temperature and water chemistry and is more robust against fouling than pressure-driven membrane separation processes.[8-10] The key components of an ED device are cation and anion exchange membranes, which carry fixed charges that permit the permeation of ions of opposite charges (i.e., counter-ions) while obstructing the passage of similarly charged ions (i.e., co-ions).[11] Conventional ion exchange membranes offer high permselectivity between counter ions and co-ions, however, efficient separation of ions of similar charges is more difficult to achieve. A variety of methods have been explored to create ion exchange membranes with tailored selectivity. The

most notable examples include amending the surface of an ion exchange membrane with an oppositely charged layer to create monovalent ion-selective membranes for table salt production[12] and proton-selective membranes for fuel cell-related applications.[13-15] Recent studies reported that incorporating crown ethers in a cation exchange membrane (CEM) enables selective removal of Cs^+ relative to Na^+.[16, 17] The improvement effect was observed when crown ethers were confined in a thin layer on the membrane surface, enabling an ion-gating mechanism, and this effect was lost when the crown ethers were incorporated throughout the polymer matrix.[17] The preferential removal of specific ions derives from ion binding abilities of the crown ether molecules, in which the oxygen atoms in the central cavity are attractive to metal ions (Scheme 1) and the size and conformation of the cavity determine binding specificity.[18-21] In addition to crown ethers, other macrocyclic ion sequestrants such as calixarenes have been designed to selectively extract various metal ions. The structure of calixarenes contains multiple phenolic units bridged by methylene groups, forming a three-dimensional bucket shape (Scheme 2).[22, 23] The most common calixarene compound is calix[4]arene, which contains four phenolic units. The phenol groups are easily functionalized with pendant ionizable groups thus affording a large degree of structural and chemical modularity.[24] Calixarenes have found applications in extraction of barium and radium,[23] heavy metals,[25] and lanthanide and actinide separation.[26] The selectivity of the ion sequestrants is controlled by metal-host conformational matching and chemical coordination.

Although a variety of ion sequestrants have been produced and they are routinely used in solvent extraction processes, conjugating electrodialysis membranes with ion sequestrants is a novel concept that has not been examined closely except for a limited number of studies using crown ethers as additives to ion exchange membranes.[16, 17] The capabilities of ion sequestrants other than crown ethers and the effects of pertinent system parameters have not been investigated closely.

The objective of this study was to examine the use of cation exchange members modified with crown ether or calixerene-based sequestrants for selective separation of Ba^{2+} and Mg^{2+} from brine solutions. Ba^{2+} is of interest due to its elevated concentration in deep formation water posing significant scaling concerns [4]. Mg^{2+} is a hardness ion found ubiquitously in natural water (the other hardness ion, Ca^{2+}, was not evaluated due to interference with instrument analysis). Compared to the prevalent method of creating a positively charged layer on a cation exchange member to achieve monovalent-ion selective separation, the proposed system here aims at using chemical sequestrants to increase membrane selectivity for dilute target ions amid complex solution matrix. Since the structure and properties of the sequestrates are amendable to tuning for specific ions, coupling sequestrants with ion exchange membranes may lead to a versatile and expandable approach for selective ion separation in lieu of the more energy intensive general desalination treatment.

Materials and Methods

Chemicals

Commercially available cation exchange membranes (CEM), PCSK™, and anion exchange membranes (AEM), PCSA™, were purchased from PCCell GmbH (Germany). Membranes were stored in 1 M NaCl solution prior to use. All salts including nitrate salts of sodium, magnesium, and barium were of ACS reagent grade. Tetrahydrofuran (THF) was dried over sodium and stored on activated molecular sieves prior to use. Anhydrous benzene and pyridine were purchased commercially (Sigma Aldrich) and used as received. All other reagents were obtained from commercial vendors and used without any further purification. Synthesis routes to both the vinyl-substituted crown ethers (**9-11,** numbers correspond to chemicals shown in the schemes) and the 'boot-strapped' calix[4]arene (**14**)[23] are shown in schemes 1 and 2, respectively.

Characterization of isolated organic products was accomplished using nuclear magnetic resonance (NMR) spectroscopy and all data is fully consistent with published spectral data.

Synthesis of Ion Sequestrants

*Synthesis of 3,4-dihydroxystyrene (**2**).* A mixture of methyl triphenylphosphonium bromide (**1**) (20.15 mmol, 7.20 g, 1.5 equiv.) in THF was treated with potassium *tert*-butoxide (33.57 mmol, 3.77 g, 2.5 equiv.). After stirring for 15 minutes at room temperature, a solution of 3,4-dihydroxybenzaldehyde (**1**) (13.39 mmol, 1.85 g, 1 equiv.) in THF was added in a dropwise fashion to the reaction mixture. After stirring overnight at room temperature, the reaction mixture was quenched with saturated NH_4Cl solution and concentrated under reduced pressure. The concentrated reaction mixture was extracted with dichloromethane (DCM), the organic layer washed with brine and subsequently dried over $MgSO_4$. The mixture was filtered, the organic solvent removed via evaporation and the residue purified by column chromatography (15 % ethyl acetate in hexanes) to the pure product as a white solid (1.09 g, 60%). ^1H (400 MHz, $CDCl_3$, 298K): 6.97 (s, 1H), 6.83 (s, 2H), 6.57 (q, 1H, J = 8Hz), 6.36 (brS, 2H), 5.54 (d, 1H, J = 16Hz), 5.09 (d, 1H, J = 12 Hz).

General Procedure for the Synthesis of Crown Ethers. To a round bottom flask equipped with a stir bar, DMF and potassium carbonate (2.18 equiv.) were added, and the mixture was warmed to 150 ^oC. To the mixture was added both **2** (1 equiv.) and the desired dichloro-species (**6**, **7** or **8**) (1 equiv.) in a slow, dropwise manner. The reaction mixture was heated at 150 °C for a further 24 h. After completion of the reaction, the solvent was removed, and the crude product extracted with DCM. The organic phase was washed with saturated $NaHCO_3$, filtered and the solvent removed under reduced pressure to afford analytically pure crown ether products, namely, vinylbenzo-15-crown-5 (VB15C5), vinylbenzo-18-crown-6 (VB18C6), and vinylbenzo-21-crown-7 (VB21C7)

(**9**, **10** or **11**), as dark yellow and viscous oils (73, 85 and, 81% respectively). **9:** ^{1}H (400MHz, $CDCl_3$, 298K): 6.96-6.91 (m, 2H), 6.81-6.79 (m, 1H), 6.61 (q, 1H, J = 4 Hz), 5.57 (d, 1H, J = 16 Hz), 5.11 (d, 1H, J = 12 Hz), 4.18-4.14 (m, 4H), 3.94-3.91 (m, 4H), 3.76-3.59 (m, 20H);^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): 148.9, 136.4, 131.2, 119.9, 113.7, 111.9, 111.5, 70.8, 69.6, 69.5, 69.0. **10:** ^{1}H (400MHz, $CDCl_3$, 298K): 6.94-6.91 (m, 2H), 6.81-6.78 (m, 1H), 6.61 (q, 1H, J = 4Hz), 5.58 (d, 1H, J = 12Hz), 5.12 (d, 1H, J = 12Hz), 4.15-4.11 (m, 5H), 3.91-3.89 (m, 5H), 3.71-3.65 (m, 12H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): 149.0, 136.5, 131.3, 120.1, 113.9, 112.0, 111.8, 70.8, 70.7, 69.7, 69.3. **11:** ^{1}H (400MHz, $CDCl_3$, 298K): 6.69-6.64 (m, 2H), 6.57-6.53 (m, 1H), 6.34 (q, 1H, J = 4Hz), 5.30 (d, 1H, J = 16 Hz), 4.85 (d, 1H, J = 12 Hz), 3.90-3.88 (m, 5H), 3.63-3.62 (m, 5H), 3.48-3.33 (m, 24 H).

