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UPHILL TRANSPORT OF PHOSPHATE ION THROUGH AN OXOMOLYBDENUM(V)-TETRAPHENYLPORPHYRIN-COMPLEX-CONTAINING BULK LIQUID MEMBRANE: EFFECT OF HALOGEN IONS ON PHOSPHATE ION FLUX

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Summary

The uphill transport of dihydrogenphosphate ion coupled with the counter-flow of a halogen ion across a bulk liquid membrane was studied by using various potassium halides (KF, KCl, KBr, and KI). The bulk membrane employed consisted of a trichlorobenzene solution containing oxomolybdenum(V) tetraphenylporphyrin complex as a mobile carrier. The feed solution phase was continuously replaced by fresh phosphate solution in order to avoid the accumulation of halogen ions and to hold the phosphate concentration to the initial level. The extraction constant, i.e., the equilibrium constant for the interfacial ligand exchange reaction, was estimated from two-phase liquid–liquid extraction experiments with a trichlorobenzene solution of the complex and an aqueous solution of the various halides. To clarify the relationship between the phosphate flux and the extraction constant, a transport equation was derived by considering aqueous film diffusion, organic film diffusion, and interfacial chemical reaction as simultaneous controlling factors. It was found that the halogen ions influence the flux via a change in the extraction constant according to their species. However, resistances due to the above three rate-controlling steps were independent of the species of halogen ion. Another characteristic of the present membrane system was that, regardless of the species of halogen ions, their concentrations at the aqueous–organic interface on the feed solution side are much larger than that of $H_2PO_4^-$.

Introduction

In recent years, active or uphill transport of matter across artificial membranes has received much attention with regard to simulating biological membrane systems and to developing a new separation technology. Different types of chemical compounds have been employed in such membrane systems as carriers; e.g., cyclic polyethers [1], chelating agents [2], redox agents [3], metal complexes of macrocyclic polyamines [4], and so forth.

In our previous study [5], a first attempt was made to apply a metalloporphyrin complex carrier, oxohalo(5,10,15,20-tetraphenylporphyrinato)molyb-

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denum(V) [MoO(X)TPP; X=Cl, Br, I], to a liquid membrane system. It was found that a supported liquid membrane containing MoO(X)TPP was able to transport dihydrogenphosphate ion against its concentration gradient. Such an uphill transport obeyed an antiport mechanism, with halogen ion transfer as the driving force, and the flux of $H_2PO_4^-$ was markedly dependent on the species of halogen ions. It is thus of interest to investigate in detail the effect of halogen ions on the flux of $H_2PO_4^-$ in order to clarify the features of the present transport system.

Here, a relationship between the phosphate flux and the extraction constant (equilibrium constant for the interfacial ligand exchange reaction) was studied as a function of the species of halogen ions. In the transport experiments, a trichlorobenzene solution containing MoO(X)TPP was used as a bulk liquid membrane. The extraction constants were estimated from two-phase liquid–liquid extraction experiments. The results obtained were analyzed by use of a transport equation, which was derived for evaluating variations in the flux with the extraction constant in connection to resistances due to aqueous film diffusion, interfacial chemical reaction and membrane diffusion as simultaneous controlling factors.

Theory

Transport of dihydrogenphosphate ion

Our previous studies [5,6] have indicated that the ligand exchange reaction of MoO(X)TPP dissolved in organic solvents with $H_2PO_4^-$ in an aqueous solution is given by

$$\overline{CX} + P^- \rightleftharpoons \overline{CP} + X^- \quad (1)$$

where the overbar refers to the organic phase, CX is the MoO(X)TPP complex, and CP is the $MoO(H_2PO_4)$TPP complex; P^- and X^- denote dihydrogenphosphate ion and halogen ion, respectively. The transport of $H_2PO_4^-$ through the complex-containing liquid membrane is illustrated in Fig. 1. The MoO(X)TPP complex-bound ligand X is replaced by $H_2PO_4^-$ in the feed solution to form $MoO(H_2PO_4)$TPP at the aqueous phase–membrane interface. At the same time, X^- is liberated into the feed solution. The resulting $MoO(H_2PO_4)$TPP complex diffuses across the membrane and, at the interface on the stripping side, it undergoes exchange with X^- and releases $H_2PO_4^-$ into the stripping solution. Regenerated MoO(X)TPP then diffuses back to the interface on the feed solution side and the cycle is repeated.

