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Determination of Optimal Conditions for Separation of Metal Ions Through Membrane Dialysis/Electrodialysis Using Statistical Experimental Methods

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1. Introduction

The membrane process for industrial application is characterized by a large market profile, such as brackish and sea water desalination, the production of ultrapure water, or hemodialysis and a large number of small market segments in the food, chemical and pharmaceutical industries, analytical laboratories and especially in the treatment and purification of industrial waste water streams (Lonsdale, 1982; Mears, 1976). It is seemed to be difficult to make a reasonably accurate forecast about the future developments of the market for membranes (Strathmann, 2004). However, due to the fact that the environmental problem of Global Warming is increasing drastically resulting in that the demand of industrial water and fresh water with the required quality are steadily decreasing worldwide (Wang, & Hsieh, 2009). There should be a need for energy efficient and affordable processes for the production of high quality water from sea and brackish water sources as well as from waste or polluted surface waters. Since membrane processes have proven to be among the most energy efficient and economic means for this purpose it is quite likely that for the foreseeable future the membrane water purification industry will continue to grow (Hwang, & Kammermeyer, 1975). The growth will also depend on further developments of membranes with improved selectivity and higher fluxes as well as better chemical, thermal and mechanical stability. Long-term experience with their application in large plants will also contribute to increase the useful life of the membranes thus making the processes more reliable and economical (Huang, 1991).

The separation of a metal ion from a multi-ionic mixture by selective transport through membrane processes was of importance from both fundamental and practical viewpoints owing to the serious lack of earth resource. For the selective permeation, the desired metal ion in a mixture has to be preferentially absorbed into the membrane phase and then be transported across the membrane phase. Subsequently, such membranes were used for desalination purposes (Helfferich, 1962). An appropriate driving force was essential for an uphill transport resulting in building up of the concentration of the permeating ion across the concentration gradient (Nobel, 1987). The driving force could be due to difference in pH of the solutions, concentration difference of the permeating species or an electrical potential. The pH difference was generally responsible for the transport in liquid membrane systems,

whereas the electrical potential difference was the driving force for the transport across ion exchange membranes. Donnan dialysis was essentially the transport of the charged species across a membrane due to concentration difference. The combined effect of electrical potential difference and concentration gradient results in the process of electro-dialysis. Ion exchange membranes, used in electro-dialysis permit the separation of the species, without any change in the phase. Depending on the type of the driving ion used, Donnan dialysis can be applied to the recovery of metal ions from wastewater. There were many studies on the use of ion exchange membranes for Donnan dialysis (Nobel, 1987; Mizutani, 1990). Electrodialysis was principally used for the production of brine from seawater. For this specific application, special cation exchange membranes were often used to reduce the permeability of alkaline earth metal ions with respect to sodium ions (Gering, & Scamehorn, 1988). Since ion exchange membranes were used for various purposes, requirements for membranes with specific properties have increased (Bungay, 1986). Ion exchange membranes find many industrial applications primarily due to their property of permselectivity.

The aim of this chapter is to introduce systematically the preferential transport behavior of a multi-ion system across the ion exchange membrane in dialysis and electrodialysis with combined use a complex agent. Then the mathematical description of the mass transport in membranes in general and in specific membrane processes is described. Finally, determination of optimal conditions for separation of metal ions through membrane dialysis/electrodialysis using statistical experimental methods are discussed in order to create an advantage position for industrial application in the future.

2. General considerations of dialysis process

Ion exchange membrane dialysis is a useful membrane process in which ions move across an ion exchange membrane based on the Donnan membrane equilibrium principle (Donnan, 1924). Application of this process can simultaneously solve two important industrial problems, for the recovery and concentration of valuable as well as for the removal of undesired ions from waste streams (Dibenedetto & Lightfoot, 1962). Many investigations of ion transfer across the ion exchange membrane have been reported (Brajter, & Slonawaska, 1988; Costa, et al., 1984; Cox & DiNunzio, 1977; Coz et al., 1984; Huang & Wang, 1992a). One of the prominent features in the development of modern technology is the cross-fertilization of ideas among different disciplines (Sata, 1991). Therefore, separation processes combined use of complex agents with cation exchange membrane for the recovery and the enrichment of heavy metal ions have received much attention in recent years (Hopfenberg et al., 1978; Huang & Wang, 1993a; Kojima et al., 1982; Kojima et al., 1991).

Dialysis is a membrane based separation process in which the concentration gradient across the membrane is the driving force resulting in a flow of material from one side of the membrane to the other. The transport is due to the solution-diffusion mechanism (Bohere, 1983). Most researchers have employed an ion exchange membrane indicating the process as diffusion or Donnan dialysis (Davis, et. al, 1971; Mizutani, 1990; Wen, & Hamil, 1981). The process is based on the Donnan equilibrium principle (Donnan, 1924) with the usual aim being the separation of ions or charged species. The transport in the Donnan dialysis is a function of two phenomena, i.e. diffusion due to the concentration gradient, and migration due to the potential gradient arising from the difference in ionic concentrations across the membrane. Another important parameter affecting the permeation of ions is the membrane

charge, which depends on the pH, and the electrolytes in the bulk solution. Dialysis is able to solve two important industrial problems, i.e. recovery of valuable materials and removal of undesired ions from waste streams (Spencer & Ellison, 1953; Wallace, 1967). The process has been used to recover various acids including organic acids (Boudet,1991) from waste streams generated in steel, metal-refining, and electro-plating industries (Wen, & Hamil, 1981), and to remove Na^+ (Takahashi, 1989), Cu^{+2} (Sudoh,1987), Ni^{+2} (Tombalakian,1967) ternary (Cu^{+2} - Ni^{+2} - Zn^{+2})ion system (Wang, & Chang, 2004), cyanides (Kim, 1979) and fluoride (Rush, & Baker, 1980).In dialysis, the improvement of permeation and selectivity is the key point for industrial applications. For this purpose, ion-exchange membranes are combined with complex agents (such as EDTA or citric acid) for the enrichment of metal ions (Ciric, & Graydon, 1962; Wang, 2004).

3. Theoretical consideration for dialysis process

The dialysis process of mass transport was indicated in Figure 1, which show schematically the mass transport through membranes separating two homogeneous phases. We 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 counterion across the cation exchange membrane is postulated to consist of three rate processe (Huang, & Wang, 1992b; Saito, et al.,1982): (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. 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.

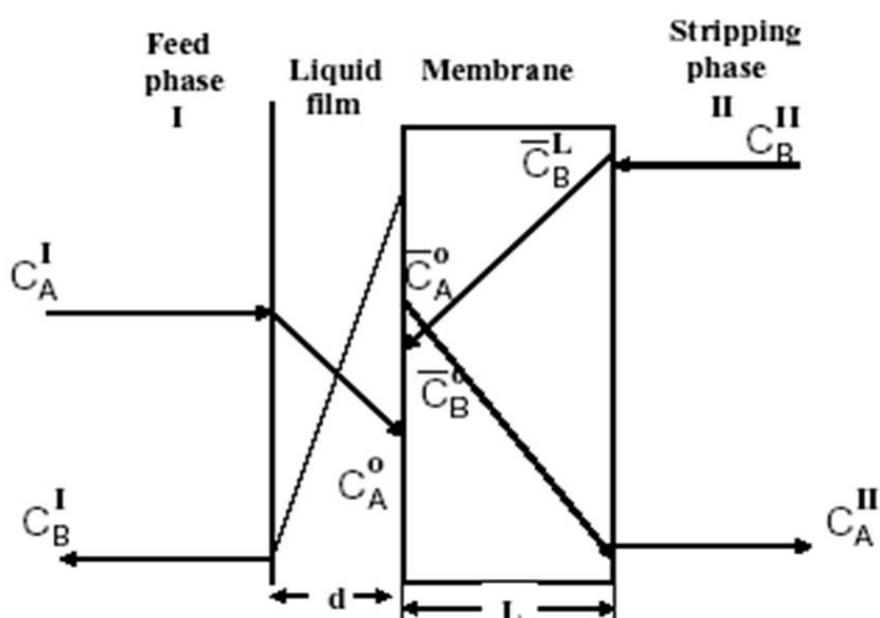


Fig. 1. Schematic diagram for theoretical consideration

First, let us consider the bulk solution-phase mass transport. If metal ion transport in one dimension, and mass flux of each ion in the solution can be represented on the basis of the Nernst-Planck equation as follows (Lightfoot & Scattergood, 1965; Saito, et al., 1991; Sherwood, 1975):

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

$$J_i = -D_i \left(\frac{dC_i}{dx} + C_i z_i F / RT \times \frac{dE}{dx} \right) \quad i = A, B, C, N \quad (1)$$

For the common anion Y , the transport flux is

$$J_Y = -D_Y \left(\frac{dC_Y}{dx} + C_Y z_Y F / RT \times \frac{dE}{dx} \right) = 0 \quad (2)$$

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 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.