Synthesis of Calixarenes. *p*-tert-butylcalix[4]arene (**12,** denoted as tBCalix4) was used as purchased. The phenolic groups in tBCalix4 were functionalized to incorporate a crown ether "boot strap" and ionizable groups to form *p*-tert-butylcalix[4]arene-crown-6 (**13**) and *p-tert*-Butylcalix[4]arene-crown-6-dicarboxylic acid (**14,** or tBCalix4-C6DA), respectively. The latter was reported to have a high affinity for Ba^{2+}.[23] The synthesis procedures for **13** and **14** are described in the SI.

Aqueous Extraction Experiments

The synthesized crown ethers were assessed for their selectivity for barium and hardness ions via aqueous extraction experiments as detailed in the SI.

Modification of CEMs with sequestrants

The surface of the membrane was deposited with a thin layer of the synthesized sequestrants to impart improved ion selectivity. Specifically, a PCSK membrane was removed from its storage solution and excess water on the surface was wiped clean. The membrane was mounted on a

glass platform with four corners of the membrane fixed using metal clamps. 120 mg of VB18C6 was dissolved in 20 mL DCM (equivalent to 18 mM) and the solution was amended with methylene blue (to reach approximately 1 mM) to enable easy visualization of the coating uniformity. 2.5 mL of the crown ether solution was evenly sprayed on the exposed surface of a PCSK membrane using a hand-held precision air brush (Aeroblend^{TM} Light), equivalent to a surface density of 0.70 μmol/cm^2. The membrane was allowed to air dry for 15 min to evaporate the solvent. The resultant membrane was rinsed with ethanol to remove excess DCM and was soaked in 1M NaCl solution for 2 days with the soaking solution replaced periodically for at least 3 cycles. Modification of the CEM with calixarenes follows a similar protocol except that the concentration of the respective sequestrant in DCM was 12.5 mM, corresponding to a surface density of 0.49 μmol/cm^2. The images of membrane before and after air-brush deposition are available in the SI (Figure S1).

Membrane Characterization

The native CEM and modified membranes were characterized using Fourier transform infrared spectroscopy (FTIR). FTIR spectra were recorded on a Nicolet iS10 infrared spectrometer using an attenuated total reflectance (ATR) attachment equipped with a diamond crystal. A small piece of the native or modified membrane was removed using a hole punch. The piece was placed in the center of the ATR and a spectrum was collected. For comparison, FTIR spectra were also collected for sequestrants VB18C6 and tBCalix4. Membrane potential was measured in barium solutions following the procedure in the SI. The morphology of the membrane surface was characterized with scanning electron microscopy (JOEL 7401 FESEM) equipped with energy-

dispersive X-ray spectroscopy (EDX). Samples were coated with 6 nm Au to alleviate surface charging.

Electrodialysis Experiments

Electrodialysis tests were set up in a four-chamber electrodialysis (ED) unit employing platinum/iridium-mixed metal oxide-coated titanium as the anode and stainless steel as the cathode (ED 64004 by PCCell GmbH, Germany). The cell dimension was 11 x 11 cm and effective membrane area was 8 x 8 cm. The configuration of the ED unit is shown schematically in Figure 1. The two compartments in the center carried diluate and concentrate flows, respectively, which were separated by either a CEM or a chemically modified CEM. The chemically modified surface faced the diluate stream unless otherwise noted. The two compartments close to the electrode ends carried electrode rinse flows. Peristatic pumps were used to recirculate the diluate, concentrate, and electrode rinse solutions between the ED unit and the respective tanks. Electrode rinse solution was 0.2 M $NaNO_3$ solution. Diluate and concentrate tanks had 0.5 L of Na^+, Mg^{2+}, and Ba^{2+} solution (as nitrate salts), and the concentration of each ion was initially the same in the two tanks to eliminate any initial concentration gradient. Prior to the start of a test, all chambers were flushed with the respective solutions for 30 min to equilibrate the membranes with solutions. Following that, a potential was applied to start the electrodialysis process. Periodically, a small aliquot of sample (< 1 mL) was drawn from the diluate and concentrate tanks. Samples were immediately diluted, filtered through 0.2 μM PTFE syringe filters (Millex-LG, Millipore), and acidified with HNO_3 for storage at 4^{o}C prior to analysis for Na, Mg, and Ba concentrations by inductively coupled plasma-mass spectrometry (ICP-MS, Perkin Elmer ELAN DRC-e). For a specific experiment, duplicate or triplicate runs

were performed using the same virgin or modified membrane. Error bars in the figures or tables represent the standard deviation of the repeated experiments. To demonstrate the stability of modified membranes, repeating runs were not performed consecutively but repeated after a set of experiments using different membrane were completed over a duration up to 3 months. Idle membranes were stored in 1M $NaNO_3$ solutions.

The flux of an ion, J_i, across the CEM is estimated by Eq. (1):

$$J_i = \left(\frac{\Delta C_{i,D}}{\Delta t}\right)\frac{V_D}{A} \quad (1)$$

Where $\Delta C_{i,D}$ is the change in the concentration of the respective ion in the diluate tank at two sampling times, V_D volume of the diluate solution, and A effective membrane area.

The transport number, t_i, of species i is calculated as in Eq.(2):

$$t_i = \frac{Z_i \cdot J_i}{\sum Z_i \cdot J_i} \quad (2)$$

Where Z_i is the nominal charge of the ion i.

The selectivity of the membrane for species i over j, $P_{i/j}$ was estimated using Eq. (3):

$$P_{i/j} = \frac{t_i/t_j}{Z_i\bar{C}_i/Z_j\bar{C}_j} \quad (3)$$

where $\bar{C}_i$ or $\bar{C}_j$ is the average concentration of the respective ion in diluate. Since concentrations varied linearly with time in the initial phase of the ED test, the average concentrations were estimated from a linear fit of the data of the first 90 min.

The average current efficiency of an electrodialysis experiment was evaluated using Eq. (4):

$$\eta = \frac{(\sum Z_i \cdot J_i) \cdot A}{I} \quad (4)$$

where I is the applied current and other parameters are defined in the previous equations.

Results and Discussion

Crown ether-based ionophores have been studied for the extraction of various metal ions. The size and conformation of the central cavity are key factors affecting ion extraction efficiency and selectivity.[18-20, 24] VB15C5, VB18C6, and VB21C7 were synthesized in this study and their affinity for target ions were evaluated using aqueous/solvent extraction experiments over a pH range of 4 to 8. The results (Figure S2) show that VB18C6 extracted Ba^{2+} and hardness ions more efficiently than 5 or 7-oxygen crown ethers, consistent with prior reports.[27, 28] The extraction of VB18C6 was less affected by pH changes than other candidate crown ethers; it was therefore selected to modify CEM in the subsequent experiments. Another class of sequestrants of interest are calixarenes. The molecular structures of calixarenes consist of phenolic units bridged by methylene carbons forming a central cone-shaped cavity (Scheme 2). Within the class, calix[4]arene, with four phenolic units, is the most common and possesses high affinity for alkaline earth and f-block elements.[25, 26] In this study, PCSK membranes were amended with VB18C6 or tBCalix4 and the resultant membranes were immersed in NaCl solution for three cycles to remove unattached residues. The native and modified membranes were characterized using ATR-FTIR spectroscopy (Figure 2). Both the VB18C6 and tBCalix4 modified membranes exhibit signals that correlate with the respective sequestrants. Specifically, for the VB18C6 modified membrane, the signals in the range of 2848 to 2962 cm^{-1} corresponding to C-H stretching show excellent agreement with VB18C6 (Figure 2a). Additionally, a signal at 1075 cm^{-1}, corresponding to C-O stretching, is also present in the modified membrane. For the tBCalix4 modified membrane, signals in the range of ca. 2860 to 3140 cm^{-1} corresponding to C-H and O-H stretching show excellent agreement with calix[4]arene (Figure 2b and Figure S3 for enlarged views of the regions of interest). The signal at 1362 cm^{-1} in both calix[4]arene and

