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Uphill and Selective Transport of Thiocyanate Ion through a Bulk Liquid Membrane Containing Ferric Tetraphenylporphyrin Complex as a Mobile Carrier

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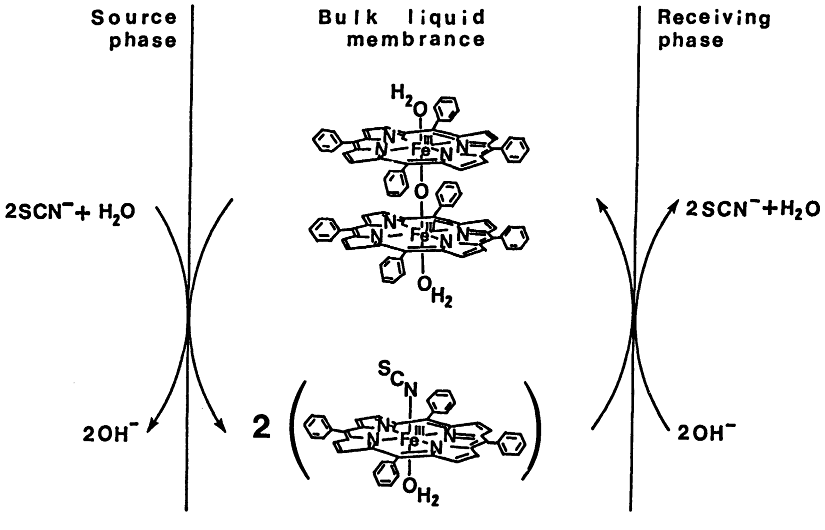
Ferric complex of tetraphenylporphyrin is useful as a carrier for preparing a bulk liquid membrane system in which SCN^- ion is selectively transported against its concentration gradient by coupling with the flow of OH^- ion coming from the opposite direction.

Different types of chemical compounds have been employed as a mobile carrier in constructing liquid membranes through which solutes can be transported against their concentration gradients.1) Previously we made the first application of a metallo-porphyrin complex to a liquid membrane system. It was proved that oxo-molybdenum complex of tetraphenylporphyrin is useful as the carrier for performing uphill transport of dihydrogenphosphate ion when being coupled with the counter-flow of halogen ions.2) The present purpose is to clarify the function of metallo-porphyrin complexes as the carrier with respect to their selectivity of transporting ions. This communication describes the excellent property of ferric tetraphenylporphyrin complex which is capable of transporting SCN^- ion against its concentration gradient across a bulk CH_2Cl_2 membrane (see Scheme 1) and also of practicing such an uphill transport even when various anions coexist in the system. To our knowledge, this is the first demonstration of the selective and uphill transport system of SCN^- ion, although crown ether mediated facilitated transport of guanidinium thiocyanate through a bulk membrane of chloroform has been reported.3)



Scheme 1.

Chloro(5,10, 15, 20-tetraphenylporphyrinato)-iron(III), FeTPPCl, was prepared according to the method of Fleischer et al.4) Full elemental analysis of the obtained complex gave results consistent with the formulation of $C_{44}H_{28}N_4FeCl$. The UV-visible spectrum of FeTPPCl in $CHCl_3$ also agreed with the literature.4) To prepare a membrane solution, 0.05 - 0.5 mmol of FeTPPCl was dissolved in 0.5 dm^3 of the purified dichloromethane, then thoroughly shaken with an aqueous NaOH solution (0.1 mol/m^3). Preliminary investigations of the obtained membrane solution by spectroscopic methods and elemental analysis5) showed that it contained an oxo-bridged dimer of ferric tetraphenylporphyrin complex, $O(FeTPP)_2$.4) Taking this into account, there are two approaches for expressing the carrier concentration ([carrier]), i.e., on molalities of the starting FeTPPCl complex and of the resulting $O(FeTPP)_2$ complex. It should be noted that the former was adopted in all the experiments described below.

The transport experiments were carried out at 25±0.1 °C, using a permeation cell consisting of two connected compartments (0.25 dm^3 each). The interfacial area of each compartment was adjusted to 28.3 cm^2 by means of a Teflon limiting ring.6) The two aqueous phases (0.1 dm^3 each), which were placed on both sides on top of the membrane solution (0.25 dm^3), consisted of the KSCN solutions ranging in initial concentration ($[KSCN]_0$) from 0.2 to 2 mol/m^3. The initial pH (pH_0) of one aqueous phase (source phase) was kept at 5.0 by use of an acetate buffer (0.1 mol/m^3), while the pH_0 of the other phase (receiving phase) was varied from 7 to 11 by a phosphate (0.03 mol/m^3) or a carbonate buffer (0.05 mol/m^3). In an experiment for evaluating the selectivity of the carrier for SCN^- ion, three buffer solutions were used which also included an equimolar (1 mol/m^3) mixture of KCl, KNO_2, KNO_3, and K_2SO_4. Both aqueous and organic phases of each cell compartment were continuously stirred at 60 rpm. The thiocyanate concentrations of both aqueous phases were determined by the pyridine-pyrazolone method.7)

