FULL PAPER

Concave Carrier Molecules: Selective Transport of Copper(II) and Lead(II) Nitrates through Supported Liquid Membranes

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Abstract. Concave 1,10-phenanthrolines **1** are selective and efficient carrier molecules for membrane transport of copper(II) and lead(II) ions. With competitive membrane transport experiments the selectivity patterns of three concave 1,10-phenanthroline membrane carriers have been determined. Measurements with copper(II) and lead(II) nitrates confirmed the predicted selectivities and revealed high transport rates for **1a** and **1b**. While **1b** shows a high preference for copper(II) nitrate, **1a** transports lead and copper nitrates equally well, but with much higher flux. In bulk liquid membranes, the carrier mediated ion flux remained constant over an extended period, whereas it decreased significantly in reused supported liquid membranes, which indicates rapid loss of carrier from the membrane under these conditions.

Ion-selective electrodes [1] are used as chemical sensors for many analytical applications. Their selectivity originates from mediated transport of ions through a hydrophobic membrane. The transport selectivity, however, is generally determined by a substrate-specific receptor molecule present in the membrane, where it can act as a carrier between source and receiving aqueous phase. Most of the work with artificial membranes has been focused on carrier-facilitated transport of metal cations by macrocyclic receptors, and many data from transport experiments under various conditions are available [2]. While the large variety of crown ether compounds, podants and calixarene derivatives provides an ample source of suitable ionophores for alkali and earth alkali metal ions, the choice of selective carriers for transition metal ions is far more restricted [1b]. We report here membrane transport properties of concave 1,10-phenanthrolines [3], which posses the structural requirements to act as selective carriers for transition metal ions: 1,10-phenanthroline is a well known ligand for binding of transition metal cations, and we expect the concave shielding to keep the metal ion binding reversible and to provide binding selectivity.

Results and Discussion

Although the rate of cation cotransport for a new carrier molecule can be predicted if only one cation is involved [4] this is certainly difficult for unusual structures, such as concave 1,10-phenanthrolines. To facilitate the testing of transport selectivities of new carrier molecules towards several cations we have recently introduced a new method [5] by which a competitive cation transport is monitored with simultaneous element analysis by inductively coupled plasma optical emission spectroscopy (ICP-OES) [6]. A single experiment of this kind reveals the transport selectivity of a carrier towards several cations. With a set of ten metal nitrates, including alkali, alkali earth and transition metal cations in the source phase, the membrane transport ability
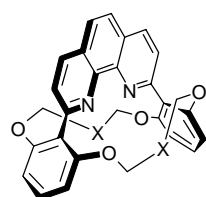
1a X = $(CH_2)_6$
1b X = $(CH_2)_8$
1c X = $(CH_2OCH_2)_2$

of the three concave carriers **1a–c** were investigated in bulk liquid membranes (BLM, CHCl₃) and supported liquid membranes (SLM). Table 1 summarizes the results.

Table 1 Ion flux [a] in competitive ion cotransport experiments with concave carriers **1a–c**

carrier	time (h)	**1a**	**1b**	**1c**
transport through bulk liquid membranes (BLM) [b]				
$Cu(NO_3)_2$ [c]	24	0.32	2.48	0.39
	120	0.39	2.07	1.07
$Pb(NO_3)_2$ [c]	24	0.03	0.08	1.27
	120	0.11	0.14	1.08
$Cd(NO_3)_2$ [c]	24	< 0.015	– [d]	0.20
	120	< 0.003	0.01	0.21
$Zn(NO_3)_2$ [c]	24	< 0.025	– [d]	0.10
	120	< 0.005	0.01	0.04
transport through supported liquid membranes (SLM) [e]				
$Cu(NO_3)_2$ [c]	24	< 0.04	0.42	– [d]
	96	0.05	0.04	– [d]
$Pb(NO_3)_2$ [c]	24	0.06	< 0.013	– [d]
	96	0.07	< 0.003	– [d]

[a] All values J for ion flux are derived from two experiments and two independent measurements of the metal ion concentration in the receiving phase. They are given in [10^{-8} mol m^{-2} s^{-1}] with an estimated error of +/– 15%. [b] The source phase contained 5 mL of an aqueous solution (10% HNO₃) of a mixture of the following nitrates in a concentration of 0.152 mol L^{-1} each: $Al(NO_3)_3$, $Ca(NO_3)_2$, $Cd(NO_3)_2$, $Cu(NO_3)_2$, $Fe(NO_3)_3$, KNO_3, $Mg(NO_3)_2$, $NaNO_3$, $Pb(NO_3)_2$, $Zn(NO_3)_2$; carrier concentration: 8×10^{-4} mol L^{-1}; volume receiving phase: 20 mL HNO₃ (10%); membrane phase: 30 mL CHCl₃. [c] Only the metal salts which were transported with a flux > 0.01×10^{-8} mol m^{-2} s^{-1} are given. [d] Not determined. [e] Carrier concentration: 2.3 mg in 350 mL *ortho*-nitrophenyl octyl ether (102×10^{-4} mol L^{-1}); volume receiving phase: 12 mL HNO₃ (10%); membrane phase: 350 mL *ortho*-nitrophenyl octyl ether in microporous polypropylene; source phase: as described above, volume 12 mL.

