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Masataka Tanigaki[a]; Tetsuo Shiode[ab]; Masami Ueda[a]; Wataru Eguchi[a]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, KYOTO UNIVERSITY, KYOTO, JAPAN [b] Nippon Kokan Co. Ltd., Kawasaki, Japan

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Facilitated Transport of Zinc Chloride through Hollow Fiber Supported Liquid Membrane. Part 1. Transport Mechanism

MASATAKA TANIGAKI, TETSUO SHIODE,* MASAMI UEDA, and WATARU EGUCHI

DEPARTMENT OF CHEMICAL ENGINEERING
KYOTO UNIVERSITY
KYOTO, JAPAN

Abstract

The facilitated transport of zinc chloride through a liquid membrane of tri-*n*-octylamine dissolved in *n*-dodecane with 2-ethylhexyl alcohol, supported on a microporous polyethylene hollow fiber, has been studied in a series of three papers. This first paper deals with the transport mechanism. The distribution of zinc chloride between the liquid membrane phase and the aqueous hydrochloric acid solution was clarified. The characteristics of the support membrane and of the flow system were examined through phenol transport experiments. The initial permeation rate of zinc chloride was explained by the sum of film resistances in the two aqueous phases and a membrane phase resistance.

INTRODUCTION

Hollow fiber supported liquid membrane (HFSLM) is expected to be a simple and energy-saving operation for the recovery and enrichment of metals from dilute aqueous solutions (*1–8*). However, it has not yet been successfully demonstrated as an industrially feasible operation.

This series of three papers describes a study to solve engineering problems involved in HFSLM operations. The system chosen is the permeation of zinc chloride through HFSLM of tri-*n*-octylamine diluted

*Presently at Nippon Kokan Co. Ltd., Kawasaki, Japan.

in *n*-dodecane. 2-Ethylhexyl alcohol was added to the liquid membrane phase to make the extraction mechanism simple. Tri-*n*-octylamine works as a carrier for the facilitated transport of zinc chloride through a liquid membrane. Uphill transport and the mutual separation of metals are also possible with this system when the chloride ion concentrations in the feed and in the strip solutions are adjusted, as has been demonstrated for iron and zinc with benzene as the diluent (*9*, *10*).

This first paper deals with the mechanism of facilitated transport. The distribution equilibrium of zinc chloride was studied to obtain a basic understanding of the permeation mechanism. The characteristics of the support membrane and the flow system were examined by phenol permeation experiments. The permeation flux of zinc chloride at the initial stage is described as the sum of film resistances in the two aqueous phases and a liquid membrane phase resistance. The time course change in the permeation flux is discussed in the second paper.

EXPERIMENTAL

Reagent

Tri-*n*-octylamine (R_3N) from Tokyo Kasei Co. was alternatively washed with 1 kmol/m^3 aqueous hydrochloric acid solution, 1 kmol/m^3 aqueous sodium hydroxide solution, and deionized water several times (*11*). Zinc chloride, hydrochloric acid, sodium hydroxide, lithium chloride, phenol, 2-ethylhexyl alcohol (EHA), and *n*-dodecane of analytical purity grade were used without further purification.

Distribution Experiments

The distribution equilibrium of phenol between *n*-dodecane containing 6 vol% EHA and deionized water or 0.4 kmol/m^3 sodium hydroxide aqueous solution was measured by a standard procedure. The distribution of hydrochloric acid (0.1 to 1.0 kmol/m^3) between water and *n*-dodecane containing R_3N (0.025 to 0.2 kmol/m^3) and 6 vol% EHA was also studied. For the distribution experiments of zinc chloride, the aqueous phase was hydrochloric acid solutions (0.1 to 1.0 kmol/m^3) and the organic phase was *n*-dodecane containing R_3N (0.025 to 0.1 kmol/m^3) and EHA (6 vol%). All experiments were carried out at 298 K.

