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Studies of Ion Transport through a Liquid Membrane by Using Crown Ethers

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Abstract

Studies on ion transport through a liquid membrane system composed of two extraction processes have been carried out. Kinetic models based on extraction processes with consideration of the controlled parameters were developed for mediated ion transport through liquid membranes, especially those using crown ethers as the ion carrier. A study of the concentration change in the receiving or source phase envisages the determination of the equilibrium constant by a kinetic method corresponding to the chemical reaction at the interface as well as the maximum initial flux through the membrane. The equilibrium constant values determined by the kinetic process were checked by the solvent extraction method.

INTRODUCTION

The study of the transport of ions in an extraction process composed of two liquid phases (source and receiving), when these phases are separated by a liquid membrane phase which is immiscible in these phases, is an interesting approach for investigation. If chemical species are soluble in the membrane phase, they can pass through the liquid membrane into other phases. The transport of chemical species may be accomplished by simple diffusion or by an ion carrier (*1–4*). In this paper the extraction process utilizes an active crown ether as a chemical carrier which can react reversibly with the solute of interest. A carrier transports the ion through the membrane and releases it at the other boundary.

The modern version of the conventional two-phase solvent extraction technique, membrane ion transport, is a possible alternative (*5*). It is explored in this research study. In this paper the applications include comparison of the modified version of the transport of ions through a liquid membrane by the solvent extraction method. The application also includes the determination of potassium ion concentration with respect to time by using computer simulation studies based on kinetic models.

EXPERIMENTAL

All reagents used were analytical grade. Dibenzo-18-crown-6 (DBC), dicyclohexano-18-crown-6, benzene, and 1,2-dichloroethane were obtained from Katayama Chemicals. Methylene blue, picric acid, and potassium perchlorate were obtained from Wako Pure Chemical Industries Ltd. Potassium picrate was prepared from picric acid and potassium hydroxide. The solutions of dibenzo-18-crown-6 and dicyclohexano-18-crown-6 were prepared in benzene. The initial concentrations of DBC (2×10^{-3} mol/L), dicyclohexano-18-crown-6 (DCC) (2×10^{-3} mol/L), potassium picrate (1×10^{-3} mol/L), and potassium perchlorate (8×10^{-5} mol/L) were used.

The concentrations of picrate and perchlorate ions in the aqueous and organic phases were determined by spectrophotometrical methods. The concentration of perchlorate ion was determined by using methylene blue as a complexing reagent. The potassium ion concentration was determined by atomic absorption spectrophotometer. Benzene solution (150 mL) was transferred into 150 mL of aqueous solution in a cylindrical vessel at 30°C. The desired concentrations of crown ether, potassium picrate or potassium perchlorate, or crown ether complexes were used in an appropriate solution phase before commencing the experiment. The aqueous and organic phases were stirred independently by two flat-blade stirrers moving in opposite directions at the desired rotation speeds (Fig. 1). After a definite interval of time, the potassium ion concentration in the organic or the aqueous phase was determined and the extraction rate was estimated.

RESULTS AND DISCUSSION

Figure 2 illustrates the transport of ions from the source phase through the liquid membrane phase to the receiving phase. In Fig. 2, *s* represents the source phase, *r* the receiving phase, and *m* the membrane phase. This ion transport process can be represented by two extraction processes; namely, ion transport from the aqueous phase to the organic phase, which is a forward extraction process, and ion transport from the organic phase to the aqueous phase, which is a backward extraction process. These two extraction processes can be represented as an extraction system by considering the whole system as a bulk solution. Thus, it illustrates the transport of ions through a bulk liquid membrane. The rate of transport of ions (N) in the proposed kinetic studies can be represented by Eq. (1). How-

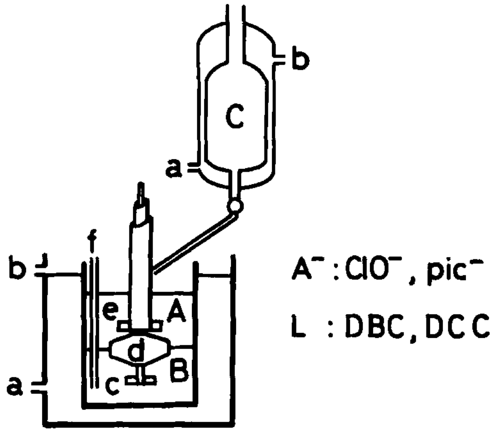

FIG. 1. Apparatus for kinetic studies: A and C, 150 mL benzene solution containing KLA; B, 150 mL water; a, thermostated water inlet; b, outlet; c and e, stirrer blades connected to stirrer motor; d, partition plate; f, tube for sampling.