$$z_A J_A + z_B J_B + z_C J_C + z_N J_N = 0 \quad (3)$$

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

$$z_A C_A + z_B C_B + z_C C_C + z_N C_N + z_Y C_Y = 0 \quad (4)$$

The potential gradient in eqn.1 and 2 can be eliminated by using eqn.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:

$$C_i = \left\{ C_i^0 \left[Q^0 \right]^{z_i} - \left[J_i / D_i Q^{z_i} \right] \right\} / Q^{z_i} \quad i = A, B, C, N \quad (5)$$

where

$$Q^0 = z_A C_A^0 + z_B C_B^0 + z_C C_C^0 + z_N C_N^0 \quad (6.1)$$

$$Q = Q^0 - \left(\frac{J_A}{D_A} + \frac{J_B}{D_B} + \frac{J_C}{D_C} + \frac{J_N}{D_N} \right) x \quad (6.2)$$

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 (Wang, & Hsieh, 2008; Wills, & Lightfoot, 1961):

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

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 (Tomicki, 1991), in which the constancy of the electric field existed in the membrane, can be adopted in this study. Eqn. 7 can be reduced to the following:

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

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 (Lake& Melsheimer, 1978):

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

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 $x=L$, eqn. 8 can be integrated to obtain the concentration profile in membrane. The concentration profiles in membrane are given as:

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

where

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

Based on the Teorell-Meyer-Sievers hypothesis (Dranoff & Lapidus, 1957; Tombalakian, et al.,1967), 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_{Na}^i , can be defined as

$$K_{Na}^i = \frac{\bar{C}_i}{C_i} \times \frac{C_{Na}^2}{\bar{C}_{Na}^2} \quad (11)$$

Substituting eqn.5 and 10 into eqn. 11, we obtained

$$\frac{\left[J_i / q\bar{D}_i (e^{qL} - 1) \right]}{\left[J_{Na} / q\bar{D}_{Na} (e^{qL} - 1) \right]^2} = K_{Na}^i \frac{\left[C_i^0 (Q^0)^2 - (J_i / D_i Q_d^2) \right]}{\left[C_{Na}^0 (Q^0) - (J_{Na} / D_{Na} Q_d) \right]^2} \quad (12)$$

where

$$Q = Q^o - \left(\frac{J_A}{D_A} + \frac{J_B}{D_B} + \frac{J_C}{D_C} + \frac{J_N}{D_N} \right) d$$

and d denotes the thickness of stagnant liquid film.

Eqn.(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 eqn.12 by the iterative technique under the restrictions of eqn.(3) and (4) as the apparent selective coefficient K_{Na}^i , obtained from equilibrium measurement, respectively. The dimensionless permeation transport of metal ion A relative to sodium ion, P_{i-Na} , in ion exchange membrane dialysis can be defined by

$$P_{i-Na} = (J_i/J_{Na}) / (C_i^o/C_{Na}^o) \quad (13)$$

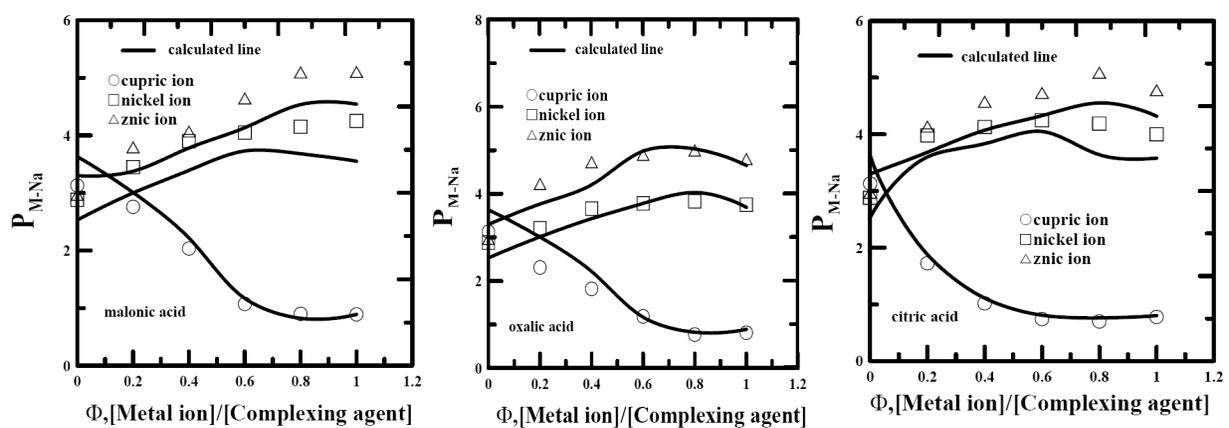


Fig. 2. Effect of the stoichiometric ratio of complex agent to metal ions on the dimensionless permeation fluxes of metal ions in the feed solution at pH 4.0 and $[CuCl_2] = [NiCl_2] = [ZnCl_2] = 0.001M$.

As can be seen from Figures 2 (a), (b) and (c) the experimental results show that the preferential transport behaviors of ternary system (Cu^{+2} - Ni^{+2} - Zn^{+2}) through dialysis process combined using the respective complex agent, malonic acid, citric acid and oxalic acid, respectively (Wang, & Hsieh, 2008). In the experiment with solutions of investigated metal ions and a complexing agent with a total sodium ion concentration of 0.1M in the feed compartment, the dimensionless permeation fluxes of metal ions were measured as the stoichiometric ratio of the complexing agent to metal ions $\Phi = [\text{complex agent}]/[\text{metal ions}]$, varied from 0 to 1.0 at pH 4.0 for the investigated system. The experimental results show that the uptake of metal ions in the cation exchange membrane is changed by adding a complex agent in the solution phase, and both the anion ligands and the kinds of metal ions can differentiate the permeation fluxes of metal ions so as to increase the membrane selectivity of the metal ions. The optimal dimensionless permeation flux ratio of $P_{Zn-Na}/P_{Ni-Na}/P_{Cu-Na}$ is obtained about 5.3/3.6/0.7. As a result, the combined use of a cation exchange membrane and a complex agent seem to be a feasible process for the simultaneous separation and

concentration of metal ions. However, more experimental work on multi-ions system with the dialysis method seems to be needed in order to develop an ion fractionation process for the enrichment of metal ions as well as the separation of metal ions from waste water in industrial practice.

The experimental results in Figures 3, (a) (b) and (c) show that the values of P_{Cu-Na} decreases with an increasing pH value of feed solution, but a peak of P_{Ni-Na} and P_{Zn-Na} arise with the change of the pH value of solution under the conditions of various complex 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 (Zeleznik & Gordon, 1968). The higher pH value leads to the complex agent releasing more complex ligands to react with cupric ion as well as makes it in an advantage position to react with nickel ions and zinc ions to form complexes when the values of pH is larger 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 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 complex agents. The maximum values of $P_{Cu-Na}/P_{Ni-Na}/P_{Zn-Na}$ is found to be 0.78/4.30/4.85 in case of using the citric acid as the complex 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 0.70/3.0/4.6 for the respective complex agent being malonic acid and oxalic acid at pH 4.0.

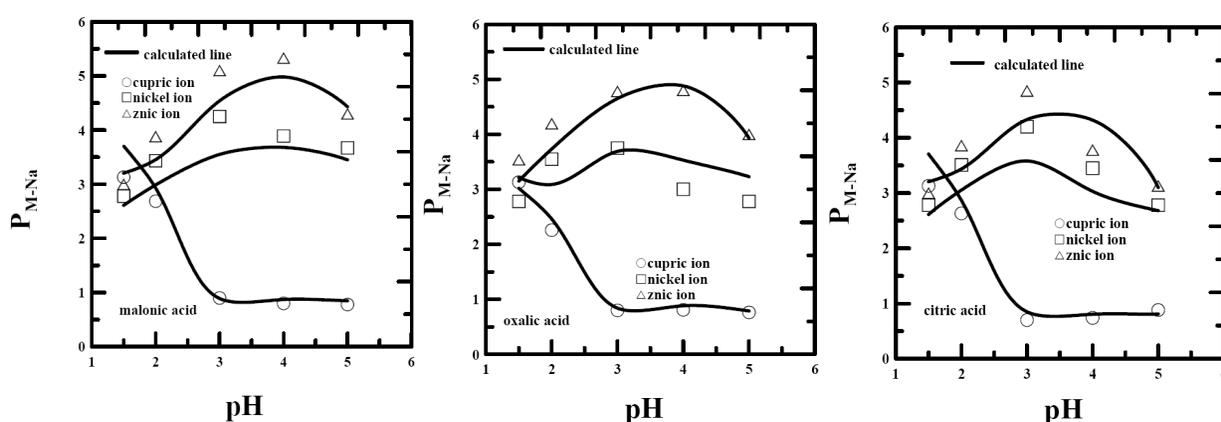


Fig. 3. Effect of the pH of solution on the dimensionless permeation fluxes of metal ions at $[CuCl_2] = [NiCl_2] = [ZnCl_2] = 0.001M$.

It can be concluded that preferential transport of metal ions with ternary system across the cation-exchange membrane can be effectively enhanced by the addition of a complex agent. The suitable complex agents are found to be malonic acid for the investigated system $Cu^{2+}-Ni^{2+}-Zn^{2+}$. The kinds of complex agents, the stoichiometric ratio of complex 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 hypothesis, a theoretical approach calculated from Eqn. 12 with numerical calculation is in agreement with the experimental data. Data from the present investigation have shown that the cation-exchange membrane with use of a

suitable complex 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 from cation-exchange membrane being the separation interface; the driving force being the concentration gradient of counter ion; the suitable complex agent being the separation agent and the pH value is the separation index.