Support Membrane

A microporous polyethylene hollow fiber, EHF 270T, kindly supplied by Mitsubishi Rayon Co., was used as the support membrane. The inside diameter is 270 μm, the wall thickness is 55 μm, the porosity is 70%, and the average pore size is ~0.3 μm.

Organic Phase

n-Dodecane with 6 vol% EHA, presaturated with water, was used as the organic phase for the phenol permeation experiments. R_3N solutions of 0.025 to 0.1 kmol/m^3 in *n*-dodecane with 6 vol% EHA, presaturated with 1 kmol/m^3 aqueous hydrochloric acid solution, were used for the zinc permeation experiments.

Feed Solutions

The feed solution for the phenol permeation experiment was prepared by dissolving phenol in deionized water which was presaturated by *n*-dodecane with 6 vol% EHA. The phenol concentration was ~0.1 kmol/m^3. The feed solution used for the zinc permeation experiment was prepared by dissolving a predetermined amount of zinc chloride in a 1 kmol/m^3 hydrochloric acid aqueous solution presaturated with the organic phase being used. The zinc concentration was ~2.5×10^{-4} kmol/m^3.

Strip Solutions

The strip solution used for the phenol permeation experiments was a 0.4 kmol/m^3 sodium hydroxide aqueous solution presaturated with *n*-dodecane with 6 vol% EHA. That for the zinc permeation experiment was a 0.1 kmol/m^3 hydrochloric acid aqueous solution presaturated with the organic phase for all experiments. Approximately 1.0×10^{-3} kmol/m^3 lithium chloride was added to the strip solution to check the breakage of the liquid membrane. However, the lithium chloride was not detected in the exit feed solution for the entire series of experiments.

Analysis

The phenol concentrations in the aqueous and in the organic phases were measured spectrophotometrically. Zinc concentrations in the aqueous solution and in the organic phase were measured by atomic absorption spectroscopy. The acid concentration was analyzed by titration with aqueous sodium hydroxide solutions. The R_3N concentration in the organic phase was determined by nonaqueous titration in the presence of glacial acetic acid against perchloric acid (*12*).

HFSLM Permeation Experiments

A schematic diagram of the experimental set-up used for the permeation experiment is shown in Fig. 1. A hollow fiber of ~21 or 28 cm length was glued at both ends to Pyrex glass capillaries of 1.4 mm i.d. with adhesive epoxy resin. The feed solution runs through the hollow fiber because of the head pressure of the feed solution tank. The stripping solution circulates outside the fiber by means of a micro tube pump. The

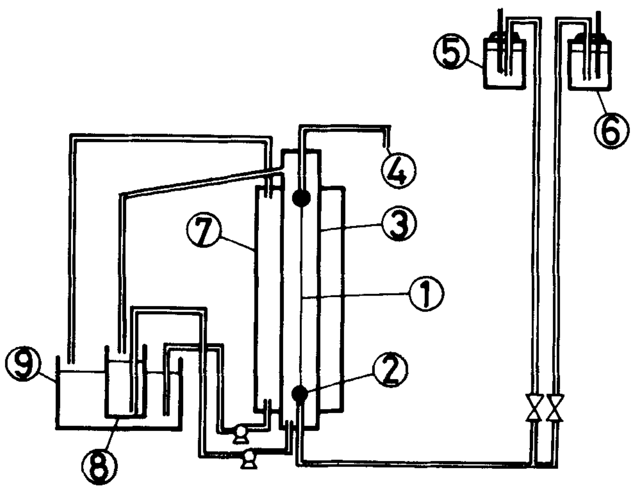

FIG. 1. Schematic diagram of the experimental set-up for the HFSLM experiments. ① Hollow fiber. ② Adhesive resin. ③ Permeation column. ④ Sample of exit raffinate solution. ⑤ Feed solution tank. ⑥ Organic phase tank. ⑦ Water jacket. ⑧ Strip solution tank. ⑨ Constant temperature bath.

permeation column, made of methyl methacrylate resin, was maintained at 298 K by constant temperature water circulating outside the column.