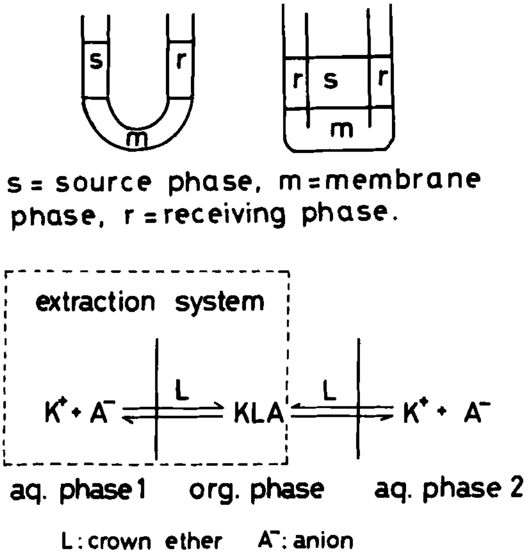

FIG. 2. Schematic presentation of extraction and ion transport systems.

ever, it can be illustrated by considering a bulk liquid membrane (Fig. 3). The forward transport rate of ions from the source phase to the membrane phase is given by $N_{f,s}$, and the backward transport rate of ions from the membrane phase to the source phase is given by $N_{b,s}$. The transport rate of ions from the membrane phase to the receiving phase, which is the forward extraction rate, is represented by $N_{f,r}$, and the backward transport rate of ions from the receiving phase to the membrane phase is given by $N_{b,r}$. Here, f and b stand for the forward and backward extraction processes. Thus, it could illustrate the mechanism path of ion transport in a bulk liquid membrane.

The transport rate of ions (N) in the proposed kinetic studies can be calculated by plotting the values of concentration of potassium ion vs time and using values of V and S. Equation (2) gives the backward ion transport rate (N_b) of the extraction process, and Eq. (3) gives the forward ion transport rate (N_f) of the extraction process.

$$N = (V/S)(dC_{K^+}/dt) \tag{1}$$

$$N_b = k_b[K^+LA^-]_0 \tag{2}$$

$$N_f = k_f[K^+][L]_0[A^-] \tag{3}$$

where V and S are volume and contact surface area, respectively. In our experiments, the values of V and S and the units of k_b and k_f are as follows: $V = 0.15$ L, $S = 35.8$ cm^2, k_b in L/cm^2·s, k_f in L^3/mol^2·cm^2·s.

The extraction equilibrium of potassium ion (K^+) with crown ether (L) and picrate or perchlorate anion (A^-) is given by

$$K^+ + L_0 + A^- \rightleftharpoons KLA_0 \tag{4}$$

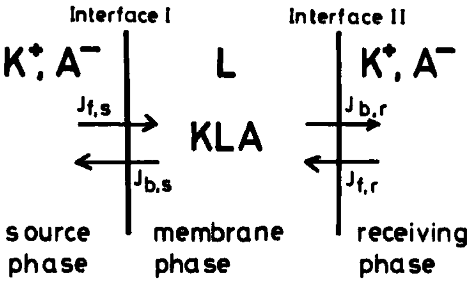

FIG. 3. Schematic representation of ion transport based on complexation kinetics.

The extraction equilibrium constant (K_{ex}) can be represented by

$$K_{ex} = \frac{[\mathrm{KLA}]_0}{[\mathrm{K}^+][\mathrm{L}]_0[\mathrm{A}^-]} \tag{5}$$

Since the extraction studies have been carried out at higher pH (*6*), there is no extraction of potassium ion with picrate ion into the organic phase. The forward extraction and backward extraction rates for the above extraction process are given by Eqs. (6) and (7), respectively:

$$N_f = k_f[\mathrm{K}^+][\mathrm{L}]_0[\mathrm{A}^-] \tag{6}$$

$$N_b = k_b[\mathrm{KLA}]_0 \tag{7}$$

At the equilibrium state where $N_f = N_b$, K_{ex} is given by

$$K_{ex} = k_f/k_b \tag{8}$$

The distribution ratio of the potassium ion (D_{K}) is expressed by

$$D_{\mathrm{K}} = [\mathrm{KLA}]_0/[\mathrm{K}^+] \tag{9}$$

The free concentrations of potassium ion, crown ether, and anion can be calculated from Eqs. (10), (11), and (12), respectively:

