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Preferential transport behaviors of ternary system cupric–nickel–zinc ions through cation-exchange membrane with a complexing agent by dialysis

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Abstract

Preferential transport behaviors of ternary metal ion system were studied in a stirred batch cation-exchange membrane dialyzer. Cu^{2+}–Ni^{2+}–Zn^{2+} system was chosen for investigation. Malonic acid, oxalic acid and citric acid were employed, respectively, as a complexing agent in order to enhance the discrepancy in transport fluxes of metal ions. The results show that the effective order of complexing agents is malonic acid > oxalic acid > citric acid. The stoichiometric ratio of complexing agent to metal ions and the pH value of the feed solution are the primary factors on the preferential transport behaviors of metal ions. The optimal dimensionless permeation flux ratio of $P_{\mathrm{Zn-Na}}/P_{\mathrm{Ni-Na}}/P_{\mathrm{Cu-Na}}$ is obtained about 5.3/3.6/0.7. On the basis of the Nernst–Planck equation and interface equilibrium, a theoretical model of the system is established. The predicted results obtained by theoretical model are in good agreement with the experimental results.

Keywords: Preferential transport; Complexing agent; Dialysis

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1. Introduction

The clean technology using ion-exchange membranes has been taken into great account in chemical industry [1]. Ion-exchange membrane dialysis is a useful process for ion separation, in which ions move across membrane based on the Donnan membrane equilibrium principle [2]. Among various techniques that have been used for ion separation and concentration, Donnan dialysis is an efficient method in pretreatment stage in industrial applications because of its permselective transport within low ionic concentration [3]. Many investigations of ion transfer across the ion-exchange membrane have been reported [4,5]. One of the prominent features in the development of modern technology is the cross-fertilization of ideas among different disciplines. Therefore, a separation process combined cation-exchange membrane with complexing agents for the recovery and enrichment of heavy metal ions has received much attention in recent years [6,7].

Preferential transport behaviors of binary metal ion system using membrane dialysis in the presence of complexing agents had been studied in our previous researches [8–11]. The experimental results show that the uptake of metal ions in the cation-exchange membrane can be changed by adding a complexing agent in the solution phase, and both the anion ligands and the kinds of metal ions can differentiate the equilibrium uptake of metal ions so as to increase the membrane selectivity of the metal ions. These results are in accordance with the reports of other investigators [12–14]. Based on these results, the combined use of a cation-exchange membrane and a complexing agent seem to be a feasible method for the simultaneous separation and concentration of metal ions [15,16]. However, it is seemed to need more experimental work on multi-ion membrane dialysis in order to develop an ion fractionation process that can be applied to the enrichment and separation of metal ions in wastewater treatment.

The aim of this paper is to study the preferential transport behaviors of ternary ions system across the cation-exchange membrane in a batch dialyzer with a complexing agent. Cu^{+2}–Ni^{+2}–Zn^{+2} ions system was chosen for the experimental investigation because they are often associated in electroplating waste solutions of electronic industry. The complexing agents used in this study include malonic acid, oxalic acid and citric acid. The influences of the stoichiometric ratios of the complexing agent to the metal ions and the pH values of the feed solution on the dimensionless permeation fluxes of metal ions have been

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Nomenclature

a_i	activity of species i in solution
C_i	concentration of ion i (kmol m^{-3})
D_i	diffusion coefficient ion i (m^2 s^{-1})
E	electric potential (V)
f	molar activity coefficient
F	Faraday's constant (9.648 × 10^4 C mol^{-1})
J_i	permeation flux of ion i (mol m^{-2} s)
$K_{\mathrm{B}}^{\mathrm{A}}$	apparent selectivity coefficient
L	thickness of ion-exchange membrane (m)
R	universal gas constant (8.314 kJ kmol^{-1} K$^{-1)}$
X	normal direction to the ion-exchange membrane (m)
z_i	valence of ion i

Greek symbols

Φ	stoichiometric ratio of complexing agent to metal ions
Ψ	electrical potential (V)

Superscript

-	in the membrane phase

investigated. A theoretical model is formulated on the bases of the Nernst–Planck equation and membrane–solution interface equilibrium. The theoretical approach can be obtained by using the numerical calculation of model equations.

2. Theoretical consideration

Consider an ion-exchange system in which a cation-exchange membrane separates two electrolyte solutions, i.e., one is the feed phase consisting of three bivalent cations species i with the common anion Y^-, and the other is the stripping phase composed of the N–Y electrolyte solution. The mechanism of the transport of counter ion across the cation-exchange membrane is postulated to consist of three rate processes [13,14]: (1) diffusion through the two liquid films adjacent to the membrane surface, (2) the ion-exchange reaction occurring at two membrane–solution interfaces, and (3) diffusion through the membrane.

It is assumed that the concentration of N–Y electrolyte solution and the agitation speed in the stripping side are sufficiently high to ignore the mass-transfer resistance of the stripping phase as compared to the other ones [17]. Furthermore, the film–membrane system has been allowed to adjust to a steady state during the dialysis operation, so that the ionic flux of the membrane is equal to that of the liquid phase [18]. The schematic transport mechanism is illustrated in Fig. 1.

Firstly, consider the mass transport of the counter ion in the liquid film of the feed phase. Based on to the Nernst–Planck diffusion equation, the transport flux of ion i can be expressed as the following [9–11].