The flowing organic phase was impregnated into the micropores inside the hollow fiber by circulating it for a short period of time (5 to 10 min). Each permeation experiment was started when the flow of the organic phase was replaced by that of the feed solution. The exit raffinate solution was periodically sampled, and the flow rate, q_1, and the concentrations of phenol or zinc chloride, hydrochloric acid, and lithium chloride were measured.

The HFSLM system is illustrated in Fig. 2. The feed aqueous solution inside and the strip aqueous solution outside the hollow fiber are denoted as phases (1) and (2), respectively. The liquid membrane phase supported in the micropores of the hollow fiber wall is denoted as phase (m). The average permeation flux of phenol or zinc chloride, J, based on the inner surface area, A_1, is determined by

$$J = (q_1/A_1)(c_1^{(i)} - c_1^{(o)}) \tag{1}$$

Diffusion Coefficients Used

The diffusion coefficient used for phenol in the aqueous phase was 8.9×10^{-10} m^2/s (*13*). That for zinc chloride in the aqueous phase was calculated by the Nernst equation to be 7.0×10^{-10} m^2/s. The diffusion

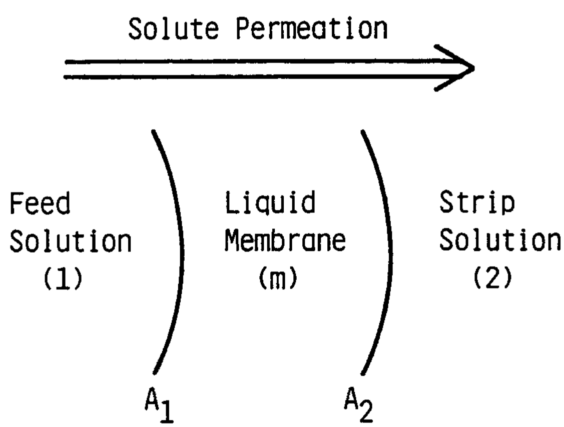

FIG. 2. HFSLM configuration. A_1 and A_2 are the inner and the outer surface areas of the support membrane, respectively.

coefficients of phenol and of the zinc complex in the organic phase were estimated using the Wilke-Chang equation (*14*) to be 1.4×10^{-9} and 2.3×10^{-10} m^2/s, respectively. The viscosity of the organic phases, necessary for the estimation of diffusion coefficients, were measured by the capillary method.

RESULTS AND DISCUSSIONS

Distribution Equilibrium of Phenol

The distribution coefficient of phenol between *n*-dodecane with 6 vol% EHA and deionized water was found to be $K_{D,\mathrm{Ph}} = 1.42$. That between *n*-dodecane with 6 vol% EHA and 0.4 $kmol/m^3$ sodium hydroxide aqueous solution was less than 6×10^{-3}.

Distribution Equilibrium of Zinc Chloride

Preliminary measurement of the distribution equilibrium of zinc chloride with the organic phase of *n*-dodecane with only R_3N revealed the appearance of a second organic phase, especially at high acid concentrations in the aqueous phase. This suggests the complicated nature of the extraction behavior with a variety of zinc and of hydrochloric acid complexes with R_3N in the organic phase. EHA (6 vol%) was then added to the organic phase. Even with EHA, high complexes appeared at high metal loadings. In the following, we deal with the cases of relatively low loading of metal only. The experimental data on distribution equilibrium were analyzed following the method described in Refs. *15* and *16*.

