Supplementary Material (ESI) for Chemical Communications

Supporting information

Carrier-mediated Electrodialysis

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Contents:

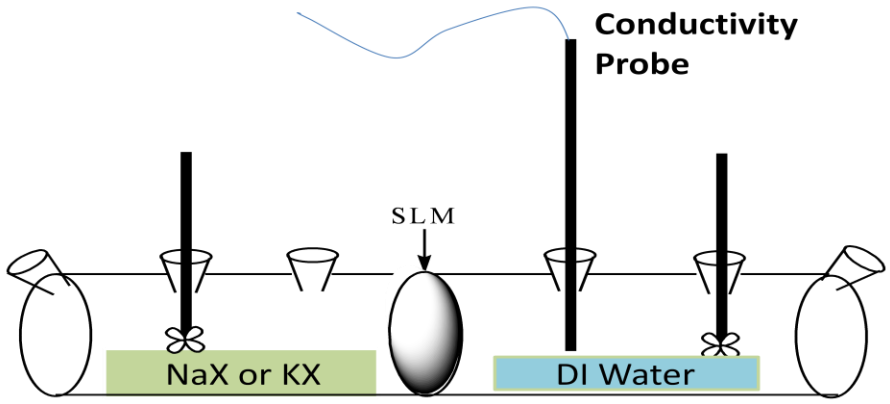
Membrane preparation. Valinomycin was purchased from Sigma Aldrich (99%). The calix[4] ethyl ester was prepared according to established procedures[1, 2]. Square swatches of Celgard® 2400 (donated by Celgard LLC), approximately 4 cm on a side, were placed in a Petri dish and bathed in NPOE containing 0.009 M carrier. The dish was subjected to vacuum (approx. 10 kPa), for 30 minutes. The membranes were then removed and stored in a sealed container. Prior to use, the membrane was placed on a flat glass surface and wiped with a Kimwipe® until the surface appeared to be dry. Weight of the NPOE/carrier solution was approximately 1 mg/cm^2.

Table S1 Summary of Celgard® 2400 Film Properties.

Film Property	
Thickness	25 µm[3]
Tortuosity	3.15[4]
Porosity	37-41%[3]
Pore Dimensions	0.12 x 0.04 µM[3]

Dialysis experiments. The rate of carrier-mediated transport of salt across a SLM was determined by conductivity measurements (Radiometer model CDM3 conductivity meter with PP 1042 probe.) The dialysis cell is shown in Figure 1.

Figure 1: Cell for dialysis experiments



Each side had a nominal volume of 50 mL. Membrane area was 10 cm^2. Both sides were stirred at 240 rpm with mechanical stirrers. Chloride and nitrate salts were purchased from Fluka Analytical, and were TraceSELECT® grade. These salts were guaranteed to be of a high purity to minimize unwanted interference from competing ions, and came with certificates of analysis.

Sodium perchlorate was purchased from ACP and had a high but known amount of potassium contamination (ca. 500 ppm.) Potassium perchlorate was purchased from Fisher Scientific Company and was of unknown purity.

Salt solutions were prepared at concentrations between 10^{-4} and 1 M. Activities were calculated from a two parameter Debye Hückel model[5]. Salt solutions were added to the left side of the cell; deionized water was used as receiving phase on the right. Conductivity was measured on the right and converted to concentration via calibration curves done for each salt. Temperature was 21 ±1 °C.

Extraction and diffusion coefficients were calculated based on the model of Reinhoudt et al[6, 7] according to equation 1.

(1) $$J = \frac{D_m}{2dm}\left(-K_{ex}a_s^2 + \sqrt{(K_{ex}a_s^2)^2 + 4S_0K_{ex}a_s^2}\right)$$

where J is the flux of salt, D_m is the diffusion coefficient, dm is the membrane thickness corrected for tortuosity, K_{ex} is the extraction constant (defined below), a_s is the activity of the salt in the left aqueous phase of the cell, and S_0 is the initial carrier concentration. This equation is valid only at the outset of the experiment before any salt has been transported, since the activity of salt on only one side of the cell is considered.

The extraction constant is defined by equation 2.