This transport process can be viewed according to a theory which accounts for the flux of $H_2PO_4^-$ by considering aqueous film diffusion, interfacial reaction and membrane diffusion as simultaneous controlling factors. Although Huang and Juang [7] recently arrived at such a theory for a supported liquid membrane system, it can not be directly applied to the present bulk membrane

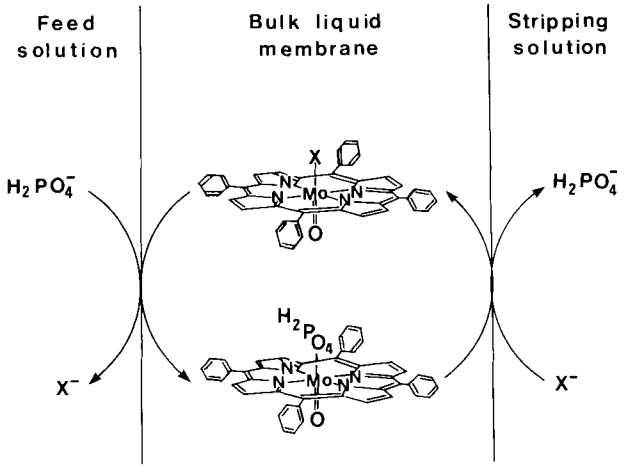

Fig. 1. Model for uphill transport of dihydrogenphosphate ion through the bulk liquid membrane containing the molybdenum complex as a mobile carrier.

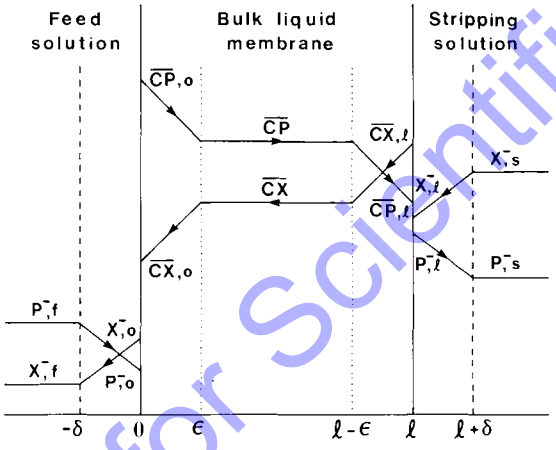

Fig. 2. Schematic concentration profile for the bulk liquid membrane system.

system. This is because the resistance of carrier diffusion in the bulk membrane under continuous stirring appears to be dominant only within the laminar film, not in all the regions of the membrane solution. We have therefore developed an alternative theoretical approach suitable for the present system.

The concentration profile in a bulk liquid membrane system is shown schematically in Fig. 2. Under continuous stirring of both aqueous and organic phases, the following assumptions are permissible: (a) linear concentration gradients exist throughout the system; (b) the diffusional resistances of $H_2PO_4^-$ and X^- within the bulk phases of both feed and stripping solutions

are negligible; (c) the resistance of carrier diffusion within the bulk phase of the membrane solution is also negligible. In a quasi-steady state, the following expressions should hold:

$$J_p = (D_p/\delta)([P^-]_f - [P^-]_o) = k_A([P^-]_f - [P^-]_o) \quad (2)$$

$$J_{cp} = (D_{cp}/2\epsilon)([\overline{CP}]_o - [\overline{CP}]_l) = 2k_O([\overline{CP}]_o - [\overline{CP}]_l) \quad (3)$$