$$[\mathrm{K}^+] = C_{\mathrm{K}}^0 - (V/V_0)[\mathrm{KLA}]_0 \tag{10}$$

$$[\mathrm{L}]_0 = C_{\mathrm{L}}^0 - [\mathrm{KLA}]_0 \tag{11}$$

$$[\mathrm{A}^-] = C_{\mathrm{A}}^0 - (V/V_0)[\mathrm{KLA}]_0 \tag{12}$$

By substituting the value of $[\mathrm{KLA}]_0/[\mathrm{K}^+]$ from Eq. (9) into Eq. (5) and taking the logarithm of both sides of the new equation, we have

$$\log D_{\mathrm{K}}/[\mathrm{A}^-] = \log K_{ex} + \log [\mathrm{L}]_0 \tag{13}$$

Simulation studies of the kinetic process were carried out by solving differential equations numerically by using an NEC computer. Equations (14), (15), and (16) are proposed to predict the potassium ion concentration with respect to time in the source, the receiving, and the membrane phases, respectively:

$$-\frac{dC^s_{K^+}}{dt} = -\frac{dC^s_{A^-}}{dt} = (K_f[K^+]_s[L]_m[A^-]_s - K_b[KLA]_m)\frac{S_1}{V_s} \qquad (14)$$

$$\frac{dC^r_{K^+}}{dt} = \frac{dC^r_{A^-}}{dt} = (K_b[KLA]_m - K_f[K^+]_r[L]_m[A^-]_r)\frac{S_2}{V_r} \qquad (15)$$

$$\frac{dC^m_{KLA}}{dt} = \left(\frac{dC^s_{K^+}}{dt}\right)\frac{V_s}{V_m} - \left(\frac{dC^r_{K^+}}{dt}\right)\frac{V_r}{V_m} \qquad (16)$$

where s = source phase, m = membrane phase, and r = receiving phase.

(A) Forward Extraction Process

Rotation Speed Dependency

Studies of the extraction of ions with various rotation speeds from 50 to 165 rpm for dibenzo-18-crown-6, dicyclohexano-18-crown-6, potassium picrate, and potassium perchlorate systems have been done systematically. During the rotation speed dependency studies the same initial concentrations of all chemical species were used. The concentrations of potassium, picrate, or perchlorate ions were determined in the organic phase for definite time intervals at different constant rotation speeds. The determined concentrations were plotted against time. By using the slope of this plotted line and Eq. (1), the N_f value was determined with respect to rotation speed. Thus N_f values at the same initial concentrations of the chemical species were determined with the variation of rotation speed. The determined N_f values were plotted against rotation speed for the forward extraction process (Fig. 4).

Figure 4 shows the relation between N_f and the rotation speed for DBC, DCC, potassium perchlorate, and potassium picrate systems. It was observed that the N_f value increases with an increase in the rotation speed: 75–125 rpm for DCC–KPic, 70–135 rpm for DCC–$KClO_4$, 70–115 rpm for DBC–$KClO_4$, and 70–110 rpm for DBC–KPic systems. Hence, these are the regions controlled by the diffusion process. Furthermore, the N_f value is independent of increasing rotation speed: 125–155 rpm for DCC–KPic, 135–165 rpm for DCC–$KClO_4$, 115–165 rpm for DBC–$KClO_4$, and 110–165 rpm for DBC–KPic. This is the region which is the rate-determining step. It is controlled by chemical reaction. Further experimental studies were carried out in this region. Therefore, the proposed kinetic model is based on chemical reaction. After this region of rotation speed, an increase

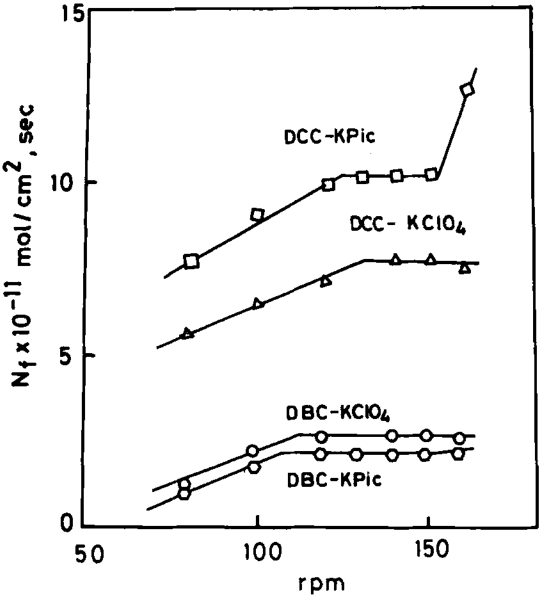

FIG. 4. Effect of rpm on N_f for DCC–KPic, DCC–KClO$_4$, DBC–KClO$_4$, and DBC–KPic systems:

