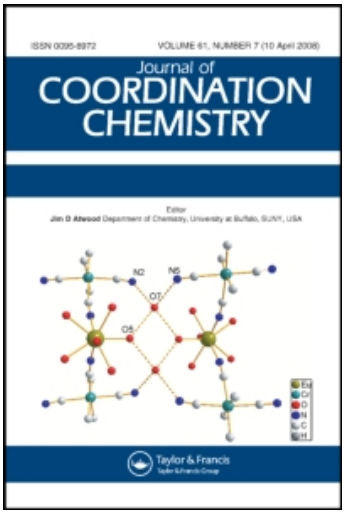

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Shoichiro Yoshida[a]; Tadashi Watanabe[a]
[a] Institute of Industrial Science, University of Tokyo, Minato-ku, Tokyo, Japan

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KINETICS OF ION TRANSPORT BY MACROCYCLIC CARRIERS IN LIQUID MEMBRANE SYSTEMS

SHOICHIRO YOSHIDA and TADASHI WATANABE
Institute of Industrial Science, University of Tokyo,
Roppongi, Minato-ku, Tokyo 106, Japan

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Abstract The relationship between the extractability of a metal ion (K^+ or Pb^{2+}) and the rate of its transfer by neutral macrocyclic carriers (dibenzo-18-crown-6, dicyclohexano-18-crown-6, 18-crown-6, and polynactin) was investigated in chloroform membrane systems. The experimentally determined apparent rate constants are compatible with the diffusion-limited process. Both the rate of ion uptake and the rate of ion transport depend crucially on the extractability of the metal ion rather than on the apparent rate constant.

Keywords: Macrocyclic carriers, extractability, diffusion-limit process

INTRODUCTION

Carrier-containing liquid membranes are promising for the construction of selective ion transport systems. It is known that an optimum value of the stability constant (K_s) of a carrier-cation complex exists for cation transport in such systems; when K_s becomes higher or lower than this optimum value, the rate of transport decreases.[1] In a previous work, we demonstrated that the rate of transport is controlled by the rate of uptake in the region of low K_s and by the rate of release in the region of high K_s.[2] These findings suggest that the extractability of the metal ion controls the concentration gradient of the complex in the membrane and the overall ion transport.[3] We describe herein how the extractability and the kinetic parameters influence the rates of individual steps (uptake, release, and transport) of ion transfer in chloroform membrane systems.

MATERIALS AND METHODS

Dibenzo-18-crown-6 (DB18C6), dicyclohexano-18-crown-6 (DC18C6), and 18-crown-6 (18C6) were reagent-grade chemicals obtained from Merck Chemical Co., Ltd. Polynactin was a gift from the Research Laboratories, Chugai Pharmaceutical Co., Ltd. The polynactin was a macrotetrolide antibiotic composed of 5% dinactin, 30% trinactin, and 65% tetranactin.

The rates of ion transport, ion uptake, and ion release were measured for the five carrier-salt combinations: DB18C6-potassium picrate(K^+Pic^-), DC18C6-K^+Pic^-, 18C6-K^+Pic^-, polynactin-KSCN, and 18C6-$Pb(NO_3)_2$. The procedure is reported in a previous paper.[3] The extraction constants were determined as previously reported.[3]

ION TRANSFER ACROSS THE INTERFACE

Figure 1 depicts the concentration profiles for the transfer of n-valent cation (M^{n+}) and univalent anion (A^-) in a liquid membrane system. If the diffusion of a metal-carrier complex in the