Here, J_p is the flux of $H_2PO_4^-$ in the aqueous laminar film, and J_{cp} is the permeation rate of the complex-bound $H_2PO_4^-$ through the membrane. D_p and D_{cp} are the diffusivities of $H_2PO_4^-$ in the aqueous laminar film and of the complex-bound $H_2PO_4^-$ in the organic laminar film, respectively; k_A and k_O are the mass transfer coefficients in the aqueous and organic films, respectively; and δ and ϵ are the thicknesses of the aqueous and the organic film, respectively. $[P^-]$ is the concentration of $H_2PO_4^-$ in the aqueous solution, and $[\overline{CP}]$ is the concentration of the complex-bound $H_2PO_4^-$ in the membrane. The subscripts f, o, and l refer to the positions shown in Fig. 2. In eqn. (3), $[\overline{CP}]_l$ is negligible compared with $[\overline{CP}]_o$ under conditions of $[P^-]_l \ll [X^-]_l$. Thus, eqn. (3) becomes:

$$J_{cp} = (D_{cp}/2\epsilon)[\overline{CP}]_o = 2k_O[\overline{CP}]_o \quad (4)$$

The formation rate of $MoO(H_2PO_4)TPP$, R, at the feed solution interface is given as:

$$R = k_1[\overline{CX}]_o[P^-]_o - k_{-1}[\overline{CP}]_o[X^-]_o \quad (5)$$

where k_1 and k_{-1} are the interfacial reaction rate constants and $[CX]$ is the concentration of $MoO(X)TPP$. When the quasi-steady state is reached, a representation in the overall flux of $H_2PO_4^-$, J, can be obtained by applying a relation of $J = J_p = J_{cp} = R$:

$$J = \frac{k_1[\overline{CX}]_o[P^-]_f}{1 + (k_{-1}[X^-]_o/2k_O) + (k_1[\overline{CX}]_o/k_A)} \quad (6)$$

Since the interfacial reaction is the equilibrium reaction shown in eqn. (1), the extraction constant, K_{ex}, can be defined as

$$K_{ex} = k_1/k_{-1} = ([\overline{CP}]_o[X^-]_o)/([\overline{CX}]_o[P^-]_o) \quad (7)$$

We can therefore recast eqn. (6) into the following form:

$$1/J = \frac{1}{k_1[\overline{CX}]_o[P^-]_f} + \frac{[X^-]_o}{2k_O K_{ex}[\overline{CX}]_o[P^-]_f} + \frac{1}{k_A[P^-]_f} \quad (8)$$

In this equation, the first term becomes the main resistance when the process is governed by an interfacial chemical reaction. The second and third terms are dominant resistances in the cases of organic film diffusion control and aqueous film diffusion control, respectively. Equation (8) seems to be useful

for analyzing and discussing a relationship between J and K_{ex} experimentally determined as a function of the species of halogen ions.

Determination of K_{ex}

We consider a system consisting of an organic phase including $MoO(H_2PO_4)TPP$ and $MoO(X)TPP$ complexes and an aqueous phase including $H_2PO_4^-$ and X^- ions, which were equilibrated by shaking the organic solution of $MoO(H_2PO_4)TPP$ with the aqueous solution of potassium halide (KX). Because the ligand exchange reaction in eqn. (1) occurs during such a shaking procedure, the equilibrium constant K can be written as

$$K=([\overline{CX}]_e[P^-]_e)/([\overline{CP}]_e[X^-]_e) \tag{9}$$

where the brackets with the subscript e refers to the equilibrium concentrations of the species. As the degree of substitution (Y) of the phosphate ligand in $MoO(H_2PO_4)TPP$ with X^- from the aqueous phase can be expressed by

$$Y=\frac{[\overline{CX}]_e}{[\overline{CX}]_e+[\overline{CP}]_e}=\frac{[\overline{CX}]_e}{C_t} \tag{10}$$