tBCalix4 the modified membrane corresponds to CH_2 bending.[29] The IR features confirm the deposition of sequestrants on the membrane surface. A comparison of the SEM images of the unmodified and VB18C6 modified membranes shows the presence of a surface coating upon the deposition of the macrocycles (Figure S4). EDX analysis shows that membrane modification led to a marked decrease in the relatively intensity of S signals (emanating from the sulfonate groups of the underlying PCSK membrane), consistent with the presence of an attenuating surface layer. A magnified view of the modified membrane reveals that the surface layer was not entirely homogeneous and was ruptured when there was uneven surface topography (Figure S4d).

Effects of Membrane Modifications

The performance of the original and modified CEM was evaluated in a four-chamber ED unit shown schematically in Figure 1. The initial diluate and concentrate solutions were of the same composition containing Na^+, Mg^{2+}, and Ba^{2+} at 200, 5, and 5 mM, respectively. The dissimilar levels of the target ions and the background cation (i.e., Na^+) serve to simulate the ion composition in natural brines, in which the presence of Na^+ is expected to dominate over multi-valent cations.[3, 30] Figure 3a shows the normalized concentrations of ions in the diluate solution at various time. Using the original CEM, Mg^{2+} and Ba^{2+} were depleted more rapidly than Na^+, suggesting the membrane has an innate albeit relatively weak permselectivity for alkaline earth metal ions over Na^+. Between Ba^{2+} and Mg^{2+}, Ba^{2+} is marginally preferred. The results are consistent with the behavior of a strong acid cation exchange membrane for which the selectivity order for ions of the same valence correlates inversely with the size of the hydrated ions.[31] In comparison to the native CEM, the membrane modified with VB18C6, with the modified surface facing the diluate stream, afforded more rapid transport of Ba^{2+} and Mg^{2+} (Figure 3b). The improvement was more pronounced for Ba^{2+}, corresponding to 34% and 92% increases in Mg^{2+}

and Ba^{2+} fluxes, respectively, when compared to the unmodified membrane. When the membrane was installed in the opposite orientation (i.e., the modified surface facing the concentrate), the enhanced selectivity was not observed. The result confirms that the interface between membrane and diluate solution exerts a critical influence on the selectivity of the membrane. All subsequent tests were conducted with the chemically modified surface facing the diluate.

Figure 4 compares the separation efficiencies of membranes loaded with VB18C6 and tBCalix4, respectively. Having a thin layer of crown ether or calixarene on the membrane surface rendered more efficient removal of Ba^{2+} and Mg^{2+} than the original membrane, with tBCalix4 showing stronger selectivity for the two ions than VB18C6. The selectivity of barium over sodium was 6.88 with tBCalix4-amended CEM, while that of the crown-ether modified membrane and the unaltered membrane was 3.16 and 1.79, respectively. It was also evident in Table 1 that, at the same current density, the flux of Na^{+} was not affected to a significant degree by chemical modifications; however, the fluxes of the divalent ions were markedly higher than the original membrane. The higher selectivity exhibited by the modified membranes therefore arises chiefly from the enhanced transport of Ba^{2+} and Mg^{2+}. Note that the differences in the separation performance of the VB18C6-coated membrane in Figure 3b and 4b are due to changes in electrolyte composition, and all subsequent tests used the same composition as in Figure 4 (i.e., with 100 mM Na^{+}, 5 mM Mg^{2+}, and 1 mM Ba^{2+}). The change was to simulate the relative ion concentrations in natural brine, where Ba^{2+} is expected to be at a lower concentration than Na^{+} or Mg^{2+}.

Effect of Operating Conditions on Ion Selectivity

The migration of ions at different current density was evaluated (Figure 5). With the original membrane, the selectivity of Ba^{2+} and Mg^{2+} over Na^{+} decreased from 3.4 to 1.1 as the current

density increased from 2.3 to 6.3 mA/cm^2, while the composition of the initial diluate and concentrate was held constant in all tests. As Mg^{2+} and Ba^{2+} were minority electrolytes, the current was largely carried by Na^+ movement. Ion flux data in Table 1 shows that, with the original membrane, Na^+ flux increased with the current density, but Mg^{2+} and Ba^{2+} fluxes showed signs of plateauing above 2.3 mA/cm^2. The latter occurred due to the onset of diffusion limitation in the boundary layer, since the divalent ions were of lower concentrations in the bulk solution and were depleted more quickly than Na^+. The data shows that the innate selectivity possessed by the membrane may only manifest in a low electric field, and this selectivity is increasingly masked by the film diffusion effect as current increases.

Amending the membrane with VB18C6 or tBCalix4 increased Ba^{2+} or Mg^{2+} selectivity over Na^+ to up to 4 times that of the original CEM (Figure 5). tBCalix4 clearly rendered the membrane to be more selective than VB18C6. Ion flux data indicated more efficient migration of Ba^{2+} and Mg^{2+} across the modified membranes, while that of Na^+ was marginally affected by membrane modifications (Table 1). The results imply that the adsorption of sequestrants on the membrane surface does not impede the movement of background non-interacting electrolytes. Rather, the presence of sequestrants facilities the transport of ions with which the sequestrants have high affinities. The increases in the ion flux of Ba^{2+} and Mg^{2+} due to VB18C6 and tBCalix4 amendment are noticeable at a high current loading where concentration depletion at the interface between the membrane and the boundary layer is expected to occur. As a result, the relative increase in selectivity (i.e., the ratio of the selectivity of the modified membrane vs. that of the native membrane) brought about by surface amendment is more significant at a higher current density.

In this study, the flowrates of diluate and concentrate streams were kept the same and they were systematically varied to examine the effect of diffusional transport. As shown in Figure S5, a stronger flow field favored the extraction of Ba^{2+} and Mg^{2+} over Na^{+}, which supports our earlier observation that the divalent minority ions were prone to diffusion limitation in the boundary layer, and more vigorous flow suppressed the boundary layer and accelerated diffusional transport. The presence of VB18C6 increased the selectivity for the divalent ions, with the beneficial effect being more noticeable at the lowest flowrate. It can be inferred that grafting the membrane surface with sequestrants is able to reduce the transport resistance of the target ions through the boundary layer. Plausibly, this is brought by specific interactions between the surface-residing macrocycles and the target ions as well as increased turbulence created by the uneven texture of the modified membranes.

