CHEMISTRY LETTERS, pp. 425-428, 1988.

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,<sup>1)</sup> 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.<sup>2)</sup> A solution (20 ml) of the purified n-butyl

n-octanoate containing MoO(Cl)TPP  $(3X10^{-5} \text{ M}, \text{ M} = \text{mol/dm}^3)$  was shaken with a 0.1 M aqueous KH<sub>2</sub>PO<sub>4</sub> solution until the Cl ligand was completely exchanged with H<sub>2</sub>PO<sub>4</sub><sup>-,3)</sup> 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<sup>2</sup>, was fixed tightly between a pair of cylindrical glass cells. The transport experiments were carried out at 30 °C with stirring (about 60 rpm).

initial concentrations of  $KH_2PO_4$  in both aqueous phases (200 ml each) on the leftside (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.<sup>4)</sup> 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<sub>2</sub>PO<sub>4</sub> through the complexcontaining 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 KHCO3 (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<sub>2</sub>PO<sub>4</sub>. This is consistent with the following facts: (a) the membrane refuses to carry free charges because MoO(H<sub>2</sub>PO<sub>4</sub>)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 thetransfer of  $H_2PO_4^{-1}$  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<sup>-</sup>) ions on the L side (b). X<sup>-</sup>:  $\blacktriangle$ , F<sup>-</sup>; O, Cl<sup>-</sup>;  $\triangle$ , Br<sup>-</sup>;  $\square$  and  $\bigcirc$ , I<sup>-</sup>. The initial concentrations of X<sup>-</sup> ions on the R side were 0.05 M, except that the initial 0.05 M ( $\square$ ) and 0.1 M ( $\bigcirc$ ) of I<sup>-</sup> were used to investigate the effect of the amount of X<sup>-</sup> 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%.

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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<sup>-</sup>; for example, the data of J (mol cm<sup>-2</sup> h<sup>-1</sup>) estimated from the initial slopes of the transport curves using KCl are as follows: 7.1X10<sup>-9</sup> ( $H_2PO_4^-$ ; L side), 6.8X10<sup>-9</sup> ( $H_2PO_4^-$ ; R side), 7.0X10<sup>-9</sup> (Cl<sup>-</sup>; L side). This indicates that the transport of  $H_2PO_4^-$  occurs via the following 1:1 ligand exchange reaction:

MOO(X)TPP (organic phase) +  $H_2PO_4$  (aqueous phase) MOO( $H_2PO_4$ )TPP (organic phase) + X (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<sup>-</sup> 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<sup>-</sup> 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;<sup>5</sup>)

$$K = \{ [MOO(H_2PO_4)TPP] \cdot [X^{-}]_{a} \} / \{ [MOO(X)TPP] \cdot [H_2PO_4^{-}]_{a} \}$$

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,  $[MoO(H_2PO_4)TPP]_0$  and  $[MoO(X)TPP]_0$ were determined by spectrophotometric measurement of the organic layer after shaking dichloromethane containing  $MoO(H_2PO_4)TPP$  ( $1X10^{-5}$  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 ( $I^-$ ).<sup>6</sup>) For F<sup>-</sup>, 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 <u>hard</u> ligands with donor atoms having relatively high electronegativity and low polarizability.<sup>7)</sup> 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.

The authors are deeply indebted to Drs. M. Sugiura and T. Shinbo, National Chemical Laboratory for Industry (Ibaraki, Japan), for their helpful encouragement and discussion.

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(Received November 27, 1987)

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