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Separation Science and Technology

Publication details, including instructions for authors and subscription information:
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Online publication date: 04 January 2003

To cite this Article Yu, Zhiqiang and Admassu, Wudneh(2003) 'Critical Change in Apparent Conductance and Ion Exchange Limit in Membrane Electrodialysis', Separation Science and Technology, 38: 7, 1561 — 1583

To link to this Article: DOI: 10.1081/SS-120019093

URL: http://dx.doi.org/10.1081/SS-120019093

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SEPARATION SCIENCE AND TECHNOLOGY
Vol. 38, No. 7, pp. 1561–1583, 2003

Critical Change in Apparent Conductance and Ion Exchange Limit in Membrane Electrodialysis

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ABSTRACT

As the rates of ion transport in membrane and electrolytic solution become comparable in membrane electrodialysis, the separation efficiency may be limited by the capability of ion exchange of the membrane. An experimental study of current vs. voltage characteristics of dilute electrolytic solutions (KCl, NaCl, and LiCl) was carried out by a laboratory scale membrane electrodialysis unit to show this phenomenon. The observed current vs. voltage characteristics show that in a low electrical field ($0 \leq E \leq 100$ volt/m), there is a critical change in the apparent conductance of the system with the increased initial ion concentration. This critical phenomenon suggests that in a low electrical field the ion transport is limited by the rate of ion exchange within the membrane. The sequence of these critical phenomena for the solutions of KCl, NaCl, and LiCl indicates that the ion exchange limit may be related to the ion's size as well.

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DOI: 10.1081/SS-120019093 0149-6395 (Print); 1520-5754 (Online)

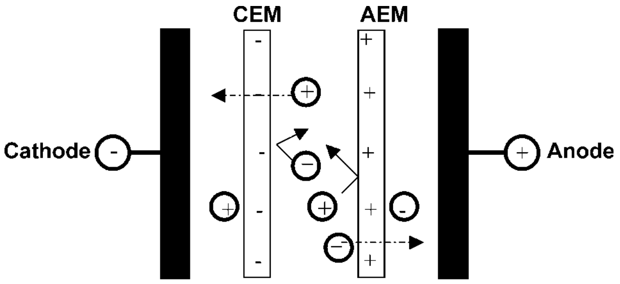
www.dekker.com

Key Words: Membrane electrodialysis; Apparent conductance; Ion exchange limit; Limiting current density.

INTRODUCTION

Membrane Electrodialysis

Currently, to reduce the corrosion in recovery boiler and therefore avoid the frequent pulp and paper mill system closure, the removal of K^+, Na^+, and Cl^- from the recycling process stream becomes critical. The traditional removal technologies include precipitation[1–5] electrochemical metal recovery[6] solvent extraction[7] and ion exchange.[8,9] Compared with these technologies, the membrane electrodialysis (MED) process can also be used as a second stage treatment for the pulp and paper mill to effectively remove K^+, Na^+, and Cl^- from the recycling process stream. In general, the advantages of using MED process to remove ions from the recycling process stream are[10–12]: (1) the controllable selectivity by membrane and electric potential variations; (2) the high removal efficiency; (3) no chemical addition required both in separation process and membrane cleanup operation, for example, the problem of membrane fouling could be treated by reversing the applied electric potential to recover the ions; and (4) the compactness, and also easily can be operated.



CEM: Cation-exchange Membrane

AEM: Anion-exchange Membrane

Figure 1. Schematic diagram of MED.

MED normally consists of anion exchange membrane and cation exchange membranes arranged alternately in parallel between an anode and a cathode. Instead of a single pair of membranes as shown in Fig. 1, usually there will be hundreds of such pairs of membranes in the actual process MED unit to raise the separation efficiency. In the electric field, as a consequence of the driving force (the external electric field or electric potential difference), anions (Cl^-) in a solution permeate through the anion-transfer membrane and cations (K^+ and Na^+) permeate through the cation ion membranes, resulting in concentration and dilution in adjoining compartments. As a second stage treatment, MED operation unit with a Venturi scrubber in a Kraft recovery boiler system is shown in Fig. 2. The concentrated dust from the electrostatic precipitator passes through a Venturi scrubber that contains K^+, Na^+, and Cl^- in the rinsing stream that will be sent to the MED process. The dilute stream from MED is recycled back to the Venturi scrubber as a rinsing stream. The concentrate from MED unit could be sent to another MED for further

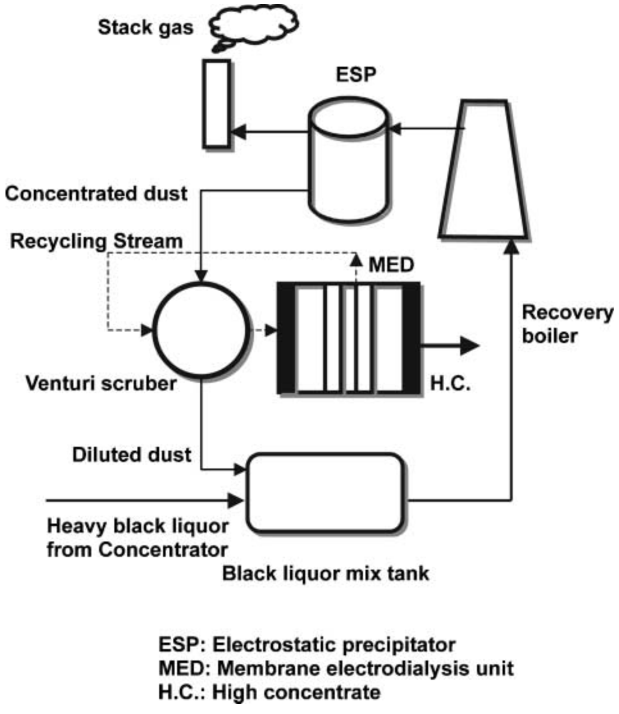


Figure 2. The position of MED in the pulp and paper recovery boiler system.