eqn. (9) is rewritten as

$$K=\left(\frac{YC_t}{C_{xi}-YC_t}\right)\left(\frac{Y}{1-Y}\right) \tag{11}$$

Here, C_t denotes the total complex concentration of the organic solution, and C_{xi} is the initial KX concentration of the aqueous solution. Under the conditions of $C_{xi} \gg C_t$, eqn. (11) becomes:

$$K=\left(\frac{C_t}{C_{xi}}\right)\left(\frac{Y^2}{1-Y}\right) \tag{12}$$

or

$$\log\frac{Y^2}{1-Y}=\log\frac{C_{xi}}{C_t}+\log K \tag{13}$$

Equation (13) implies that plots of $\log[Y^2/(1-Y)]$ against $\log(C_{xi}/C_t)$ becomes a straight line with slope = 1, and the K value is determinable by means of the intercept. We can therefore estimate the value of K_{ex} by using the relationship $K=1/K_{ex}$.

Experimental

Bulk membrane

A complex of $MoO(Cl)TPP$ (1.05×10^{-3} mol), prepared as in the previous studies [5,6], was dissolved in 1.5×10^{-3} m^3 of purified 1,2,4-trichlorobenzene.

The complex solution was shaken with an aqueous KH_2PO_4 solution (10^2 mol/m^3) until the Cl ligand was completely replaced by $H_2PO_4^-$. The completion of this ligand exchange reaction was detected spectrophotometrically, because $MoO(H_2PO_4)TPP$ in trichlorobenzene showed a characteristic spectrum having three absorption bands in the ultraviolet and visible regions. The wavelength and absorptivity (in parentheses) of each absorption maximum are: 475 nm (4.65×10^3 m^2/mol) for the Soret band; 607 nm (9.8×10^2 m^2/mol) for the β band; 649 nm (8.1×10^2 m^2/mol) for the α band. The obtained $MoO(H_2PO_4)TPP$-containing organic layer was equilibrated with a stripping solution containing both $H_2PO_4^-$ (1 mol/m^3) and X^- (5×10^2 mol/m^3), and then used as a bulk membrane.

Transport experiment

The apparatus used is illustrated in Fig. 3. The permeation cell consists of two compartments (each 1.57×10^{-3} m^3) connected by a glass tube. The two aqueous solutions (each 2×10^{-4} m^3), which were separated by a bulk membrane (total 3.23×10^{-4} m^3) placed at the bottom of each compartment, initially contained 1 mol/m^3 of KH_2PO_4. In addition, the stripping solution (right-hand side compartment in Fig. 3) included 5×10^2 mol/m^3 of each KX salt to provide driving force. Unless otherwise noted, the feed phase was continuously replaced by supplying freshly prepared feed solution at a constant flow rate (2×10^{-4} m^3/hr). This was done in order to avoid the accumulation of X^- ions and also to hold the phosphate concentration to the initial level. Both aqueous and organic phases in each half cell were stirred at 60 rpm during the measurement. The permeation cell and the feed vessel for the fresh phosphate solution were immersed in a water-bath controlled at 25 ± 0.1°C. The concen-

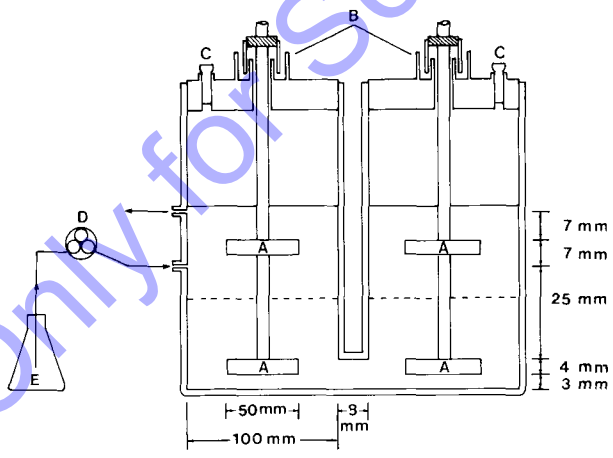

Fig. 3. Apparatus used for the transport experiments. A: stirrer blade, B: paraffin seal, C: sampling port, D: peristaltic pump, E: feed vessel.

trations of phosphate and halogen ions in the aqueous phases were determined by a colorimetric method and ion chromatographic analysis, respectively [5].