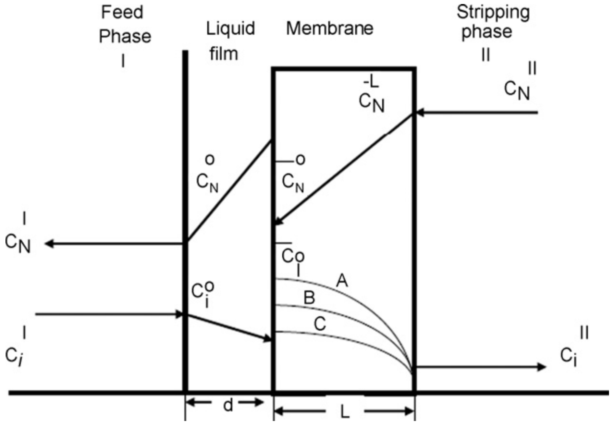

Fig. 1. The schematic mechanism of preferential transport behavior in ion-exchange membrane dialysis for a multi-ionic system.

For the metal ions and counter ion i, the transport flux is

$$J_i = -D_i\left(\frac{\mathrm{d}C_i}{\mathrm{d}x} + \frac{C_i z_i F}{RT}\frac{\mathrm{d}E}{Ex}\right), \quad i = \mathrm{A, B, C, N} \tag{1}$$

For the common anion Y, the transport flux is

$$J_{\mathrm{Y}} = -D_{\mathrm{Y}}\left(\frac{\mathrm{d}C_{\mathrm{Y}}}{\mathrm{d}x} + \frac{C_{\mathrm{Y}} z_{\mathrm{Y}} F}{RT}\frac{\mathrm{d}E}{\mathrm{d}x}\right) = 0 \tag{2}$$

where A, B and C denote the coded metal ions, N denotes the counter ion. E, D_i and C_i denote the diffusion potential, the diffusion coefficient and the concentration of ion i in the liquid phase, respectively. F, x and z_i denote the Faraday's constant, the distance normal to the membrane and the valence of ion i, respectively.

On the basis of the mass balance in the steady state, the following equation can be obtained:

$$z_{\mathrm{A}}J_{\mathrm{A}} + z_{\mathrm{B}}J_{\mathrm{B}} + z_{\mathrm{C}}J_{\mathrm{C}} + z_{\mathrm{N}}J_{\mathrm{N}} = 0 \tag{3}$$

The electroneutrality condition must be satisfied at any location of the electrolyte solution, i.e.,

$$z_{\mathrm{A}}C_{\mathrm{A}} + z_{\mathrm{B}}C_{\mathrm{B}} + z_{\mathrm{C}}C_{\mathrm{C}} + z_{\mathrm{N}}C_{\mathrm{N}} + z_{\mathrm{Y}}C_{\mathrm{Y}} = 0 \tag{4}$$

The potential gradient in Eqs. (1) and (2) can be eliminated by using Eqs. (3) and (4). Then, the concentration distribution of ion i in liquid film can be obtained by integrating these equations with the boundary condition, $C = C_i^0$ at $x=0$, as follows:

$$C_i = \frac{C_i^0[Q^0]^{z_i} - [J_i/D_i Q^{z_i}]}{Q^{z_i}}, \quad i = \mathrm{A, B, C, N} \tag{5}$$

where

$$Q^0 = z_{\mathrm{A}}C_{\mathrm{A}}^0 + z_{\mathrm{B}}C_{\mathrm{B}}^0 + z_{\mathrm{C}}C_{\mathrm{C}}^0 + z_{\mathrm{N}}C_{\mathrm{N}}^0 \tag{6.1}$$

$$Q = Q^0 - \left(\frac{J_{\mathrm{A}}}{D_{\mathrm{A}}} + \frac{J_{\mathrm{B}}}{D_{\mathrm{B}}} + \frac{J_{\mathrm{C}}}{D_{\mathrm{C}}} + \frac{J_{\mathrm{N}}}{D_{\mathrm{N}}}\right)x \tag{6.2}$$

Next, let us consider the membrane–phase mass transport. If common ion, do not exists in the membrane and metal ions transport in one dimension, then the mass flux of each ion in the membrane can be expressed as follows [9–11]:

$$J_i = -\bar{D}_i\left(\frac{\mathrm{d}\bar{C}_i/\mathrm{d}x + \bar{C}_i z_i F}{RT \times \mathrm{d}\bar{E}/\mathrm{d}x}\right), \quad i = \mathrm{A, B, C, N} \tag{7}$$

where $\bar{E}$, $\bar{D}_i$ and $\bar{C}_i$ denote the diffusion potential, the diffusion coefficient and the concentration of ion i in the membrane, respectively.

Assume that the experiments are operated at steady state; the effect of ionic strength of solution on the mass transport is negligible. This is consistent with the Goldman approximation [18,19], in which the constancy of the electric field existed in the membrane, can be adopted in this study. Eq. (7) can be reduced to the following:

$$\frac{J_i}{\bar{D}_i} = -\left(\frac{\mathrm{d}\bar{C}_i/\mathrm{d}x + \bar{C}_i z_i F}{RT \times \bar{E}/L}\right), \quad i = \mathrm{A, B, C, N} \tag{8}$$

where L denotes the thickness of the membrane and $\bar{E}$ denotes the membrane potential that can be estimated by using the multi-ionic potential theory as follow [11]:

$$\bar{E} = \frac{RT}{z_i F}\ln\left\{\frac{\sum_j(\bar{D}_j a_j^{\mathrm{I}}/\bar{f}_j)}{\sum_k(\bar{D}_k a_k^{\mathrm{II}}/\bar{f}_k)}\right\} \tag{9}$$

where a and f denote the activity and the molar activity coefficient; the subscripts j refer to ions A, B, C and N in compartment I and the subscript k refers to counter ion N in compartment II.