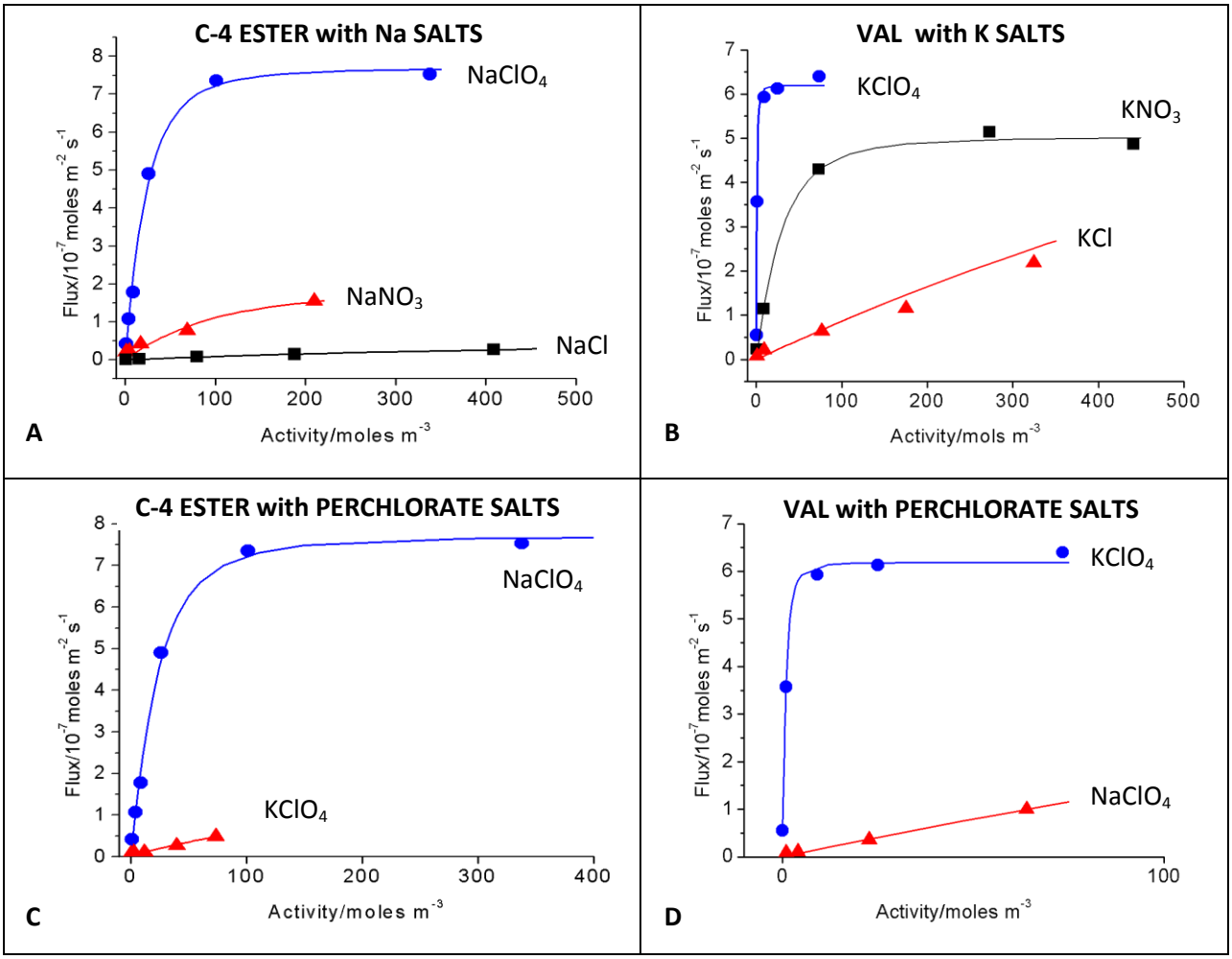
(2) $$I_s^+ + X_s^- + S_m \leftrightarrows IS_m^+ + X_m^-$$

$$K_{ex} = \frac{[IS_m^+][X_m^-]}{[I_s^+][X_s^-][S_m]}$$

Subscripts s and m refer to aqueous and membrane phases respectively. Although equation 2 is written with concentration terms, we actually used activities for all species in the calculations, and assumed that the activity coefficient for all (dilute) membrane species was 1.

Figure 2 gives experimental flux vs activity points for both carriers with a variety of salts.

Figure 2: Dialysis experimental data and fitted curves (equation 1)



Extraction and diffusion coefficients were derived from a fit of experimental data of flux as a function of source phase salt activity at five (usually) different concentrations using a Micromath® Scientist model of equation 1. The fitting program used salt activity as the independent variable, flux as the dependant variable and K_{ex} and D as the parameters to be fitted. Data are summarized in Tables 1 and 2. Statistical errors reported in the extraction and diffusion coefficients were calculated based on a 95% certainty. The method is not very reliable for systems in which the flux does not saturate. Duplicates were not performed for these experiments.

