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Uphill Transport of Dihydrogenphosphate Ion through a Liquid Membrane Containing Oxomolybdenum(V) Tetraphenylporphyrin Complex as a Mobile Carrier

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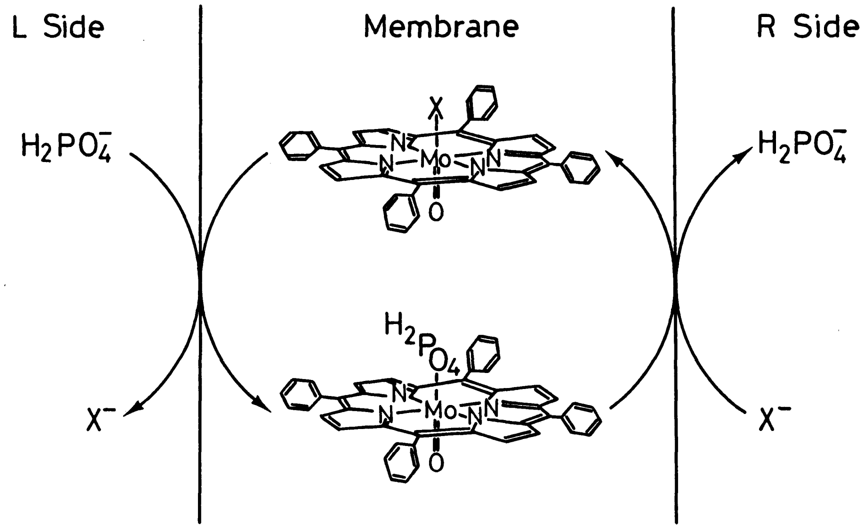
Oxomolybdenum(V) tetraphenylporphyrin complex is useful as a carrier for preparing a polymer-supported liquid membrane system in which $H_2PO_4^-$ ion is transported against its concentration gradient by coupling of a ligand exchange reaction.

In recent years, active or uphill transport of matter across artificial membranes has drawn much attention with regard to simulating biological membrane systems, and to developing a new separation technology. Although several complexing agents were employed in such membrane systems as a carrier,$^{1)}$ no attempt was made to use metallo-porphyrin complexes. Here we report the first application of a metallo-porphyrin complex, oxohalo(5,10,15,20-tetraphenylporphyrinate)molybdenum(V) [MoO(X)TPP; X = Cl, Br, I], to a liquid membrane system in which $H_2PO_4^-$ is transported against its concentration gradient as shown in Scheme 1.



Scheme 1.

The sample, MoO(Cl)TPP, is the same complex as used in our previous study on a selective phosphate ion exchanger.$^{2)}$ A solution (20 ml) of the purified n-butyl n-octanoate containing MoO(Cl)TPP ($3X10^{-5}$ M, M = mol/dm^3) was shaken with a 0.1 M aqueous KH_2PO_4 solution until the Cl ligand was completely exchanged with $H_2PO_4^-$.[3)] The liquid membrane was prepared by soaking a microporous poly(propylene) film (Duragard 2502) in the complex solution. The membrane, having the effective area of 68 cm^2, was fixed tightly between a pair of cylindrical glass cells. The transport experiments were carried out at 30 °C with stirring (about 60 rpm). The initial concentrations of KH_2PO_4 in both aqueous phases (200 ml each) on the left-side (L side) and right-side (R side) were adjusted to $1X10^{-4}$ M, while that of KX (X = F, Cl, Br, I) on the R side was 0.05 or 0.1 M. The phosphate concentration was determined colorimetrically.[4)] The concentrations of halogen ions (L side) were measured with an ion chromatographic analyzer (Yokokawa-Hokushin model IC 100).

Figure 1 shows the time vs. transport curves of $H_2PO_4^-$ through the complex-containing liquid membrane, observed by adding various KX salts into the R side. During the transfer from the R to L side of X^- ions, except for F^-, the phosphate ion was transported from the L to R side against its concentration gradient. This phenomenon of the phosphate transfer also occurred, even when a difference in the salt concentration between both aqueous phases was cancelled by adding KI (0.05 M) and $KHCO_3$ (0.05 M) into the R and L sides of the phosphate solution, respectively. It becomes evident that in the present system the membrane potential is not a factor governing the uphill transport of $H_2PO_4^-$. This is consistent with the following facts: (a) the membrane refuses to carry free charges because MoO(H_2PO_4)TPP and MoO(X)TPP are electroneutral complexes, (b) no transport is observed by the use of F^- having an ability to form a very stable complex with the carrier (see below), and (c) other ions (K^+, H^+, and OH^-) and H_2O do not move during the measurement. From these results, it can be said that the transfer of $H_2PO_4^-$ is not only against its concentration gradient, but also against its electrochemical potential gradient.