Figure 3 shows the results of the distribution of hydrochloric acid. The ratio of the hydrochloric acid concentration in the organic phase, $\bar{C}_H$, to the total R_3N concentration, $\bar{C}_N$, is second order to the hydrochloric acid concentration in the aqueous solution, C_H, when C_H is low but becomes unity for $C_H > 0.03$ $kmol/m^3$, independent of $\bar{C}_N$. This suggests the formation of a 1-1 acid complex in the organic phase.

$$\overline{R_3N} + H^+ + Cl^- \rightleftharpoons \overline{R_3NHCl} \tag{2}$$

The equilibrium constant of Eq. (2) can be expressed as

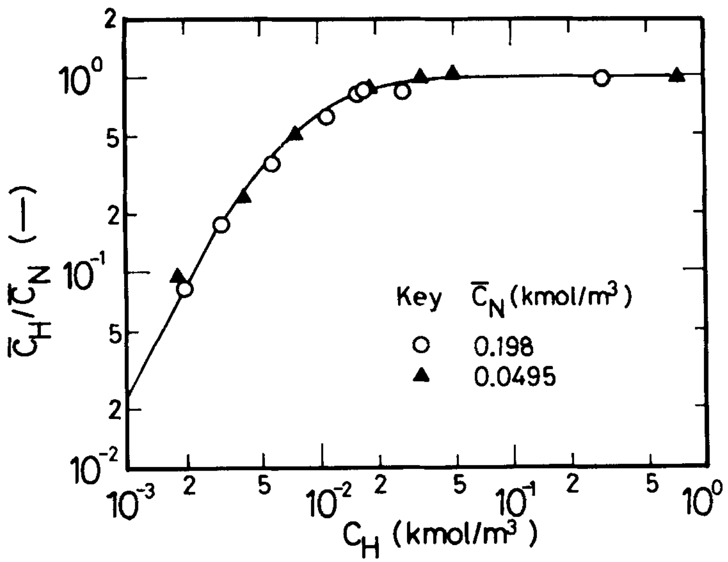

FIG. 3. Distribution equilibrium of hydrochloric acid at 298 K between deionized water and *n*-dodecane containing 6 vol% EHA and R_3N.

$$\tilde{K}_H = \frac{[\overline{R_3NHCl}]}{[\overline{R_3N}][H^+][Cl^-]} = \frac{\bar{y}_{NH}(\overline{R_3NHCl})}{\bar{y}_N(\overline{R_3N})y_H^2C_H^2} \tag{3}$$

Let us define

$$\tilde{K}_H = K_H\frac{\bar{y}_N}{\bar{y}_{NH}} = \frac{(\overline{R_3NHCl})}{(\overline{R_3N})y_H^2C_H^2} \tag{4}$$

The total acid and amine concentrations in the organic phase can then be expressed as

$$\bar{C}_H = (\overline{R_3NHCl}) = \tilde{K}_H(\overline{R_3N})y_H^2C_H^2 \tag{5}$$

$$\bar{C}_N = \bar{C}_H + (\overline{R_3N}) \tag{6}$$

Equation (5) suggests that $\bar{C}_H$ is proportional to $y_H^2C_H^2(\bar{C}_N - \bar{C}_H)$. The experimental data lie on a straight line of unity slope as seen in Fig. 4, and the constant $\tilde{K}_H$ was found to be 0.0246 m⁹/mol³. The mean activity coefficient of hydrochloric acid, y_H, was obtained from a standard

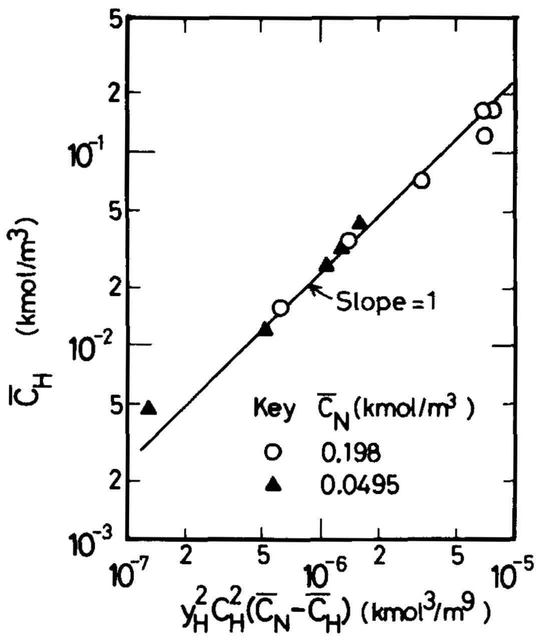

FIG. 4. Test of the distribution data of hydrochloric acid.