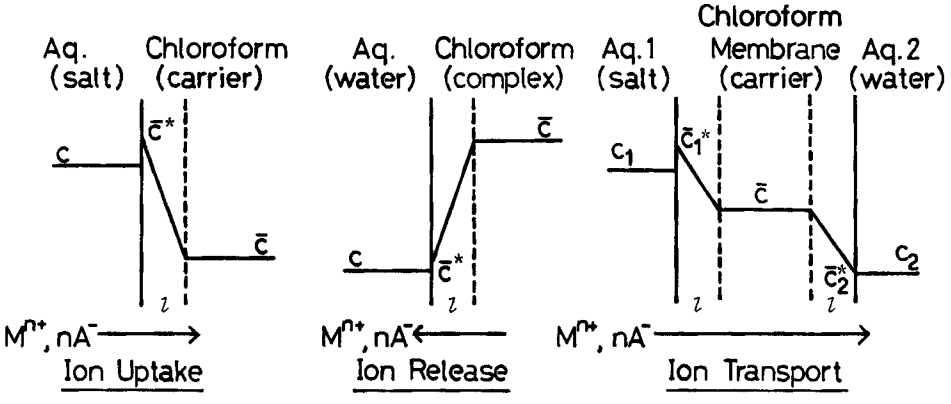

FIGURE 1. Concentration profiles for the ion transfer in a liquid membrane system.

membrane solution phase is the rate-determining step, the rates of ion uptake (J_u), ion release (J_r), and ion transport (J) should be proportional to the concentration gradient in the membrane solution phase as in eqs. 1, 2, and 3, where k_u, k_r, and k are defined as the apparent rate constants of uptake, release, and transport, respectively.

$$J_u = k_u(\bar{C}_M^* - \bar{C}_M) \tag{1}$$

$$J_r = k_r(\bar{C}_M - \bar{C}_M^*) \tag{2}$$

$$J = k(\bar{C}_{M1}^* - \bar{C}_{M2}^*) \tag{3}$$

In the case where the complexation readily attains an equilibrium at the interface, the metal concentration ($\bar{C}_M^*$) at the interface on the membrane side is related to the concentration in the aqueous phase by eq 4 which is derived from the extraction

$$\bar{C}_M^* = K_a' \bar{C}_L^\circ a_\pm^{(n+1)} / (1 + K_a' a_\pm^{(n+1)}) \tag{4}$$

equilibrium, where K_a' is the conditional extraction constant relative to activity of species and $\bar{C}_L^\circ$ is the total concentration of carrier in the membrane solution phase. Since $\bar{C}_M$ in eq 1, $\bar{C}_M^*$ in eq 2 and $\bar{C}_{M2}^*$ in eq 3 are negligibly small at the early stage of ion transfer, eq 1 through 3 can be rewritten as follows.

$$J_u = k_u K_a' \bar{C}_L^\circ a_\pm^{(n+1)} / (1 + K_a' a_\pm^{(n+1)}) \tag{5}$$

$$J_r = k_r \bar{C}_M \tag{6}$$

$$J = k K_a' \bar{C}_L^\circ a_\pm^{(n+1)} / (1 + K_a' a_\pm^{(n+1)}) \tag{7}$$

In the range of low activity of salt ($1 >> K_a' a_\pm^{(n+1)}$) in the aqueous phase, a plot of log J or log J_u against log $a_\pm$ was linear with a slope of 2 for univalent cations[3] and with a slope of 3 for bivalent cations (Figure 2). Further, the plot of J or J_u vs. $a_\pm^{(n+1)}/(1 + K_a' a_\pm^{(n+1)})$ indeed gives a straight line over a wide range of salt concentrations in the aqueous phase (Figure 2). J_r increased linearly with an increase in the concentration of the metal-carrier complex in the membrane solution phase, as expected from eq 6. These results demonstrate the validity of eqs. 5-7 in analyzing the ion transfer at the aqueous phase/membrane interface.

