

Notes

Highly selective and efficient membrane transport of zinc as its thiocyanate complex anion using K^+ -dibenzo-18-crown-6 as a carrier

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A simple, selective and efficient liquid membrane system for the transport of Zn^{2+} ion has been designed. In this system, potassium-dibenzo-18-crown-6 is used as a carrier for the uphill transport of zinc as $Zn(SCN)_4^{2-}$ complex ion through a chloroform membrane, using cysteine as a suitable stripping agent in the aqueous receiving phase. Under the optimal experimental conditions, the amount of zinc transported through the liquid membrane after 90 min is found to be 97 ± 1 percent. The selectivity and efficiency of zinc transported from aqueous solutions containing Ag^+ , Sr^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Cd^{2+} , Pb^{2+} , Hg^{2+} , Pd^{2+} , Fe^{3+} , Bi^{3+} and Cr^{3+} ions have been studied.

Use of liquid membranes for metal ion transport has received extensive attention during the past two decades^{1,2}. Macrocyclic crown ethers have been widely used to mimic biological membranes and to separate metal ions, particularly alkali and alkaline earth cations^{3,4}. However, comparatively less attention has been paid to transport of transition and heavy metal ions⁵. We have recently designed some bulk liquid membranes for selective and efficient transport of transition and heavy metal ions using macrocyclic crown ethers as suitable ion carriers^{6,12}. Despite the fundamental role of zinc in the biological, medical and environmental processes¹³⁻¹⁵ as well as its increased industrial use¹⁵, work reported on its transport across liquid membranes is quite sparse^{6,17}. In this paper, we have used K^+ -dibenzo-18-crown-6 as a carrier for the highly efficient and selective transport of zinc ion as $Zn(SCN)_4^{2-}$ counter anion through a bulk chloroform membrane.

Experimental

Dibenzo-18-crown-6 (DB18C6) and other macrocyclic ligands used were purchased from Merck Chemical Company and used as received. Reagent grade chloroform (Merck) was used as the membrane organic solvent. All other chemicals used in this study were of the highest purity available from either Merck or Fluka Chemical Companies and used without further purification except for vacuum drying. Triply distilled water was used throughout. The atomic absorption spectrophotometer used for the measurement of metal ion concentrations was a Shimadzu AA-670 instrument. Mercury was determined in solution using cold vapour atomic absorption spectrometry (CVAAS). pH measurements were made with a Metrohm 632 pH-meter using a combined glass electrode. A bulk type liquid membrane cell^{11,17} was used.

All transport experiments were carried out at ambient temperature. A cylindrical glass cell (inside diameter 4.0 cm) holding a glass tube (inside diameter 2.0 cm), thus separating the two aqueous phases, was used^{11,17}. The inner aqueous phase (source phase) contained zinc nitrate (5 ml, 1.0×10^{-3} M) and potassium thiocyanate (0.6 M). The outer aqueous phase (receiving phase) contained cysteine at pH 7 (5 ml, 0.4 M). The chloroform solution (20 ml) containing 6.0×10^{-3} M DB18C6 which lay below these aqueous phases, bridged the two aqueous phases. The organic layer was slowly stirred by a Teflon-coated magnetic bar (3 cm $\times$ 5 mm diameter). Metal concentration was determined using AAS. Reproducibility was confirmed as $\pm 5\%$ or better. A similar transport experiment was carried out in the absence of the carrier for reference.

Results and discussion

In preliminary experiments, it was found that DB18C6-mediated transport of zinc nitrate in the chloroform membrane system is negligible. This is due to relatively high hydration energy of Zn^{2+} ion¹⁸ and its weak interaction with DB18C6¹⁹. However, in the presence of excess KSCN, zinc ion forms a relatively stable and bulky complex anion²⁰

$\text{Zn}(\text{SCN})_4^{2-}$ with low hydration energy which can easily accompany K^+ -DB18C6 cation into the membrane phase. The experimental variables such as concentration of KSCN in the source phase, nature and concentration of the stripping agent in the receiving phase, pH of the aqueous phases and nature and concentration of the macrocyclic polyether in the organic membrane phase were then optimized in order to achieve the highest efficiency and selectivity for the transport of a $1.0 \times 10^{-3} \text{ M}$ solution of zinc nitrate across the membrane system used.

