Separation & Purification Reviews

Ion Separation by Charge-Mosaic Membrane System

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ION SEPARATION BY CHARGE-MOSAIC MEMBRANE SYSTEM

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ABSTRACT

Macromosaic cell and neutralization dialysis are new separation methods and they are called charge-mosaic membrane systems because they involve a pair or pairs of a cation- and an anion-exchange membrane. They are very simple and easy to be constructed and the permeability of ions across the membrane is very high in the system without any external driving force other than a concentration gradient. The system can be used for deionization, the separation of electrolytes from nonelectrolytes, and other purposes. The transport rates can be predicted on the basis of a circulating current in the macromosaic cell or Donnan dialysis in the neutralization dialysis.

I. INTRODUCTION

A charge-mosaic membrane proposed by Sollner in 1932[1] is composed of cation-exchange parts and anion-exchange parts and the salt permeability across the membrane is extremely high. When salt solution and pure water are separated to each other by a cation- or an anion-exchange membrane, counter ions are permeated through an ion-exchange membrane under a concentration gradient but only a trace amount diffuses because the diffusion of cations alone or

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anions alone breaks an electrical neutral condition at the membrane
surface and an electric field is formed to transport the ions
backward.   In a mosaic membrane, anions are permeated through the
anion-exchange parts, cations are permeated through the cation-
exchange parts, and the cations and anions approach to each other to
form a circulating current[2].   The ion transport is facilitated by
this circulating current in a mosaic membrane and the large salt
flux causes the water flux in the same direction, which is called
negative osmosis, while osmosis occurs in a usual membrane and water
is transported across the membrane from the diluted solution to the
concentrated solution.   Salts can be enriched by the permeation
through the mosaic membrane under a pressure gradient to the
contrast of reverse osmosis, where salts are rejected by a membrane.
The salt enrichment by a mosaic membrane is called piezodialysis[3]
and it is more effective than reverse osmosis because the minor
components, salts are enriched in the permeated solution and the
source phase solution is deionized.   Mosaic membranes are also
effective to separate electrolytes from nonelectrolytes[4].

Many charge-mosaic membranes have been developed but there have
been no mosaic membranes with sufficient permeation characteristics
although many years have passed since the first proposition by
Sollner[1].   Weinstein et al. reported a mosaic membrane where a
single layer of alternating cation- and anion-exchange beads were
embedded in an inert silicone rubber film and negative osmosis
through the membrane[2].   Many other methods have been reported to
prepare mosaic membranes but they are not sufficient because it is
very difficult to make a cation-exchange part in the vicinity of an
anion-exchange part and vice versa.   Fujimoto et al., however,
reported recently a very good mosaic membrane prepared from
pentablock co-polymer and it is very effective in both piezodialysis
and the separation between electrolytes and nonelectrolytes[5].

My group also prepared a mosaic membrane and reported the
selective permeability of metal ions but the negative osmosis

through the membrane was very small[6]. In the early work of charge-
mosaic membranes, however, a charge-mosaic membrane system was
constructed with a cation-exchange membrane, an anion-exchange
membrane, three compartments separated by the membranes, and two
probe electrodes and a circulating current was determined in the
cell as a model of a charge-mosaic membrane[7]. Sollner also studied
fundamental characteristics of mosaic membranes with a mosaic
membrane system[8]. Then, the authors began to develop an effective
charge-mosaic membrane system. The system is composed of an anion-
exchange membrane, a cation-exchange membrane, and two solution
compartments separated by the membranes to each other and the
circulating current flows perpendicularly to the membranes[9]. We
call the system a macromosaic cell. The cell is the same as the
electrodialysis cell except that the current is short-circuited by a
salt solution. This cell is very simple but the circulating current
is as high as that of a mosaic membrane. We developed later another
new method called neutralization dialysis on the basis of Donnan
dialysis[10], which needs a pair of ion-exchange membranes and a cell
similar to a macromosaic cell and is a very effective deionization
method[11].

Those methods need not special membranes but commercial ion-
exchange membranes, which are Selemion AMV and CMV (Asahi Glass Co.
Ltd.) in this paper, and are very simple but their efficiencies are
very high. These systems will have many applications. In this
review, the principles and the applications will be demonstrated.