Based on the boundary conditions $\bar{C}_i = \bar{C}_i^0$ at $x = 0$ and $\bar{C}_i = 0$ at $x = L$, Eq. (8) can be integrated to obtain the concentration profile in membrane. The concentration profiles in membrane are given as

$$\bar{C}_i = \frac{J_i}{q\bar{D}_i}\left[\frac{\mathrm{e}^{qL}}{\mathrm{e}^{qx}-1}\right], \quad i = \mathrm{A, B, C, N} \tag{10}$$

where

$$q = \frac{z_i F}{RT}\left(\frac{\bar{E}}{L}\right)$$

Based on the Teorell–Meyer–Sievers hypothesis [10,14], a pseudo-equilibrium state between each metal ion and counter ion Na^+ is assumed to exist at the film–membrane interface, respectively. An apparent selectivity coefficient, K^i_{Na}, can be defined as

$$K^i_{\mathrm{Na}} = \frac{\bar{C}_i}{C_i}\frac{C^2_{\mathrm{Na}}}{\bar{C}^2_{\mathrm{E}}} \tag{11}$$

Substituting Eqs. (5) and (10) into Eq. (11), we obtained:

$$\frac{J_i/q\bar{D}_i(\mathrm{e}^{qL}-1)}{[J_{\mathrm{Na}}/q\bar{D}_{\mathrm{Na}}(\mathrm{e}^{qL}-1)]^2} = K^i_{\mathrm{Na}}\frac{C_i^0(Q^0)^2-(J_i/D_i Q_d^2)}{[C^0_{\mathrm{Na}}(Q^0)-(J_{\mathrm{Na}}/D_{\mathrm{Na}}Q_d)]^2} \tag{12}$$

where

$$Q = Q^0 - \left(\frac{J_{\mathrm{A}}}{D_{\mathrm{A}}} + \frac{J_{\mathrm{B}}}{D_{\mathrm{B}}} + \frac{J_{\mathrm{C}}}{D_{\mathrm{C}}} + \frac{J_{\mathrm{N}}}{D_{\mathrm{N}}}\right)d$$

and d denotes the thickness of stagnant liquid film.

Eq. (12) is a general equation describing the preferential transport behaviors of ternary bivalent ions sharing with the same counter ion across the cation-exchange membrane. The permeation flux ratio of the metal ions, J_i/J_{Na}, can be calculated numerically from Eq. (12) by the iterative technique under the restrictions of Eqs. (3) and (4) as the apparent selective coefficient K^i_{Na}, obtained from equilibrium measurement, respectively.

The dimensionless permeation transport of metal ion A relative to sodium ion, $P_{i\text{–Na}}$, in ion-exchange membrane dialysis can be defined by

$$P_{i\text{–Na}} = \frac{J_i/J_{\mathrm{Na}}}{C_i^0/C^0_{\mathrm{Na}}} \tag{13}$$

3. Experimental

3.1. Materials

The ion-exchange membranes used in this work were Selemion CMV and AMV, produced by Asahi Glass Co. Ltd. The properties of the membranes have been describes in an earlier paper [8]. The membranes were changed to the same form before all experiments. The membranes soaked in a 0.5 M NaCl solution for at least 8 h until the original counter ion in the membrane was completely replaced by sodium ions. All electrolyte solutions were prepared from de-ionized water and extra pure chemicals without further purifications.

3.2. Apparatus

3.2.1. Dialysis cell

The stirred batch dialyzer used in this experiment consisted of two separable acrylic compartments. The membrane was sandwiched between both compartments by two pieces of rubber gasket to prevent leakage. The effective transfer area of the membrane was $4.3 \times 10^{-3}\ \mathrm{m}^2$. The volume of the feed compartment was $5.5 \times 10^{-4}\ \mathrm{m}^3$, and that of the stripping compartment was half of that. Each solution in the compartments was agitated by a two-blade stirrer. All runs were thermostatically controlled at 298 K.

3.2.2. Permeation measurements

The feed solution containing metal ions, a complexing agent, and 0.1 M NaCl was placed in the feed compartment. To the stripping compartment, only 1.0 M NaCl was added except for the other specifications. Both solutions were stirred at 1600 rpm; a further increase in stirring did not increase ionic flux. A pseudo-steady state was attained by pre-dialysis for a half-hour, and then the solution in the compartments was replaced with fresh solutions. During the dialysis, 2 ml of solution were taken from the stripping compartment at each preset time interval. The concentrations of metal ions were determined by use of an atomic absorption spectrophotometer (Model 551, Instrumentation Laboratory Inc.). However, the measured concentration had to be corrected due to the change of solution volume during sampling. The dimensionless permeation fluxes of the metal ions were calculated from linear slopes of the ionic concentration versus time curve with using the least squares method [9,10].

3.2.3. Equilibrium measurement

In the measurement of ion-exchange membrane equilibrium, a piece of sodium-form membrane was soaked in an electrolyte solution containing the investigated metal ions and a complexing agent, and shaken over 20 h. After equilibrium the membrane was quickly wiped with filter paper and stripped with 0.5N sodium chloride solution at least five times. The amount of metal ions in the stripping solution was determined by atomic absorbance measurements. The apparent selectivity coefficients are calculated from Eq. (11).