The influence of the concentration of KSCN in the range 0.0 to 1.0 M in the source phase on the zinc ion transport was investigated. The percentage of Zn^{2+} transported into the receiving phase increased with the potassium thiocyanate concentration in the source phase until reagent concentration of about 0.6 M was reached, beyond which the transport efficiency remained more or less the same (~86-87%). It should be noted that, at such high concentrations of potassium thiocyanate, one would expect a competitive permeation of $(\text{K}^+\text{-DB18C6})\cdot\text{SCN}^-$ with $(\text{K}^+\text{-DB18C6})_2\cdot\text{Zn}(\text{SCN})_4^{2-}$ through liquid membrane which is likely to lower the transport rate of the zinc ion. In such case of competitive transport, the concentration of K^+ ion in the receiving phase must always be greater than twice that of Zn^{2+} ion. However, in all experiments carried out, it was found that approximately twice as many K^+ ions as Zn^{2+} were transported which is indicative of negligible co-transport of KSCN in the system.

The nature of amino acid used as a stripping agent for Zn^{2+} ion in the receiving phase considerably influences the permeability of the membrane system for $\text{Zn}(\text{SCN})_4^{2-}$ ion. It was seen that, in the presence of cysteine in the receiving phase, 88% of zinc ion transports through the liquid membrane during 60 min, while the use of other amino acids viz., glycine, histidine, arginine and alanine give much lower transport efficiency (55-70%). This is due to the increased formation constant of Zn^{2+} -cysteine complex in comparison with other Zn^{2+} -amino acid complexes.²¹ However, in the absence of any stripping agent in the receiving phase, the zinc transport is negligible. The optimum concentration of cysteine in the receiving phase was also studied and found to be 0.4 M when ~90% transport efficiency was observed.

The influence of pH of the source and receiving phases on the transport of Zn^{2+} was investigated. It

was found that maximum zinc transport occurred at the receiving phase $\text{pH} > 7$. At lower pH values there was a decrease in the percentage transport of zinc, due to the diminished complex ability of the amino acid at such pH values. On the other hand, the best pH region of the source phase for the maximum transport of Zn^{2+} ion was found to be between 3 and 6. At pH values < 3 in the source phase, most of the SCN^- ion exists in the form of HCN, resulting in a diminished amount of $\text{Zn}(\text{SCN})_4^{2-}$ ion necessary for the successful extraction of zinc ion into organic phase. While at $\text{pH} > 6$, the formation of some $\text{Zn}(\text{OH})_2$ precipitate caused a decrease in transport efficiency of zinc ion.

The permeability of the membrane system designed for transport of Zn^{2+} was also found to be critically dependent on the nature of the macrocycle used as carrier in the organic membrane phase. Among the five 18-crowns investigated in the present study, DC18C6, 18C6 and DB18C6 were found to be suitable carriers for the transport of zinc, mainly due to their appropriate cavity sizes for K^+ ion²² and, consequently, the higher stability of their complexes (Table 1). It is interesting to note that, despite better transport efficiency of Zn in the presence of DC18C6 and 18C6, in this study DB18C6 was used as a carrier ligand due to its lower bleeding in the aqueous phases as well as its much lower price. In the case of macrocycles of smaller cavity sizes (i.e. 15C5 and B15C5), due to the diminished stability of their K^+ complexes, the transport of zinc ion through the liquid membrane was found to be very low. It should be noted that, despite the proper cavity size of A18C6 and DA18C6 for K^+ ion, their use as carrier ligand