processing or recycled back for further concentration. The highly concentrated electrode rinse streams then could be sent to incineration or other operations before they reach saturation points. Because the washing stream of ESP usually contains Na^+, K^+, Cl^-, SO_4^{2-}, and CO_3^{2-}, which are soluble in water, the membrane-fouling problem here can have much less concern than in other applications.

Ion Exchange Membrane

Ion exchange membrane is a key component in the MED process. Conventionally, the ion exchange technology combines the processes of adsorption and desorption. In the adsorption process, the ion-exchange resin usually are held in a fixed bed and the concentrated solution is passed continuously through the bed by which the target ions are adsorbed by the ion-exchange resin until the ion-exchange resin is nearly saturated and the separation can no longer be achieved. In the desorption process, the saturated ion-exchange resin is switched to a second solution to release the ions previously adsorbed until the saturated resin can be regenerated. But, in the MED process, there are no such steps of material “switching” for the ion-exchange membrane as the conventional ion exchange resin does. The ion-exchange membrane works as a screen or a charged network providing the selectivity of ion permeability because of its charge preference.

Modern ion-exchange membranes typically consist of cross-linked vinyl polymers with charged groups chemically bonded to the polymer. For example, the cation exchange membranes typically consist of cross-linked vinyl polymers having negatively charged sulfonate groups bonded to the polymer network.[13] The negative charges of the sulfonate groups are electrically balanced by positively charged cations (known as counter-ions). These counter-ions are appreciably dissociated from the bound (negatively charged sulfonate) groups into water absorbed by the membrane and are mobile in solution. The high concentration of counter-ions in the sheet-form ion-exchange membrane results in low electrical resistance. The high concentration of bound (negatively charged sulfonate) groups tends to exclude negatively charged ions from solution in contact with membrane and is responsible for its high ion selectivity. Similarly, anion exchanged membranes generally have positive-charged quaternary ammonium groups chemically bonded to the polymer.[13] In this case, the counter-ions are negatively charged and are principal carriers of electrical current.

The ion-exchange membrane used in MED is known as nonporous membrane because its pore size is comparable to the molecular size. Usually, the pore size of ion-exchange membrane used for MED is about 10 to 100 Å.[14] These pores form connections of numerous tortuous tunnels in which the ions migrate. In the low electric field, the rigid body model usually is valid for ions migrating inside the membrane (which assumes ion deformation is negligible).[15] The cations, such as Li^+, Na^+, and K^+, have radii much smaller than the dimensions of the tortuous tunnels inside the membrane. If the interaction between the ions is negligible compared with the interaction between ion and the polymer structure of the membrane, the ion transport inside the so-called ion exchange membrane actually is the ion migration under the local effective electric field. As shown in Fig. 3, inside a cation exchange membrane the cations migrate under the driving force from the local effective electric field, which is a superposition of the external electric field, the electric field created by the surrounding charged groups bonded in polymer structure, and the surrounding ions in migration.

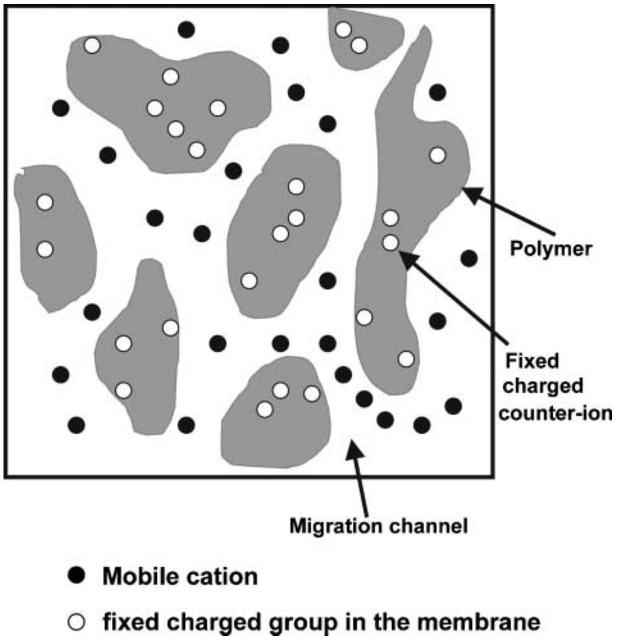


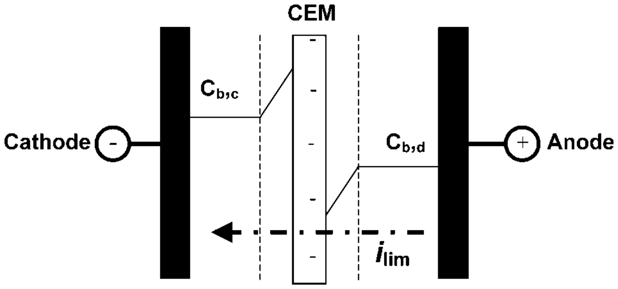
Figure 3. Ion transport inside a cation exchange membrane.