textbook (17). The solid line in Fig. 3 is the calculated values of $\bar{C}_H/\bar{C}_N$ with the above value of $\tilde{K}_H$. Note that for $C_H > 0.03$ kmol/m^3, R_3N is completely saturated with acid.

Zinc chloride is supposed to be extracted according to

$$m(\overline{R_3NHCl}) + n(Zn^{2+} + 2Cl^-) \rightleftharpoons \overline{(R_3NHCl)_m(ZnCl_2)_n} \qquad (7)$$

The equilibrium constant for this reaction is

$$K_{Z,m,n} = \frac{[\overline{(R_3NHCl)_m(ZnCl_2)_n}]}{[\overline{R_3NHCl}]^m([Zn^{2+}][Cl^-]^2)^n} \qquad (8)$$

When $C_Z \ll C_H$,

$$[Zn^{2+}][Cl^-]^2 = y_Z y_{Cl}^2 C_Z C_H^2 \qquad (9)$$

$y_Z y_{Cl}^2$ is supposed to be a function of the ionic strength or, in this case, a function of C_H only:

$$y_Z y_{Cl}^2 = F(C_H) \tag{10}$$

With the above considerations, we can define

$$\tilde{K}_{Z,m,n} = K_{Z,m,n} \frac{\bar{y}_{NH}^m}{\bar{y}_{Z,m,n}} = \frac{(\overline{(R_3NHCl)_m(ZnCl_2)_n})}{(\overline{R_3NHCl})^m(FC_H^2C_Z)^n} \tag{11}$$

and the total zinc and R_3N concentrations in the organic phase are expressed as

$$\bar{C}_Z = \sum_m \sum_n \{n\tilde{K}_{Z,m,n}(\overline{R_3NHCl})^m(FC_H^2C_Z)^n\} \tag{12}$$

$$\bar{C}_N = \sum_m \sum_n \{m\tilde{K}_{Z,m,n}(\overline{R_3NHCl})^m(FC_H^2C_Z)^n\} + (\overline{R_3NHCl}) \tag{13}$$

Note that the whole R_3N is saturated with hydrochloric acid, and that the free amine concentration $(\overline{R_3N})$ is negligible in Eq. (13).

Equations (12) and (13) indicate that $\bar{C}_Z$ is a function of $\bar{C}_N$ and $F(C_H)C_H^2C_Z$. Although $F(C_H)$ is unknown at this stage, the $F(C_H)$ values relative to that at a certain reference C_H concentration can be determined. We select this reference condition as $C_H = 0.5$ kmol/m^3. In this case $\bar{C}_Z$ can be expressed as

$$\bar{C}_Z = \sum_m \sum_n \{n\tilde{\tilde{K}}_{Z,m,n}(\overline{R_3NHCl})^m(fC_Z)^n\} \tag{14}$$

where

$$\tilde{K}_{Z,m,n} = \tilde{\tilde{K}}_{Z,m,n}(FC_H^2)^n_{|C_H=0.5} \tag{15}$$

and

$$f = (FC_H^2)/(FC_H^2)_{|C_H=0.5} \tag{16}$$

The parameter f is a function of C_H only and is determined so that the experimental values of $\bar{C}_Z$ at constant $\bar{C}_N$ for different C_H coincide with that for $C_H = 0.5$ kmol/m^3.