4. Results and discussion

4.1. Effect of various kinds of complexing agents on the dimensionless permeation fluxes of metal ions

The organic complexing agents, including malonic acid, oxalic acid and citric acid were introduced, respectively, into the feed solution of 0.001 M investigated metal ions and 0.1 M NaCl in each run. The stripping solution contained 1.0 M NaCl. The dimensionless permeation fluxes of metal ions were measured from the linear slopes of ionic concentration versus time curves with the least squares method [8,9]. These results are tabulated in Table 1.

In the investigated system Cu^{2+}–Ni^{2+}–Zn^{2+}, the dimensionless permeation fluxes of metal ions, $P_{i\text{–Na}}$, are varied from 0.7 to 5.3 for dialysis operation with various kinds of complexing agents. Without using a complexing agent in the feed phase, the dimensionless permeation fluxes of metal ions have the order as the following $P_{\text{Cu–Na}}$ (3.13) > $P_{\text{Zn–Na}}$ (3.03) > $P_{\text{Ni–Na}}$ (2.78). This can be explained from the fact that the driving force of the permeation flux across the membrane is nearly constant because the difference of ionic strength between feed solution (0.1 M NaCl) and stripping solution (1.0 M NaCl) has been maintained constant during experiment. The rate-determining step of dimensionless permeation fluxes across the membrane is the resistance of mass transfer included the solution phase as well as the membrane phase. The experimental results in our previous paper indicate that the diffusion coefficients of metal ions have the order cupric ion > zinc ion > nickel ion for both solution phase and membrane phase [10,11]. Therefore, the cupric ions have the advantage position to permeate through the membrane from the feed side to the stripping solution as compared to the zinc ion and nickel ion. This lead to the dimensionless permeation fluxes of metal ions have the following order $P_{\text{Cu–Na}} > P_{\text{Zn–Na}} > P_{\text{Ni–Na}}$ in the case of without using complexing agent.

Table 1
Effect of complexing agents on the dimensionless permeation fluxes of metal ions at pH 4.0, Φ 1.0 and $[CuCl_2] = [NiCl_2] = [ZnCl_2] = 0.001$ M

Complexing agent	$P_{\text{Cu–Na}}$	$P_{\text{Ni–Na}}$	$P_{\text{Zn–Na}}$
Malonic acid	0.70	3.60	5.30
Oxalic acid	0.78	3.80	4.85
Citric acid	0.80	3.90	4.80
Without using	3.13	2.78	3.03

In case of using complexing agents in the feed solution, the different change of the dimensionless permeation fluxes for the investigated system Cu^{2+}–Ni^{2+}–Zn^{2+} can be observed in Table 1. It is found that the difference values of $P_{i\text{–Na}}$ are obtained under the condition of various kinds of complexing agents. This is due to the fact that metal ions will compete with each other to react with complexing ligands to from complexes which are hardly permeated through the membrane [10–13]. The difference in the concentration gradients of free metal ions across the membrane can be obtained because of the difference in stability and quantity of complexes. The larger the difference that exists between stability constants of metal ion complexes, the higher difference that the permeation flux of metal ions can be attained [19]. The effect of various kinds of complexing agents on the preferential transport of Cu^{+2}–Ni^{+2}–Zn^{+2} ions system is found to be in the following order: malonic acid > oxalic acid > citric acid.

4.2. Effect of the stoichiometric ratio of complexing agent to metal ions on the dimensionless permeation fluxes of metal ions

In the experiment with solutions of investigated metal ions and a complexing agent with a total sodium ion concentration of 0.1 M in the feed compartment, the dimensionless permeation fluxes of metal ions were measured as the stoichiometric ratio of the complexing agent to metal ions Φ = [complexing agent]/[metal ions], varied from 0 to 1.0 at pH 4.0 for the investigated system of Cu^{2+}–Ni^{2+}–Zn^{2+}. These results are shown in Figs. 2–4 for the respective complexing agents being malonic acid, oxalic acid and citric acid.

As can be seen from Figs. 2–4, the experimental results show that the values of $P_{\text{Cu–Na}}$ decrease steeply as Φ ranges from 0 to 0.5, and it approaches a limiting value of when Φ increase

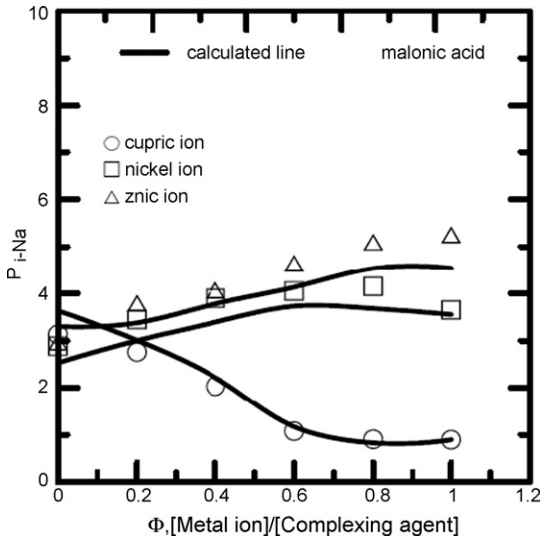

Fig. 2. Effect of the stoichiometric ratio of complexing agent to metal ions on the dimensionless permeation fluxes of metal ions for malonic acid at pH 4.0 and $[CuCl_2] = [NiCl_2] = [ZnCl_2] = 0.001$ M.