4. General considerations of electro dialysis process

Ion exchange membrane electro dialysis is a membrane separation process (Leitz, F. B. & Eisenamann, 1981;) in which ions transport across ion-permselectivity membranes from one fluid to another under an applied direct electric field. As shown in Figure 4, there are at least five element parts for electro dialysis applications: (1) direct current supply, which proves effective to initializing ion migration; (2) electrodes, where the oxidation/reduction reactions occur to realize the transformation from ionic conduction to electron conduction and thus provide the original driving force for ion migration; (3) ion exchange membranes, the key components which permit the transport of counter ions and block the passage of co-ions; (4) solvents, which make a continuum for ion transport by filling the space between electrodes and membranes; (5) electrolytes, the current carriers between cathode and anode. In such a way, it should be able to deionize one stream so as to produce a purified stream that can be either discharged or reused and a concentrated electrolyte stream that can be disposed of or processed for recovery of dissolved salts. The cations and anions permeate through cation selective and anion selective membranes, respectively as a result of applied electrical energy. In electro dialysis, electrolytes permeate through the membranes and, the solvent and nonelectrolytes generally do not permeate through the membranes. The solution from which electrolytes are removed gets depleted of salt and the solution which receives the solute gets enriched with salt. Owing to its distinguished functions, applications of ion exchange membrane electro dialysis have been widely conducted on desalination of brackish water (Farrell & Smith,1962; Korngold et al., 1987; Seto et al., 1978), recovery of metal ions from waste water (Gering. & Scamehorn, 1988; Itoi et al.,1980), purification of protein solutions (Lounis & Gavach, 1990), recovery of acids (Graillon et al., 1996), and removal of inorganic impurities from sugar solutions (Sandeaux et al.,1991).

One of the prominent features in the development of modern science and technology is the cross-fertilization of ideas among different disciplines (King, 1980). The combined use of complex agents with ion exchange membranes has received much attention. It has been found that different kinds of complex agents can differentiate the permeation fluxes of metal ions across the membrane. Therefore, the permselectivity of metal ions through membrane dialysis can be effectively increased resembling a support liquid membrane characterized by its high selectivity of metal ions. Some fundamental work on the preferential transport of ions through an ion exchange membrane with electro dialysis in the absence of complex agents was done by many researchers (Huang & Wang, 1993b; Kitamoto & Takashima, 1964; Margerum, 1965). It was proved that the applications of ion exchange membrane electro dialysis with complex agents to be an effective technique not only for concentration of metal ions but also for their separation.

In this section, preferential transport of ions through a cation exchange membrane electro dialysis has been discussed combined using complex agents. Based on the Nernst-Planck equation (Wang, 2004; Keister & Kasting, 1986)and interfacial quasi-equilibrium hypothesis (Rosenberg.& Tirrell, 1957), a theoretical approach was obtained with numerical

calculation and compared with the experimental results. Then the mathematical description of the mass transport in membranes in general and in specific membrane processes is described. Finally, determination of optimal conditions for separation of metal ions through membrane electro dialysis using statistical experimental methods are discussed in order to create an advantage position for industrial application in the future.

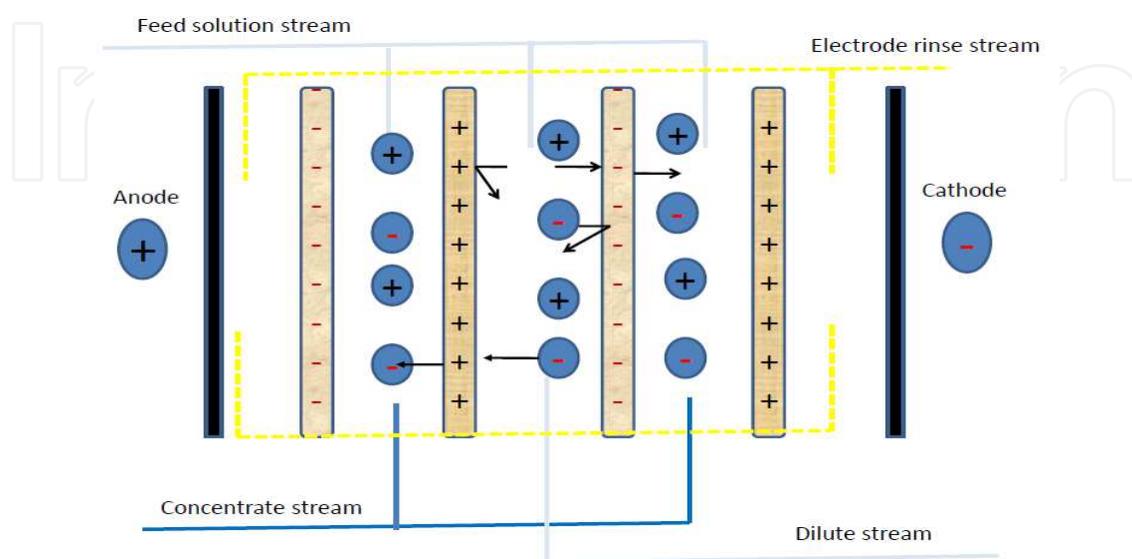


Fig. 4. Schematic drawing illustrating the principle of an electro dialysis process; - and, + refer anion and cation selective membranes, respectively.

5. Theoretical considerations of electro dialysis process

Consider a cation exchange membrane in an electrolyte solution which consists of cations *A* and *B* with a common anion *C*(-1). When an electric field is applied to this electro dialysis system, the cations pass through the diffusion liquid film in the desalinating compartment from the bulk dilute solution to the cation exchange membrane surface, then transfer through the membrane into the concentrate compartment.

First, let us consider the mass transport in the diffusion liquid film adjacent to the membrane surface. According to experimental conditions, the following assumptions can be made (1) Anions cannot pass through the cation exchange membrane (2) Electroneutrality holds in all parts of the membrane-solution system. (3) There are no pressure and temperature gradients across the system. (4) Solvent transport can be neglected (Belfort & Guter, 1972). Otherwise, assumed that the electro dialysis cell has been operated at a constant current density, and during this operation the membrane-film system has been allowed to adjust to a steady state. At this point the Nernst-Planck flux equation can be written for the ionic fluxes, *J_i*, in each liquid film and in the membrane (Huang & Wang, 1992a; Keister & Kasting, 1986; Kuroda et al., 1983).

$$J_i = -D_i \left(\frac{dC_i}{dx} + C_i z_i F / RT \times \frac{dE}{dx} \right) \quad i = A, B, C, N \tag{14}$$

where *E*, *D_i* and *C_i* denote the electrical field, the diffusion coefficient and the concentration of ion *i* in the liquid phase, respectively. *F*, *x* and *z_i* denote the Faraday constant, the distance normal to the membrane and the valence of ion *i*, respectively.

On the basis of electroneutrality condition is assumed to be existed in all part of systeme, the following equation can be obtained.

$$z_A C_A + z_B C_B + z_Y C_Y = 0 \quad (15)$$

By means of the simultaneous application of the one flux equation of anion and two flux equations of cations with using the boundary condition: $C = C^o$ at $X=0$, the concentration profiles of cations in the film can be derived,

$$C_Y = C_Y^o \exp[F/RT\Psi X] \quad i=A, B, C, N \quad (16)$$

where

$$\Psi = (dE / dX) = \text{constant } t$$

The electric flux transport by each ionic species can be expressed as

$$I = Z_A F J_A + Z_B F J_B = t_A I + t_B I \quad (17)$$

Substituting Eqns. (16) and (17) into Eqns. (14) and (15), the concentration profile of cation can be formulated by integrating method to give:

$$C_i = \left\{ C_i^o [C_Y^o]^{z_i} - P [C_Y^o]^{z_i} [1 - \exp[Z_i F \Psi X / RT]] \right\} / C_Y^{z_i} \quad i = A, B \quad (18)$$

where

$$P = t_i I R T / (Z_i F)^2 D_i \Psi$$

Next, consider the mass transport in the membrane phase. The driving force of permeation flux is mainly due to the electric migration, and the normal diffusion as well as convective transport can be neglected. Therefore the ionic concentration in the membrane can be derived from Nernst-Planck equation as following (Yamabe & Seno, 1967):

$$\bar{C}_i = \frac{t_i I}{Z_i F D_i} \frac{RT}{Z_i F \Psi_m} \quad (19)$$

Here \bar{C}_i, \bar{D}_i and Ψ_m represent the ionic concentration, ionic diffusivity and membrane potential in the membrane phase; the subscripts i and k refer to ions and to all components in the system, respectively.