Extraction experiment

The trichlorobenzene solution of $MoO(H_2PO_4)TPP$ (1.17×10^{-2} mol/m^3; 5×10^{-6} m^3) was shaken with aqueous KX solutions (3×10^3–2 mol/m^3; 5×10^{-6} m^3) in a sealed vial at 25 ± 0.1°C until equilibrium was established. To determine the Y value, spectrophotometric measurement of the organic solution was carried out at 607 nm, corresponding to a maximum absorption of the β band for $MoO(H_2PO_4)TPP$, using a Hitachi 200-20 spectrophotometer. The attainment of equilibrium was checked by investigating the time course of spectral changes of the organic layer. The distribution equilibrium was reached in less than 20 min.

Results and discussion

Change in K_{ex} with the species of halogen ions

Extraction experiments with the aqueous solutions of KCl, KBr and KI showed that $MoO(H_2PO_4)TPP$ in trichlorobenzene was partially converted into the corresponding $MoO(X)TPP$ complexes. When aqueous KF solution was employed, however, the conversion was almost quantitative because of the very great stability of $MoO(F)TPP$. The Y values for the halogen ions other than F^- were determined from the spectroscopic data by using the following equation:

$$Y=\frac{A_{cm}-A_{cx}}{A_{cp}-A_{cx}} \tag{14}$$

Here, A_{cp} denotes the absorbance of $MoO(H_2PO_4)TPP$, A_{cx} is that of $MoO(X)TPP$, and A_{cm} is that of a mixture of both species. As shown in Fig. 4, the logarithmic plots of $[Y^2/(1-Y)]$ vs. (C_{xi}/C_t) revealed a linear relationship. The least squares method gave a correlation coefficient of 0.994 ± 0.004. The slopes of straight lines were within the range of 1.03 ± 0.05. These agree with the prediction from eqn. (13), and thus the values of K_{ex} can be calculated from the K values determined by means of the intercepts of the straight lines. The results are summarized in Table 1.

Nappa and Valentine [8] have reported that the equilibrium constant for a ligand exchange reaction of the zinc(II)–tetraphenylporphyrin complex with R_4AsX ($R=C_6H_5$ or C_2H_5; X=F, Cl, Br, and I) in dichloromethane solution increased with an increase in the electronegativity of ligand X. Also, it has been found that the spectral behavior of Zn(X)TPP is identical to that of MoO(X)TPP [9]. Therefore, the observed change in K_{ex} with the species of X^- ions is explicable in relation to their electronegativity.

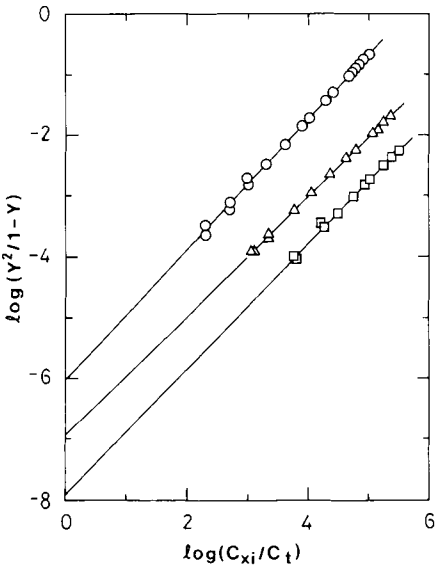

Fig. 4. Plots of log $[Y^2/(1-Y)]$ vs. log(C_{xi}/C_t) for estimation of K_{ex} values. ○: Cl^-, △: Br^-, □: I^-.