KClO$_4$ system	KPic system
DCC = 4×10^{-4} mol/L	DCC = 3×10^{-4} mol/L
DBC = 4×10^{-4} mol/L	DBC = 5×10^{-4} mol/L
KClO$_4$ = 4.4×10^{-2} mol/L	K^+ = 10^{-2} mol/L
	Pic^- = 2×10^{-4} mol/L

in rotation speed causes N_f values to increase for the DCC–KPic system. In our experimental studies it was observed that the contact surface area was disturbed at high rotation speeds. This may be the cause for the increase in N_f values for the DCC–KPic system. The other reason may be hydrophobic, hydrophilic, and the shape and size of picrate ion and DCC in comparison with those of perchlorate ion and DBC.

The relationships between the concentration of potassium, picrate, or perchlorate ion in the organic phase versus time at different initial concentrations of potassium, picrate, perchlorate, and crown ether at constant rotation speed are given for the DCC–KPic system (135 rpm) and for the DBC-KPic system (130 rpm) in Fig. 5, and for the DBC–KClO$_4$ system (140 rpm) and the DCC–KClO$_4$ system (150 rpm) in Fig. 6. The rotation speeds were selected from the chemical reaction region. By using the slopes of the lines and Eq. (1), the N_f values were determined for these systems.

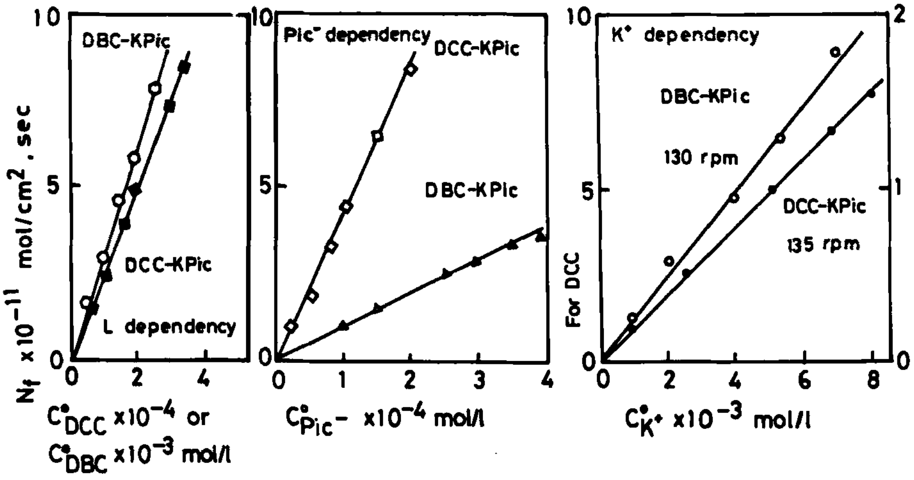

FIG. 5. Relation between N_f and initial concentration (C^0) of K$^+$, Pic$^-$, and L. DCC = 3 × 10^{-4} mol/L, DBC = 5 × 10^{-4} mol/L, Pic$^-$ = 2 × 10^{-4} mol/L, K$^+$ = 10^{-2} mol/L, L = DCC or DBC. DCC–KPic system, 135 rpm; DBC–KPic system, 130 rpm.