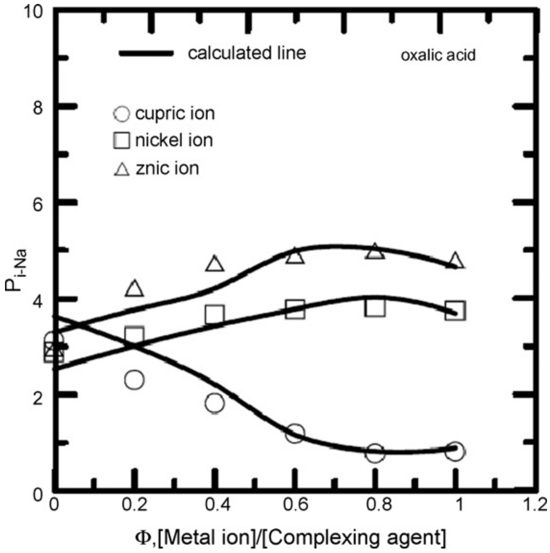

Fig. 3. Effect of the stoichiometric ratio of complexing agent to metal ions on the dimensionless permeation fluxes of metal ions for oxalic acid at pH 4.0 and $[CuCl_2] = [NiCl_2] = [ZnCl_2] = 0.001$ M.

from 0.5 to 1.0 for various kinds of complexing agents. This is due to the fact that the stability constants of cupric ions with these complexing ligands are larger than those of nickel ion and zinc ion complexes [15]. While the cupric ions compete with the nickel ions and zinc ions for complexing ligands, it is in an advantageous position for forming complexes, which hardly permeate through the membrane. Thus, an increase of the Φ value leads to an increase in the formation of cupric ion complexes as well as an increase in fluxes of nickel and zinc ions. Consequently, there is a steep increase of nickel ion flux $P_{\text{Ni–Na}}$ and zinc ion flux $P_{\text{Zn–Na}}$ as Φ ranges from 0.0 to 0.5. The changes may result from the suppression of cupric ions fluxes as well as the higher concentrations of free nickel ion and zinc ion without capture by complexing ligands. When $\Phi > 0.5$, i.e., the concentration of complexing agent is larger than that of cupric ion, the reaction of the cupric ion and complexing ligands to form complexes approach a limiting state, so that the cupric flux appears to be a minimum value.

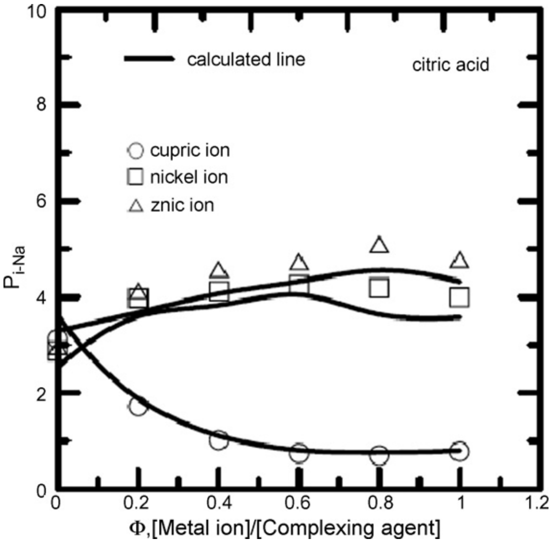

Fig. 4. Effect of the stoichiometric ratio of complexing agent to metal ions on the dimensionless permeation fluxes of metal ions for citric acid at pH 4.0 and $[CuCl_2] = [NiCl_2] = [ZnCl_2] = 0.001$ M.

It can be seen from Fig. 2 in the case of complexing agent being malonic acid that the dimensionless permeation fluxes of nickel ion and zinc ion, increases as Φ ranges from 0.0 to 0.5 and attained a limiting value while $\Phi > 0.5$. This can be explained by the fact the stability constants of nickel ion complexes ($\times 10^{\sim 4.1}$) and zinc ion complexes ($\times 10^{\sim 3.8}$) are smaller that the dissociate constants of complexing agent ($\times 10^{\sim 5.7}$) [15,16]. While the concentration of hydrogen ion nearly equal to that of metal ion, the nickel ion and zinc ion compete with hydrogen ion react with complexing ligands in a disadvantage position for residual amount of complexing ligands to form complexes at low pH value. Therefore, the difference of the concentration gradient between free metal ions of Cu^{2+}–Ni^{2+}–Zn^{2+} system approaches the limiting state. The optimal value of $P_{\text{Zn–Na}}/P_{\text{Ni–Na}}/P_{\text{Cu–Na}}$ can obscured as 5.3/3.6/0.70 when the Φ value ranges from 0.7 to 1.0.