Figure 5 shows the reduced relations of the distribution equilibrium thus obtained with the f values listed in the figure. In the region of small fC_Z in Fig. 5, $\bar{C}_Z$ is proportional to fC_Z, which indicates that $n = 1$ in this region. We assume that $n = 1$ for the whole concentration region and further assume that m takes a unique value. Then Eqs. (14) and (13) reduce to

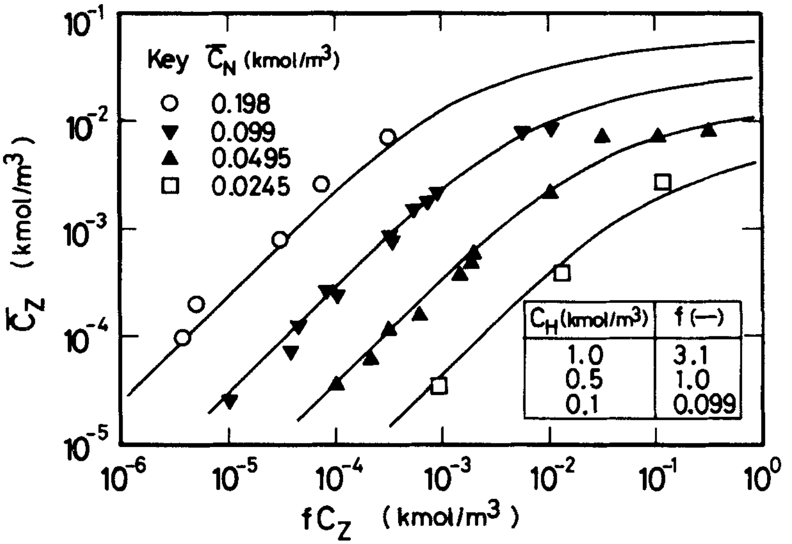

FIG. 5. Distribution equilibrium of zinc chloride between aqueous hydrochloric acid solution and *n*-dodecane with 6 vol% EHA and R_3N at 298 K.

$$\bar{C}_Z = \tilde{K}_{Z,m,1}(\overline{R_3NHCl})^m(fC_Z) \tag{17}$$

$$\bar{C}_N = m\bar{C}_Z + (\overline{R_3NHCl}) \tag{18}$$

If we choose a certain value of m, $(\overline{R_3NHCl})$ can be calculated by Eq. (18) and a log-log plot of $\bar{C}_Z/fC_Z$ vs $(\overline{R_3NHCl})$ should become a straight line of slope m. The best match was obtained when $m = 3$ as shown in Fig. 6, and the $\tilde{K}_{Z,3,1}$ value was found to be 2.92×10^{-6} m^9/mol^3. The solid lines in Fig. 5 were calculated with $\tilde{K}_{Z,3,1}$, which agree with the experimental values. The distribution coefficient $K_{D,Z}$ can now be calculated by

$$K_{D,Z} = \bar{C}_Z/C_Z = 2.92 \times 10^{-6}f(\overline{R_3NHCl})^3 \tag{19}$$

together with

$$\bar{C}_N = 3 \times 2.92 \times 10^{-6}fC_Z(\overline{R_3NHCl})^3 + (\overline{R_3NHCl}) \tag{20}$$

HFSLM Permeation Experiments

The average permeation flux of the solute, J, can be expressed as

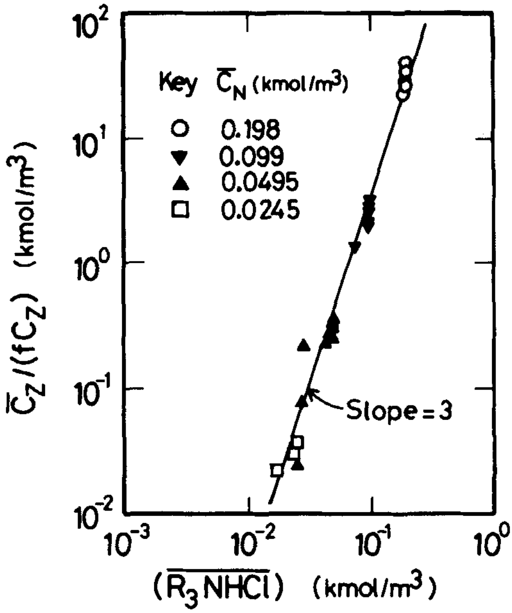

FIG. 6. Test of the distribution data of zinc chloride with $m = 3$.