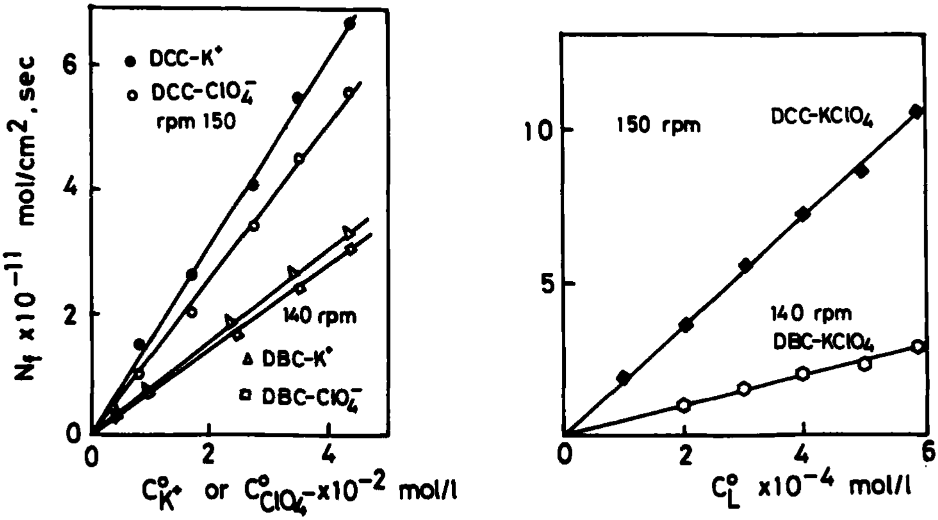

FIG. 6. N_f versus C^0 of K$^+$, ClO$_4^-$, and L$_0$; L = KClO$_4$. (●) DCC = 4 × 10^{-4} mol/L, ClO$_4^-$ = 4.4 × 10^{-2} mol/L, $C^0_{K^+}$ dependency. (○) DCC = 3 × 10^{-4} mol/L, K$^+$ = 4.4 × 10^{-2} mol/L, $C^0_{ClO_4^-}$ dependency. (△) DBC = 6 × 10^{-4} mol/L, ClO$_4^-$ = 4.4 × 10^{-2} mol/L, $C^0_{K^+}$ dependency. (□) DBC = 7 × 10^{-4} mol/L, K$^+$ = 4.4 × 10^{-2} mol/L, $C^0_{ClO_4^-}$ dependency. (■) KClO$_4$ = 4.4 × 10^{-2} mol/L, C^0_{DCC} dependency. (o) KClO$_4$ = 4.4 × 10^{-2} mol/L, C^0_{DBC} dependency.

N_f *Dependency on Initial Concentrations of* K^+*,* Pic^-*, and Crown Ether*

Figure 5 shows the relationship between N_f values and the initial concentrations of K^+, Pic^-, and crown ether. It can be observed from the plots that the N_f value is directly proportional to the initial concentrations of potassium, picrate, and crown ethers. This indicates that the rate-determining step is at the water–benzene interface, which is a chemical reaction of ion-pair formation in the forward extraction process. The value of k_f can be calculated for these systems by using the slope of the straight lines (Fig. 5) and the initial constant concentrations of the other two chemical species (Eq. 3).

N_f *Dependency on Initial Concentrations of* K^+*,* ClO_4^-*, and Crown Ether*

Figure 6 shows the relationship between N_f and initial concentrations of potassium ion, perchlorate, and crown ether. From the plots it can be seen that the N_f values are directly proportional to the initial concentrations of potassium or perchlorate ion and crown ether. Thus it shows that the rate-determining step is at the water–benzene interface, which is a chemical reaction of ion-pair formation. By using the slope of the straight line (Fig. 6) and initial constant concentrations of the other two chemical species (Eq. 3), the value of k_f can be calculated for these systems. The k_f values determined for these systems are listed in Table 1.

(B) Backward Extraction Process

Rotation Speed Dependency

The rotation speed dependency for the backward extraction process has been studied from 50 to 175 rpm for dibenzo-18-crown-6, dicyclohexano-18-crown-6, potassium picrate, and potassium perchlorate systems. In the studies of rotation speed dependency, the initial concentrations of crown

TABLE 1
Rate Constant Values for Different Systems[a]

		DBC	DCC
KPic	k_b	1.25×10^{-6}	9.8×10^{-7}
	k_f	2.6×10^{-2}	0.16
$KClO_4$	k_b	1.25×10^{-6}	1.66×10^{-6}
	k_f	2.48×10^{-5}	9.2×10^{-5}

[a] $N_b = k_b[K^+LA^-]_0$, k_b in L/cm²·s. $N_f = k_f[K^+][L]_0[A^-]$, k_f in L³/mol²·cm²·s.

ether, potassium ion, and picrate or perchlorate anion were kept constant. The concentration of potassium or perchlorate or picrate ion was determined in the aqueous phase at the definite time interval at constant rotation speed. The determined concentrations were plotted against time. From the slope of the plots and using Eq. (1), N_b values were calculated with respect to rotation speed. Thus the N_b values at the same concentrations of chemical species with the variation of rotation speed have been determined. The determined N_b values were plotted against rotation speed for the backward extraction process (Fig. 7).

