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Membrane Carrier Selectivities Identified by Competition Transport Experiments

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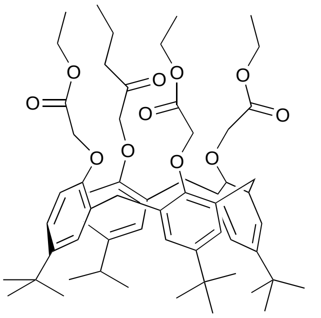
With a single experiment the transport selectivity of a membrane carrier towards a given set of metal cations can be determined.

Here we report an approach that facilitates the testing of carrier selectivities in the transport through supported and bulk liquid membranes.[1a] A single competition transport experiment with ten metal nitrates and subsequent simultaneous metal ion analysis of the receiving phase with ICP-OES[8] yields the transport selectivity pattern of a carrier for a given set of metal cations and the experimental conditions applied. The unrestricted choice of metal salts used in the procedure allows a rapid screening of membranes for separation technology. However, it must be emphasized that the observed selectivities are only valid for the employed mixture: coupling between the movements of different ions is likely in a multi-component system. Thereby transport rates might change with the source phase composition.



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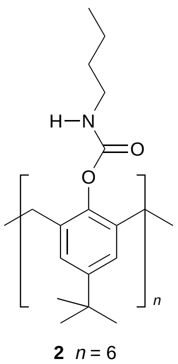
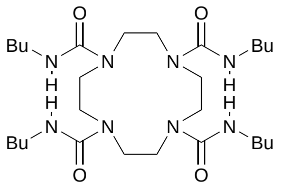


2 $n = 6$
3 $n = 8$



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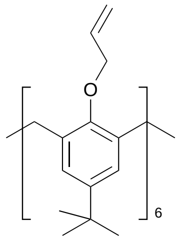

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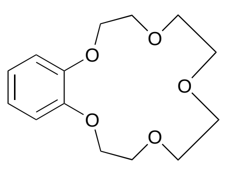

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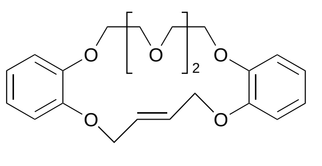

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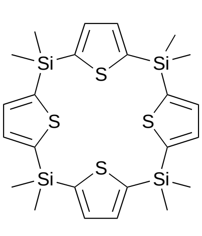

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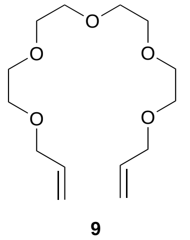

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Compound **1** is well known to bind and transport sodium ions selectively.[9] However, complete selectivity was not expected and therefore **1** was used as a membrane carrier to investigate multielement transport experiments. By standard procedures **1** was incorporated into a porous polypropylene membrane with *ortho*-nitrophenyl octyl ether (NPOE) as solvent.[7] The so obtained SLM was used in transport experiments with an aqueous source phase containing equimolar amounts (0.15 mol L^{-1}) of ten nitrate salts. The analysis of the receiving phase after 168 h shows the expected high preference for sodium nitrate transport (Fig. 1). However, some transport of potassium and lead nitrate was also detected. To monitor the entire transport process, *i.e.* the ion concentration of the source and receiving phase before and after ion flux, lower salt concentrations had to be used. A source phase with ten nitrate salts, each of a concentration of 50 mg L^{-1}, proved to be useful (Fig. 2).

Competitive transport experiments were used to determine the transport properties of new or not yet tested carrier molecules **2**–**5** and **7**. The results are summarized in Table 1. With benzo-crown[5] (**6**) as carrier, multielement competitive transport experiments trough BLMs were performed. Chloroform, dichloromethane or freon were used as the organic membrane phase. The transport selectivity patterns of **1** and **7**–**9** in dichloromethane were measured accordingly. For podant **9** an unexpectedly high lead transport

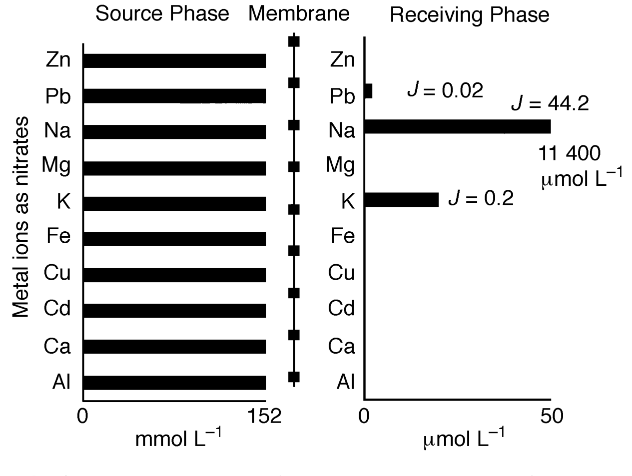

Fig. 1 Competitive transport of metal nitrates through an SLM with carrier **1**. Concentration in receiving phase after 168 h; transport rates J are given in $[10^{-8}\ \mathrm{mol\ m^{-2}\ s^{-1}}]$[12]