Based on the Teorell-Meyer-Sievers hypothesis (Tombalakian, et al., 1967), a pseudo-equilibrium state between each metal ion is assumed to exist at the film-membrane interface, respectively. An apparent selectivity coefficient, K_B^A , can be defined as

$$K_B^A = \frac{\bar{C}_B^{Z_B}}{\bar{C}_A^{Z_A}} \times \frac{C_B^{Z_A}}{C_B^{Z_B}} \quad (20)$$

Substituting eqn 16 and 19 into eqn. 20, we obtained

$$\frac{\{C_A^o - P(1 - \exp[Z_A F \Psi \delta / RT])\}^{Z_B}}{\{t_A IRT / (Z_A F)^2 \bar{D}_A \Psi_m\}^{Z_B}} = K_B^A \frac{\{C_B^o - P(1 - \exp[Z_B F \Psi \delta / RT])\}^{Z_A}}{\{t_B IRT / (Z_B F)^2 \bar{D}_B \Psi_m\}^{Z_A}} \quad (21)$$

where δ denotes the thickness of stagnant liquid film, $t_A + t_B = 1$.

Eqn.21 is a general equation describing the preferential transport behaviors of metal ions sharing with the same counter-ion across the cation-exchange membrane in electro dialysis process. In the above equation, C_i , D_i , t_i , U_i and Z_i refer to the concentration, diffusivity, transport number, mobility and charge of ion I , respectively. F , I , L and $K_{A/B}$ are the Faraday constant, current density, film thickness and selectivity coefficient, respectively. The superscripts o and $-$ represent the bulk solution phase and the membrane phase. Since the selectivity coefficient $K_{A/B}$ can be obtained from equilibrium measurement and film thickness L estimated from I-V curves (Mandersloot et al., 1965), the transport number t_A and t_B can then be calculated by numerical method at each operating condition.

In general, the permselectivity of ion A relative ion B , T_B^A in ion exchange membrane electro dialysis can be defined by (Cowan & Brown, 1959):

$$T_B^A = (J_A / J_B) / (C_A^o / C_B^o) = (Z_B t_A / Z_A t_B) / (C_A^o / C_B^o) \quad (22)$$

The permselectivity coefficient can also be determined experimentally from the following equation derived from a shell mass balance [Huang & Wang, 1992b].

$$T_B^A = \ln(C_{A,o}^o / C_{A,t}^o) / \ln(C_{B,o}^o / C_{B,t}^o) \quad (23)$$

where $C_{i,o}^o$ is the initial concentration of ionic species i in the bulk solution, and $C_{i,t}^o$ is that of the bulk solution at time t .

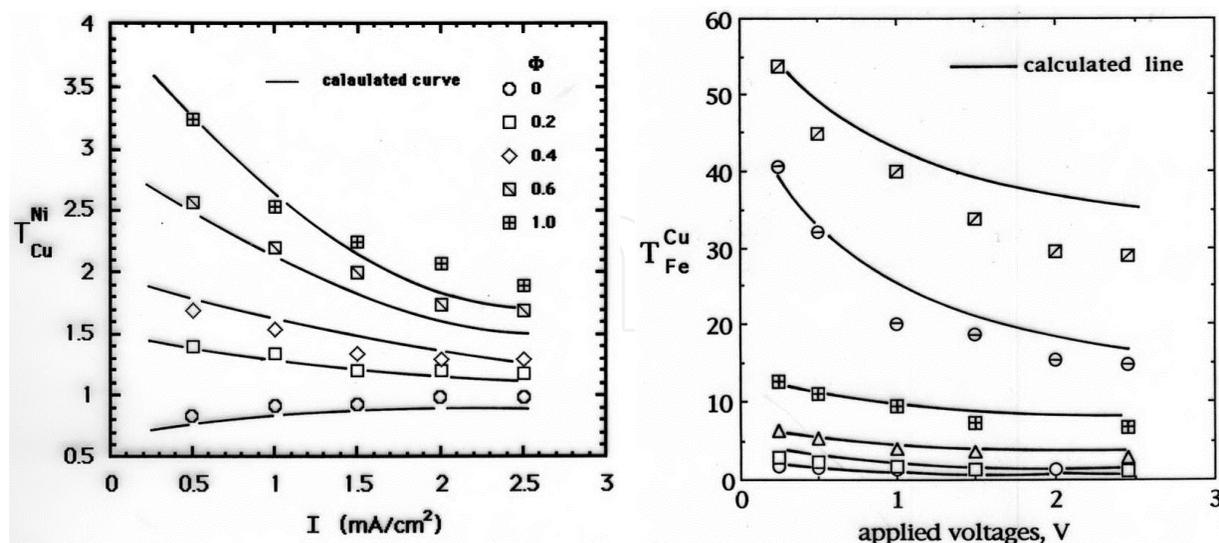


Fig. 5. Preferential transport behaviors of metal ions in a five compartment electro dialyzer with using citric acid as a complex agent at $[CuCl_2] = [NiCl_2] = [FeCl_3] = 0.015M$.

The preferential transport of nickel and cupric ions as well as ferric and cupric ions through cation exchange membranes was studied with electro dialysis in chloride solutions

containing a complex agent (Huang & Wang, 1993b). Citric acid was employed as complex agents in order to increase the permselectivity of metal ions. As can be seen from Figures 5 (a) and (b), citric acid was found to be an effective complex agents to increase the permselectivity coefficient T_{Cu}^{Ni} from 0.83 to 3.32 and T_{Cu}^{Fe} from 0.85 to 58.78. The values of T_{Cu}^{Ni} and T_{Cu}^{Fe} increase as the stoichiometric ratio of complex agent to metal ions and pH of complex solutions increase, but decrease with an increased current density and applied voltages. Based on the Nernst-Planck equation and interfacial quasi-equilibrium hypothesis, a theoretical approach obtained from numerical calculation is consistent with the experimental data. The experimental results show that electro dialysis combined with the use of complex agents has been demonstrated to be a useful technique not only for the enrichment of metal ions but also for their separation.

6. Optimization method of dialysis/electrodialysis process

As a result, the combined use of a cation exchange membrane and a complex agent seem to be a feasible process for the simultaneous separation and concentration of metal ions. However, many factors such as membrane and complex agent sources, pH of solution, concentrations of complex agent and metal ions are important variables affecting permselectivity of metal ions. It is seemed to need a simple model to optimize such an ion fractionation process that the enrichment of metal ions as well as the separation of metal ions from waste water in industrial practice because of economic consideration.

Conventional practice of single variable optimization by maintaining other variables involved at a specified constant level does not depict the combined effect of all the variables involved. It was reported that the complexities and uncertainties associated with industry separation usually come from lack of knowledge of the sophisticated interactions among various variables. Unlike traditional optimization, statistical optimization methods can take into account the interactions of variables in generating the process response. These limitations of a single variable optimization can be eliminated by using of experimental design and response surface methodology (Dean & Voss, 1999). A combination of variables generating a certain optimum response can be identified through Box-Behnken design and the use of response surface methodology. This pattern is designed by using statistical methods to yield the most information by a minimum number of experiments and had been successfully applied to the optimization of various engineer process (Wang & Hsieh, 2009).

In general usage, statistics experimental design is the design of any information-gathering exercises where variation is present, whether under the full control of the experimenter or not. However, in statistics, these terms are usually used for controlled experiments. A methodology for designing experiments was proposed by Ronald A. Fisher, (Montgomery, 1991). As an example, he described how to test the hypothesis that a certain lady could distinguish by flavour alone whether the milk or the tea was first placed in the cup. While this sounds like a frivolous application, it allowed him to illustrate the most important ideas of experimental design. In statistics, Box-Behnken designs are experimental designs for response surface methodology, devised by George E. P. Box and Donald Behnken (Khuri & Cornell, 1987), to achieve the following goals:

- Each factor, or independent variable, is placed at one of three equally spaced values. (At least three levels are needed for the following goal.)

- The design should be sufficient to fit a quadratic model, that is, one containing squared terms and products of two factors.
- The ratio of the number of experimental points to the number of coefficients in the quadratic model should be reasonable .
- The estimation variance should more or less depend only on the distance from the centre (this is achieved exactly for the designs with 4 and 7 factors), and should not vary too much inside the smallest (hyper)cube containing the experimental points.

Each design can be thought of as a combination of a two-level (full or fractional) factorial design with an incomplete block design. In each block, a certain number of factors are put through all combinations for the factorial design, while the other factors are kept at the central values. For instance, the Box-Behnken design for 3 factors involves three blocks, in each of which 2 factors are varied through the 4 possible combinations of high and low. It is necessary to include centre points as well (in which all factors are at their central values). In statistics, response surface methodology (RSM) explores the relationships between several explanatory variables and one or more response variables. The method was introduced by G. E. P. Box and K. B. Wilson in 1951 (Dean, & Voss, 1999). The main idea of RSM is to use a sequence of designed experiments to obtain an optimal response. Box and Wilson suggest using a second-degree polynomial model to do this. They acknowledge that this model is only an approximation, but use it because such a model is easy to estimate and apply, even when little is known about the process.