II. MACROMOSAIC CELL

Circulating Current Generation in a Macromosaic Cell

Figure 1 shows the apparatus of macromosaic cell and the scheme
of circulating current generation[9]. The current is short-circuited
by an external salt solution, source phase solution in a beaker, and
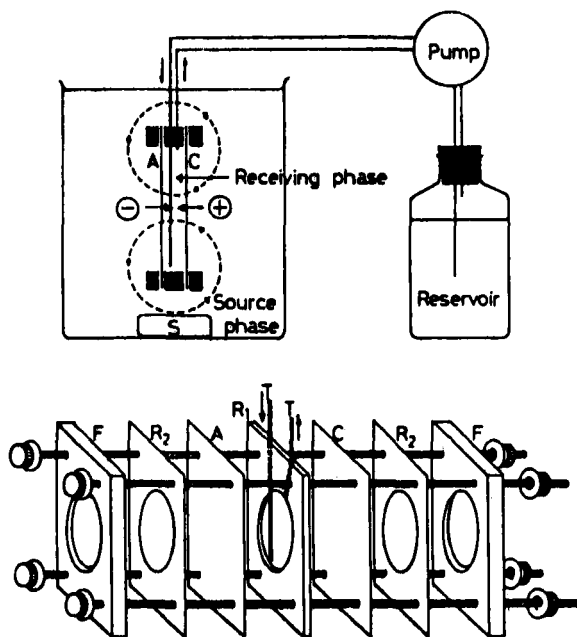cations and anions are permeated across the cation-exchange membrane

FIGURE 1

Macromosaic cell and schematic circulating current (Ref. 9): (---),
schematic circulating current; C, cation-exchange membrane; A,
anion-exchange membrane; ♠, cation; ⊖, anion; S, stirrer chip; T.
Teflon tubing; R_1 and R_2, silicone rubber sheets; F, acrylic resin
frame.

and the anion-exchange membrane, respectively and a circulating
current is generated in this cell. The driving force of the ion
transport is the membrane potential generated by the concentration
difference across a membrane. A thin silicone rubber sheet (3 mm)
with a pore of 38 mm diameter is interposed between a cation- and an
anion-exchange membrane and they are tightened to each other with
acrylic resin frames. This cell is immersed in a salt solution in a
beaker, which is stirred with a stirrer. The receiving phase

solution in the compartment between two membranes is pumped from a
reservoir.

   Ion flux, J_I in this macromosaic cell can be calculated from
the circulating current, I_c which is defined as the sum of the
membrane potentials divided by the sum of the resistance of the
cell, R_t as shown in the following equation.

$$J_I = \frac{I_c}{nF} = \frac{1}{nFR_t} \times \frac{2RT}{nF} \ln \frac{C_s}{C_r} \qquad (1)$$

where F is the Faraday constant, n is the valence of the ion, R is
the gas constant, T is the absolute temperature, C_s and C_r are the
concentration of the source phase solution and that of the receiving
phase solution, respectively. The resistance of each membrane
resistance is between 2.0 and 3.5 ohm·cm^2 and the resistance in the
cell is practically equal to the sum of the solution resistances,
which can be calculated from the molar conductivity, the salt
concentration, and the thickness of the compartment.

Ion Transport in a Macromosaic Cell

   Figure 2 shows the measured values and the calculated curve of
the ion flux in the cell as the function of the receiving phase
concentration, when the concentration of the source phase is
maintained constant. In the low concentration range, the flux
increases with the increase of the concentration because of the
decrease of the resistance of the receiving phase solution. In the
concentration range higher than 0.01 mol/L, however, the flux
decreases with the concentration because of the decrease of the
membrane potential which is the driving force. The ion flux
increases with the decrease of the thickness of the receiving phase
compartment because of the decrease of the solution resistance in
the receiving phase compartment. The figure also show a
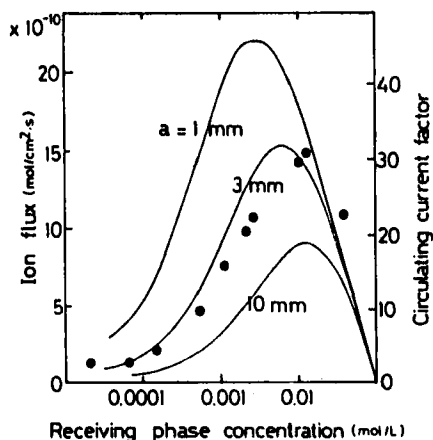circulating-current factor, A which is defined as follows.