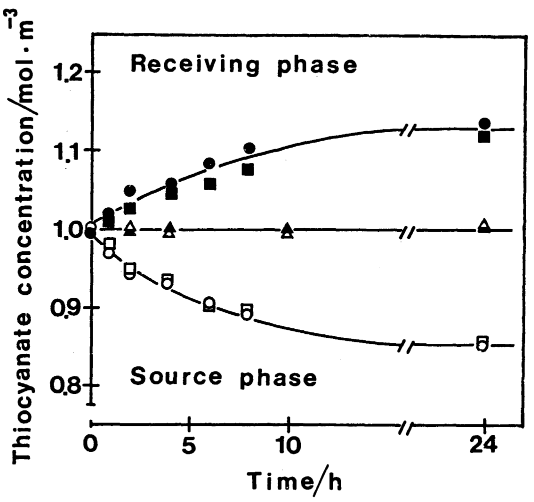


Fig. 1. Time dependence of thiocyanate concentrations on the source (△,○,□) and receiving (▲,■,●) sides in the presence (△, ▲and □,■) and absence (○,●) of all the common anions described in the text. The experimental conditions were: [carrier] = 0 mol/m^3 (△,▲) and 1 mol/m^3 (○,●and □,■); pH_0 = 5.0 (source side) and 10.0 (receiving side). The carrier-free membrane solution was used in a control experiment. Each plot shows the average of three determinations. The standard deviations average ± 8% with none being greater than ± 11%.

Figure 1 shows the concentration changes of SCN^- ion on the source and the receiving sides during the transport experiments in the presence and absence of the common anions. It is found that SCN^- ion is transported from the source to the receiving phase against its concentration gradient. Since there are no large differences in the transport curves in the presence and absence of various potassium salts, the uphill transport of SCN^- is little affected by the common anions used here. It can thus be said that the present metallo-porphyrin carrier has the function of selectively transporting SCN^- through the bulk membrane.

A small increase in pH on the source side was observed in the transport experiments employing the buffer solutions. Thus, a careful experiment without the use of the buffer solutions was carried out under the following conditions: $[\mathrm{KSCN}]_0$ of both sides = 1 mol/m^3; [carrier] = 1 mol/m^3; pH of the receiving side = 11.02 (adjusted with NaOH). The pH value of the source side varied from 6.70 to 9.24 when the transport of SCN$^-$ was allowed to continue for 1 h. The flux (J) of OH$^-$ on the source side was 1.70×10^{-7} mol/m^2·s, as estimated from the observed pH change. This value compares favorably with the J values of SCN$^-$ on the source side (1.77×10^{-7} mol/m^2·s) and on the receiving side (1.36×10^{-7} mol/m^2·s). Therefore, the thiocyanate transfer is found to follow an antiport mechanism with OH$^-$ transfer as the driving force.

Other important characteristics of the present transport system can be seen from changes in the J value of SCN$^-$ with [carrier], $[\mathrm{KSCN}]_0$, and pH$_0$ of the receiving phase (see Fig. 2). A plot of J against [carrier] at $[\mathrm{KSCN}]_0 = 2$ mol/m^3 is found to be linear on both source and receiving sides. However, the J vs. [carrier] curve at $[\mathrm{KSCN}]_0 = 1$ mol/m^3 levels off in the range of [carrier] > 1 mol/m^3. Such a leveling off in J is also observed in the results at a fixed [carrier] (1 mol/m^3) when increasing pH$_0$ of the receiving side or $[\mathrm{KSCN}]_0$. It is therefore indicated that the SCN$^-$ transport is controlled by diffusion in the organic laminar film within the bulk membrane phase as lowering [carrier] compared to $[\mathrm{KSCN}]_0$ on the source side and/or OH$^-$ concentration on the receiving side. In contrast, when raising [carrier] relative to one or both of them, aqueous film diffusion becomes a dominant factor. These are consistent with the general features of mass transfer across a liquid membrane.