A prior knowledge and understanding of the process and process variables under investigation are necessary for achieving a more realistic model. Based on the results of preliminary experiments, we selected the significant variables from screening experimental variables in first. Then the Box-Behnken design and response surface methodology (RSM) were employed to obtain the optimal variable conditions for higher permselectivity of metal ions. Each variable had three levels to be examined at high level (+1), medium level (0) and low level (-1). The high and low levels we selected for this study represented the extremes of normal operating ranges. The range and the levels of the experimental variables investigated in this study are given in the Table 1. Based on Box-Behnken design, a set of 17 experiments was carried out for for each complex agent, respectively. In developing regression model, the experimental variables were coded according to the following equation:

$$x_i = \frac{X_i - X_0}{\Delta X} \quad (24)$$

where x_i is the coded value of the variable X_i , X_0 is the value of X_i at the center point and ΔX is the step change value. Once the experiments were performed, the regression model could be constructed by fitting the experimental results. According to the RSM methodology, a second-order polynomial model was used to fit the experimental variables using the following equation :

$$Y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_1^2 + b_5x_2^2 + b_6x_3^2 + b_7x_1x_2 + b_8x_1x_3 + b_9x_2x_3 \quad (25)$$

where Y is the permselectivity of metal ions; b_0, \dots, b_9 are coefficients of the model; x_1, x_2, x_3 are the coded variables.

In this study, Design-Expert package (version 6.0.10, Stat-ease Inc., Minneapolis, USA) was used for regression analysis of the data obtained, to estimate the coefficients of regression model and to search the optimal conditions. The fit of regression model attained was checked by the multiple correlation coefficients (R^2). The optimization process was depicted in Figure 6.

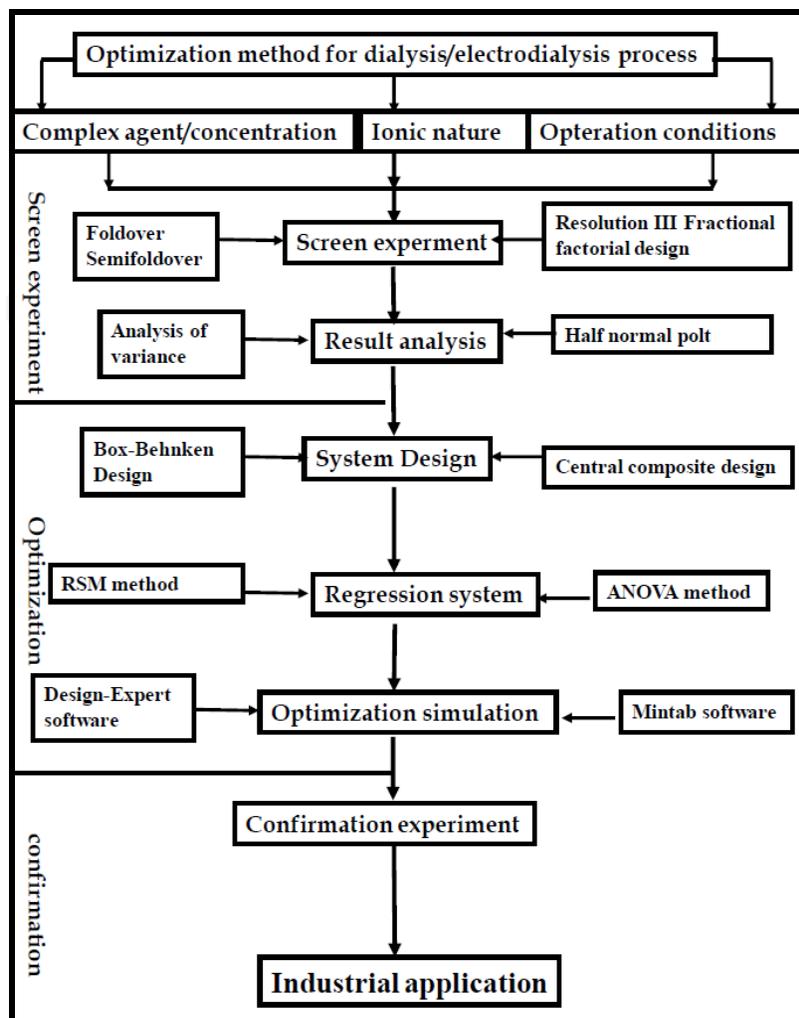


Fig. 6. The flowchart of optimization process

Statistical experimental methods were used to optimize the variable conditions of membrane dialysis process with a complex agent. Permselectivity of metal ions has been investigated in a two-compartment dialyzer with reflux flow. Cu^{+2} - Ni^{+2} ion system was chosen for the experimental investigation. Oxalic, malonic acid, acid and citric acid were selected as a complex agent used in the investigated solution in order to increase the discrepancy between transport fluxes of metal ions. The concentration ratio of complex agent to metal ions (X_1), pH value of investigated solution (X_2) and concentration of metal ions (X_3) were conducted to be optimized. The Box-Behnken design and Response surface methodology were employed in the design of experiments and the analysis of results. The experimental results indicated that oxalic acid is a better complex agent in this study.

The Box-Behnken design and experimental results are shown in the Table 2. The experimental data indicates that permselectivity of metal ions can be enhanced with use of a complex agent. This is due to the fact that metal ions will compete with each other to react with complex ligands to form complexes which are hardly permeated through the membrane, while the complex agent is added in feed. 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 (Ng & Snyder, 1981; Kuroda, 1983). Thus, the various permselectivity of metal ions can be observed in Table 2 for various kinds of complex agent

included oxalic acid, malonic acid and citric acid. From the experimental results in Table 2, the means of permselectivity of metal ions are 2.31 for malonic acid as complex agent; 4.24 for oxalic acid as complex agent; 1.95 for citric acid as complex agent, respectively. It shows that the effect of complex agent on permselectivity of metal ions for Cu+2-Ni+2 ion system has the following order: oxalic acid >malonic acid >citric acid. The permselectivity of metal ions can be enhanced with a complex agent under suitable conditions. 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 permselectivity of metal ions can be obtained. These experimental results were analyzed using statistical software package Design-Expert 6.0.

Trial no.	Variables			Permselectivity (Y)		
	x ₁	x ₂	x ₃	oxalic	malonic	citric
1	-1	-1	0	0.91	0.91	0.91
2	1	-1	0	2.20	1.30	1.25
3	-1	1	0	0.95	0.95	0.95
4	1	1	0	10.88	5.25	4.13
5	-1	0	-1	0.87	0.87	0.89
6	1	0	-1	6.00	3.86	3.03
7	-1	0	1	0.93	0.93	0.93
8	1	0	1	5.78	3.53	2.40
9	0	-1	-1	2.43	1.53	1.20
10	0	1	-1	5.50	2.34	2.78
11	0	-1	1	1.13	1.03	1.03
12	0	1	1	9.43	4.30	3.78
13	0	0	0	5.03	2.53	1.88
14	0	0	0	4.95	2.45	1.98
15	0	0	0	5.20	2.40	2.05
16	0	0	0	4.95	2.53	1.89
17	0	0	0	5.20	2.45	1.99

Table 1. The Box-Behnken design and results for dialysis with using a complex agent

1. For oxalic acid as complex agent

According to the RSM methodology, a second-order polynomial model, Eqn.(25), was used to fit the experimental variables. Multiple regression analysis of the experimental results gave the following equation:

$$Y = 5.07 + 2.65x_1 + 2.65x_2 + 0.42x_3 - 1.14x_1^2 - 0.19x_2^2 - 0.53x_3^2 + 2.16x_1x_2 - 0.07x_1x_3 + 1.08x_2x_3 \quad (26)$$

The results of analysis of variable (ANOVA) for regression model show that x₁, x₂, x₁², x₁ x₂ and x₂ x₃ have significant effect on permselectivity of metal ions because the value of P<F is less than 0.05 (Montgomery, (1991). The R² (multiple correlation coefficient) of the regression equation obtained from analysis of variance is always larger than 0.9685 (a value >0.75 indicates aptness of the model), which means that the model can explain 96.85% variation in the response (Wang & Hiesh, 2009).

2. For malonic acid as complex agent

From the analysis of sequential model and lack of fit, a second-order regression model was suggested. Multiple regression analysis of the experimental results gave the following equation:

$$Y = 2.47 + 1.28x_1 + 1.02x_2 + 0.16x_3 - 0.17x_1^2 - 0.20x_2^2 + 0.98x_1x_2 - 0.098x_1x_3 + 0.59x_2x_3 \quad (27)$$

The results of analysis of variable (ANOVA) for regression model are given that x_1 , x_2 , $x_1 x_2$ and x_2x_3 have significant ($P < 0.05$) effect on permselectivity of metal ions. The results showed the R^2 (multiple correlation coefficient) of the regression equation obtained from analysis of variance is 0.9807 (a value > 0.75 indicates aptness of the model), which means that the model can explain 98.07% variation in the response.

3. For citric acid as complex agent

From the analysis of sequential model and lack of fit, a second-order regression model was suggested. Multiple regression analysis of the experimental results gave the following equation:

$$Y = 1.96 + 0.89x_1 + 0.91x_2 + 0.03x_3 - 0.27x_1^2 + 0.12x_2^2 + 0.12x_3^2 + 0.71x_1x_2 - 0.17x_1x_3 + 0.29x_2x_3 \quad (28)$$

The results of analysis of variable (ANOVA) for regression model are show that x_1 , x_2 and $x_1 x_2$ have significant ($P < 0.05$) effect on permselectivity of metal ions. The R^2 (multiple correlation coefficient) of the regression equation obtained from analysis of variance is always larger than 0.9680 (a value > 0.75 indicates aptness of the model), which means that the model can explain 96.80% variation in the response.