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Table 1 Transport rates through supported liquid membranes[a]

Carrier	Al	Ca	Cd	Cu	Fe	K	Mg	Na	Pb	Zn
1[b]	–[c]	–	–	–	–	0.2	–	44.2	0.02	–
1[b,d]	–	–	–	–	–	–	–	5.9	–	–
2[e]	–	–	–	–	–	–	–	2.8	–	–
3[e]	–	–	–	–	–	–	–	0.3	–	–
4[e]	–	–	–	–	–	–	–	5.3	–	–
5[e]	–	–	–	–	–	–	–	–	–	–
6[e]	–	–	–	–	–	45	–	1.6	0.4	–
7[e]	–	–	–	–	–	13	–	–	0.08	–

[a] All transport rates are given in [10^{-8} mol m^{-2} s^{-1}].[12] Source phase concentration 0.15 mol L^{-1} for each metal salt unless otherwise stated. [b] Transport for 168 h. [c] Not detectable; concentration in receiving phase < 0.2 mg L^{-1}. [d] Source phase concentration 50 mg L^{-1} for each metal salt. [e] Transport for 24 h.

Table 2 Carrier mediated competitive transport through bulk liquid membranes[a]

Carrier	Al	Ca	Cd	Cu	Fe	K	Mg	Na	Pb	Zn
6[b]	–[c]	–	–	–	–	0.2	–	2.4	0.01	–
6[d]	–	–	–	–	–	24.6	–	10.7	0.14	–
6[e]	–	–	–	–	–	–	–	0.1	–	–
1[f]	–	–	–	–	–	0.7	–	176	0.05	–
7[g]	–	–	–	–	–	0.2	–	–	–	–
8[h]	–	–	–	–	–	–	–	1.7	–	–
9[f]	–	–	–	–	–	1.4	–	0.6	26	–

[a] All rates are given in [10^{-8} mol m^{-2} s^{-1}].[12] Source phase concentration 0.15 mol L^{-1} for each metal salt and dichloromethane bulk liquid membrane unless otherwise stated. [b] Source phase concentration 1000 mg L^{-1} for each metal salt; chloroform as organic phase; 120 h transport time. [c] Not detected; concentration in receiving phase < 0.2 mg L^{-1}. [d] Source phase concentration 1000 mg L^{-1} for each metal salt; dichloromethane as organic phase; 120 h transport time [e] Source phase concentration 1000 mg L^{-1} for each metal salt; freon (trichlorotrifluoroethane) as organic phase; 120 h transport time. [f] 24 h transport time. [g] 24 h transport time; chloroform bulk liquid membrane. [h] 48 h transport time.

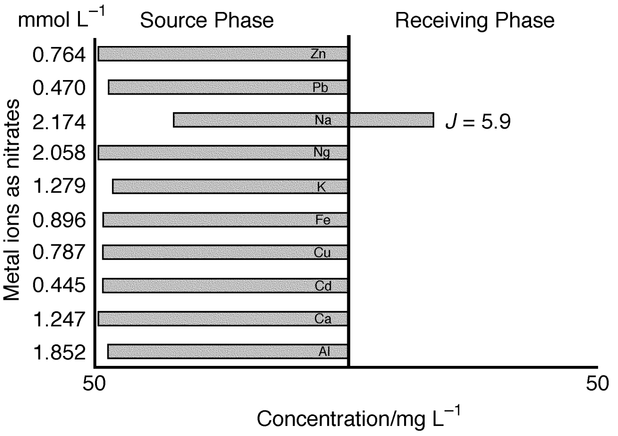

Fig. 2 Competitive transport of metal nitrates through an SLM with carrier **1**. Concentration in source and receiving phase after 168 h; transport rates J are given in [10^{-8} mol m^{-2} s^{-1}]

rate was found in dichloromethane. The results are summarized in Table 2.

In summary we have shown that the laborious testing of membrane carrier selectivities towards a given set of metal cations and specific conditions can be reduced to a single transport competition experiment using ICP-OES for simultanous ion analysis.

Technique used: ICP-OES

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12 The reported fluxes are transient fluxes for the given experimental conditions. However, if the experiments are repeated for different periods of time a kinetic analysis of the competitive transport is possible. From such measurements steady state fluxes can be derived. All experiments were performed at 20(±3) °C. The solutions were constantly stirred at 50 rpm.