TABLE 1

Change in K_{ex} values with the species of halogen ions

Halogen ion	$K_{ex} \times 10^{-6}$ (−)
I^-	79.4
Br^-	8.51
Cl^-	1.12
F^-	–

Transport curves

Figure 5 shows the transport curves obtained with and without continuous replacement of the feed solution. The following important features were observed for the results obtained without the replacement procedure: (a) there is no difference in the magnitude of change in the concentration of $H_2PO_4^-$ between the feed and stripping sides (see curves B and C); and (b) the concentration changes of $H_2PO_4^-$ on both sides (curves B and C) are in fair agreement with that of Cl^- on the feed solution side (curve D). These clearly indicate that the uphill transport of $H_2PO_4^-$ is coupled with the 1:1 ligand exchange reaction shown in eqn. (1).

Another important feature of Fig. 5 was the marked difference in the transport curves depending on whether or not the replacement procedure was car-

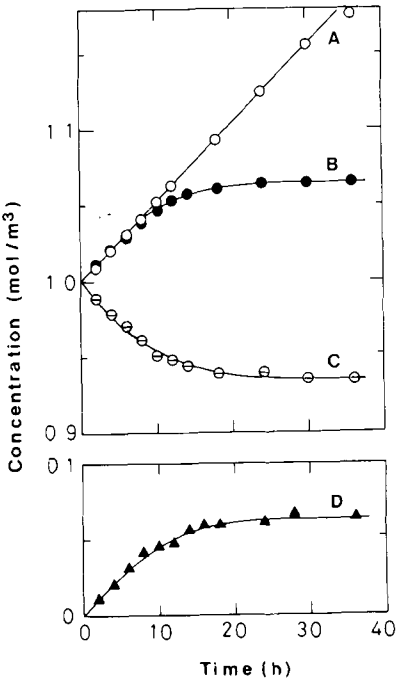

Fig. 5. Time-dependent concentration changes of $H_2PO_4^-$ and Cl^- ions on the feed and stripping sides. A and B: $H_2PO_4^-$ on the stripping side, C: $H_2PO_4^-$ on the feed side, D: Cl^- on the feed side. Straight line A was obtained with replacement of the feed solution, whereas the others were obtained without the replacement procedure.

ried out. Performance of this procedure resulted in a linear increase in the $H_2PO_4^-$ concentration of the stripping solution over time (see straight line A). In contrast, the transport curves of $H_2PO_4^-$ and Cl^- without replacement leveled off with the passage of time (see curves B, C, and D). These findings reveal that the accumulation of halogen ions in the feed solution has a marked effect on the transport rate of $H_2PO_4^-$ across the membrane.

The effect of the species of halogen ions was further studied by replacing the feed solution. The incorporation of KF in the stripping solution did not cause phosphate transfer because the very stable MoO(F)TPP was formed (see previous section). However, the other halides (KCl, KBr, and KI) brought about the uphill transport of $H_2PO_4^-$ against its concentration gradient, and the transport curves were linear plots (see Fig. 6). The correlation coefficients were within the range of 0.991 ± 0.004. The fluxes of $H_2PO_4^-$ were thus determined from the slope of each straight line. The results obtained are listed in Table 2. The comparison of these results with those in Table 1 strongly suggests the dependence of J on K_{ex}.