FIGURE 2

Effect of receiving-phase concentration on ion flux and circulating current factor in macromosaic cell (Ref. 9): (●), observed value; (——), calculated value; a, thickness of receiving phase compartment; receiving phase, KCl soln.(50 mL); source phase, 0.1 M KCl soln.(1 L).

$$A = J_M / (J_A + J_C) \tag{2}$$

where J_M is the ion flux through a membrane in the cell and J_A and J_C are the salt flux through an anion- and a cation-exchange membrane. The maximum value obtained in this experimental condition is 31 and this value is as high as that obtained by a representative mosaic membrane[2].

The transport efficiency is higher in a multiple mosaic cell than in a single type cell and the deionization is possible in the multiple cell. Figure 3 show the ion transport through the cell when compartment A, B, and C contain the solutions of a same concentration but there are concentration differences between other compartments. The ions in compartment B are permeated to other
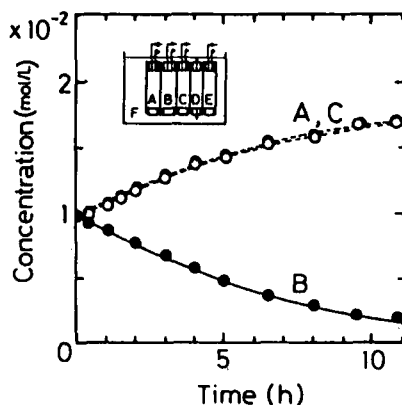
FIGURE 3

Uphill transport of salt in multiple macromosaic cell (Ref. 9):
compartment A, B, and C, 0.01 M KCl soln.(50 mL); compartment D and
F, 0.1 M KCl soln.(1 L); compartment E, 0.01 M KCl soln.(0.5 L).

compartment against the concentration gradient and the solution is
deionized although the initial concentration is the same to those in
the adjacent compartments. The ion flux continues to flow until the
sum of the membrane potential becomes zero as follows.

$$E_{AB} + E_{BC} = - (E_{CD} + E_{DE} + E_{EF} + E_{FA}) \qquad (3)$$

where E_{XY} is the membrane potential between compartment X and
compartment Y. Furthermore, the diffusion flux of nonelectrolytes
such as sucrose is very low and it is possible to separate
nonelectrolytes from electrolytes in the cell.

III. NEUTRALIZATION DIALYSIS

Principle of Neutralization Dialysis

Neutralization dialysis[11] is developed recently from a
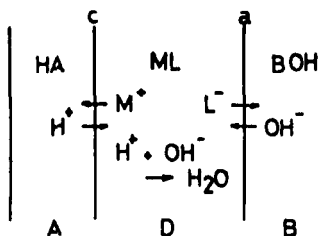macromosaic cell. Its principle is based on Donnan dialysis[10] and

FIGURE 4

Schematic ion transport in neutralization dialysis (Ref. 11): a,
anion-exchange membrane; c, cation-exchange membrane; A, acid
solution compartment; D, deionization compartment; B, base solution
compartment.

the deionization scheme is shown in Figure 4. The salt solution in
the deionization compartment is separated from an acid solution and
a base solution by a cation-exchange membrane and an anion-exchange
membrane, respectively. The cations are exchanged with proton and
the anions are exchanged with hydroxide ion across each membrane.
The proton reacts with the hydroxide ion to yield water molecule
just after their permeations to the deionization compartment and the
deionization and the neutralization occur simultaneously in the
compartment. In this method, the large concentration differences of
proton and hydroxide ion caused by the neutralization reaction are
the driving force of the ion transport and as a consequence this
method is called as neutralization dialysis. The cell of this
method resembles to a macromosaic cell except that the cell involves
three compartments. A dual membrane tube method proposed by
Dasgupta et al. was also effective for deionization although it was
developed for the membrane suppressors for ion chromatography[12]. An
ion-exchange membrane tube was inserted inside another ion-exchange
membrane tube and a salt solution was deionized between the tubes on
the same basis when an anion-exchange membrane tube was inserted
inside a cation-exchange membrane tube.