But in the case of complexing agent being oxalic acid and citric acid, the stability constants of nickel ion complexes and zinc ion complexes are slightly larger than the dissociation constants of complexing agent [15]. Consequently, nickel ions and zinc ions can overcome hydrogen ions to react with the residual quantity of complexing ligands in the formation of nickel ion complexes and zinc ion complexes that may not occur in the case of complexing agent being malonic acid. The experimental results in Figs. 3 and 4 indicate that the performances of $P_{i\text{–Na}}$ values are similar as that of foregoing discussion when varied Φ from 0 to 0.5 because the situation between the stability constants of metal ion complexes is the same as above description. But when Φ increased from 0.7 to 1.0, there is a decrease of $P_{\text{Ni–Na}}$ and $P_{\text{Zn–Na}}$ values. Meanwhile, the values of $P_{\text{Ni–Na}}$ and $P_{\text{Zn–Na}}$ are increased sharply as Φ from 0 to 0.5, resulting from the formation of cupric ion complexes which decrease the dimensionless permeation fluxes of cupric ion. Since the formation of nickel ion complexes and zinc ion complexes decreases the permeation fluxes of nickel ion and zinc ion, there is a decrease of $P_{\text{Ni–Na}}$ and $P_{\text{Zn–Na}}$ at Φ values ranging from 0.7 to 1.0. The larger the difference exists between stability constants of metal ion complexes, the higher the difference that the values of $P_{i\text{–Na}}$ can be obtained.

In order to study the effect of the stoichiometric ratio of the complexing agent to the metal ions on the permeation flux on the basis of Eq. (12), the apparent selectivity coefficient K^i_{Na} were measured from the ion-exchange membrane equilibrium. These results are tabulated in Table 2 for the respective complexing agents being malonic acid, oxalic acid and citric acid. It is noted that the relationship between the Φ value and the apparent selectivity coefficient is similar to that between the Φ values and the permeation flux of the metal ions. These results confirm that the competitive formation of complexes between metal ions is the primary factor on the preferential transport behavior of metal ions in multi-ion system.

The theoretical values $P_{i\text{–Na}}$ are calculated by a trial-and-error numerical method with Eqs. (5), (10) and (12) while

Table 2
Effect of the stoichiometric ratio of complexing agent to metal ions on the apparent selectivity coefficient at pH 4.0 and $[\mathrm{CuCl_2}] = [\mathrm{NiCl_2}] = [\mathrm{ZnCl_2}] = 0.001$ M

Φ	Malonic acid			Oxalic acid			Citric acid		
	$K^{\mathrm{Cu}}_{\mathrm{Na}}$	$K^{\mathrm{Ni}}_{\mathrm{Na}}$	$K^{\mathrm{Zn}}_{\mathrm{Na}}$	$K^{\mathrm{Cu}}_{\mathrm{Na}}$	$K^{\mathrm{Ni}}_{\mathrm{Na}}$	$K^{\mathrm{Zn}}_{\mathrm{Na}}$	$K^{\mathrm{Cu}}_{\mathrm{Na}}$	$K^{\mathrm{Ni}}_{\mathrm{Na}}$	$K^{\mathrm{Zn}}_{\mathrm{Na}}$
0	43.4	34.26	37.8	43.4	34.2	37.8	43.4	34.2	37.8
0.2	33.3	37.8	43.5	30.5	37.8	43.4	23.8	41.3	45.0
0.4	27.8	39.8	47.0	11.6	40.3	52.5	20.8	45.3	50.4
0.6	13.4	43.6	52.5	1.6	31.3	43.4	15.6	45.4	51.3
0.8	13.4	43.0	52.0	0.8	30.3	40.8	7.8	34.3	39.3
1.0	8.6	42.8	51.3	1.6	28.6	38.4	7.0	30.0	34.3

the apparent selectivity coefficients K^{i}_{Na} are obtained from the corresponding values in Table 2, respectively. The membrane potentials are calculated from multi-ion theory with the assumption of the unity activity coefficient [8] and physical properties obtained from previous work [10,11]. The calculated results of $P_{\mathrm{Zn\text{–}Na}}/P_{\mathrm{Ni\text{–}Na}}/P_{\mathrm{Cu\text{–}Na}}$ are shown with solid lines in Figs. 2–4, respectively. It can be seen that the agreement between the theoretical line and experimental data is acceptance.

4.3. *Effect of the pH value of solution on the dimensionless permeation fluxes of metal ions*

The mixed solutions of investigated metal ions and a complexing agent including with a total sodium concentration of 0.1 M were introduced into the feed compartment under various pH values. The dimensionless permeation fluxes of metal ions were separately measured from linear slopes of the ionic concentration versus time curve with the least squares method. These results are shown in Figs. 5–7 for the respective complexing agent system being malonic acid (Φ 1.0), oxalic acid (Φ 1.0) and citric acid (Φ 1.0).

The experimental results in Figs. 5–7 show that the values of $P_{\mathrm{Cu\text{–}Na}}$ decreases with an increasing pH value of feed solution, but a peak of $P_{\mathrm{Ni\text{–}Na}}$ and $P_{\mathrm{Zn\text{–}Na}}$ arise with the change of the pH value of solution under the conditions of various complexing agents. This can be explained from the fact that the stability constants of metal ion complexes have the following order zinc ion complex < nickel ion complex < cupric ion complex [15]. The higher pH value leads to the complexing agent releasing

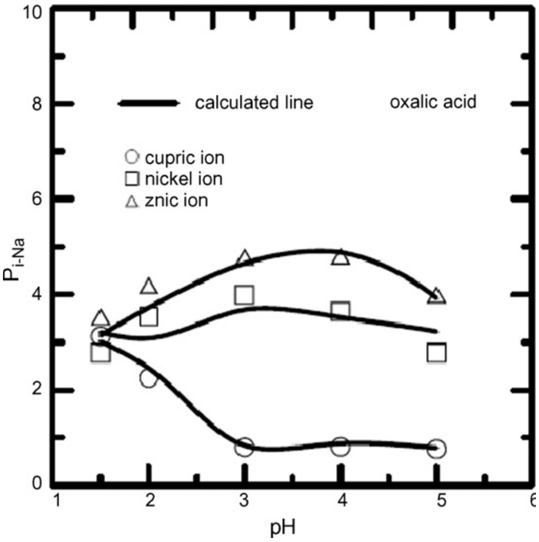

Fig. 6. Effect of the pH of solution on the dimensionless permeation fluxes of metal ions for oxalic acid at Φ 1.0 and $[\mathrm{CuCl_2}] = [\mathrm{NiCl_2}] = [\mathrm{ZnCl_2}] = 0.001$ M.