Figure 7 shows the relation between N_b values and rotation speed for DBC, DCC, potassium perchlorate, and potassium picrate systems. It can be observed from these plots that the N_b value increases with an increase in rotation speed: 50–100 rpm for the DCC–$KClO_4$ system, 50–125 rpm for the DCC–KPic system, 50–125 rpm for the DBC–KPic system, and 50–125 rpm for the DBC–$KClO_4$ system. This indicates that this region is controlled by the diffusion process. With a further increase in rotation

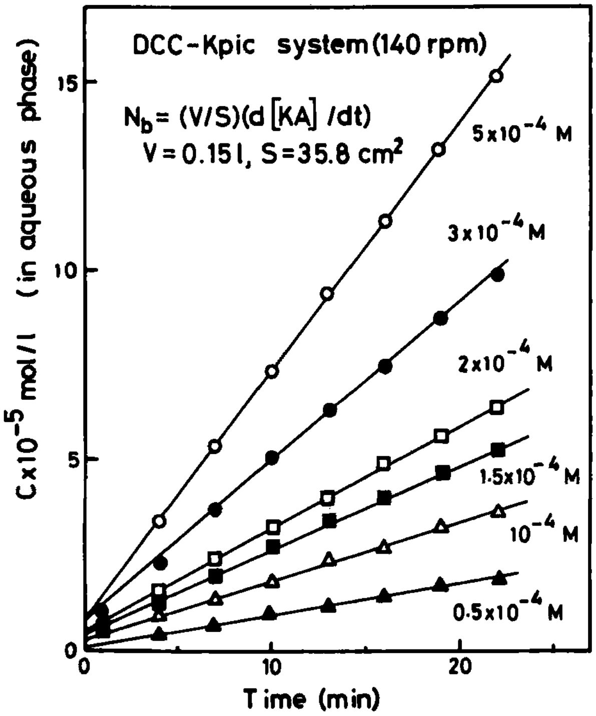

FIG. 7. Effect of rotation speed on N_b at constant KLA concentration. DCC–Pic$^-$ = 10^{-4} *M*, DBC–Pic$^-$ = 10^{-4} *M*, DCC–ClO_4^- = 6.33×10^{-5} *M*, DBC–ClO_4^- = 1.67×10^{-5} *M*.

speed, N_b is independent of the rotation speed. The values in this region were 100—135 rpm for the DCC–$KClO_4$ system, 125–165 rpm for the DCC–KPic system, 125–165 rpm for the DBC–KPic system, and 125–175 rpm for the DBC–$KClO_4$ system. This is the region of rotation speed which is the rate-determining step. It is controlled by chemical reaction. Further studies were carried out in this range of rotation speed. Thus, the kinetic model proposed in this study is based on chemical reaction. Furthermore, with an increase in rotation speed, an increase in N_b value was observed for the systems DCC–$KClO_4$ (135–165 rpm), DCC–KPic (165–175 rpm), and DBC–KPic (165–175 rpm). In the experimental studies it was observed that the contact surface area was disturbed due to a further increase in rotation speed. Therefore, this may be the cause for the increase in N_b values. The other possible cause was explained earlier.

The determination of N_b values was carried out with a variation of KLA_0 complex concentration. From the plot of the concentration of potassium or picrate or perchlorate ion in aqueous phase versus time, the value of N_b was determined by using the slope of the straight line (Fig. 8) and the extraction rate (Eq. 1).

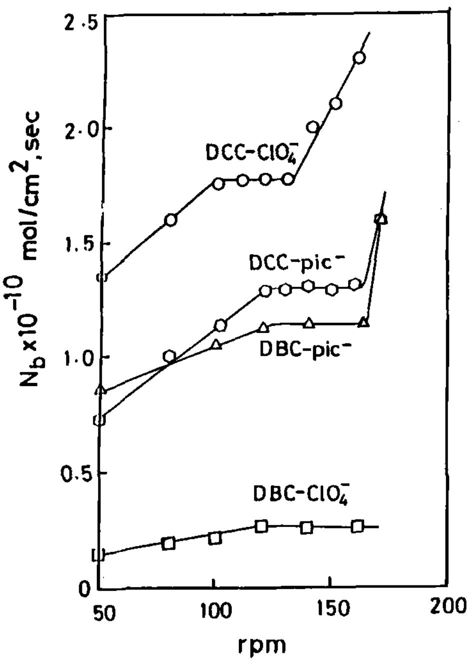

FIG. 8. Time dependency on potassium picrate concentration in the aqueous phase.