To assess the effect of background electrolytes, the concentration of Na^{+} was adjusted between 0.1 to 0.5 M while keeping those of Mg^{2+} and Ba^{2+} constant. As shown in Figure 6, the unmodified membrane exhibited minor variations in ion selectivity across the range of Na^{+} concentration evaluated. In contrast, the selectivity of the modified membranes was very sensitive to the feedwater salinity. $P_{Ba/Na}$ and $P_{Mg/Na}$ of calixarene-modified CEM decreased from 6.9 to 3.4 and 4.6 to 2.6 respectively, as Na^{+} concentration increased from 0.1 to 0.5 M. Similar trends were observed of VB18C6-modified membrane. Overall, the effect of ion sequestrants was markedly attenuated as the feed water becomes increasingly saline. Several factors may have contributed to this behavior. In the classic solution-diffusion model, the permeability of polymer membranes for salts is governed by the sorption coefficients of the salts and their diffusivity in the polymer matrix.[32, 33] When a membrane is exposed to a solution with a high salt concentration, the water content in the membrane declines due to osmotic de-swelling.[34, 35] As a

result, the membrane is less able to accommodate ions of higher hydration energies. If membrane de-swelling was the main contributing factor, one would expect to see similar effects on ion selectivity among the native and modified membranes. However, it was observed that the sequestrant-modified CEMs were more strongly affected by an increasing sodium concentration, suggesting that factors other than membrane de-swelling may contribute to diminished ion selectivity in solution with a high salt concentration. Another cause that may explain for the attenuated sensitivity of sequestrant-modified membranes in a saline solution is that the oxygen atoms in the ether groups of crown ethers or hydroxyl groups of calixarenes carry partial negative charges, which attract divalent metal ions through ion-dipole interactions.[36] An increasing salt concentration in the bulk solution would attenuate such interactions and reduce ion binding specificity, which is consistent with the results of extraction experiments (Figure S6), in which we saw a substantial decrease in the extraction efficiency of Mg^{2+} by VB18C6 with an increasing sodium concentration. Taken together, the sequestrants-ion interactions play a dominant role in the resultant membrane's separation properties. When such interactions were diminished in solutions of high ionic concentrations, the selective effect brought by the sequestrants is significantly attenuated.

Effect of Calixarene with Ionizable Groups

The three-dimensional cone structure of calixarenes and their conformational flexibility give rise to their high chelating ability. Using the calixarene structure as a scaffold, an extensive family of calixarene-based ionophores have been created.[25] *p-tert*-Butylcalix[4]arene-crown-6-dicarboxylic acid (i.e., tBCalix4-C6DA), which has two of the phenolic groups of calix[4]arene connected with a polyether unit, forming a 'boot strap' for the cone opening, and two methoxy carboxylic groups attached to two remaining phenol rings, was reported to extract alkaline and

alkaline earth metals more efficiently than calix[4]arene.[25] tBCalix4-C6DA was synthesized in this study and was applied to the CEM. In contrary to expectation, this membrane performed significantly worse in terms of barium extraction as compared to membrane with tBCalix4 (Figure 7). Ion flux data reveals that there is a large reduction in barium flux relative to that of VB18C6 or tBCalix4-modified membrane (Table 1). A reasonable explanation for the large difference between calix[4]arene and its boot-strapped-di-carboxylic derivative is that, with the ionizable acid groups, Ba^{2+}, and to a less extent Mg^{2+}, were strongly retained by the chelating molecule via metal-host coordination as well as charge interactions, and the dual effects created a stable complex causing the metal ions to be firmly trapped. This results are similar to prior studies, where attempts were made to increase ion binding affinity by incorporating phosphonic acid groups in CEMs.[37] This effort, however, resulted in low transport numbers of multivalent cations due to strong binding between the multivalent cations and the phosphonic groups.

General Consideration of Membrane Surface Modification with Sequestrants

It is generally considered that the permselectivity of an ion exchange membrane in a mixed salt solution is mainly influenced by the affinity of the membrane for specific ions and the mobility of ions across the polymer phase.[36] Various techniques have been studied to enhance the selectivity of ion exchange membranes. This includes depositing an oppositely charged thin layer on an ion exchange membrane,[11, 12, 15, 38] adjusting the degree of cross-linking of the bulk polymer matrix or addition of a dense surface layer,[39, 40] and coating membranes with multiple layers of polyelectrolytes.[41, 42] These methods act to increase or deter the mobility of the ions through electrostatic interactions or size-dependent sieving effects. To increase the affinity of membranes for specific ions, weak acids (e.g. carboxylic acids) or metal chelating moieties (e.g., amine groups) were incorporated into the membrane structure;[36, 43] however, the latter approach

has generated mixed outcomes in the literature. On one hand, strong chemical binding between component ions and ion exchange groups was shown to impair the movement of the ions and lead to overall decreases in the separation selectivity and current efficiency.[36, 37] On the other hand, the creation of a surface layer enriched in crown ethers on Nafion 117 rendered improved selectivity for Cs^+ over lighter alkaline metal ions.[16, 17] The diverging results suggest that there is a delicate balance between ion affinity and mobility when embedding chemical sequestrants into ion exchange membranes. Peppering chelating agents throughout the membrane phase will increase the concentrations of the target ions in the membrane, but they may also make ions less mobile. The quantities, spatial distribution, and binding specificity of the chelating groups are expected to exert large effects on a membrane's separation performance. Previous studies suggest that, instead of creating membranes in which sequestrants were distributed homogeneously throughout the bulk polymer, confining sequestrants in a surface layer will boost selectivity without causing an excess drop in transport resistance [[17]]. The results of this study confirm the validity of this surface modification approach.

In prior studies of membrane separation, the effect of boundary layer on ion selectivity tends to be overlooked. Similar to other membrane separation processes, the boundary layer imposes an opposing effect against the innate selectivity of the membrane. An ion that moves more efficiently across the membrane will be depleted more severely in the boundary layer, thereby reducing its concentration near the entrance to the membrane. If the more selective ion is a minority electrolyte (as in this study), it would encounter concentration limitation at a lower current density; accordingly, its apparent selectivity with respect to a non-selective major ion will decrease with the current density. This effect, shown schematically in Figures 8a and 8b, agrees with our experimental observations. When a thin layer of sequestrant molecules is

attached to the membrane surface, it may increase the concentration of the target ion at the membrane-solution interface, giving rise to a greater concentration gradient across the membrane in the direction of ion flow (Figure 8c). The effect is most evident at a medium to high current density or in a mild flow field when there is significant concentration depletion in the solution phase adjacent to the membrane. It is worth noting that membrane potential measurements in barium solutions in the absence of an applied current registered slightly lower trans-membrane potentials for the modified membranes in comparison to the original membrane (Table S1). The results inform that, in the absence of an electrical field or when concentration polarization is insignificant, the surface-residing sequestrants slow down transport of barium to a moderate degree due to binding with the metal ion or partial coverage of surface ion-exchange groups by the sequestrants. The sequestrant layer is expected to affect predominantly the transport of multivalent cations relative to monovalent cations or anions. However, when there is a strong field that drives rapid ion migration and creates surface depletion, the chemical amendments can facilitate the transport of target ions via a combination of chemical and physical (e.g., increased surface turbulence due to roughened texture) effects. This is likely the mechanism underlying the improvements in barium and magnesium selectivity brought about by tBCalix4 and VB18C6 amendments.