Table 1 Calix[4] Ester membrane - Extraction and Diffusion Coefficients

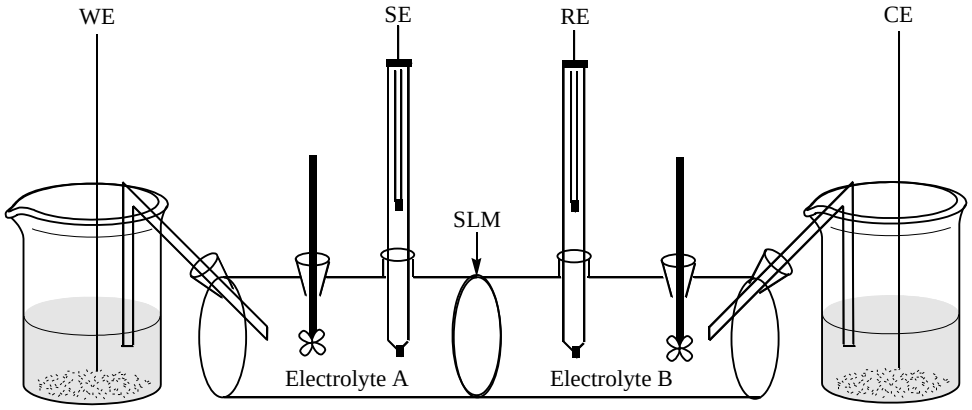
Salt	Log K_{ex} / M^{-1}	D (x 10^{12} m^2 s^{-1})
NaCl	1.5 ± 0.5	0.14 ± 0.08
$NaNO_3$	2.9 ± 0.7	0.51 ± 0.38
$NaClO_4$	4.1 ± 0.2	2.14 ± 0.14
$KClO_4$	2.8 ± 1.1	0.29 ± 1.67

Table 2 Valinomycin membrane - Extraction and Diffusion Coefficients

Salt	Log K_{ex} /M^{-1}	D (x 10^{12} m^2 s^{-1})
KCl	0.9 ± 1.2	2.8 ± 15
KNO_3	3.9 ± 0.1	1.4 ± 0.3
$KClO_4$	6.9 ± 0.15	1.72 ± 0.08
$NaClO_4$	1.9 ± 1.3	1.67 ± 18

Electrodialysis. The electrodialysis cell is shown in Figure 3 below. Cell volumes were 50 mL per side, and membrane area was 10 cm^2. A potentiostat (PARSTAT 2263), maintained the required potential difference between sense and reference electrodes (double junction glass Ag/AgCl electrodes), by flowing current between platinum working and counter electrodes. The platinum electrodes were connected to the system via agar salt bridges made with 0.1 M of the same electrolyte as was in the cell compartment to which it was connected. This isolated the acidic and caustic products of electrode reactions to the beakers external to the cells. Beakers were filled with 0.1 M of the same salt as was in the salt bridges. Both cells were stirred mechanically at approximately 240 rpm. Beakers were stirred by magnetic stirring. Temperature was 19 to 22 °C during the experiments.

Figure 3 Electrodialysis Cell



Cation concentrations were measured by atomic emission using a Varian AA-475 model spectrophotometer. Samples were prepared using 10 mL of analyte and 10 mL of a solution consisting of 2000 ppm Cs (as CsCl), and 10% HNO_3 as ionization suppressors. Calibrations were done at 4 different concentrations of cation. Calibration solutions were made with the same electrolyte as was in the cell. For example, if potassium was to be measured in a 0.1 M solution of $NaNO_3$, the calibration solutions were made with the appropriate amount of potassium, one measure of 0.1 M $NaNO_3$ and an equal measure of ionization suppressor solution. This ensured that both calibration standards and samples varied only in the analyte to be determined. Sodium emission was measured at 589 nm and potassium emission was measured at 766.5 nm. The detection limit was 0.005 ppm. Each calibration solution was measured four times and the sample was measured four times. The technique was accurate to within 10%.

Anions were determined by ion chromatography using a Dionex DX-120 ion chromatograph. Samples were not diluted and sample size was 1 mL. Calibration curves were run using four different concentrations of anion. Detection limit was 0.05 ppm. Each calibration solution was measured four times and the sample was measured four times. The technique was accurate to within 10%.

Ion Accounting Experiments. This gives the full picture of ion and electron flow, and is illustrated in the first figure in the paper. This experiment requires that both cation and anion be different on the two sides of the cell in order to maintain a zero background signal for the ion analyses.