N_b Dependency on Initial Concentrations of Crown Ether–Potassium Picrate and Crown Ether–Potassium Perchlorate

Figure 9 shows the relationship between N_b and the initial concentration of KLA_0 for the crown ether–potassium picrate and crown ether–potassium perchlorate systems. From the plots it can be observed that the N_b value is directly proportional to the KLA_0 concentration. Thus the rate-determining step of the backward extraction process is decomposition of the ion-pair at the water–benzene interface. The slope of the straight line gives the value of k_b, the backward extraction rate constant. The k_b values determined for the crown ether–potassium picrate and crown ether–potassium perchlorate systems are listed in Table 1.

(C) Determination of K_{ex} Values by the Solvent Extraction Method

The K_{ex} values for the DBC–potassium picrate, DCC–KPic, DBC–$KClO_4$, and DCC–$KClO_4$ systems have not been determined under experimental conditions. Therefore, K_{ex} values were determined for these systems by the solvent extraction method. Figure 10 shows plots of log D_K/A^- versus log L_0 for DCC and DBC and potassium picrate and potassium perchlorate systems (Eq. 13). The K_{ex} values determined from these plots (Fig. 10) for these systems are listed in Table 2.

(D) Comparison of k_f and k_b Values

The k_f and k_b values were determined by the equilibrium kinetic method. These values are given in Table 1. The k_f values are much larger than the k_b values. This shows that the forward extraction process is predominant to the backward extraction process. The k_f values of the picrate systems

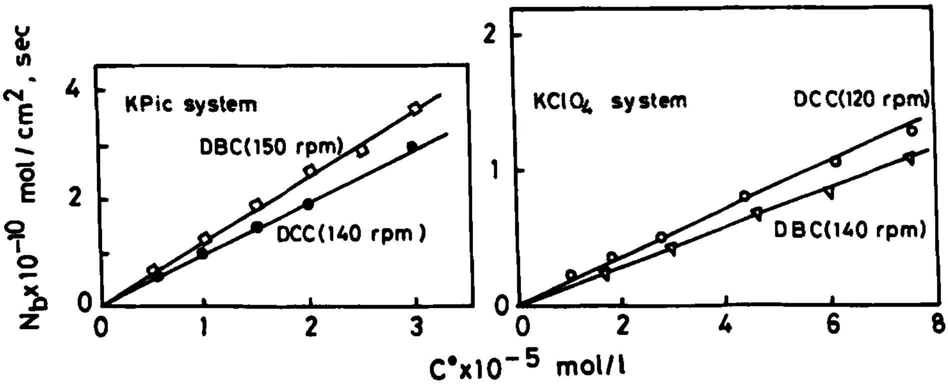

FIG. 9. Plots of N_b versus C^0 of $K^+LA_0^-$.

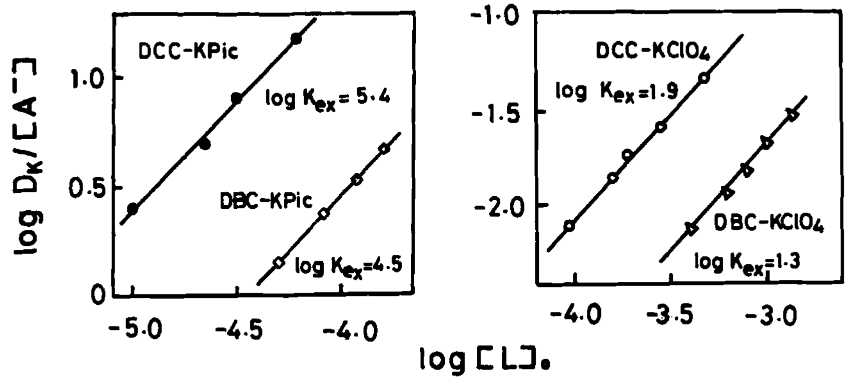

FIG. 10. Plots of log $D_K/[A^-]$ versus log $[L]_0$ for the DCC–KPic, DCC–KClO$_4$, DBC–KPic, and DBC–KClO$_4$ systems. The curve marked "a)" is from K. Toei et al., *Bull. Chem. Soc. Jpn.*, *48,* 60 (1975).

are higher than those of the perchlorate systems. Therefore, it can be concluded that the picrate ion is more suitable for ion transport studies.