Conclusions

The results obtained in this study show that surface amendment of crown ether and calixarenes-based macrocycles (specifically, VB18C6 and calix[4]arene) increased the selectivity of the resultant cation exchange membranes for Ba^{2+} and Mg^{2+} relative to Na^{+}, with calix[4]arene-modified membrane exhibiting greater selectivity improvements for the divalent ions than crown ether-amended counterparts. The optimal selectivity was achieved at moderate to high current

density (3.1 to 6.3 mA/cm^2) at the given ion composition (mole ratio of Ba/Mg/Na = 1/5/100). The principal advantage of the chemically enhanced electrodialysis is that it is a customizable approach and can be extended to other ions of interest; nonetheless, several aspects should be considered when using ion-specific sequestrants to adjust membrane selectivity. For one, the optimal sequestrant does not necessarily need to be a strong chelating agent, as the latter may form stable complexes that hamper ion movement as manifested in the case of tBCalix4-C6DA. Another aspect to reckon is that, in this study the sequestrants are present as a non-continuous layer (Figure S4) due to the method of sequestrants deposition while electrodeposition or surface polymerization processes tend to give rise to a more homogeneous layer [15,44]. Though the membrane boosts the transport of the divalent ions, it does not significantly affect the migration of background ions (i.e., Na^+). This will present a limit to which enhancement in selectivity can be achieved. A continuous and non-porous layer that can effectively reduce the flux of the major ions may render the membrane to be more selective, although this may come at a cost of increased membrane electrical resistance and a lower current efficiency.

Acknowledgement

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Supporting Information: descriptions of aqueous extraction, calixarene synthesis, and membrane potential measurements, membrane potential data, pH of ED experiments, membrane imaing and characterization data, and additional data showing effects of flowrate and Na concentration on selectivity. These data are available free of charge at: https://pubs.acs.org/.

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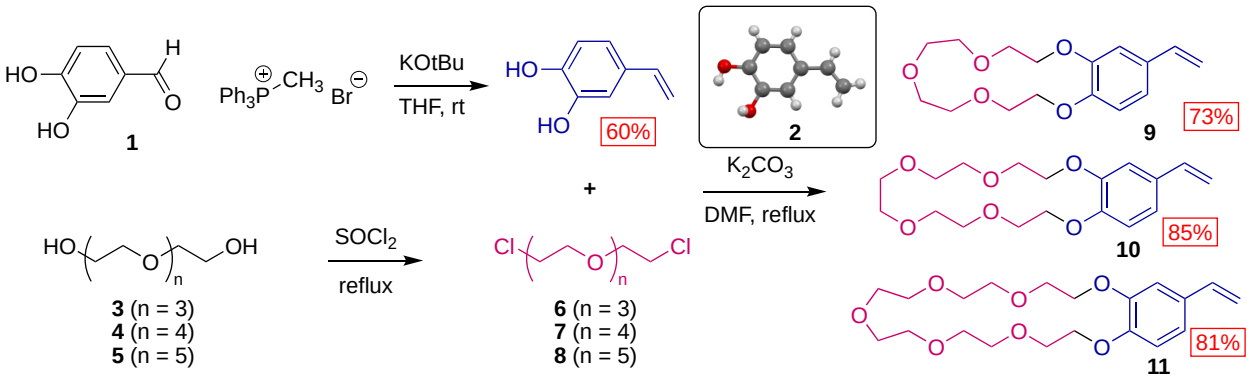
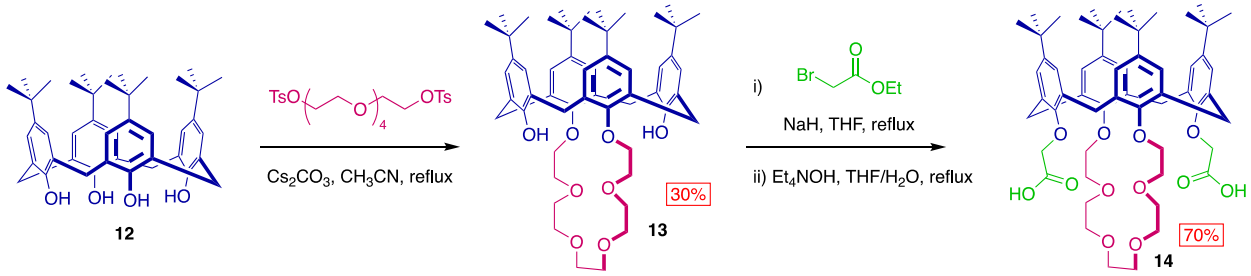


Scheme 1. Synthesis of vinyl-substituted benzo-crown ethers. The molecular structure of **2** (inset) was obtained by single-crystal X-ray diffraction experiments.



Scheme 2. Synthesis of 'boot-strap' *p-tert*-Butylcalix[4]arene-crown-6-dicarboxylic acid.[23]

Table 1. Ion flux of the original and modified CEM (units: 10^{-3} mole/m^2·min).[^]

		Current Density (mA/cm2)		
		2.3	3.1	6.3
Unmodified CEM	Na	9.38 ± 1.90	12.1 ± 2.38	29.4 ± 1.1
	Mg	1.72 ± 0.0	2.35 ± 0.56	2.40 ± 0.23
	Ba	0.38 ± 0.0	0.49 ± 0.14	0.50 ± 0.04
	Current Efficiency	102% ± 4%	85% ± 15%	74% ± 3%
CEM with VB18c6	Na	9.08 ± 0.49	12.9 ± 0.92	29.4 ± 1.2
	Mg	2.73 ± 0.04	2.46 ± 0.50	5.08 ± 1.32
	Ba	0.69 ± 0.03	0.82 ± 0.24	1.16 ± 0.22
	Current Efficiency	109% ± 4%	100% ± 17%	108% ± 11%
CEM with calix[4]arene	Na	5.77 ± 2.04	10.2 ± 1.5	31.3 ± 1.03
	Mg	2.59 ± 0.10	3.13 ± 0.51	6.85 ± 1.82
	Ba	0.65 ± 0.02	0.80 ± 0.23	1.69 ± 0.51
	Current Efficiency	85% ± 13%	94% ± 15%	92% ± 7%
CEM with calix[4]arene-C6DA	Na	7.97	15.5	
	Mg	2.38	2.38	
	Ba	0.48	0.50	
	Current Efficiency	94%	110%	

[^] Experiments were performed using feed solution containing 100 mM Na, 5 mM Mg, and 1 mM Ba, respectively. The initial pH of the feed solution was approximately 7.5. The final pH of concentrate and diluate was tabulated in Table S2. Uncertainty values correspond to one standard deviation.