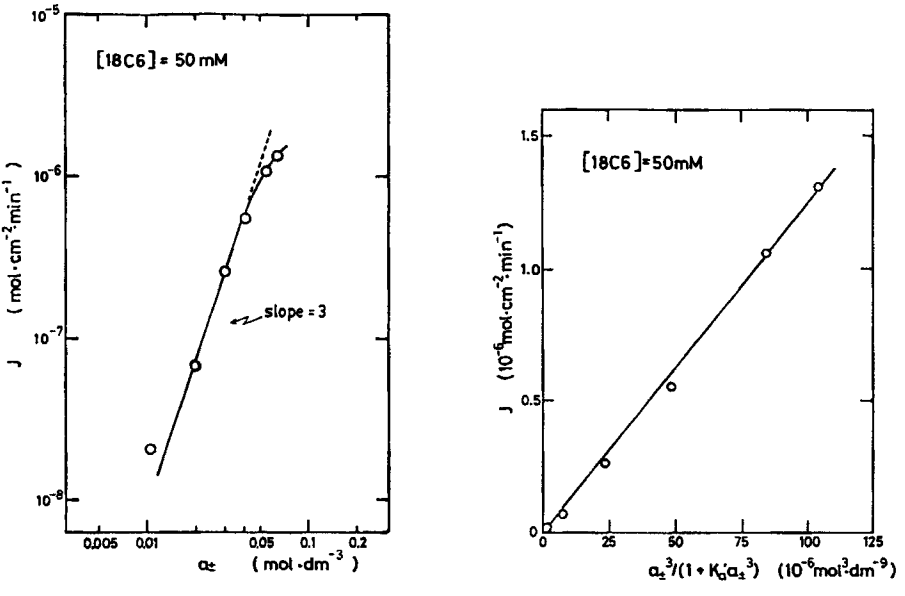

FIGURE 2. Left: dependence of the rate of Pb^{2+} transport by 18-crown-6 on the activity of $Pb(NO_3)_2$ in the source phase. Right: J vs. $a_\pm^3/(1 + K_a' a_\pm^3)$ for the 18-crown-6•$Pb(NO_3)_2$ system.

The apparent rate constants were calculated from eqs 5-7 by introducing the experimentally determined extraction constants. The kinetic parameters determined in this manner are summarized in Table 1.

TABLE 1. Rates of transport (J), apparent rate constants of ion transport (k), ion uptake (k_u) and ion release (k_r), and overall extraction constants (K_a') for the five macrocyclic carrier-salt combinations examined.

carrier [a]	salt	$\bar{c}_L^\circ$	k	k_u	k_r	K_a'	J [b]
		(10^{-3}M)	(10^{-4}cm/s)			(dm^6/mol^2)	(10^{-9}mol/cm^{2}min)
DB18C6	K^+Pic^-	2	7.0	11	15	3.70×10^4	3.0
DC18C6	K^+Pic^-	2	2.3	5.5	8.4	6.93×10^5	11.5
18C6	K^+Pic^-	2	2.6	9.4	11	8.02×10^5	13.7
PN	KSCN	100	1.2	5.7	5.1	6.0×10^2	792
18C6	$Pb(NO_3)_2$	50	7.1	13	16	5.98×10^3 [c]	1310
18C6	$Pb(NO_3)_2$	100	4.4	___	___	3.09×10^3 [c]	1210

[a] DB18C6, DC18C6, 18C6, and polynactin(PN) are, respectively, dibenzo-18-crown-6, dicyclohexano-18-crown-6, 18-crown-6, and a macrotetrolide antibiotic composed of 5% dinactin, 30% trinactin, and 65% tetranactin.
[b] The source phase (Aq. 1) is water containing 10^{-3}mol/dm^3 potassium picrate (K^+Pic^-) and 10^{-1}mol/dm^3 KSCN or $Pb(NO_3)_2$. [c] K_a' values in dm^9/mol^3.

The apparent rate constants are of the order of the value calculated from the diffusion coefficient (D, $\simeq 10^{-5}$cm^2 s^{-1}) and the thickness of the Nernst layer (l, 50-300 μm).

$$k_u,\ k_r = D/l \simeq (4\text{-}20)\times10^{-4}\text{cm s}^{-1}$$
$$k = D/2l \simeq (2\text{-}10)\times10^{-4}\text{cm s}^{-1}$$

Thus, a diffusion-limited process is applicable to the present experimental data.

RELATIONSHIP BETWEEN THE EXTRACTABILITY AND THE RATE OF ION TRANSFER

The rate of transport depends on the parameter kK_a'. The extractability of a metal ion makes a relatively large contribution to the magnitude of kK_a'. For a higher extractability, the concentration gradient of the metal-carrier complex in the membrane phase is steeper, so that the rates of uptake and transport should increase as K_a' increases.

When K_a' is very high, the concentration of the complex at the interface on the release side ($\bar{C}_{M2}^{*}$) is no longer negligible in comparison with the concentration in the bulk solution ($\bar{C}_M$). In such a case, the rate of release decreases with an increase in the extractability, so that the transport of ion does not proceed so fast as would be expected from its high affinity to the carrier.

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