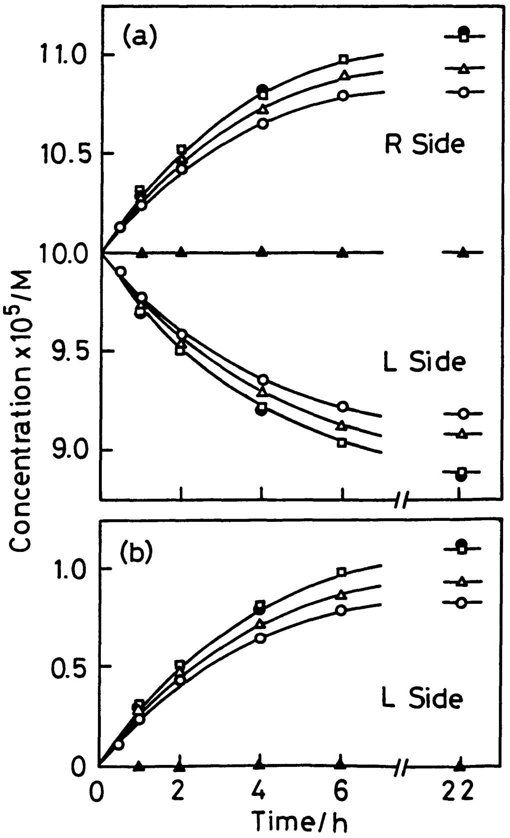


Fig. 1. Time dependence of concentrations of $H_2PO_4^-$ ion on the R and L sides (a) and of various halogen (X^-) ions on the L side (b). X^-: ▲, F^-; ○, Cl^-; △, Br^-; □ and ●, I^-. The initial concentrations of X^- ions on the R side were 0.05 M, except that the initial 0.05 M (□) and 0.1 M (●) of I^- were used to investigate the effect of the amount of X^- on the formation of MoO(X)TPP on the R side. The other conditions for the transport experiments are described in the text. Each plot shows the average of three determinations. The standard deviations average ± 8% with none being greater than ± 15%.

Another important feature of the present membrane system is that there are no differences in the flux (J) values of $H_2PO_4^-$ on the L and R sides or in the J values of $H_2PO_4^-$ and X^-; for example, the data of J (mol cm^{-2} h^{-1}) estimated from the initial slopes of the transport curves using KCl are as follows: 7.1×10^{-9} ($H_2PO_4^-$; L side), 6.8×10^{-9} ($H_2PO_4^-$; R side), 7.0×10^{-9} (Cl^-; L side). This indicates that the transport of $H_2PO_4^-$ occurs via the following 1:1 ligand exchange reaction:

$$\mathrm{MoO(X)TPP\ (organic\ phase)} + H_2PO_4^-\ \mathrm{(aqueous\ phase)} \rightleftarrows \mathrm{MoO(H_2PO_4)TPP\ (organic\ phase)} + X^-\ \mathrm{(aqueous\ phase)}$$

The mechanism could be interpreted as shown in Scheme 1. The complex-bound ligand X is replaced by $H_2PO_4^-$ in the bulk water to form $MoO(H_2PO_4)TPP$ at the aqueous phase-membrane interface on the L side. At the same time, X^- is liberated into the aqueous phase. The resulting $MoO(H_2PO_4)TPP$ complex diffuses across the membrane, and at the interface on the R side, it exchanges with X^- and releases $H_2PO_4^-$ into the aqueous phase. Regenerated MoO(X)TPP then diffuses back to the interface on the L side and the process is repeated.

No marked difference in the transport curves was observed when the experiments were carried out using the initial KI concentrations of 0.05 and 0.1 M (see Figure 1); indicating that the amount of X^- on the R side suffices for the formation of MoO(X)TPP under the conditions used here. Therefore, the transport of $H_2PO_4^-$ would be governed by the ligand exchange reaction on the L side. Assuming equilibrium across the phase boundary, this reaction could be characterized by the following type of an equilibrium constant;[5)]

$$K = \{[\mathrm{MoO(H_2PO_4)TPP}]_o \cdot [X^-]_a\}/\{[\mathrm{MoO(X)TPP}]_o \cdot [H_2PO_4^-]_a\}$$

where the brackets refer to the concentration of the species, and the subscripts o and a denote the organic and aqueous phases, respectively. A rough estimation of K was made by investigating the distribution ratios between CH_2Cl_2 and H_2O layers for the phosphate and halide. Experimentally, $[MoO(H_2PO_4)TPP]_o$ and $[MoO(X)TPP]_o$ were determined by spectrophotometric measurement of the organic layer after shaking dichloromethane containing $MoO(H_2PO_4)TPP$ (1×10^{-5} M; 5 ml) with an aqueous KX solution (0.5 M; 5 ml) in a sealed vial until the equilibrium had been established. The obtained values of log K (CH_2Cl_2/H_2O) were 5.20 (Cl^-), 5.58 (Br^-), and 6.61 (I^-).[6)] For F^-, the data could not be obtained under the employed experimental conditions, because of the very great stability of MoO(F)TPP. The order of K values is that expected from the transport experiments. This supports the conclusion that the uphill transport of $H_2PO_4^-$ is coupled with the ligand exchange reaction.

It has been known that zinc(II)-tetraphenylporphyrin complex preferentially binds hard ligands with donor atoms having relatively high electronegativity and low polarizability.[7)] The values of K obtained here increased in the same order as those of the equilibrium constant for a ligand exchange reaction of the zinc complex with R_4AsX (R = ph or Et; X = F, Cl, Br, and I) in CH_2Cl_2. Therefore, the active transport of H_2PO_4- by the molybdenum complex carrier seems to be directly influenced by the electronegativity of halogen ion used as a driving force.

The present liquid membrane system can be applied to the uphill transport of cyanate ion. It is our view that since many kinds of metallo-porphyrin complexes are currently available, their application in liquid membranes could be useful in constructing carrier-mediated uphill transport systems for various solutes.

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References

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3) The completion of this exchange reaction was determined by the characteristic absorption bands in the UV-visible spectrum of $MoO(H_2PO_4)TPP$: λ_{max} nm (logε) 475(4.62), 607(3.98), 649(3.89).

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