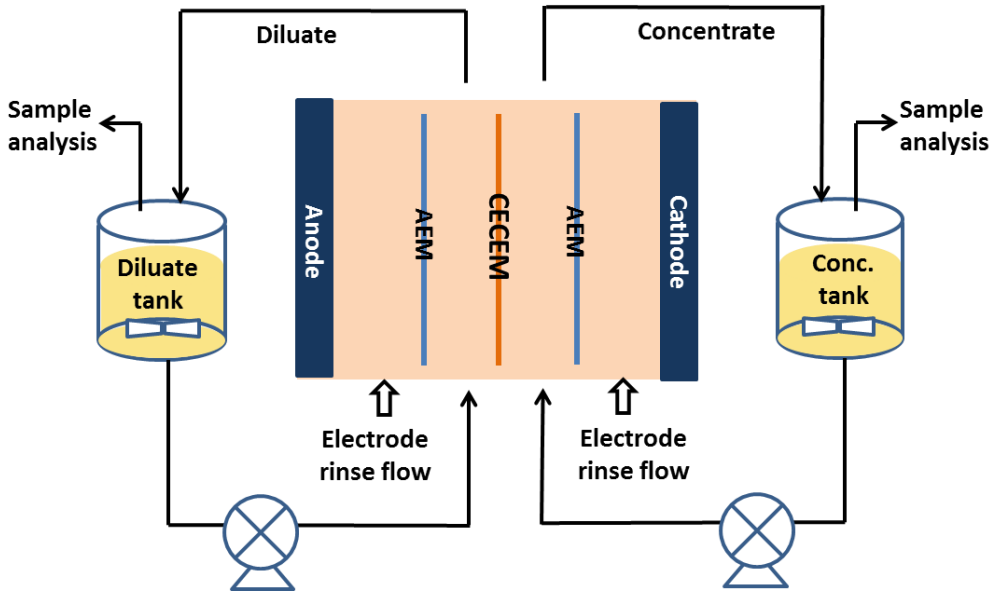
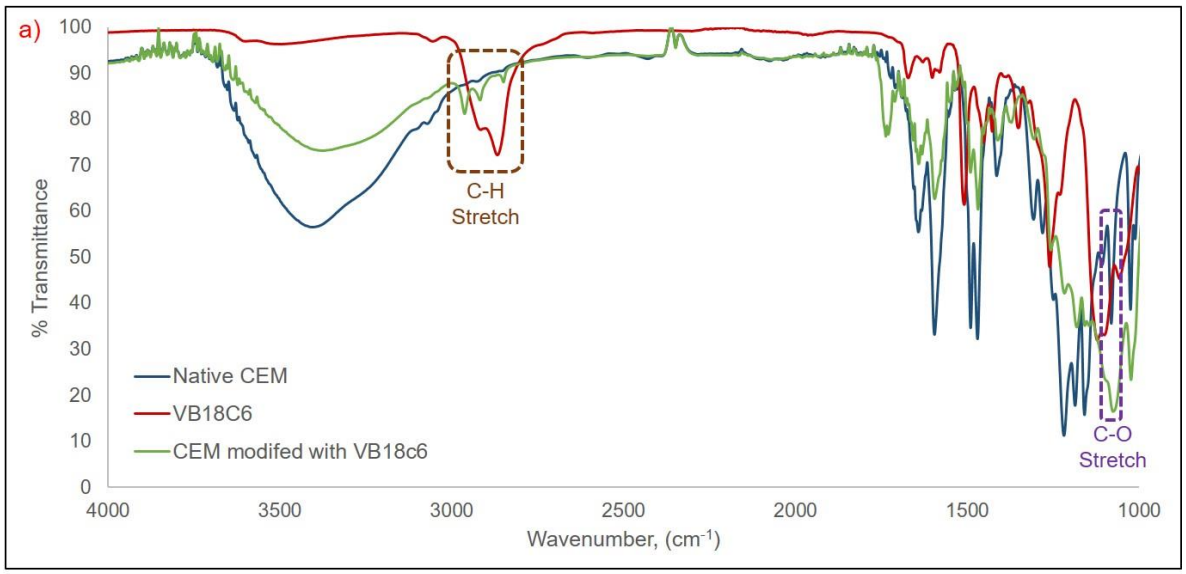
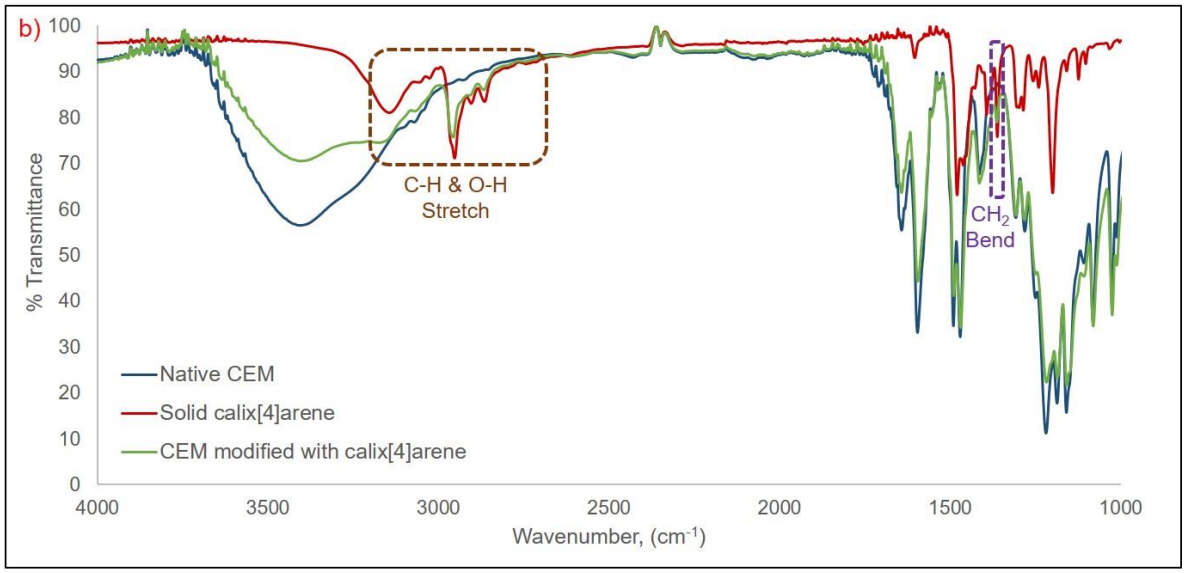


Figure 1. Schematics of an eletrodialysis unit. 4-chamber configuration was employed. Membrane surface area was 64 cm^2 and the volume of diluate and concentrate tanks were 500 mL each.


a)
% Transmittance
Wavenumber, (cm-1)
C-H
Stretch
C-O
Stretch
Native CEM
VB18C6
CEM modifed with VB18c6


b)
% Transmittance
Wavenumber, (cm-1)
C-H & O-H
Stretch
CH2
Bend
Native CEM
Solid calix[4]arene
CEM modified with calix[4]arene

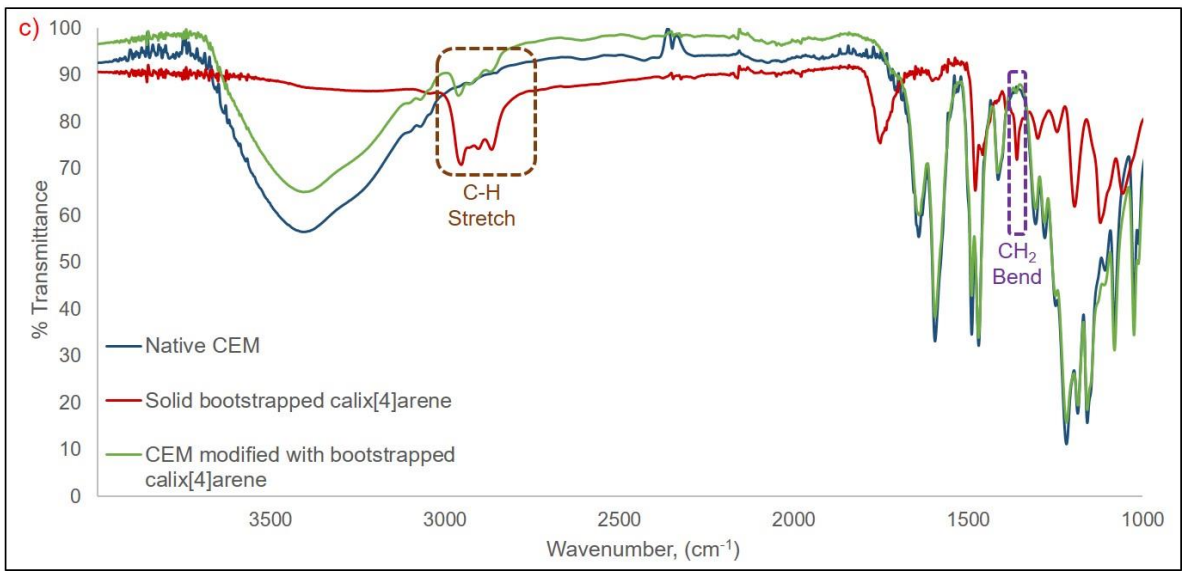

c)
% Transmittance
Wavenumber, (cm-1)
C-H
Stretch
CH2
Bend
Native CEM
Solid bootstrapped calix[4]arene
CEM modified with bootstrapped
calix[4]arene

Figure 2. FTIR spectra of original CEM and that coated with VB18C6 (a), tBCalix4 (b), and tBCalix4-C6DA (i.e., bootstrapped calix[4]arene), respectively.