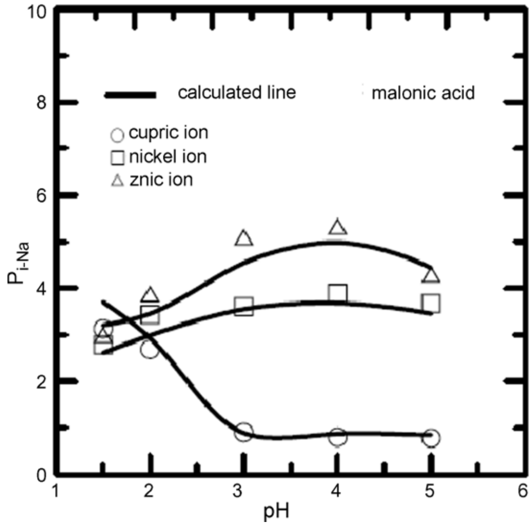

Fig. 5. Effect of the pH of solution on the dimensionless permeation fluxes of metal ions for malonic acid at Φ 1.0 and $[\mathrm{CuCl_2}] = [\mathrm{NiCl_2}] = [\mathrm{ZnCl_2}] = 0.001$ M.

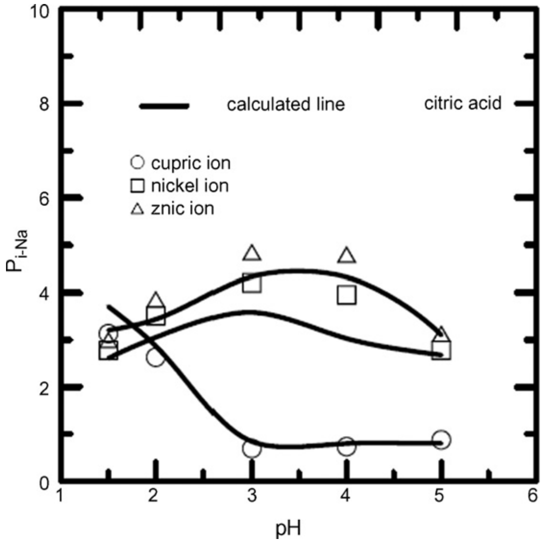

Fig. 7. Effect of the pH of solution on the dimensionless permeation fluxes of metal ions for citric acid at Φ 1.0 and $[\mathrm{CuCl_2}] = [\mathrm{NiCl_2}] = [\mathrm{ZnCl_2}] = 0.001$ M.

Table 3
Effect of the pH of solution on the apparent selectivity coefficient at Φ 1.0 and $[CuCl_2] = [NiCl_2] = [ZnCl_2] = 0.001$ M

pH	Malonic acid			Oxalic acid			Citric acid		
	K_{Na}^{Cu}	K_{Na}^{Ni}	K_{Na}^{Zn}	K_{Na}^{Cu}	K_{Na}^{Ni}	K_{Na}^{Zn}	K_{Na}^{Cu}	K_{Na}^{Ni}	K_{Na}^{Zn}
1.5	15.3	15.6	20.4	7.0	14.0	17.6	22.3	23.4	27.8
2.0	15.8	39.7	48.2	6.5	27.8	38.8	19.8	39.7	48.2
3.0	12.3	42.8	52.3	1.7	33.4	39.8	9.8	33.4	39.8
4.0	8.6	42.8	51.3	1.6	28.6	38.4	7.0	30.0	34.3
5.0	2.1	31.3	42.3	0.8	23.4	30.0	7.0	23.4	30.0

more complexing ligands to react with cupric ion. As a result, it is in a disadvantage position to react with nickel ions and zinc ions to form complexes when the values of pH are less than 3.0. Thus, the values of $P_{Ni–Na}$ and $P_{Zn–Na}$ increase sharply as the pH value varies from 2.0 to 3.0, resulting from the formation of cupric ion complexes which decrease the cupric ion flux. There is a decrease the values of $P_{Ni–Na}$ and $P_{Zn–Na}$ at pH values ranging from 4.0 to 5.0 because the formation of nickel ion complexes and zinc ion complexes may be happened to decreases the nickel ion flux and zinc ion flux. The optimal values of preferential transport behavior can be obtained while the pH value of solution ranges from 3 to 4. The optimal values of pH are found to be 3.0 and 4.0 for various kinds of complexing agents. The maximum values of $P_{Cu–Na}/P_{Ni–Na}/P_{Zn–Na}$ is found to be 0.70/4.10/4.85 in case of using the citric acid as the complexing agent at pH 3.0. The optimal value of $P_{Cu–Na}/P_{Ni–Na}/P_{Zn–Na}$ is found to be 0.70/3.60/5.3 and 0.78/3.80/4.85 for the respective complexing agent being malonic acid and oxalic acid at pH 4.0.