Current vs. Voltage Characteristics of the System

Many researchers have focused on the distributions of ion concentration and/or electrical potential in the membrane-electrolyte system.[15–20] Because of either external electrical field or electrical potential difference, the transport of ions forms certain concentration and electrical potential distributions in the interfaces between the membrane and electrolyte solution. These distributions determine the removal efficiency and process limits. One important concept in these processes is the limiting current density i_{lim}, which is defined as the current density at which the ion concentration tends to zero at the membrane surface in the dialysate channel. As shown in Fig. 4, i_{lim} is the maximum current that could pass through a given membrane area without creating adverse effects (i.e., higher electrical resistance, large change of pH value, and lower current utilization). An analytical expression of i_{lim} can be obtained using the continuity of flux in the boundary layer at the membrane surface and in the membrane[21]:

$$\mathrm{i}_{\mathrm{lim}} = \frac{\mathrm{DF}}{\delta}\frac{\mathrm{C}_{\mathrm{B}}^{+}}{(\mathrm{t}_{\mathrm{m}}^{+} - \mathrm{t}_{\mathrm{s}}^{+})}, \tag{1}$$

where, $\mathrm{C}_{\mathrm{B}}^{+} = \mathrm{C}^{+}|_{x=\delta}$ is the bulk concentration of cation in the dialysate channel; δ is the thickness of the boundary layer; D is the diffusion coefficient and F is the Faraday constant; t is the transport number and the subscripts m and s refer to membrane and electrolyte solution. Eq. (1) provides an estimation of the limiting current density, which depends on the bulk concentration of ion C_{B}^{+} and thickness of boundary layer.



$C_{b,c}$: Bulk concentration in concentrate
$C_{b,d}$: Bulk concentration in dialyte
i_{lim} : Limiting current density

Figure 4. Ion concentration distribution in MED unit.

However, the concept of i_{lim} is derived under the hypothetical condition that the ion exchange membrane has an infinite capability rate of ion transport inside the membrane. This means ions in the electrolytic solution reaching the membrane surface can immediately enter the membrane and pass through the network by ion exchange without any limitation. In realty, this will not be always true. There will be times when the rate of ion exchange in the membrane becomes the limiting step and impedes ion migration in the electrolytic solution. A question that naturally arises is what happens when the rate of ion transport in ion exchange membrane becomes comparable to that in aqueous electrolytic solution?

Based upon research by Gnusin,[22] under some conditions the limiting current density actually would not be measurable because the zero concentration of ions at the membrane-solution interface was practically and theoretically unreachable or the diffusion layers at membrane surface did not exist.

So it is necessary to estimate the rates of ion transport in membrane and in electrolytic solution theoretically and measure it experimentally. In a given electric field, the electric current is a measure of ion migration. Because the magnitude of the electrical current directly relates to the rate of ion transport in the electrolyte solution and ion exchange membrane, the measurement of current vs. voltage characteristics will help to determine the rates of ion transport in different regions. Usually, the current vs. voltage characteristics show a linear relationship. The ratio of current vs. voltage is known as the electrical conductance and plays an important role in the ionic separation process. The electrical conductance is not only depends on the ion concentration, but also depends on the rate of ion transport. Generally, it is difficult to measure individual conductance for ion transport in the electrolytic solution and in the ion exchange membrane separately. Therefore, an apparent conductance σ as given by the gradient of the plot of I–V curve can be used to describe the combined system. In the constant electric field, the change of electric current, and then apparent conductance, will represent the change of the rate of ion transport.

In this article, the measurement of current vs. voltage characteristics of dilute electrolytic solutions (KCl, NaCl, and LiCl) was carried out in a laboratory scale MED unit. The observed experimental results show that there is a critical change in the apparent conductance for all these systems. These critical phenomena suggest that in a low electrical field, the separation efficiency is limited by the rate of ion exchange within the membrane. The ion exchange limit can be described by the ion accumulation inside the membrane near the membrane surface. The sequence of these critical phenomena for the solutions of KCl, NaCl, and LiCl indicates that the ion exchange limit may be related to the ion's size as well.

EXPERIMENTAL

The experimental set up of a laboratory scale unit for membrane electrodialysis process is shown in Fig. 5.

The MED tank was made of Plexiglass and consisted of three channels: two concentrate channels at each side and one dilute channel at middle. In the concentrate channel the electrodes were set in and filled with deionized water (DIW), whereas the dilute channel was filled with a known concentration of KCl, or NaCl, or LiCl solution. As shown in Fig. 5, these three channels were