Analysis of the receiving phase after 24 h and 120 h revealed that out of ten metal nitrates offered for transport in the source phase only four were carried by compounds **1a–c** through the separating chloroform layer: $Cu(NO_3)_2$, $Pb(NO_3)_2$, $Cd(NO_3)_2$ [7] and $Zn(NO_3)_2$. Other metal cations were not detected with ICP-OES in the receiving phase. Within the detection limit no metal salts were transported without carriers in the BLM under the same experimental conditions. Compound **1a** transports both copper(II) and lead(II) nitrate [8]. Transport of zinc(II) and cadmium(II) nitrates could not be detected. Compound **1b** is far more selective: the determined flux for copper(II) nitrate exceeds lead(II) nitrate transport by a factor of fifteen. Some transport of zinc(II) and cad-mium(II) nitrate was found, but compared to the cop-per(II) nitrate flux these fluxes were smaller by two orders of magnitude. With compound **1c** as carrier in the chloroform phase, a significant transport of $Cu(NO_3)_2$, $Pb(NO_3)_2$, $Cd(NO_3)_2$ and $Zn(NO_3)_2$ was observed. For measurements over 120 h similar values for

the ion flux of copper(II) and lead(II) nitrate were obtained, while cadmium(II) and zinc(II) nitrate were transported to a smaller extent. Compound **1c** is a less selective carrier than **1a** or **1b**.

Compared to BLM a much smaller ion flux of similar magnitude for copper(II) and lead(II) nitrate was observed with **1a** when incorporated as a carrier in a supported liquid membrane (SLM). With compound **1b** as carrier in a SLM only the transport of copper(II) nitrate from the mixture of ten nitrates was observed with high ion flux. However, the flux drops dramatically if the membrane is used for a longer time, indicating loss of the carrier from the membrane under the experimental conditions.

The ion fluxes derived from competition experiments are only valid for the applied conditions. To obtain conventional values for ion flux and to confirm the proposed selectivities a series of transport experiments with **1a** and **1b** as carriers in SLMs and single metal nitrates was performed. The transport from the source phase, now containing only copper(II) or lead(II) nitrate, into the receiving phase, which was free of any salts or acids (pure water [9]), was followed conductometrically. Ion fluxes were derived as an average from three independent experiments from the measurement of increasing conductivity in the receiving phase over 24 h using known procedures [10, 11]. To investigate the stability of the membranes experiments were repeated up to three times. The results revealed a selective transport of copper(II) nitrate with **1b** as carrier. Although some lead(II) nitrate is transported, the observed selectivity $S = 1.0 (\pm 0.3)$ [12] is remarkably high. Unfortunately, the ion flux drops to half of its initial value, if the membrane is reused indicating "bleeding out" of the carrier under the experimental conditions. Significantly higher ion flux was determined for **1a**, but without discrimination between copper(II) and lead(II) nitrate. Again, the ion flux dropped to approx. half of its value if membranes were reused. For compound **1c** an ion flux for lead(II) nitrate of $J = 1.3 \pm 0.3$ 10^{-8} mol m^{-2} s^{-1} was measured. Table 2 summarizes the results.

In conclusion, we have shown that the concave 1,10-phenanthrolines **1a–c** transport four transition metal nitrates selectively through BLM and SLM out of a mixture of ten alkali, alkali earth and other metal nitrates. The selectivities, which were predicted from competitive transport measurements, were confirmed by single salt transport experiments. Compound **1a** shows high, but approximately equal transport of copper(II) and lead(II) nitrate through BLMs and SLMs. Compound **1c** provides smaller transport rates and is even less selective. The best selectivity was found for **1b** either as a carrier in BLM or SLM: copper(II) nitrate is efficiently transported with a flux ten times larger than the flux determined for lead(II) nitrate. Compound **1b** can therefore be regarded as a new copper-selective ionophore