$$J = k_{ov}\{C_1 - (K_{D2}/K_{D1})C_2\}_{lm} \tag{21}$$

Here, k_{ov} is the overall mass transfer coefficient based on the inner surface of the hollow fiber. Subscript lm refers to the logarithmic mean of the values in { } at the inlet and at the exit. The total resistance, $1/k_{ov}$, is the sum of three resistances when the surface reaction rate is fast:

$$\frac{1}{k_{ov}} = \frac{1}{k_1} + \frac{A_1}{k_m K_{D1} A_{lm}} + \frac{K_{D2}A_1}{k_2 K_{D1} A_2} \tag{22}$$

The inside film mass transfer coefficient, k_1, can be evaluated using the analogy of heat and mass transfer at the inside of the circular tube (*8*). The membrane mass transfer coefficient, k_m, is expressed as

$$k_m = D\varepsilon/\tau\delta \tag{23}$$

The tortuosity factor of the present support membrane, τ, has been determined to be 1.4 (*8*).

In the case of phenol permeation through the liquid membrane of *n*-

dodecane with 6 vol% EHA, the strip-side resistance is negligible because $K_{D2} \ll K_{D1}$. The observed overall resistance in this case approximately agreed with the calculated sum of the inside feed film resistance and the membrane resistance.

To determine the value of k_2, the feed solution was made to run on the outside and the strip solution on the inside of the hollow fiber. In this case the overall resistance is the sum of the outside feed solution film and the membrane resistances. The k_2 values obtained at different flow rates, q_2, are shown in Fig. 7. The value of k_2 for phenol was found to be 1.6×10^{-6} m/s, irrespective of the flow rate. The k_2 value for zinc chloride can then be calculated by

$$k_{2,\mathrm{Z}} = (D_{\mathrm{Z}}/D_{\mathrm{Ph}})k_{2,\mathrm{Ph}} \tag{24}$$

Figure 8 shows the overall resistances in the case of zinc permeation through the liquid membrane of R_3N in *n*-dodecane with 6 vol% EHA. The circles indicate the observed overall resistances, and the lines show the calculated films, membrane, and total resistances. The agreement between the observed and the calculated overall resistances is satisfactory, which indicates that the reaction resistances are negligible in this system and that the permeation of zinc chloride in the present system can be explained by the sum of the three resistances.

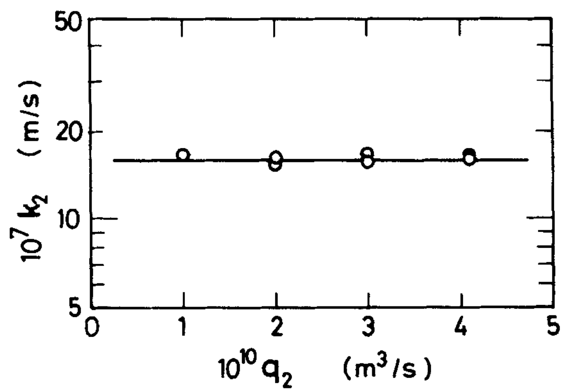

FIG. 7. Outside film mass transfer coefficient, k_2, at 298 K, determined from phenol permeation experiments.