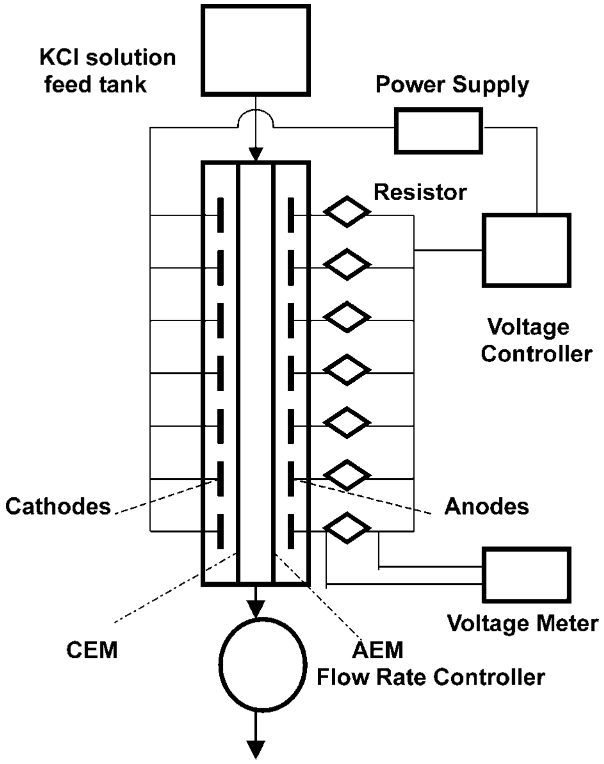


Figure 5. Experimental set-up of the MED unit.

separated by two ion exchange membranes: one cation exchange membrane close to the cathode and one anion exchange membrane close to the anode. The cation exchange membrane and anion exchange membrane are the products of IONICS Company at Watertown, Mass. The cation exchange membrane (TYPE CR 67 HMR-412) is made of acrylic based resin; the anion exchange membrane (TYPE 204-SZRA-412) is made of styrene divinylbenzene based resin. The dimensions of cation exchange membrane and anion exchange membrane were $10 \times 18 \times 0.05$ cm. The space between cation exchange membrane and anion exchange membrane was 1 cm. The electrodes consisted of seven pairs, of which the anodes were made of copper and the cathodes were made of gold plated copper plates. The space between anodes and cathodes was 10 cm. The voltages on these pairs of electrodes were controlled by a power supply and voltage controller that provided a constant electrical potential difference. A voltage meter was used to monitor the voltage drop on the resistor in the circuit of each pair of electrodes, and then the related electrical current density could be calculated. In the case of static batch (flow rate of electrolytic solution = 0), all cathodes and anodes were

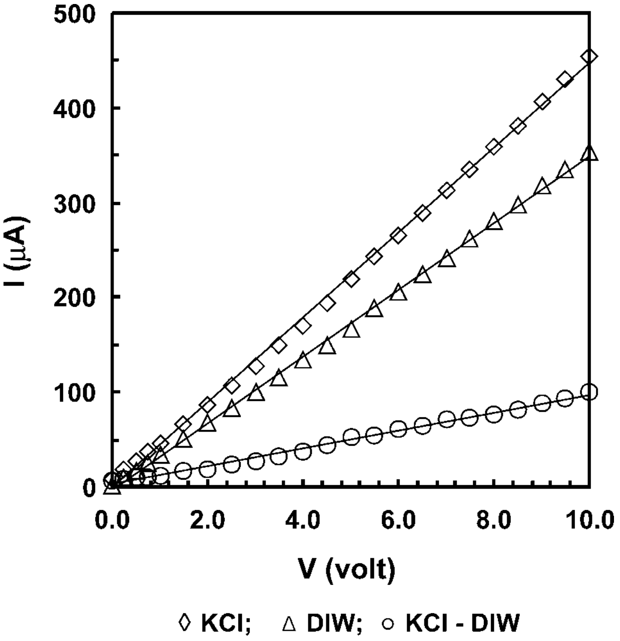


Figure 6. I–V curves for KCl solution at 300 ppm.

connected into a single pair of electrodes. Therefore, the measured electrical current is an average value. The dilute, flowing out of MED tank, went to a collecting tank from which samples were drawn. The electrical potential difference across the electrode was between 0 and 10 volts, so that the electrical field strength was in the region $0 \leq E \leq 100$ volt/m.

In the electrical field, the contributions to the electrical current included the movements of H^+, OH^-, K^+, Na^+, Li^+, and Cl^-. So, to limit the influence of H^+ and OH^-, I–V curve was generated by filling the three channels with DIW. These data were taken and were deducted from the I–V curve measured with various ion concentration of KCl, NaCl, and LiCl to limit the contribution of H^+ and OH^-. Figure 6 shows the difference between the I–V characteristics of KCl solution of 300 ppm and that of DIW. Figures 7 and 8 show the I–V characteristics of KCl, NaCl, and LiCl solution of 300 ppm and 1000 ppm, respectively. The I–V characteristics of KCl solution at various concentrations and external electrical potential differences are shown in Fig. 9. Similar behaviors were observed for NaCl and LiCl solutions.

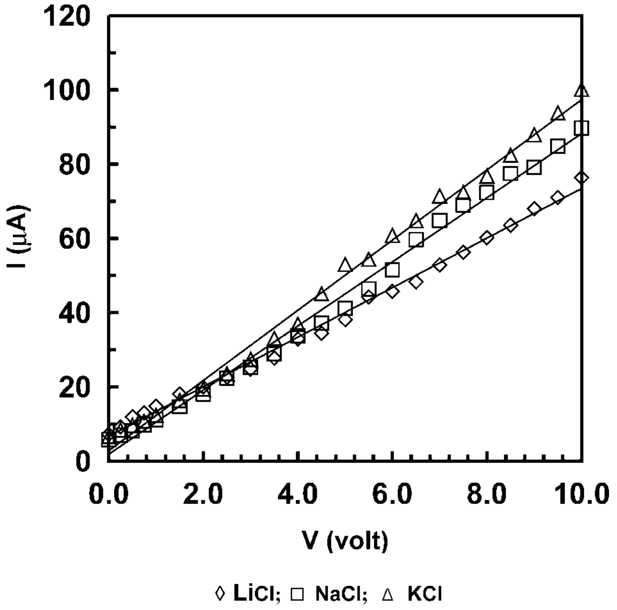


Figure 7. I–V curves for KCl, NaCl, and LiCl solutions at 300 ppm.