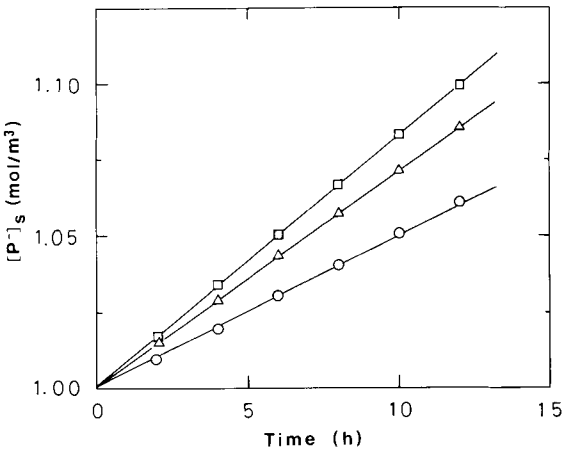

Fig. 6. Time-dependent concentration changes of $H_2PO_4^-$ on the stripping side obtained by using different halogen ions and by replacing the feed solution. Symbols as in Fig. 4.

Comparison of J *with* K_{es}

In order to compare the values of J and K_{ex} for different X^- ions, eqn. (8) was converted into a more convenient form by the elimination of $[\overline{CX}]_o$. The following equation was derived thus from eqn. (7):

$$\frac{1}{[\overline{CX}]_o} = \frac{1}{C_{tc}}\left(K_{ex}\frac{[P^-]_o}{[X^-]_o}+1\right) \tag{15}$$

Here, $C_{tc}(=[\overline{CP}]_o+[\overline{CX}]_o)$ denotes the total carrier concentration of the bulk membrane. By combining eqn. (15) with eqn. (8), followed by rearrangements using the relationship of $K_{ex}=k_1/k_{-1}$, we obtain

$$\frac{[P^-]_f C_{tc}}{J} = \frac{A}{K_{ex}} + B \tag{16}$$

$$A=\frac{[X^-]_o}{2k_O}+\frac{1}{k_{-1}} \qquad B=\frac{[P^-]_o}{2k_o}+\frac{C_{tc}}{k_A}+\frac{[P^-]_o}{k_{-1}[X^-]_o}$$

TABLE 2

Fluxes of dihydrogenphosphate ion obtained by using different halogen ions as driving force

Halogen ion	Flux $\times 10^8$ (mol/m²-sec)
I^-	5.93
Br^-	5.15
Cl^-	3.47
F^-	0

This becomes the same form as the transport equation of Baker et al. [2], concerning the carrier-mediated coupled transport of Cu^{2+}, when the two following requirements are satisfied: (a) in the Baker system the carrier-bound Cu^{2+} concentration at the interface on the stripping side is negligibly small, and (b) in our system the resistances due to both aqueous film diffusion and interfacial reaction are negligible.

In eqn. (16), the terms $[P^-]_f$ and C_{tc} remain unchanged during the experiments. Thus, the plots of $[P^-]_f C_{tc}/J$ against $1/K_{ex}$ were investigated by use of the data in Tables 1 and 2. The result obtained is expressed by an approximately linear relationship (see Fig. 7), indicating the constancy of terms A and B in eqn. (16). The values of $[X^-]_o$ and $[P^-]_o$ in eqn. (16) appear to remain almost constant through all the transport experiments employing different KX salts, because the feed phase was continuously replaced by fresh phosphate solution. Thus, the observed constancy of A and B means that the species of X^- as a driving force has little influence on $1/k_A$ (resistance due to aqueous film diffusion), $1/k_O$ (that due to organic film diffusion), and also $1/k_{-1}$ (that due to interfacial ligand exchange reaction). In particular, the minute change of k_{-1} with the species of X^- could suggest that the variation in K_{ex} corresponds mainly to that in k_1. In conclusion, it becomes apparent that, in the present membrane system, the species of halogen ions affects the flux only through changes induced in K_{ex}.

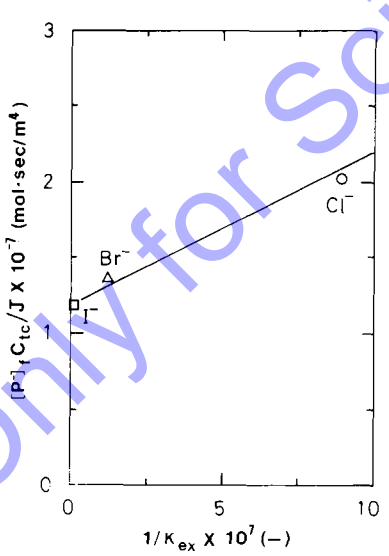

Fig. 7. Linear relationships between $[P^-]_f C_{tc}/J$ and $1/K_{ex}$.