Trial no.	Permselectivity					
	Oxalic acid		Malonic acid		Citric acid	
	Actual	Predicted	Actual	Predicted	Actual	Predicted
1	0.91	0.79	0.91	0.77	0.91	0.72
2	2.20	1.58	1.30	1.39	1.25	1.09
3	0.95	1.57	0.95	0.86	0.95	1.12
4	10.88	11.19	5.25	5.39	4.13	4.32
5	0.87	0.25	0.87	0.75	0.89	0.72
6	6.00	5.69	3.86	3.52	3.03	2.84
7	0.93	1.24	0.93	1.27	0.93	1.12
8	5.78	6.40	3.53	3.65	2.40	2.57
9	2.43	2.36	1.53	1.68	1.43	1.55
10	5.50	5.49	2.34	2.55	2.78	2.78
11	1.13	1.04	1.03	0.82	1.03	1.03
12	9.43	8.95	4.30	4.05	3.78	3.43
13	5.03	5.07	2.53	2.47	1.88	1.96
14	4.95	5.07	2.45	2.47	1.98	1.96
15	5.20	5.07	2.40	2.47	2.05	1.96
16	4.95	5.07	2.52	2.47	1.89	1.96
17	5.20	5.07	2.45	2.47	1.99	1.96

Table 2. Comparisons of the predicted values and actual values for dialysis process

Once the optimal level of the process variables is identified for each complex agent, the confirmation experiment was conducted to validate the optimization model. As shown in Table 2, comparisons of experimental value and predicted value of regression model, it was observed that agreement was satisfactory. The results also indicate that the model could be a simple method to stimulate the permselectivity behaviors of metal ions through membrane dialysis with a complex agent.

In the preceding section there is a demonstration case that statistics based experimental designs were used to optimize preferential behavior for the electrodialysis process combined use a complex agent. $\text{Cu}^{+2}\text{-Ni}^{+2}$ and $\text{Cu}^{+2}\text{-Fe}^{+3}$ ions system were chosen for the experimental investigation. Citric acid was employed as a complex agent used in the investigated solution in order to increase the discrepancy between transport fluxes of metal ions. The Box-Behnken design and experimental results are tabulated in the Table 3. Once the experiments were performed, the regression model could be constructed by fitting the experimental results with a second-order polynomial. The optimal conditions of selected variables were searched using the regression model and also by analyzing the response surface method. Based on Box-Behnken design, a set of 17 experiments was carried out. According to the RSM methodology, a second-order polynomial model was used to fit the experimental variables. The statistical software package Design-Expert 6.0 was used to analyze the experimental results.

Trial no.	Variables			Permselectivity	
	X_1	X_2	X_3	$\text{Cu}^{+2}\text{-Ni}^{+2}$	$\text{Cu}^{+2}\text{-Fe}^{+3}$
1	-1	-1	0	0.91	0.85
2	1	-1	0	1.30	12.20
3	-1	1	0	0.95	1.03
4	1	1	0	4.25	42.78
5	-1	0	-1	0.87	2.43
6	1	0	-1	3.86	36.00
7	-1	0	1	0.93	0.88
8	1	0	1	3.53	25.78
9	0	-1	-1	1.43	9.43
10	0	1	-1	2.34	25.50
11	0	-1	1	1.23	11.23
12	0	1	1	4.50	23.50
13	0	0	0	2.53	15.03
14	0	0	0	2.45	14.95
15	0	0	0	2.40	15.20
16	0	0	0	2.53	14.95
17	0	0	0	2.45	15.20

Table 3. The Box-Behnken design and results for electrodialysis process

The results of analysis of variance (ANOVA) for regression model are listed in Table 4 for $\text{Cu}^{+2}\text{-Ni}^{+2}$ system. It is indicated that the main effect X_1 , X_2 and two-variable interaction X_1X_2 had significant effect ($P < 0.05$) on permselectivity of metal ions. The R^2 (multiple correlation coefficient) of the regression equation obtained from analysis of variance is always larger than 0.9436 (a value >0.75 indicates aptness of the model), which means that the model can

explain 94.36% variation in the response. By using the regression analysis method, the regression model for Cu²⁺-Ni²⁺ system in the coded form was established as follows:

$$Y = 5.06 + 2.65x_1 + 2.70x_2 + 0.52x_3 - 1.24x_1^2 - 0.092x_2^2 - 0.43x_3^2 + 2.16x_1x_2 - 0.07x_1x_3 + 1.18x_2x_3 \quad (29)$$

Effect	Sum of Squares	DF	Mean Square	F- Value	Prob>F
X ₁	6.35	1	6.35	68.98	< 0.0001
X ₂	6.57	1	6.57	71.32	< 0.0001
X ₃	7.2x10 ⁻³	1	7.2x10 ⁻³	0.078	0.7855
X ₁ X ₂	2.02	1	2.02	21.89	0.0009
X ₁ X ₃	0.11	1	0.11	1.22	0.2956
X ₂ X ₃	0.34	1	0.34	3.71	0.0828

Table 4. Analysis of variance for electro dialysis of Cu²⁺-Ni²⁺ system Table 5 Analysis of variance for electro dialysis of Cu²⁺-Fe³⁺ system

Effect	Sum of Squares	DF	Mean Square	F- Value	Prob>F
X ₁	56.18	1	56.18	81.12	< 0.0001
X ₂	58.10	1	58.10	83.90	< 0.0001
X ₃	2.14	1	2.14	3.09	0.1220
X ₁ X ₂	6.34	1	6.34	9.15	0.0192
X ₁ X ₃	0.028	1	0.028	0.041	0.8455
X ₂ X ₃	0.75	1	0.75	1.08	0.3327

Table 5. Analysis of variance for electro dialysis of Cu²⁺-Fe³⁺ system

The results of analysis of variable (ANOVA) for regression model for Cu²⁺-Fe³⁺ system are tabulated in Table 5. It is indicated that the main effect X₁, X₂ and two-variable interaction X₁X₂ had significant effect (P < 0.05) on permselectivity of metal ions. The R² (multiple correlation coefficient) of the regression equation obtained from analysis of variance is always larger than 0.9678 (a value >0.75 indicates aptness of the model), which means that the model can explain 96.78% variation in the response. By using the regression analysis method, the regression model for Cu²⁺-Fe³⁺ system in the coded form was established as follows:

$$Y = 3.90 + 88.61x_1 - 28.87x_2 - 79.94x_3 - 150.52x_1^2 + 47.05x_2^2 + 189.83x_3^2 - 24.95x_1x_2 - 32.42x_1x_3 - 275.7x_2x_3 \quad (30)$$

Based on the regression model, the predicted maximum permselectivity was calculated to be 5.25 from Eq (29) Cu²⁺-Ni²⁺ system. The corresponding optimal variable conditions were 0.85 for Φ, 4.83 for pH, and current density 12.43A/dm². The predicted maximum permselectivity was calculated to be 43.5 from Eq (30) for Cu²⁺-Fe³⁺ system. The corresponding optimal variable conditions were 1.00 for Φ, 3.78 for pH, and current density 17.43A/dm². Comparisons of experimental value and predicted value of regression model), it was observed that agreement was satisfactory.

Data from the present investigation have shown that statistics based experimental designs is an effective tool to find the optimal separation conditions for the ion membrane dialysis process combined use a complex agent. It is also highlighted that an effective multi-ion fractionation process (as shown in Figure 7) could be build from cation-exchange membrane being the separation interface; the driving force being the applied electric field; the suitable complex agent being the separation agent and the pH value is the separation index.