For the investigation of the pH effect on the permeation flux on the basis of Eq. (12), the apparent selectivity coefficient K_{Na}^{i} was measured from the ion-exchange membrane equilibrium. These results are listed in Table 3 for the respective complexing agents being malonic acid, oxalic acid and citric acid. It is noted that the dependence of pH value on the apparent selectivity coefficient is similar to that of pH value on the permeation flux of the metal ions. These results coincide with the fact that the competitive formation of complexes between metal ions is the primary factor on the preferential transport behavior of metal ions in multi-ion system.

The theoretical values $P_{i–Na}$ are calculated by a trial-and-error numerical method with Eqs. (5), (10) and (12) with the same numerical method as that in foregoing description while the apparent selectivity coefficients K_{Na}^{i} are obtained from the corresponding Table 3, respectively. Comparing the solid lines of theoretical values in Figs. 5–7 with experimental results, they appears to be consistent with each other as the pH values of solution ranging from 2 to 6. The discrepancy between them may result from the assumption of quasi-equilibrium hypothesis as well as independence of metal ion concerning transport across the membrane.

5. Conclusion

The preferential transport of metal ions with ternary system across the cation-exchange membrane can be effectively enhanced by the addition of a complexing agent. The suitable complexing agents are found to be malonic acid for the investigated Cu^{2+}–Ni^{2+}–Zn^{2+} system. The kinds of complexing agents, the stoichiometric ratio of complexing agent to metal ions, the pH value of solution are the primary factors on the preferential transport behavior of metal ions across the cation-exchange membrane. On the basis of the Nernst–Planck equation and interfacial equilibrium, a theoretical approach from numerical calculation is in agreement with the experimental data.

The investigated results have shown that the cation-exchange membrane dialysis with a suitable complexing agent is found to be a feasible process for the simultaneous separation and concentration of metal ions. It is also highlighted that an effective multi-ion fractionation process could be build; cation-exchange membrane being the separation interface; the driving force being the concentration gradient of counter ion; the suitable complexing agent being the separation agent and the pH value is the separation index.

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References

[1] D. Berdous, D.E. Akretche, Recovery of metals by Donan dialysis with ion exchange textiles, Desalination 144 (2002) 213–218.
[2] A.G. Chmielewski, T.S. Urbanski, W. Migdal, Separation technologies for metals recovery from industrial wastes, Hydrometallurgy 45 (1997) 333–344.
[3] I. Dobrevsky, M. Dimova-Todorova, T. Panayotova, Electroplating rinse waste water treatment by ion exchange, Dealination 108 (1996) 277–280.
[4] S. Graillon, F. Persin, G. Pourcelly, C. Gavach, Development of electrodialysis with bipolar membrane for the treatment of concentrated nitrate effluents, Dealination 107 (1996) 159–169.
[5] S.J. Oh, S.-H. Moon, T. Davis, Effects of metal ions on diffusion dialysis of inorganic acids, J. Membr. Sci. 169 (2000) 95–103.
[6] E. Alvarez-Ayuso, A. Garcia-Sanchez, X. Querol, Purification of metal electroplating waste waters using zeolites, Water Res. 37 (2003) 4855–4862.
[7] A.T. Cherif, J. Molenat, A. Elmidaoui, Nitric acid and sodium hydroxide generation by electrodialysis using bipolar membranes, J. Appl. Electrochem. 27 (1997) 1069–1074.
[8] T.-C. Huang, J.-K. Wang, Preferential transport of nickel and cupric ions through cation-exchange membrane in electrodialysis with a complexing agent, Desalination 86 (1992) 257–271.
[9] T.-C. Huang, J.-K. Wang, Separation of cupric and ferric ions with a cation-exchange membrane in the presence of complexinging agents, Sep. Sci. Technol. 27 (1992) 1137–1155.

[10] T.-C. Huang, J.-K. Wang, Selective transport of metal ions through cation-exchange membrane in the presence of a complexinging agent, Ind. Eng. Chem. Res. 32 (1993) 133–139.

[11] T.-C. Huang, J.-K. Wang, Preferential transport of cupric and ferric ions through ion exchange membranes with dialysis in the presence of citric acid, Chem. Eng. Commun. 122 (1993) 213–225.

[12] F.G. Donnan, Theory of membrane equilibrium, Chem. Res. 1 (1924) 73–79.

[13] A. Elmidaoui, J. Molenat, C. Gavach, Competitive diffusion of hydrochoric acid and sodium chloride through an acid dialysis membrane, J. Membr. Sci. 55 (1991) 79–98.

[14] T. Kojima, S. Furusaki, K. Saito, A fundamental study on recovery of copper with a cation-exchange membrane. Part 2. Transfer rate of copper and hydrogen ion through a cation-exchange membrane, Can. J. Chem. Eng. 60 (1982) 650–658.

[15] A.E. Martell, R.M. Smith, Critical Stability Constant, Plenum, NewYork, 1974.

[16] F.M.M. Morel, Principle of Aquatic Chemistry, Wiley–Interscience, New York, 1983.

[17] K. Takahashi, K. Tsuboi, H. Takeuchi, Mass transfer across cation-exchange membrane, J. Chem. Eng. Jpn. 22 (1989) 352–357.

[18] C.P. Wen, H.F. Hamil, Metal counterion transport in Donan dialysis, J. Membr. Sci. 8 (1981) 51–68.

[19] G.B. Wills, E.N. Lightfoot, Membrane Selectivity, AIChE J. 7 (1961) 273–276.