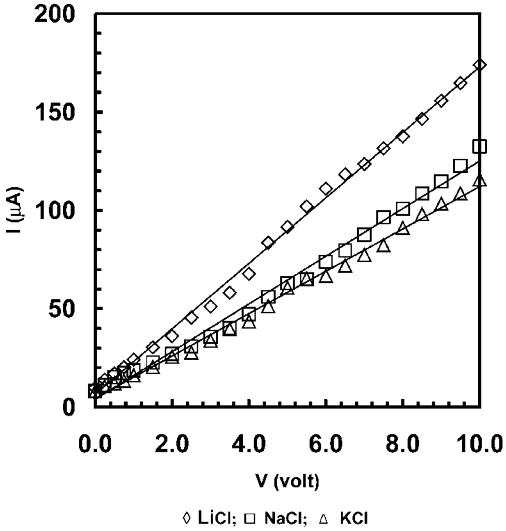


Figure 8. I–V curves for KCl, NaCl, and LiCl solutions at 1000 ppm.

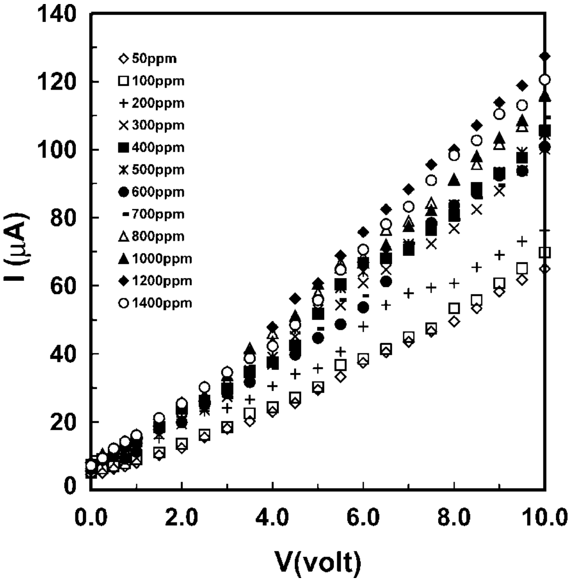


Figure 9. I–V curves at various concentrations of KCl solution.

DISCUSSION

As shown in Fig. 6, a linear I–V curve of KCl solution of 300 ppm indicates that the rate of ion transport increases proportionally with external electrical potential difference. Similar linear behavior of I–V curve of DIW exists in the same region. But these two systems have different gradients. The difference between these two curves represent the contribution that can be attributed to the transport of $K^+$and Cl^- and also show a linear relationship.

Figure 7 shows the I–V characteristics of KCl, NaCl, and LiCl solution at initial concentration of 300 ppm. Figure 8 shows the I–V characteristics of KCl, NaCl, and LiCl solution at a initial concentration of 1000 ppm. At the low initial concentration (300 ppm), the measured data of current show that the rate of ion transport of KCl is the highest, and that of LiCl is the lowest; that is, $I_K > I_{Na} > I_{Li,}$ respectively. However, at the high concentration (1000 ppm), the order of measured current is reversed (i.e., $I_K < I_{Na} < I_{Li}$). This indicates that there is a critical point in the I–V curves that relates to the rate of ion transport in these systems when operating at the low electric field ($0 \leq E \leq 100$ volt/m).

Figure 9 shows that different initial concentration of KCl solution have similar linear relationship profile of I–V curves in the low electrical field region. These indicate that in all these regions the rate of ion transport increases proportionally with the increase of the external driving force (i.e., the external potential difference). However, with the increasing initial concentration, it is observed that a critical point has been reached where the gradient in the I–V curves switches from a higher value to a lower value. The gradient in the I–V curve, or the ratio of current vs. voltage is known as the electrical conductance that plays an important role in the ionic separation process. Because the electrical conductance not only depends on the ion concentration, but also depends on the rate of ion transport, experimentally it is difficult to measure individual conductance for the electrolytic solution and the ion exchange membrane. So, an apparent conductance σ (10^{-6} ohm^{-1}) as given by the gradient of the plot of I–V curve is used to describe the combined system. All of the gradients of the I–V curves shown in Fig. 9 are plotted in Fig. 10 to show the variation of apparent conductance σ of the system. As shown in Fig. 10, for the KCl solution there is a critical point in σ at around an initial concentration $C_{0,C} = 350$ ppm. When $C_{0,C} < 350$ ppm, σ increases significantly with the increasing initial concentration. The slope of this portion of the data is $s_1 = 0.0131$ (10^{-6}/ohm/ppm). However, when $C_{0,C} > 350$ ppm, the slope of this portion of the data is $s_2 = 0.0022$(10^{-6}/ohm/ppm). The ratio of slopes of these two parts in Fig. 10 is 6:1. Such a decline in the observed slope indicates