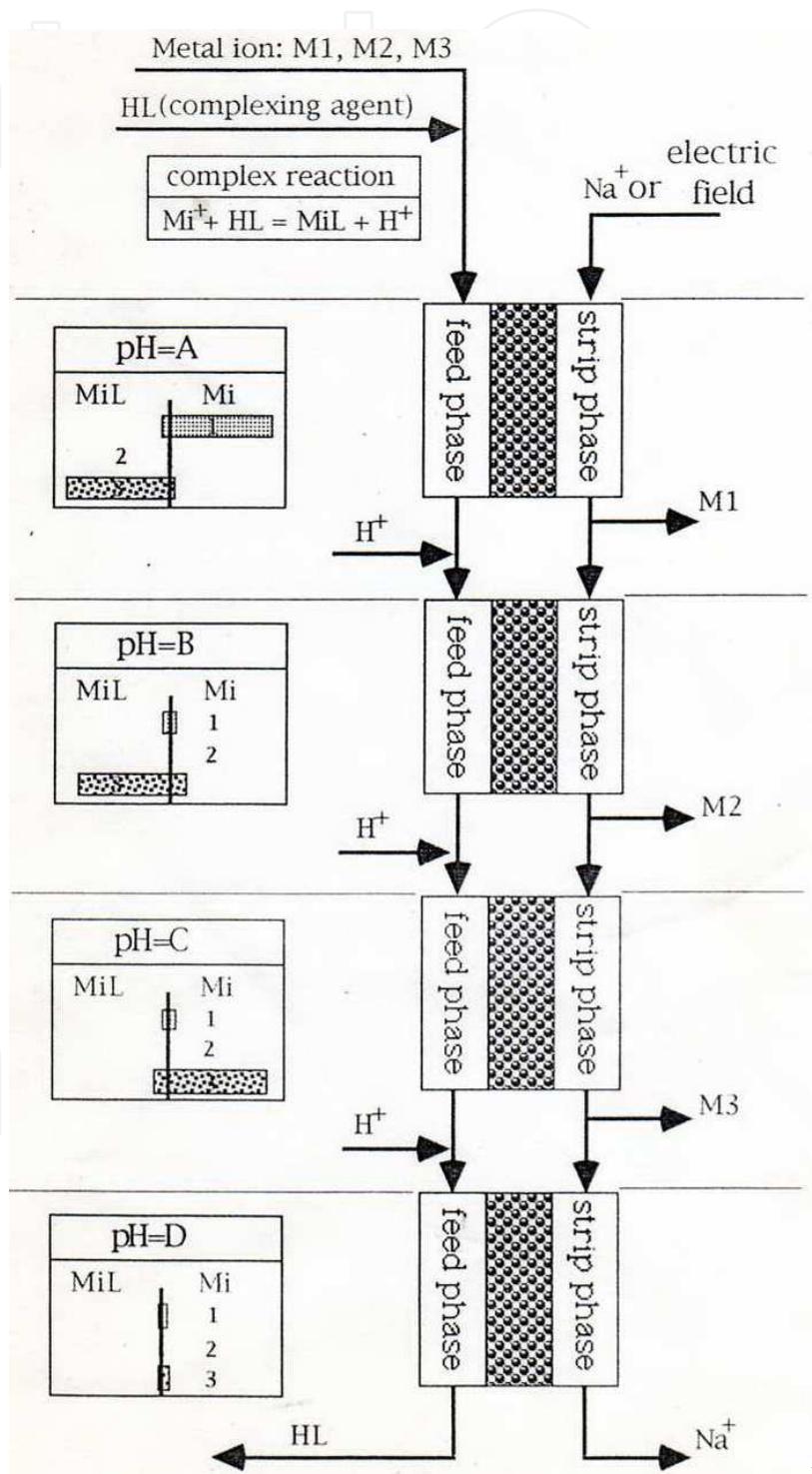


Fig. 7. Schematic mechanism of multi-ion fractionation process

7. Conclusion and outlook

Ion exchange membrane processes included dialysis and electrodialysis are used today on a large industrial scale in the production of potable and industrial process water as well as in the treatment of industrial effluents. However, today's membrane processes and components used in these processes have still severe technical and commercial limitations and there is a substantial need for basic as well as applied research to improve the processes. More recently developed processes will be discussed in more detail and their technical as well as economic advantages are described, and present and potential future applications indicated. Problems and technical limitations of these processes as well as commercial opportunities are indicated. They will be brought to industrial practice as long as the developers or users recognize that these separation technologies are versatile tools to deal with specific treatment requirements. It should also be noted that dialysis/electrodialysis separations are promising technologies for clean production and separation but have a long way to go before industrialization in most industries. The obstacles include the limited choice of membranes and the extremely high equipment cost of electrodialyzer. The increase in environmental awareness and raw material cost have accelerated the application of dialysis/electrodialysis integrations, especially in highly industrialized and densely populated countries. Accordingly, researchers should give attention to interdisciplinary knowledge and solve some interesting problems, such as membrane exploration, processes simulation, and operation optimization in dialysis/electrodialysis separation processes.

8. References

- Belfort, G. & Guter, G. A. (1972). An Experimental Study of Electrodialysis Hydrodynamics, *Desalination*, 10, 221
- Bohere, M. P. (1983). Diffusional Boundary Layer Resistance for Membrane Transport, *Ind. Eng. Chem. Fundam.*, 22, 27
- Brajter, K. & Slonawaska K. (1988). Separation of Noble Metals by Donnan Dialysis, *Sep. Sci. Technol.*, 23, 321
- Boudet, D.; Lindheimer, M.; Gavach, A. & C. (1991). Transport Properties of Anion Exchange in Contact with Hydrochloric Acid Solutions--Membranes for Acid Recovery by Electrodialysis, *J. Membr. Sci.*, 57, 57
- Bungay, P. M.; Lonsdale H. K. & DePinhp M. N. (1986). Synthetic Membrane: Science, Engineering and Application. *ASISeries*, Vol. 181
- Ciric, J. & Graydon, W. F. (1962). Ion-Exchange Membranes (IV)--Univalent Cation Transfer Rates, *J. Phys. Chem.*, 66, 1549
- Costa, E.; Lucas, A. D. & Gonzalez, M. E. (1984). Ion Exchange Determination of Interdiffusion Coefficients, *Ind. Eng. Chem. Flundam.*, 23, 400
- Cox, J. A. & DiNunzio, J. E. (1977). Dialysis Enrichment of Cations, *Anal. Chem.* 49, 1272
- Coz, J. A., Slonawska, J.; Gatchell, D. K. & Hiebert, A. G. (1984). Metal Speciation by Donnan Dialysis, *Anal. Chem.*, 56, 650
- Cowan, D. A. & Brown, J. H. (1959). Effect of Turbulence on Limiting Current in Electrodialysis Cells, *Ind. Eng. Chem.*, 51(12), 1445

- Davis, T. A.; Wu, J. S. & Baker, B. L. (1971). Use of the Donnan Equilibrium Principle to Concentrate Uranyl Ions by an Ion-Exchange Membrane Process, *AIChE J.*, 17 (4), 1006
- Dean, A. & Voss, D. (1999). *Response surface methodology. In: Design and analysis of experiments*, Springer-Verlag, New York, pp. 547-86.
- Dibenedetto, A. T. & Lightfoot, E. N. (1962). The Separation of Ions With Permselectivity Membranes, *AIChE J.*, 79
- Donnan, F. G. (1924). Theory of Membrane Equilibria, *Chem. Rev.*, 1, 73
- Dranoff, J. & Lapidus, L. (1957). Equilibria Ternary Ion-Exchange System", *Ind. Eng. Chem.*, 49, 1297
- Farrell, J. B. & Smith, R. N. (1962). Process Application of Electrodialysis, *Ind. Eng. Chem.*, 54(6), 29
- Gering, K. L. & Scamehorn, J. F. (1988). Use of Electrodialysis to Remove Heavy Metals form Wast, *Sep. Sci. Technol.*, 23 ,2231
- Graillon, S.; Persin, F.; Pourcelly, G. & Gavach, C. (1996). Development of electrodialysis with bipolar membrane for the treatment of concentrated nitrate effluents, *Desalination*, 107, 159-169.
- Helfferich, F. (1962). *Ion Exchange*, McGraw-Hill Book Company, Inc., New York
- Hopfenberg, H. B.; Lee, K. L. & Wen, C. P. (1978). Improved Membrane Separations by Selective Chelation of Metal Ions in Aqueous Feeds, *Desalination*, 24, 175
- Huang, R. Y. M. (1991). *Prevaporation Membrane Separation Process*, Elsevier, Amsterdam
- Huang, T. -C. & Wang, J. -K. (1992a). Separation of Cupric and Ferric Ions with a Cation-exchange Membrane in the Presence of Complexing Agents, *Sep. Sci. Technol.*, 27, 1137
- Huang, T. -C. & Wang, J. -K. (1992b). Preferential Transport of Nickel and Cupric Ions through Cation Exchange Membrane in Electrodialysis with a Complex Agent, *Desalination*, 86, 257
- Huang, T. -C. & Wang, J. -K. (1993a). Selective Transport of Metal Ions through Cation Exchange Membrane in the Presence of Complexing Agent, *Ind. Eng. Chem. Res.*, 32(1), 133-139
- Huang, T. -C. & Wang, J. -K. (1993b). Preferential Transport of Cupric and Ferric Ions through Ion Exchange Membrane with Electrodialysis in the Presence of Citric Acid, *Chem. Eng. Commun.*, 122, 213-225
- Hwang, S. -T. & Kammermeyer, K. (1975). *Membrane in Separations*, John Wiley & Son, New York
- Itoi, S.; Nakamura, I. & Kawahara, T. (1980). Electrodialysis Recovery Process of Metal Finish ing Waste Water, *Desalination*, 32, 393
- Keister, J. C. & Kasting, G. B. (1986). Ionic Mass Transport through a Homogeneous Membrane in the Presence of a Uniform Electric Field, *J. Membr. Sci.*, 29, 155
- Khuri, A. I. & Cornell, J. A. (1987). *Response Surfaces Design and Analysis*, Dekker, New York
- Kim, B. M. (1979). Donnan Dialysis for Removal of Chromates and Cyanides. *AIChE Symb. Ser.*, 76(197), 184
- King, C. J. (1980). *Separation Process 2th ed.*, McGraw-Hill Inc., New York