Table 2 Ion flux J [10^{-8} mol m^{-2} s^{-1}] [a]) for Cu(NO$_3$)$_2$ and Pb(NO$_3$)$_2$ transport through SLM with **1a**–**c** as carriers [b])

carrier	use of membrane [c])	**1a**	**1b**	**1c**
Cu(NO$_3$)$_2$	(1st use)	6.6 ± 0.5	1.9 ± 0.2	– [d])
	(2nd use)	4.2 ± 0.4	0.9 ± 0.1	– [d])
	(3rd use)	– [d])	0.8 ± 0.2	– [d])
Pb(NO$_3$)$_2$	(1st use)	6.6 ± 0.8	0.2 ± 0.04	1.3 ± 0.3
	(2nd use)	3.6 ± 0.1	– [d])	0.6 ± 0.2
	(3rd use)	3.1 ± 0.3	– [d])	0.5 ± 0.1

[a]) All values for J are derived as an average of three measurements. [b]) For details, see experimental section. [c]) SLMs were reused up to three times to determine their stability. [d]) Not determined.

with properties comparable to the best known examples, such as neutral dithiocarbamate disulfides or pyridine-based macrocyclic carriers [13]. However, for any application in chemical sensors the membrane stability must be increased markedly. The attachment of long alkyl chains to increase the hydrophobicity [14] of the compound or its immobilization in the membrane [15] might be envisaged.

Experimental

Compounds **1a**–**c** were synthesized according to previously reported procedures.[3] Supported liquid membranes (SLM) were prepared by standard procedures [16] from microporous polypropylene film (Accurel® PP, thickness $d_m = 100\ \mu m$, porosity = 64%, Akzo Nobel) with *ortho*-nitrophenyl octyl ether (NPOE) as solvent. The transport experiments were performed at 22 (+/–1) °C in magnetically stirred (500 rpm) permeation cell (for SLMs) or a beaker-glass-tube apparatus (for BLMs) similar to previous described setups [5, 16]. All glass apparatus were made from quartz glass to avoid contamination. Sampling vessels were polyethylene. All inorganic salts were *pro analysis* grade. Chloroform was Baker ultra resi analyzed, HNO$_3$ was 65% *p.a.* All standard solutions were prepared from high purity ICP 10 000 ppm stock standards, Johnson Matthey, Alfa Products. ICP-OES measurements were performed on a JY 70 Plus (ISA JOBIN YVON, München) with the following instrument operating parameters: power 880 W; plasma gas flow rate 14 L/min; coating gas 0.2 L/min; auxiliary gas 0.4 L/min; nebulizer type: cross flow; pressure 2.6×10^5 Pa; sample uptake rate 1 mL/min; integration time: simultaneous 5.0 s, sequential 1.0 s. For further details of the ICP-OES measurements, see ref. [5].

Transport of Cu(NO$_3$)$_2$ and Pb(NO$_3$)$_2$ through SLM was followed by conductivity measurements with conductometer LF 340-A (WTW) with cell LR 325/01 (cell constant $C = 0.1$ cm^{-1}). The measured conductivity was converted with an internal non-linear temperature compensation to conductivity at 25 °C. Concentration of the metal nitrates in the source phase was 0.1 mol L^{-1}; as receiving phase pure water was used. Conductivity was corrected for autoprotolysis of water. For calculation of concentrations, ion equivalent conductivities γ_0 [Pb(NO$_3$)$_2$] = 272.2 S cm^2 mol^{-1} and γ_0 [Cu(NO$_3$)$_2$] =

253.2 S cm^2 mol^{-1} in water at 25 °C were used [17]. The ion flux J within $t = 24$ h was calculated from $J = c\ V\ t^{-1}\ A^{-1}$, with A = 9.08 cm^2 (effective exchange area), V = 23 mL (volume receiving phase) and c = concentration receiving phase [12].

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transient of a steady state flux. However, similar values obtained for both time intervals indicate steady state transport.

[9] Pure water was produced with Seralpur Pro90c, Fa. Seral, Germany. The specifications of the pure water are better than ASTM Typ I: κ (25 °C) = 0.055 μS/cm; Na < 0.01 mg/L; Σ heavy metals < 0.005 mg/L.

[10] Although loss of carrier from the membranes changes the ion flux gradually as indicated by decreasing values of J for reused membranes, the ion flux can be regarded as a value for steady state transport within the observation intervals. Different values for J are obtained for competitive and single salt measurements with the same membranes. This reflects the influence of other metal salts present in the source phase on the transport process. Another difference which has to be taken into account is the different receiving phase: for competitive transport experiments this was aqueous HNO_3 (10%) to obtain samples for direct use in ICP-OES measurements, for conductivity measurements this was pure water. A small increase in conductivity corresponding to an ion flux of $J = 0.1 - 0.2 \times 10^{-8}$ mol m^{-2} s^{-1} for $Cu(NO_3)_2$ and $J = 0.3 - 0.4 \times 10^{-8}$ mol m^{-2} s^{-1} was observed in experiments with carrier-free membranes. The measured conductivity with carrier-loaded membranes was corrected by this value.

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