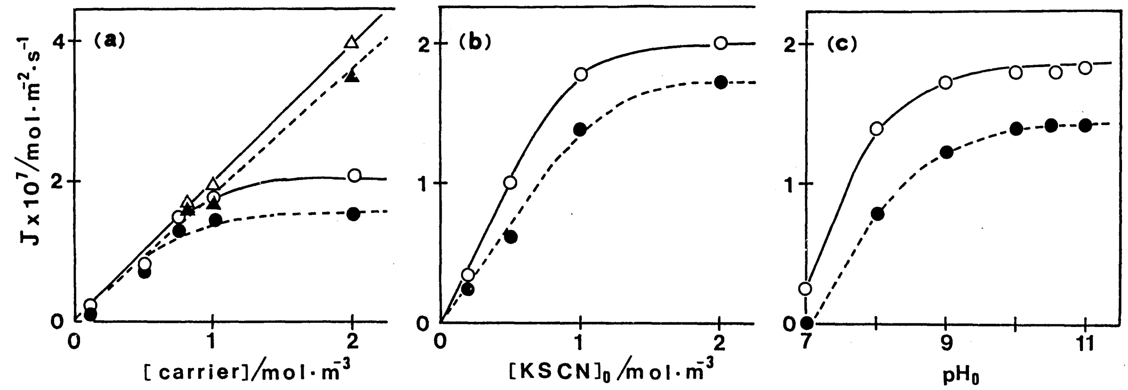


Fig. 2. Changes in the J values on the source (△, ○) and receiving (▲, ●) sides with [carrier], $[\mathrm{KSCN}]_0$, and pH$_0$ of the receiving solution. The experimental conditions in (a): $[\mathrm{KSCN}]_0$ = 1 mol/m^3 (○, ●) and 2 mol/m^3 (△, ▲), pH$_0$ = 5.0 (source phase) and 10.0 (receiving phase); in (b): [carrier] = 1 mol/m^3, pH$_0$ = 5.0 (source phase) and 10.0 (receiving phase); in (c): [carrier] = 1 mol/m^3, $[\mathrm{KSCN}]_0$ = 1 mol/m^3, pH$_0$ (source phase) = 5.0. Each plot shows the average of three determinations. The standard deviations average ± 8% with none being greater than ± 15%.

It is also found from Fig. 2 that the value of J on the receiving side comes close to that on the source side under conditions of [carrier] < 0.8 mol/m^3 or $[\mathrm{KSCN}]_0$ < 0.2 mol/m^3. These conditions seem to permit the balance of two types of carrier complexes (i.e., the oxo-bridged dimer complex and the thiocyanato complex) over all the regions of the membrane phase. Therefore, this finding suggests that in a stoichiometric relationship the thiocyanate transfer obeys the ligand exchange reaction shown in Scheme 1.[8,9] The transport mechanism could be interpreted as follows: At the aqueous-organic interface on the source side, the thiocyanato complex[10] is formed from the breakdown of the oxo-bridged dimer complex. At the same time, OH^- is liberated into the aqueous phase. The resulting thiocyanato complex diffuses across the bulk membrane, and at the interface on the receiving side, it turns the dimer complex and releases both SCN^- and H_2O into the aqueous phase. The regenerated dimer complex then diffuses back to the interface on the source side and the process is repeated.

In conclusion, it is our view that the present results strongly suggest the possibility of metallo-porphyrin carriers for constructing other liquid membrane systems which have the function of attaining uphill and selective transport of various coordinative solutes.

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References

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5) The membrane solution prepared was directly subjected to the UV-VIS measurement, while both elemental analysis and IR spectroscopy were carried out using a solid sample separated from the membrane solution by evaporating it to dryness. UV-VIS: λ_{max} nm (ε; based on the molality of the starting complex of FeTPPCl) 408 (105900), 571 (9800), 612 (4200). IR (KBr): 878 and 895 cm^{-1} (Fe-O-Fe). Anal. Found: C, 78.03; H, 4.15; N, 8.25%. Calcd for $C_{88}H_{56}N_8Fe_2O$: C, 78.11; H, 4.17; N, 8.28%.
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8) We assumed that the 6th coordination position of the Fe(III) in the carrier complex is occupied by a water molecule. Although such a coordination structure could not be supported by the results of elemental analysis and IR spectroscopy for a solid sample from the membrane solution, it seems more likely in the present transport system.
9) The transfer of water molecules from the source to the receiving phase was not yet confirmed even though several volumetric techniques have been tried.
10) The thiocyanato complex, FeTPPSCN, was obtained from sufficient shaking of the $O(FeTPP)_2$-containing membrane solution with the same KSCN solutions used as the source phase. The elemental analysis and IR spectroscopy were made for a solid complex obtained by evaporating the resulting organic solution to dryness. UV-VIS: λ_{max} nm (ε) 415 (127800), 511 (18400), 577 (3300), 665 (2400), 700 (2900). IR (KBr): 2035 cm^{-1} (SCN-Fe). Anal. Found: C, 73.07; H, 3.91; N, 9.38%. Calcd for $C_{45}H_{28}N_5FeS$: C, 72.58; H, 4.06; N, 9.40%.

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