- Kitamoto, A. & Takashima, Y. (1964). Preferential Ion Transport through Ion Exchange Membrane by Electrodiagnosis, *J. Chem. Eng. Japan*, 37, 1443
- Kojima, T.; Furusaki, S.; Takao, K. (1982). A Fundamental Study on Recovery of Copper with a Cation Exchange Membrane Part 2-- Transfer Rate of Copper and Hydrogen Ion through Cation Exchange Membrane, *Canadian J. Chem. Eng.*, 60, 650
- Korngold, E.; Kock, K. & Strathmann, H. (1987). Electrodialysis in Advanced Waste Water Treatment, *Desalination*, 24, 129
- Kuroda, O.; Takahashi, S. & Nomura, M. (1983). Characteristics of Flow and Mass Transfer Rate in an Electrodialyzer Compartment Including Spacer, *Desalination*, 46, 225
- Lake, M. A. & Melsheimer, S. S. (1978). Mass Transfer Characterization of Donnan Dialysis, *AIChE J.*, 24(1), 130
- Leitz, F. B. & Eisenmann, J. L. (1981). Electrodialysis as a Separation Process, *AIChE Sym. Ser.*, 77(204), 204
- Lightfoot, E. N. & Scattergood, E. M. (1965). Suitability of the Nernst-Planck Equation for Describing Electrokinetic Phenomena. *AIChE J.*, 11, 175
- Lonsdale, H. K. (1982). The Growth of Membrane Technology, *J. Membr. Sci.*, 10, 81
- Lounis, A. & Gavach, C. (1990). Electrotransport of Carbonate and Hydrogen Carbonate Ions in Anion Exchange Membranes. *J. Membr. Sci.*, 54, 63
- Mandersloot, W. G. B. & Hicks, R. E. (1965). Concentration Polarization on Ion-exchange Resin Membrane in Electrodialytic Demineralization, *Ind. Eng. Chem. Process Des. Dev.*, 4, 304
- Margerum, D. W.; Janes, D. L.; Rosen, H. M. (1965). Multidentate Ligand Kinetics. VII. The Stepwise Nature of the Unwrapping and Transfer of Ethylenediamine-tetraacetatonicelate from Nickel (II) to Copper (II), *J. Am. Chem. Soc.*, 87, 4463
- Matsuyama, H.; Fuji, K. & Teramoto, M. (1991). Selective Separation of Rare Earth Metals by Donnan Dialysis in the Presence of Water-Soluble Complexing Agent, *J. Chem. Eng. Japan*, 24, 253
- Mears, P. (1976). *Membrane Separation Process*, Elsevier, Amsterdam
- Mizutani, Y. (1990). Ion Exchange Membrane with Preferential Permselectivity for Monovalent Ions, *J. Membr. Sci.*, 54, 233
- Montgomery, D. C. (1991). *Design and Analysis of Experiments*, Wiley, New York, 3rd edn.
- Ng, P. K. & Snyder, D. D. (1981). Mass Transport Characterization of Donnan Dialysis: The Nickel Sulfate System, *J. Electrochem. Soc.*, 128(8), 1717
- Nobel, R. D. (1987). A Overview of Membrane Separations, *Sep. Sci. Technol.*, 22(2&3), 731
- Nott, B. R. (1981). Electrodialysis for Recovering Acid and Caustic from Ion-Exchange Regeneration Wastes, *Ind. Eng. Chem. Process Res. Dev.*, 20, 170
- Pyrzynska, K. (1991). Membrane method for preconcentrating and separating gold complexes from aqueous solutions containing other platinum group metals, *Anal. Chim. Acta*, 255, 169-175.
- Rosenberg, N. W. & Tirrell, C. E. (1957). Limiting Currents in Membrane Cells, *Ind. Eng. Chem.*, 49, 780
- Rush, W. E. & Baker, B. L. (1980). Quantitative Description of Ion Transport in Donnan Ion Exchange Membrane Systems, *Sep. Sci. Technol.*, 15(4), 1153

- Saito, K., S. Furusaki & Kojima (1982). A Method for Determination of Integral Interdiffusion Coefficient in a Cation Exchange Membrane, *J. Chem. Eng. Japan*, 15(b), 487
- Sandeaux J.; Sandeaux, R. & Gavach, C. (1991). Competition between the Electrotransport of Acetate and Chloride Ions through a Polymeric Anion Exchange Membrane, *J. Membr. Sci.*, 59, 265
- Sata, T. (1991). Ion Exchange Membranes and Separation Process with Chemical Reaction, *J. App. Electrochem.*, 21, 283
- Saito, K.; Sakairi, T.; Yonemoto, T. & T. Tadaki, (1991). Ionic Transport in a Continuous Donnan Dialyzer with Two Parallel-plate Channels, *J. Chem. Eng. Japan*, 24(5), 575
- Seto, T.; Ehara, M. L.; Komori, R.; Yamaguchi, A. & Miwa, T. (1978). "Seawater Desalination by Electrodialysis", *Desalination*, 25,
- Sherwood, T. K.; Pigford, R. L. & Wilke, C. R. (1975). *Mass Transfer*, McGraw-Hill, Book Co. Inc., New York
- Spencer, H. G. & Ellison, T. M. (1953). Effects of pH and Divalent Cations on the Transport of Univalent Cation Across a Weak Acid Membrane, *J. phys. Chem.*, 57, 687
- Stratmann, H. (2004). *Ion-exchange Membrane Separation Process*, Elsevier, Amsterdam
- Sudoh, M.; Kamei, H. & Nakamura, S. (1987). Donan Dialysis Concentration of Cupric Ions, *J. Chem. Eng. Japan*, 20(1), 34
- Takahashi, K.; Tsuboi, K. & Takeuchi, H. (1989). Mass Transfer across Cation Exchange Membrane, *J. Chem. Eng. Japan*, 22(4), 352
- Tombalakian, A. S.; Yeh, C. Y. & Graydon, W. F. (1967). Cation Exchange across Ion Exchange Membrane, *J. Phys. Chem.*, 71, 435
- Tomicki, B. (1991). A Thermodynamic Description of Membrane Equilibria, Dissipation and Transport, *J. Membr. Sci.*, 60, 169
- Wang, J.-K. & Hsieh, C.-S. (2009a). Determination of optimal conditions for separation of metal ions through membrane dialysis using statistical experimental methods, *Desalination and Water Treatment*, 2, 246-253
- Wang, J.-K. & Hsieh, C.-S. (2009). Optimization of the Medium Components by Statistical Experimental Methods to Enhance Nattokinase Activity", *Food J. Health Sci.*, 1(1), 21-27
- Wang, J.-K. & Hsieh, C.-S. (2008). Preferential transport behaviors of ternary system Cupric-Nickel-Zinc ions through cation-exchange membrane with a complex agent by dialysis, *Chem. Eng. J.*, Vol 138/1-3, 103-110
- Wang, J.-K. (2004). Preferential transport behaviors of ternary system ferric-cupric-nickel ions through cation ion exchange membrane with a complex agent by dialysis, *Desalination*, 161, 277-285
- Wang, J.-K. & Chang, C.-P. (2004). Selective transport behaviors of ternary system Cupric-Nickel-Cobalt ions through cation ion exchange membrane with a complex agent by dialysis, *Desalination*, 164, 269-280
- Wallace, R. M. (1967). Concentration and Separation of Ions by Donan Membrane Equilibrium, *Ind. Eng. Chem. Process Des. Dev.*, 6, 423
- Wen, C. P. & Hamil, H. F. (1981). Metal Counterion Transport in Donan Dialysis, *J. Membr. Sci.*, 8, 51

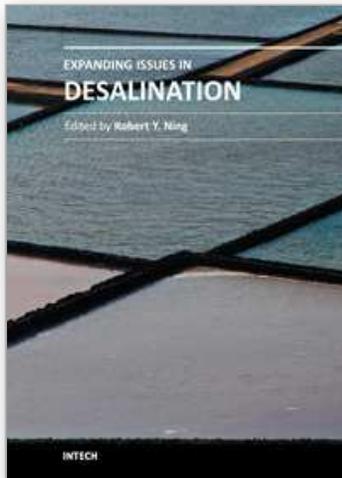
Wills, G. B. & Lighfoot, E. N. (1961). Membrane Selectivity, *AIChE J.*, 7(2), 273

Yamabe, T. & Seno, M. (1967). The Concentration Polarization Effect in Ion-Exchange Membrane Electrodialysis, *Desalination*, 2(2), 148

Zeleznik, F. J. & Gordon, S. (1968). Calculation of Complex Chemical Equilibria, *Ind. Eng. Chem.*, 60, 27

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For this book, the term “desalination” is used in the broadest sense of the removal of dissolved, suspended, visible and invisible impurities in seawater, brackish water and wastewater, to make them drinkable, or pure enough for industrial applications like in the processes for the production of steam, power, pharmaceuticals and microelectronics, or simply for discharge back into the environment. This book is a companion volume to “Desalination, Trends and Technologies”, INTECH, 2011, expanding on the extension of seawater desalination to brackish and wastewater desalination applications, and associated technical issues. For students and workers in the field of desalination, this book provides a summary of key concepts and keywords with which detailed information may be gathered through internet search engines. Papers and reviews collected in this volume covers the spectrum of topics on the desalination of water, too broad to delve into in depth. The literature citations in these papers serve to fill in gaps in the coverage of this book. Contributions to the knowledge-base of desalination is expected to continue to grow exponentially in the coming years.

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