Table 1—Effect of carrier structure on zinc transport*

Carrier ligand	Percentage transported into receiving phase	Percentage remaining in source phase
18C6	93	5
DC18C6	95	4
DB18C6	91	8
A18C6	38	60
DA18C6	25	74
15C5	25	75
B15C5	30	69

* Conditions: Source phase, 5 ml $1.0 \times 10^{-3} \text{ M}$ zinc nitrate and 0.6 M KSCN at pH 5; membrane phase, 20 ml $8.0 \times 10^{-3} \text{ M}$ of different macrocyclic ligands in chloroform; receiving phase, 5 ml of 0.4 M cysteine at pH 7; time of transport, 60 min.

Table 2—Amount of cation transport from different cation mixtures through the organic membrane*

Cation	Percentage transported into receiving phase	Percentage remaining in source phase
Mixture 1		
Zn ²⁺	90	7
Fe ³⁺	0	85
Bi ³⁺	0	100
Cr ³⁺	0	100
Mixture 2		
Zn ²⁺	90	9
Fe ²⁺	0	67
Ni ²⁺	0	99
Co ²⁺	0	95
Mixture 3		
Zn ²⁺	90	8
Ag ⁺	4	95
Cd ²⁺	8	80
Pb ²⁺	9	81
Mixture 4		
Zn ²⁺	91	8
Cu ²⁺	10	75
Hg ²⁺	85	14
Mn ²⁺	0	90
Mixture 5		
Zn ²⁺	90	9
Pd ²⁺	7	75
Sr ²⁺	5	81

*Conditions: Source phase, 5 ml 1.0×10^{-3} M of each cation and 0.6 M KSCN at pH 5; membrane phase, 20 ml 8.0×10^{-3} M DB18C6 in chloroform; receiving phase, 5 ml 0.4 M cysteine at pH 7; time of transport, 60 min.

results in diminished zinc transport. This is due to the lower complexing ability of aza-substituted crown ethers (as soft bases) towards K⁺ ion as a hard acid²³.

The effect of the concentration of DB18C6 in the organic phase on the transport efficiency of zinc was min. The reproducibility of zinc transport was investigated, and the percent of metal ion transported after 90 min from ten replicate measurements was found to be 97 ± 1 .

The selectivity of the membrane system for the transport of zinc ion over some other transition and heavy metal ions, in equimolar mixtures, was studied (Table 2). Among the different cations tried, only Hg²⁺ ion interfered seriously in transport of zinc ion. However, the interfering effect of this cation was successfully eliminated by addition of 0.1 M thiourea as a masking agent in the source phase, although the efficiency of the Zn²⁺ transport decreased by ~7%.

In order to further support the concept that tetracyanatozinc(II) complexed anion accompanied

the K⁺-DB18C6 complexed cation into membrane phase in this study, the concentration of K⁺ after the transport period in the receiving phase was determined. It was found that approximately twice as many K⁺ ions as Zn²⁺ were transported, emphasizing that almost all potassium ions are participating as (K⁺-DB18C6)₂.Zn(SCN)₄²⁻ ion pair.

Thus, based on the foregoing discussions, a possible mechanism of zinc transport through the liquid membrane system proposed is presented as follows. Initially at the source phase-membrane interface, the K⁺-DB18C6 complex is formed. Since the Zn(SCN)₄²⁻ complex anion is less hydrated than other anions present in the source, it forms an ion pair with the potassium-crown complex cation, and this ion pair distributes preferentially into the chloroform membrane. Then, at the membrane-receiving phase interface, cysteine with high affinity for mercury ion²¹ completes the transport process by removing Zn²⁺ ion from its complex anion. Finally, the free carrier (i.e. DB18C6) diffuses back across the membrane to the source phase-membrane interface, where the cycle starts again. The very high efficiency and excellent degree of selectivity for zinc transport shown by the membrane system introduced demonstrate its potential application to selective removal, concentration, or purification of Zn²⁺ ion from different real samples.

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