Deionization by Neutralization Dialysis

The deionization of univalent ions by neutralization dialysis can be explained quantitatively by the concept of Donnan equilibrium across a membrane[10].

$$\frac{[M^+]_A}{[M^+]_D} = \frac{[H^+]_A}{[H^+]_D} \qquad (4)$$

$$\frac{[L^-]_B}{[L^-]_D} = \frac{[OH^-]_B}{[OH^+]_D} \qquad (5)$$

where D, A, and B show deionization compartment, acid solution compartment, and base solution compartment, respectively. The equilibrated concentration of metal ions in the deionization compartment can be calculated from both these equations and the material balance as follows.

$$[M^+]_D = \frac{C_0 V_D}{[H^+]_A/[H^+]_D \times V_A + V_D} \qquad (6)$$

where the initial concentration and the volume of the salt solution are C_0 and V, respectively and the volume and the initial concentration of the acid solution is assumed to be equal to those of the base solution. If the flux of proton is equal to that of hydroxide ion, the concentration of proton in deionization compartment approaches to 10^{-7} mol/L and the equilibrated salt concentration in the deionization compartment becomes very small. In the actual cell, however, the proton flux is not the same as the flux of hydroxide ion and the leak of co-ion through ion-exchange membranes is not negligible.

Figure 5 show the result of deionization. A pure water with 1 Mohm·cm specific resistance could be attained in 1 hour. The
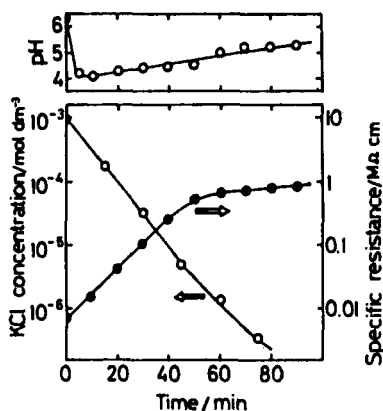
FIGURE 5

Deionization by neutralization dialysis (Ref. 11): compartment A,
0.01 M H_2SO_4(1 L); compartment B, 0.01 M $Ca(OH)_2$(1 L); compartment
D, 0.001 M KCl(75 mL); membrane area, 2 x 10 cm^2.

membrane in the cell was rectangular and the thickness of the
compartment was 0.5 mm in this experiment. The deionization speed
can be expressed by the flux of an univalent cation, J_M as follows.

$$J_M = C_{ex}P[\frac{1}{1 + C_D^H/KC_D^M} - \frac{1}{1 + C_A^H/KC_A^M}] \qquad (7)$$

where C_{ex} is the ion exchange capacity, P is the membrane
permeability, K is the selective ion exchange factor of a metal ion
to proton, C is an ion concentration, and H and M are proton and
metal ion, respectively. It is obvious from this equation that
deionization flux decreased with the increase of the salt
concentration in the acid and the base solutions but the up-hill
transport is possible. The solution pH was shifted to be low in
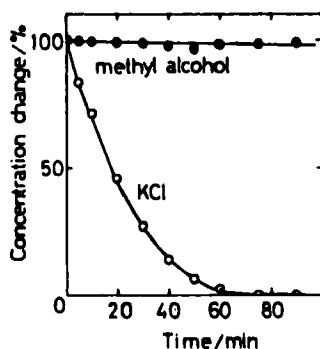deionization compartment because the proton flux was higher than the

FIGURE 6

Separation of potassium chloride from methyl alcohol (Ref. 11): compartment A, 0.01 M H_2SO_4(1 L); compartment B, 0.01 M $Ca(OH)_2$(1 L); compartment D, 0.1 M methyl alcohol + 0.01 M KCl aq. soln.(100 mL); membrane area, 2 x 10 cm^2.

hydroxide ion flux and it is one of the causes of the low specific resistance of the pure water attained by this method. The difference between fluxes of the proton and hydroxide ion was small in the multiple cell of neutralization dialysis[13].