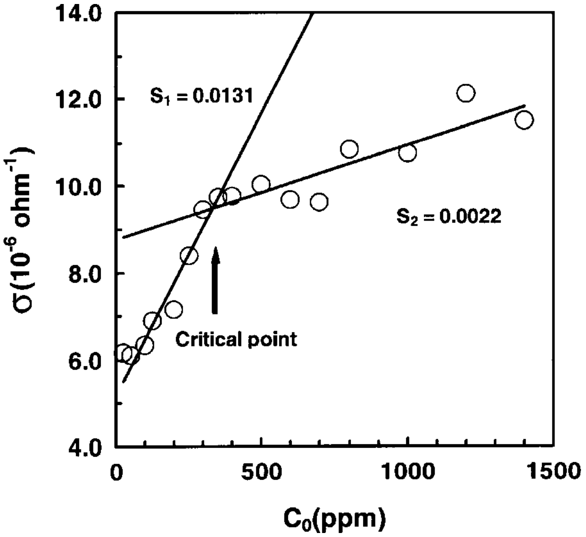


Figure 10. Apparent conductance vs. initial concentration of KCl solution.

a significant change in the rate of ion transport as a function of electrical current. This indicates that there is a critical point in the initial concentration, after which the MED separation process becomes membrane ion-exchange–limited. That is, the rate of ion exchange in membrane reaches a maximum and does not increase significantly because of the increase of ion concentration in the solution.

These behaviors are also clearly observed when the solutions of NaCl and LiCl were used. The apparent conductances for these two solutions are shown in Figs. 11 and 12.

From Fig. 11, one can observe that a critical change in the apparent conductance for NaCl solution happens at $C_{0,C} = 600$ ppm. The slope of the data of apparent conductance below $C_{0,C} = 600$ is $s_1 = 0.0073$ (10^{-6} /ohm/ppm), and above $C_{0,C} = 600$ is $s_2 = 0.0013$ (10^{-6}/ohm/ppm). The ratio of slopes of these two parts is 5.6. Similarly, from Fig. 12, such a critical change in the apparent conductance for LiCl solution occurs at $C_{0,C} = 700$ ppm. The slope of the data of apparent conductance below $C_{0,C} = 700$ is $s_1 = 0.0179$ (10^{-6}/ohm/ppm), and above $C_{0,C} = 700$ is $s_2 = 0.0055$(10^{-6}/ohm/ppm). The ratio of these slopes is 3.3. Table 1 shows a summary of these variations with ion characteristics for Li^+, Na^+, and K^+.

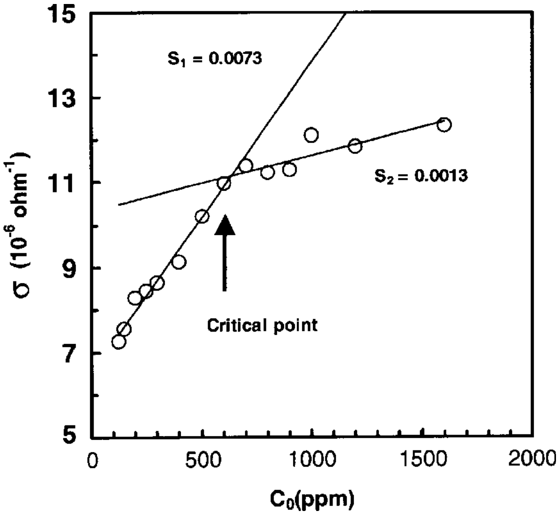


Figure 11. Apparent conductance vs. initial concentration of NaCl solution.

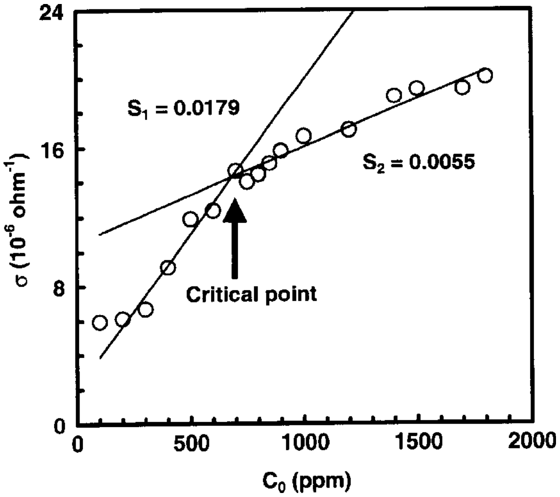


Figure 12. Apparent conductance vs. initial concentration of LiCl solution.

Table 1. Critical values for $C_{0,C}$, σ, and S_1/S_2.

Ion	Ion size, r (Å)	$C_{0,C}$(ppm)	σ (10^{-6} ohm^{-1})	S_1/S_2
Li^+	0.60	700	14.641	6.0
Na^+	0.95	600	10.980	5.6
K^+	1.33	350	9.762	3.3
Cl^-	1.81	—	—	—

From Table 1 the following observation has been made:

1. The critical point for three cations occur at different initial concentrations. For example, for Li^+, $C_{0,C} = 700$ ppm; for Na^+, $C_{0,C} = 600$ ppm; and for K^+, $C_{0,C} = 350$ ppm. The sequence at which these critical points occur is consistent with the reverse order of ion size, that is, $r_{Li} < r_{Na} < r_K$. This indicates that for a given membrane the small ion has a high value of initial concentration for critical transition point, whereas the large ion has a low value of initial concentration for critical transition point.
2. The point of such critical change in the apparent conductance divides all data into two parts: below the critical point, the apparent conductance increases at a higher rate with initial concentration; above the critical point, the apparent conductance increases at a lower rate with initial concentration. Also, at the critical points one can observe that $\sigma_{c,Li} > \sigma_{c,Na} > \sigma_{c,K}$.