Eliminating k_O and k_{-1} from eqn. (16), it follows that

$$\frac{C_{tc}[X^-]_o}{B[X^-]_o - A[P^-]_o} = k_A \tag{17}$$

Taking into account the fact that $k_A > 0$, the introduction of A (1.0×10^{13} mol-sec/m^4), B (1.2×10^7 mol-sec/m^4), and C_{tc} (0.7 mol/m^3) into eqn. (17) leads to

$$\frac{[X^-]_o}{[P^-]_o} > 8.5 \times 10^5 \tag{18}$$

This implies that, at the aqueous phase–membrane interface on the feed solution side, the concentration of halogen ions, regardless of their species, is much larger than that of $H_2PO_4^-$. Such a significant characteristic of the present membrane system could be caused by a chemical interaction which impedes the dissociation of X^- from the membrane interface, since there is no reason to assume that within the aqueous film the diffusivity of X^- is orders of magnitude less than that of $H_2PO_4^-$. In addition, when considering the difference in the transport curves obtained with and without replacement of the feed solution (see Fig. 5), it is likely that this interaction is strengthened by the accumulation of halogen ions in the feed solution.

Conclusion

The uphill transport of $H_2PO_4^-$ was studied by coupling with a flow of different halogen ions coming from the opposite direction across a bulk liquid membrane containing oxomolybdenum(V) tetraphenylporphyrin complex as a mobile carrier. A method for continuously replacing the feed solution by fresh KH_2PO_4 solution was generally adopted in this study in order to avoid the accumulation of halogen ions and to hold the phosphate concentration to the initial value. Thus, the $H_2PO_4^-$ concentration on the stripping side increased linearly with the passage of time. The flux values determined were compared with the extraction constants estimated from the two-phase liquid–liquid extraction experiments. A transport equation was derived for this purpose, considering aqueous diffusion, organic film diffusion and interfacial chemical reaction as simultaneous controlling factors. The results obtained showed the following important features: (a) the halogen ions influence the flux via a change in the extraction constant with their species; (b) resistances due to the three rate-controlling steps considered are independent of the species of halogen ions; and (c) the concentrations of halogen ions at the aqueous–organic interface on the feed solution side are much larger than that of $H_2PO_4^-$.

List of symbols

A	absorbance of species
C	concentration, mol/m^3
D	diffusivity of species, m^2/sec
J	flux or permeation rate of species, mol/m^2-sec
k_1,k_{-1}	interfacial reaction rate constants, m^4/mol-sec or (m/sec)/(mol/m^3)
k_A	mass transfer coefficient in the aqueous film, m/sec
k_O	mass transfer coefficient in the organic film, m/sec
K	equilibrium constant defined by eqn. (9)
K_{ex}	extraction constant
R	interfacial reaction rate, mol/m^2-sec
Y	degree of substitution of the phosphate ligand in MoO(H_2PO_4)TPP with X^- ions
[ ]	concentration of the species in the brackets, mol/m^3

Greek letters

δ	thickness of diffusion layer in the aqueous phase, m
ϵ	thickness of diffusion layer in the bulk liquid membrane, m

Subscripts

cm	mixture of MoO(H_2PO_4)TPP and MoO(X)TPP complexes
cp	MoO(H_2PO_4)TPP complex
cx	MoO(X)TPP complex
e	equilibrium state
f, o, l	corresponding to positions shown in Fig. 2
p	$H_2PO_4^-$ ion
t	total complex concentration
tc	total carrier concentration
xi	initial concentration of KX salts

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