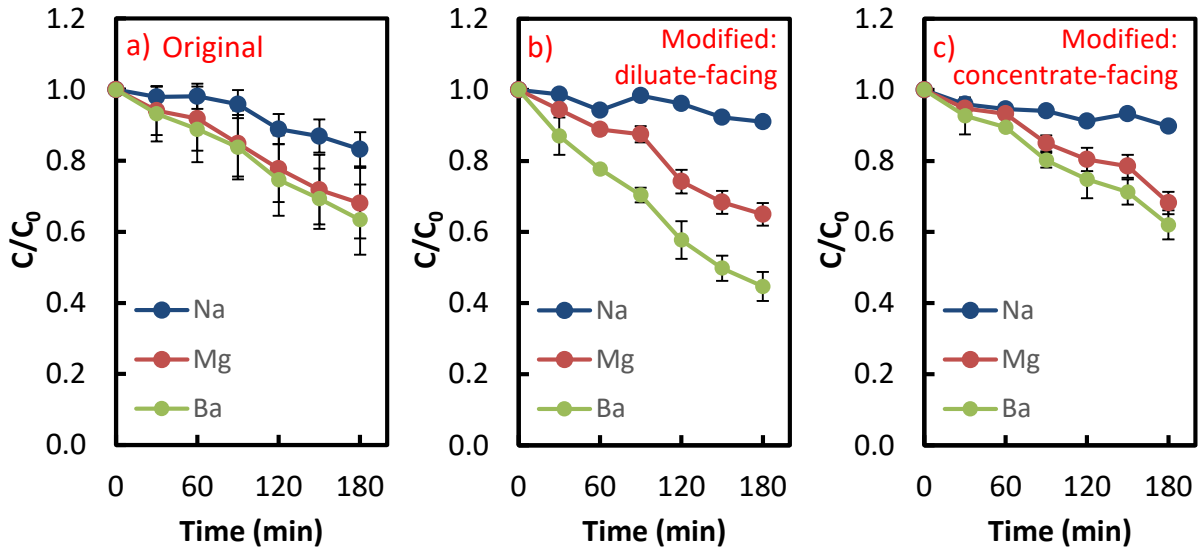


Figure 3. Concentration profiles of cations in diluate stream with (a) original CEM, and CEM deposited with VB18C6 with the loaded surface facing (b) the diluate or (c) concentrate stream, respectively. Electrolytes in the feed water were 200 mM Na, 5 mM Mg, and 5 mM Ba, respectively. Current density was 3.1 mA/cm^2. Error bars represent one standard deviation.

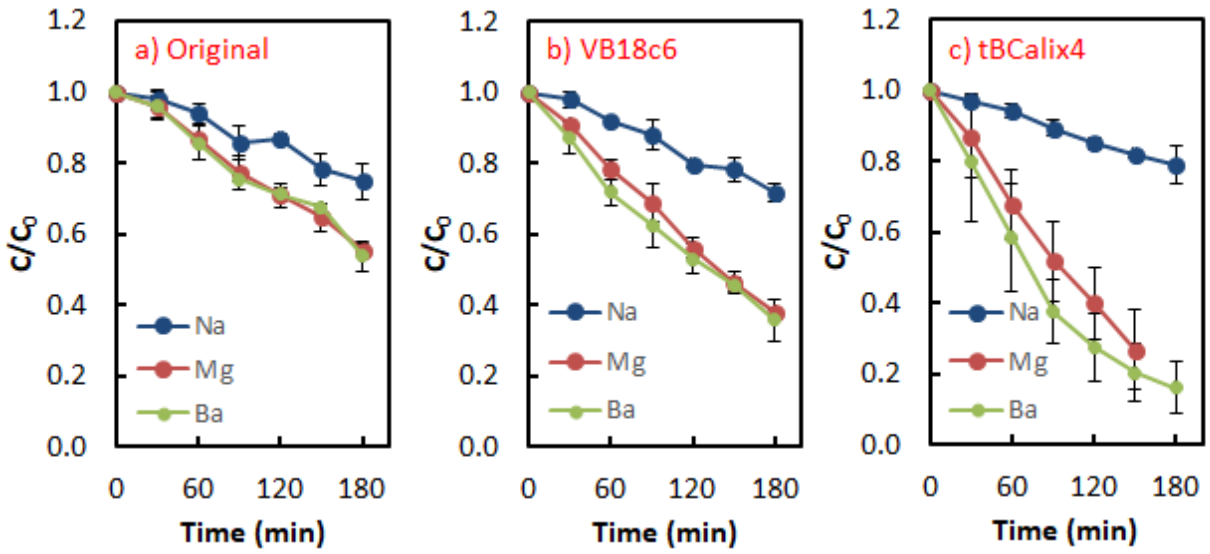


Figure 4. Concentration profiles of cations in diluate stream with (a) original CEM and CEM modified with (b) VB18C6 or (c) tBCalix4. Electrolytes in the feed water were 100 mM Na, 5 mM Mg, and 1 mM Ba, respectively. Current density was 3.1 mA/cm^2. Error bars represent one standard deviation.

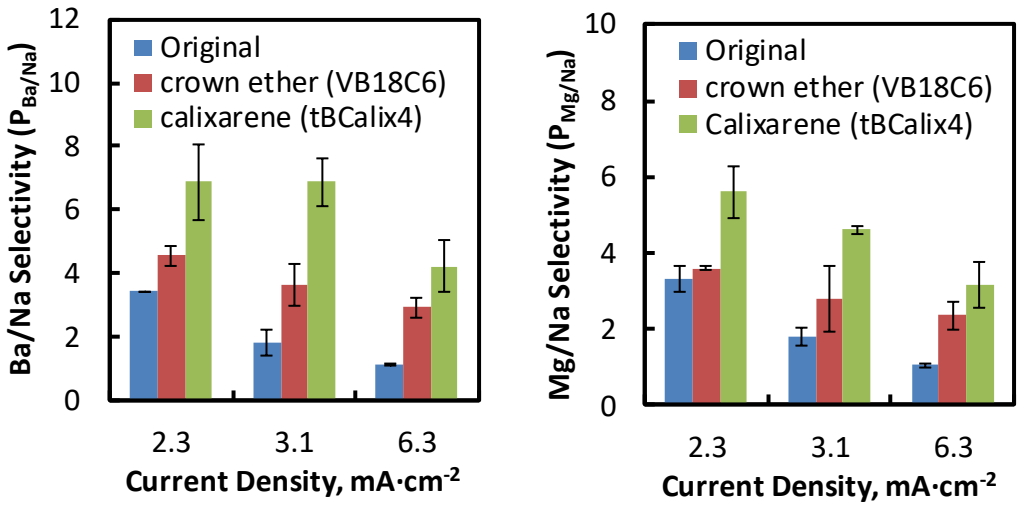


Figure 5. Effect of current density on the selectivity of (a) Ba over Na and (b) Mg over Na during electrodialysis using the unmodified and crown ether or calixarene-modified CEM. Electrolytes in the feed water were 100 mM Na, 5 mM Mg, and 1 mM Ba, respectively. Error bars represent one standard deviation.