An ion-exchange process with ion-exchange resins is very important in the preparation of a pure or a super pure water. Ion-exchange resins need, however, intermittent regeneration and the contamination occurs in the regeneration process. Neutralization dialysis is a continuous deionization process and is free from the contamination in the regeneration process because the regeneration process is equal to the deionization process in this method.

Figure 6 shows the separation of nonelectrolytes from electrolytes in the mixed aqueous solution of potassium chloride and methanol. The separation is very effective and this method can be used in the place of dialysis with a dialysis membrane.
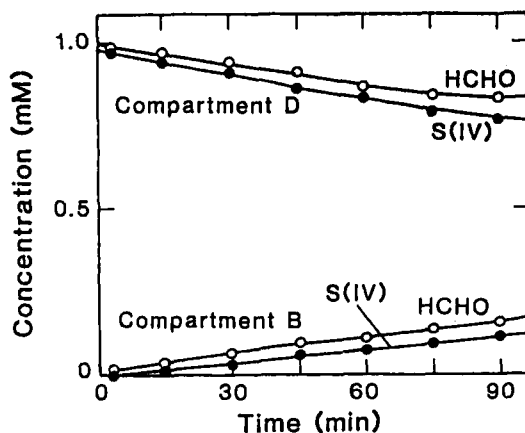
FIGURE 7

Formaldehyde and S(IV) transport through anion-exchange membrane: o,
HCHO; ●, S(IV); compartment B, 0.001 M NaOH; compartment A, 0.001 M
HCl; compartment D, 0.001 M HCHO, 0.001 M NaHSO$_3$, and 0.0001 M HCl;
membrane area, 7.7 cm^2.

Active Transport of Formaldehyde through an Anion-Exchange Membrane
via the Formation of Bisulfite Adduct

Neutralization will be useful in many fields. There have been
many papers reported on the up-hill and selective transport of
inorganic ions and amino acids with the coupled counter-transport of
proton or hydroxide ion across a liquid membrane[14,15]. The solution
pH changes in the system and the efficiency decreases with time for
the pH change. If hydroxide ion or proton is supplied through
another ion-exchange membrane in a neutralization dialysis cell, the
pH change decreases and the high efficiency continues for a long
time. Recently, the authors reported a new application of this
method for a facilitated transport of nonelectrolytes across an ion-
exchange membrane[16].

There are many reports on a facilitated and selective transport of ions through an artificial membrane[14,15] but there are only a few reports of the selective and active transport of nonelectrolytes through an artificial membrane, such as the transports of sugars through polyvinyl-polypeptide membrane[17] or hydrophobic solutes through hydrophobic membranes[18]. Formaldehyde, which is one of very important species in environment, reacts with bisulfite ion to form an adduct, hydroxymethane sulfonic acid ion, which is a conjugate base of a strong acid[19]. As a consequence formaldehyde can be transported rapidly across an anion-exchange membrane as anions with the coupled counter-transport of hydroxide ion. The stability of the anion depends strongly on pH and the ion is dissociated in an alkaline solution[19]. The solution pH is constant in the neutralization dialysis cell and the flux can be maintained constant, too. Figure 7 show the transport of formaldehyde with bisulfite ion coupled with the counter-transport of hydroxide ion. The transport of formaldehyde could not be detected in the absence of bisulfite in the formaldehyde solution. Hydroxymethane sulfonic acid is dissociated to be formaldehyde and sulfite ion in the base solution and the flux of formaldehyde is higher than that of bisulfite. Bisulfite ion is exchanged with the ion in the membrane and is transported with the coupled counter-transport of hydroxide ion while formaldehyde reacts with bisulfite ion in the membrane and is transported by hopping from one bisulfite ion to the other under its concentration gradient. There are many reactions between electrolytes and organic nonelectrolytes to form electrolytes[20] and this transport mechanism may be an important role in biomembranes.

CONCLUSION

Charge-mosaic membrane system composed of a pair or pairs of an anion-exchange membrane and a cation-exchange membrane is very simple and easy to be constructed and there will be many applications of it other than those described above.

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