At the end of the 24 hour experiment, potassium and chloride were measured on the right and sodium and nitrate were measured on the left. This gave moles of charge moved which was then converted to coulombs of charge moved as ions. The potentiostat gave the coulombs of electrons passed in the period.

Cation competition experiments. These experiments were set up with sodium and potassium salts (perchlorate, nitrate or chloride), on the left, and with LiCl or $LiNO_3$ on the right. At the end of the 24 hour experiment, potassium and sodium were measured on the right using standards containing the lithium salt matrix. Replicate flux determinations of individual ions appear averaged in the tables in cells showing error estimates. In general flux was reproducible between replicates within ±20%. Some experiments involving low sodium flux were complicated by the presence of trace sodium from glass ware and reagents; these cases have the lower precisions indicated.

Table 3 Perchlorate Salt Competition Experiment 1. Valinomycin Membrane

Applied Potential/V	-1	0	1	1.75	2
Current/10^{-5} A	-1.7	0	0.013	0.68	1.82±0.04
K Flux/10^{-7} moles m^{-2} s^{-1}	2.78	3.53 ±0.06	3.36	3.36	3.53±0.06
Na Flux/10^{-9} moles m^{-2} s^{-1}	1.69	1.24± 0.23	1.1	1.02	0.98±0.04
K/Na selectivity	160	280±70	300	320	360±10

Left compartment: $KClO_4$ 0.05M, $NaClO_4$ 0.05M. Right compartment: 10^{-5} M LiCl.

Table 4 Chloride Salt Competition Valinomycin Membrane

Applied Potential/V	-1	0	1.5	2
Current/10^{-5} A	-1.58±0.55	0	0.22 ±0.14	1.2±0.01
K Flux/10^{-7} moles m^{-2} s^{-1}	0.00135±0.0002	0.036±0.003	0.3±0.17	1.2±0.02
Na Flux/10^{-9} moles m^{-2} s^{-1}	0.71±0.14	4.7±3	2.3±.3	3.3±0.2
K/Na selectivity	0.19±0.02	0.8[a]	13±10	37±3

Left compartment: KCl 0.05M, NaCl 0.05M. Right compartment: 10^{-5} M LiCl.

[a] significant uncertainty in the value

Table 5 Chloride Salt Competition Calix[4] Ester Membrane

Applied Potential/V	0	1	2
Current/10^{-5} A	0	0.39±0.38	1.11±0.03
K Flux/10^{-8} moles m^{-2} s^{-1}	0.40±0.04	0.94±0.2	1.1±0.1
Na Flux/10^{-8} moles m^{-2} s^{-1}	0.29±0.2	1.3±0.6	5.5±0.9
K/Na selectivity	1.37±0.04	0.7±0.4	0.20±0.01

Left compartment: KCl 0.05M, NaCl 0.05M. Right compartment: 10^{-5} M LiCl.

Table 6 Chloride Salt Competition Calix[4] Ester Membrane

Applied Potential/V	0	1	2
Current/10^{-5} A	0	1.89±0.12	3.3±0.6
K Flux/10^{-8} moles m^{-2} s^{-1}	0.77±0.02	2.6±0.3	5.8±0.6
Na Flux/10^{-8} moles m^{-2} s^{-1}	0.45±0.02	20±1	26.6±2.3
K/Na selectivity	1.7±0.04	0.13±0.2	0.22±0.1

Left compartment: KCl 0.05M, NaCl 0.05M. Right compartment: 10^{-3} M $LiNO_3$.

Table 7 Cation competition at varying concentrations. Valinomycin Membrane

Concentration/M	Applied Potential/V	Current/10^{-5}A	K Flux/10^{-7} moles m^{-2} s^{-1}	Na Flux/10^{-9} moles m^{-2} s^{-1}	K/Na selectivity
0.05	0	0	2.63±0.12	3.0±0.3	87±4
0.05	2	1.51±0.01	3.8±0.2	1.8±0.06	209±5
0.025	0	0	2.1±0.06	0.86±0.04	236±3
0.025	2	1.27±0.01	2.42±0.11	0.39±0.02	610±60
0.0125	0	0	1.26±0.1	0.3±0.04	420±20
0.0125	2	1.35	1.57	0.11[a]	1400[a]

Left compartment: $NaNO_3$ and KNO_3 salts at equal concentrations as indicated. Right compartment: 10^{-5} M LiCl.

[a] significant uncertainty in the value

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