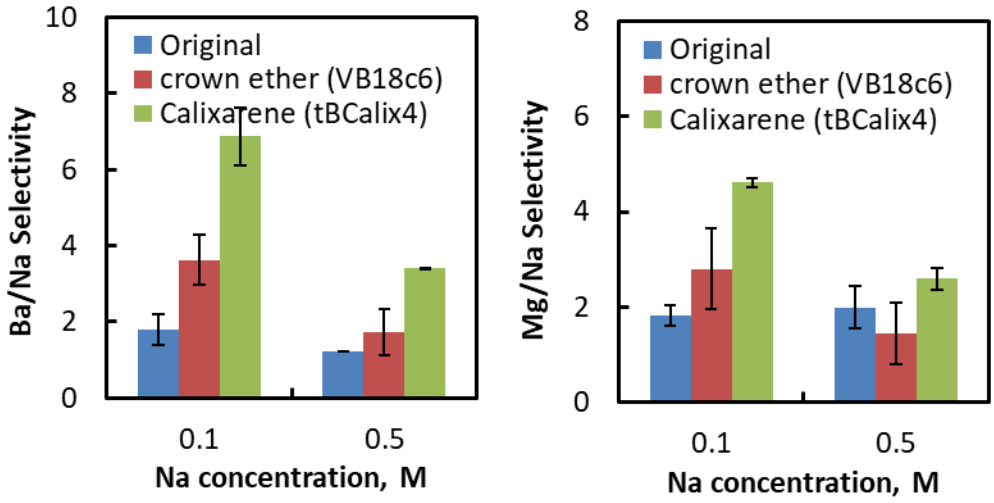


Figure 6. Effect of Na concentration on selectivity of (a) Ba over Na and (b) Mg over Na during electrodialysis. Feed water contained 5 mM Mg and 1 mM Ba, in addition to Na ion. Current density was 3.1 mA/cm^2. Error bars represent one standard deviation.

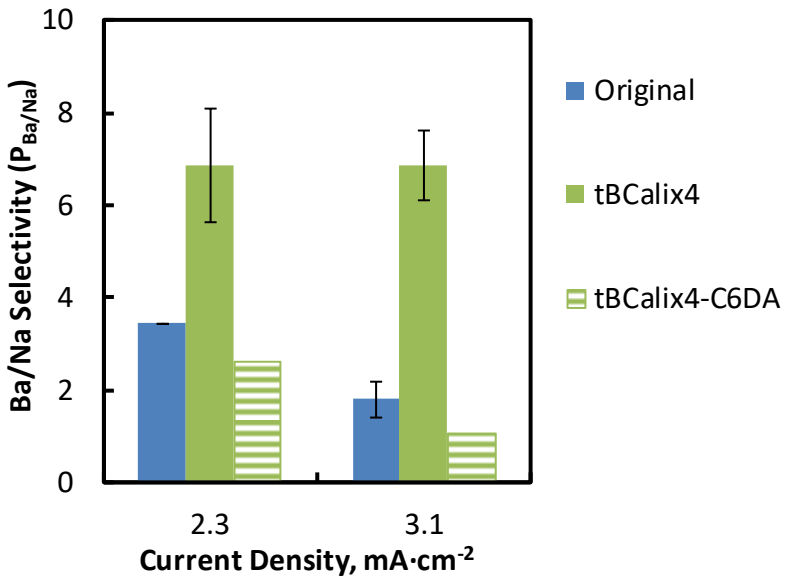


Figure 7. Comparison of ion selectivity of membranes deposited with tBCalix4 and tBCalix4-C6DA. Electrolytes in the feed water were 100 mM Na, 5 mM Mg, and 1 mM Ba, respectively. Error bars represent one standard deviation.

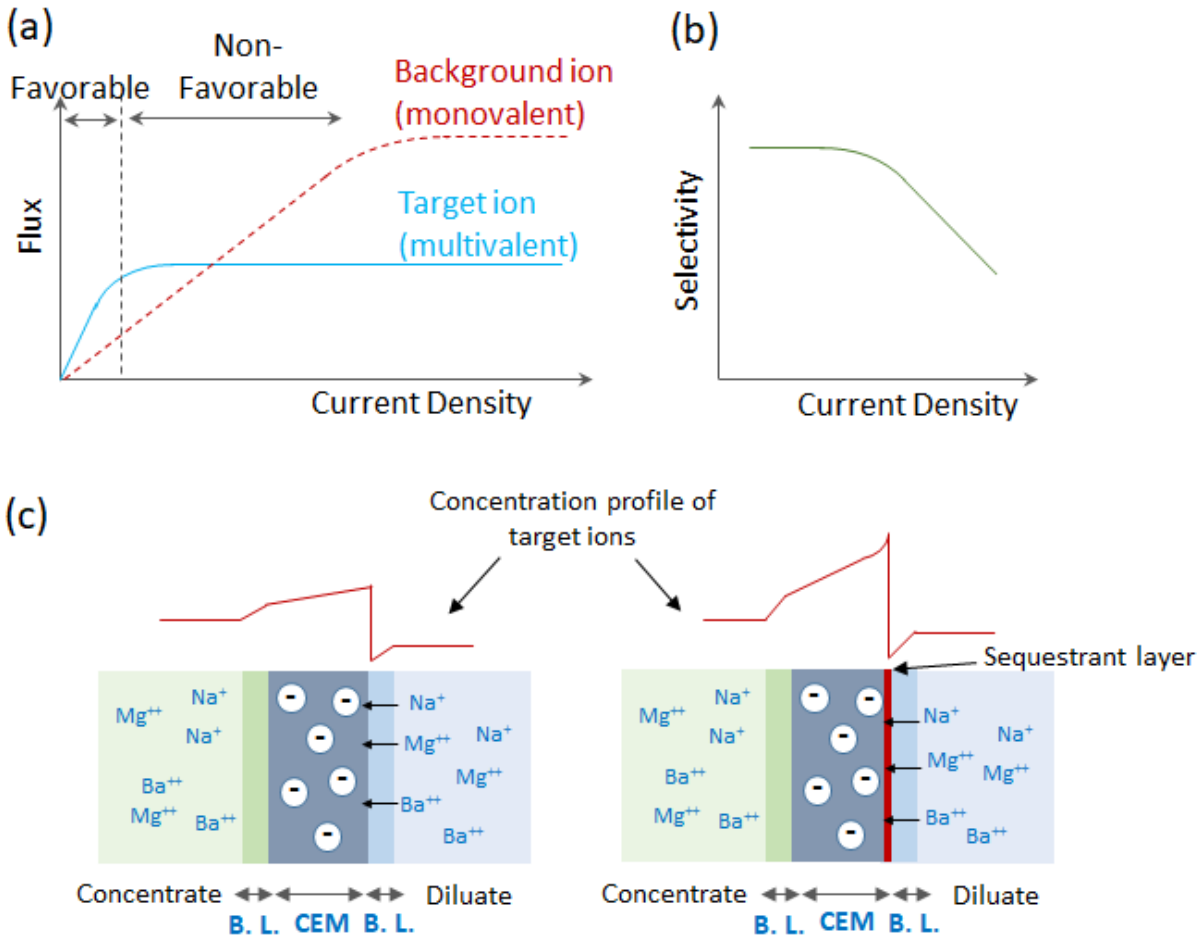


Figure 8. Conceptual model of increased barium and magnesium selectivity through surface modification with sequestrants. Flux (a) and selectivity (b) of ions in response to current density. c) Effect of membrane modification on target ion concentration profile.