These phenomena indicate that there is ion exchange limit inside the membrane. The concept of ion exchange limit inside the membrane can be described both macroscopically and microscopically. As shown in Figs. 1 and 3, the ion transport in the MED process occurs in three different regions: membrane network, bulk solution, and the interface between membrane and solution, that is, the boundary layer. In bulk concentration region, the ion transport is due to the migration under the external electrical field. In the boundary layer, both migration and diffusion determine the ion transport. However, in the membrane, because of the nature of porous structure with charged background, the migrations of ions are determined by the local effective electrical field. Because the continuity of electrical current should hold in these different regions, the magnitude of the electrical current is a direct measure of the rate of ion transport in these three regions. Two facts will determine the electrical current in these regions: the local effective electrical field and the number of ions involved in the transport. The local effective electrical field in the bulk solution is approximately equal to the external electrical field for a very dilute aqueous solution. In the boundary layer, one needs to consider the influence of ion concentration distribution. In the membrane, it will be more complicated because of the existence of charged network and porous structure. Therefore, a point-by-point calculation becomes difficult. The influence from the number of ions involved in transport is determined by the ion concentration in the boundary layer, and therefore by the initial concentration.

In Fig. 9, the linear relations in I–V curves shows that under a constant initial concentration and within a certain time period, there is a steady state of ion concentration in the boundary layer, that is, the amount of ions flowing into the membrane are equal to that flowing from the bulk solution. When the external driving force increases (i.e., the external electrical potential difference increases), the rate of ion transport proportionally increases. Therefore, the electrical current increases with the potential difference. In a low electrical field ($0 < E < 100$ volt/m), the experimental data show that there is no evidence of the decrease of the electrical current when the potential difference increases. This indicates that there is no significant depletion of ion concentration in the boundary layer. When the general method of estimating limiting current density was used[19] the data show there is no trend indicating the existence of limiting current density at this low electric field.

However, as the initial concentration increases, the ion concentration in the boundary layer becomes high with the increase of initial bulk concentration. At this time, if the external electrical field is kept the same, the local effective electrical field inside the membrane will not change, and an individual migrating ion will have the same mobility as before. Because the capability of ion exchange in the membrane is not infinity, the rate of ion exchange will not proportionally follow the increasing of ion concentration in the boundary layer. Therefore, in a macroscopic view, the increasing of the apparent conductance of the system σ vs. initial concentration will be different after the critical point, as shown in Fig. 10.

In the electric field, the ion exchange membrane has a certain capability of ion transport. As pointed out previously, such capability is determined by the membrane structure, charged background, and the external electric field. In a constant external electric field, the rate of ion transport inside the membrane is also constant, that is, the maximum number of ions that can migrate through the membrane will be a fixed value. At the low ion concentration, the amount of ions entering the membrane is less than this maximum value, so that the rate of ion transport will increase with the ion concentration in the boundary layer, and then the bulk concentration, and then the initial concentration. However, as the initial concentration approaches to a point at which there are more ions entering the membrane from the boundary layer than the maximum capability of the membrane for ion transport, some ions become crowded in the vicinity of the membrane surface, inside rather than outside. Then, a concentration distribution build up will occur in this area that would decline the rate of ion transport. Therefore, there is a critical change in the apparent conductance of the system. Figure 13 shows a schematic description of a microscopic view of this critical change in the system. For simplification, Fig. 13 shows a single

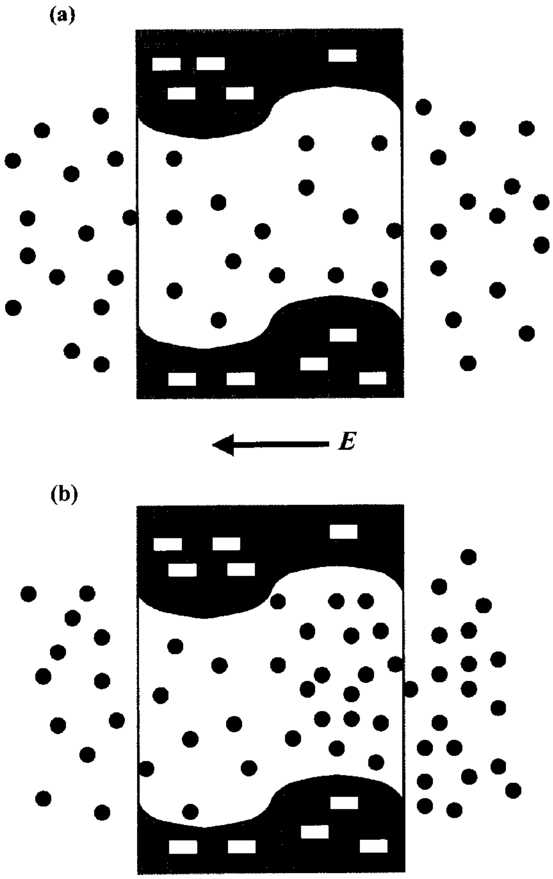


Figure 13. Schematic illustration of cation concentration inside the cation exchange membrane. (a) Low C_0, (b) High C_0.