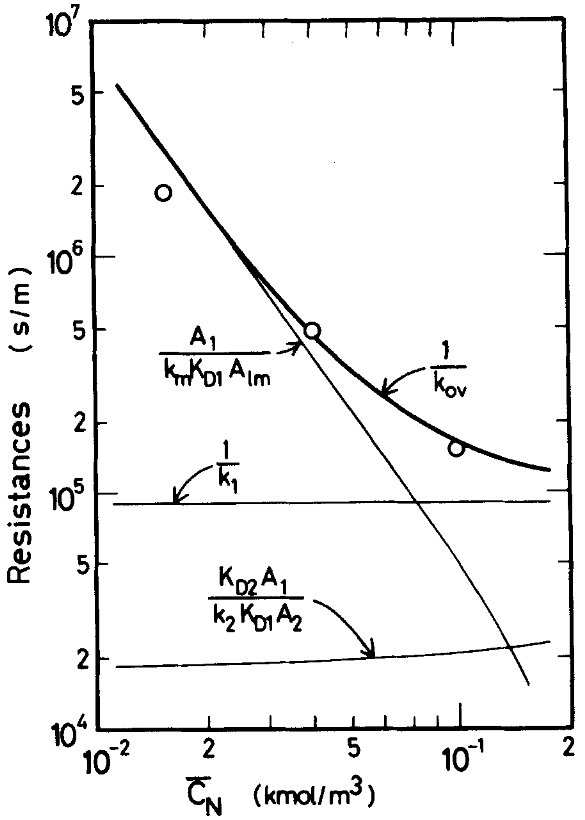

FIG. 8. Comparison of the calculated resistances with the observed one in zinc chloride permeation experiments at 298 K. C_N = 0.1 kmol/m^3, $C_{H,1}$ = 1.0 kmol/m^3, and $C_{H,2}$ = 0.1 kmol/m^3.

CONCLUSION

As a basic study to learn the mechanism of the facilitated transport of zinc chloride through a liquid membrane of *n*-dodecane with EHA which contains R_3N as the carrier, the distribution equilibrium was examined. R_3N was found to form a 1-1 complex with hydrochloric acid in the organic phase. This acid complex forms a 3-1 complex with zinc chloride at a relatively low loading of zinc chloride.

The tortuosity of the polyethylene hollow fiber, obtained through the phenol transport experiments, agreed with the value of 1.4 obtained earlier. The mass transfer coefficient outside the fiber was also obtained.

The observed overall resistance in the transport experiments of zinc chloride was well explained by the distribution equilibrium at both interfaces and the characteristics of the support membrane and the flow system.

SYMBOLS

A	surface area (m^2)
C_H	total acid concentration in aqueous phase (mol/m^3)
$\bar{C}_H$	total acid concentration in organic phase (mol/m^3)
$\bar{C}_N$	total amine concentration in organic phase (mol/m^3)
C_Z	zinc chloride concentration in aqueous phase (mol/m^3)
$\bar{C}_Z$	total zinc complex concentration in organic phase (mol/m^3)
D	diffusion coefficient (m^2/s)
F	parameter of C_H only, defined by Eq. (10)
f	parameter of C_H only, defined by Eq. (16)
J	permeation flux based on the inner surface area A_1 ($mol/m^2/s$)
K	equilibrium constant
$\tilde{K}$	reduced equilibrium constant defined by Eqs. (4) and (11)
$\tilde{\tilde{K}}$	reduced equilibrium constant defined by Eq. (15)
K_D	distribution coefficient
k_{ov}	overall mass transfer coefficient (m/s)
k_1	inside film mass transfer coefficient (m/s)
k_2	outside film mass transfer coefficient (m/s)
k_m	membrane phase mass transfer coefficient (m/s)
q	flow rate (m^3/s)
y	activity coefficient
ε	porosity
δ	wall thickness of support membrane (m)
τ	tortuosity
( )	concentration
[ ]	activity

Subscript

Cl	chlorine ion
H	hydrochloric acid or hydrogen ion
lm	logarithmic mean

m	membrane phase
N	amine
NH	amine–acid complex
Ph	phenol
Z	zinc chloride or zinc ion
1	inside the hollow fiber or inside surface
2	outside the hollow fiber or outside surface

Superscript

(i)	inlet
(o)	outlet

Acknowledgment

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