(E) Comparison of K_{ex} Values Obtained by Kinetic and Solvent Extraction Methods

Log K_{ex} values for DBC, DCC, picrate, and perchlorate systems obtained by kinetic and solvent extraction methods are listed in Table 2. The K_{ex} values obtained by these two methods are in agreement. The conclusion to be drawn is that the proposed rate equations for these systems are correct. The k_f and k_b values determined for the DCC and DBC systems are correct within the limits of errors.

(F) Simulation Curves

Figure 11 shows three different cases of simulation curves for constant log K_{ex} value and concentrations of their chemical species for dibenzo-18-

TABLE 2
Comparison between log k_f/k_b and log K_{ex}

		log (k_f/k_b)	log K_{ex}
KPic	DCC	5.2	5.4
	DBC	4.3	4.5
KClO$_4$	DCC	1.7	1.9
	DBC	1.3	1.3

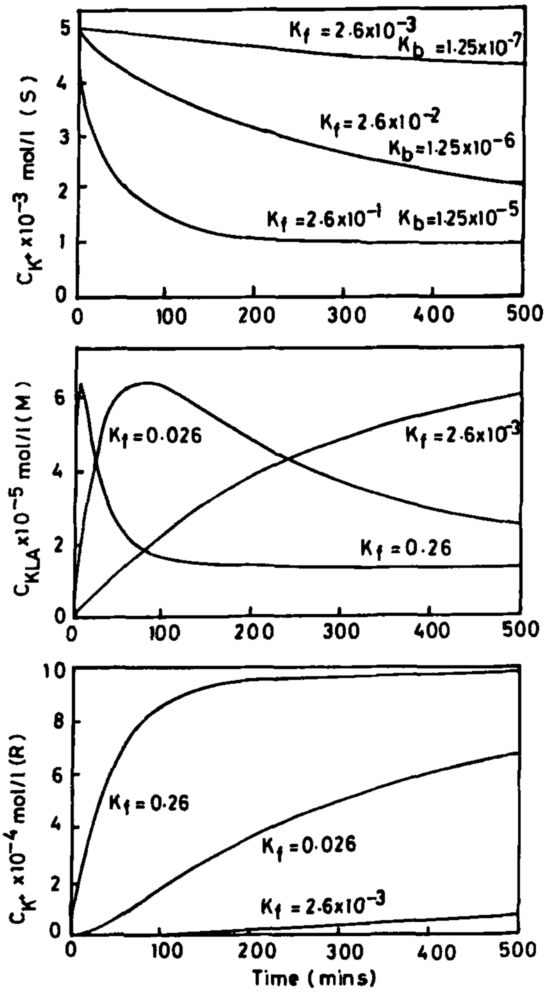

FIG. 11. Simulation curves for the DBC–KPic system. R = receiving phase, M = membrane phase, S = source phase, log K_{ex} = 4.3, V_s = 0.042 L, V_m = 0.351 L, V_r = 0.168 L, s_2 = 76.8 cm^2, s_1 = 36.3 cm^2, C_L = 7 × 10^{-4} mol/L, C_{KPic} = 5 × 10^{-3} mol/L.

crown-6–potassium picrate systems. For these studies, different parameters, such as constant surface areas s_1 and s_2, volumes of source phase V_s, membrane phase V_m, receiving phase V_r, and initial concentrations, were kept constant. The values of k_f and k_b were determined from the K_{ex} value. The change in the ion transport rate is illustrated with the variation of k_f and k_b values. The simulation studies indicate that it is important to determine the k_f and k_b values. The potassium ion concentration in the source, receiving, and membrane phases can be determined with respect to time by considering the equilibrium state as illustrated by the simulation curves.

CONCLUSION

The log K_{ex} values were determined for potassium–dibenzo-18-crown-6 and for dicyclohexano-18-crown-6 by using picrate and perchlorate as counteranions. The extraction equilibrium constant values were determined by two methods, solvent extraction and kinetic, which agree with each other. This supports the view that the proposed rate equations for kinetic studies are correct. In the kinetic studies, the k_f values determined are much larger than the k_b values. It was observed that the forward extraction process is predominant over the backward extraction process. The k_f values of picrate systems are much larger than those of perchlorate systems. It is concluded that the picrate ion is more suitable for ion transport studies with a liquid membrane compared to the perchlorate ion as the counteranion for these systems.

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