tortuous channel that crosses the membrane for ion migration. Figure 13(a) shows that at the low ion concentration there is no ion accumulation inside the membrane. Figure 13(b) shows that when the number of ions entering the membrane is over the maximum transport capability, some ions begin to crowd at the entrance, and a concentration distribution near the membrane surface will occur. This kind of ion accumulation will cause two effects on the rate of ion transport. First, this ion accumulation in the vicinity of membrane surface will reduce the depth of the electric potential well inside the membrane near the surface area and then will retard the ions outside the membrane to enter the membrane. Second, because of this concentration gradient, there will be some contributions added to the rate of ion transport from the ion diffusion. Therefore, as a combined result, this ion accumulation inside the membrane near the membrane surface will cause a critical change in the increase of apparent conductance with the initial concentration. Because this change causes extra energy dissipation, the resulting change in the rate of ion transport should be to decrease rather than to increase. That's why after the critical point, the increase of the apparent conductance of the system vs. the initial concentration becomes slow. At the same time, the ion size will definitely affect the degree of ion accumulation inside the membrane. Because the same migration channel inside the membrane will allow more small ions than large ions to migrate before reaching the ion exchange limit, as shown in Figs. 10–12, there is an order of the critical change in the apparent conductance (i.e., for Li^+, $C_{0,C} = 700$ ppm; for Na^+, $C_{0,C} = 600$ ppm; and for K^+, $C_{0,C} = 350$ ppm). Also, the values of the apparent conductance at these critical points follow the order of $\sigma_{c,Li} > \sigma_{c,Na} > \sigma_{c,K}$, as shown in Table 1. Qualitatively this shows that in ion exchange membrane, the ion exchange limit allows more ions with small size to contribute to the electric current than ions with large size. In Table 1, one can observe that the ratio of the critical points of initial concentration of 700 ppm (Li^+): 600 ppm (Na^+): 350 ppm (K^+) has a similar trend to that of the apparent conductances at these points (i.e., 14.641(Li^+): 10.980 (Na^+): 9.762 (K^+)). But when the ratio of 700 ppm (Li^+): 600 ppm (Na^+): 350 ppm (K^+) is compared with the ratio of ion size, 0.60 Å (Li^+): 0.95 Å (Na^+): 1.33 Å (K^+), the trend is reversed, giving credence to the assumption that small size ions contribute more to the electric current via high ion concentration in the membrane. In addition, there could be interaction between ions themselves and interaction between ions and membrane that could contribute to the overall ion transport, which was assumed to be negligible in the analysis that was made in this article. A theoretical investigation by Mokrani et al.[23] shows that during ion transport through ion exchange membrane, the membrane resistance becomes important as concentration increases. They found that the crossover from diffusion boundary layer control to membrane control to be at a concentrations of 0.01 to 0.1 M. This is consistent with the observation made in the current study.

Figure 14 shows the electrical current vs. initial concentration under varied electrical potential difference for the system of KCl solution. The experimental data were recalculated using the critical values of C_0 and the related data of electrical currents as scaling factors, as listed in Table 2. As shown in Fig. 15, the scaling factors have collapsed all the data into a single curve. Both NaCl and LiCl solutions show similar behaviors in these regions. These scaling results enable one to see the intrinsic property of the rate of ion transport by eliminating the extrinsic effects of external electrical potential difference. Also, these are consistent with a transition in the rate of ion transport predicted by the critical change of the apparent conductance of the system as shown in Figs. 10–12.

All these results presented in this article suggest that there is another phenomenon besides the limiting current density to consider (i.e., there can be an ion transport limitation within the membrane as the controlling step during the MED process in a low electrical field [$0 < E < 100$ volt/m]). As it was

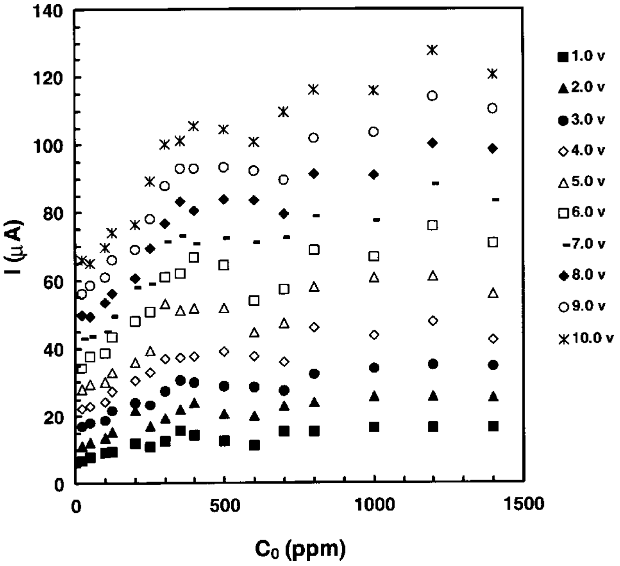


Figure 14. I vs. C_0 at constant external potential difference for KCl solution.

Table 2. Scaling parameters of $C_{0,s}$ and I_s for KCl solution.

$C_0 = C_{0,s}$ (ppm)	V (volt)	$I = I_s$ (μA)
350	300	30.530
350	6.50	66.763
350	7.00	72.953
350	7.50	78.884
350	8.00	83.224
350	8.50	87.257
350	9.00	93.152
350	9.50	99.685
350	10.00	101.23

discussed previously, this separation process limitation would occur when the rates of ion transport inside the membrane and in the electrolytic solution become comparable, and then the rate of ion exchange in the membrane becomes the limiting factor.

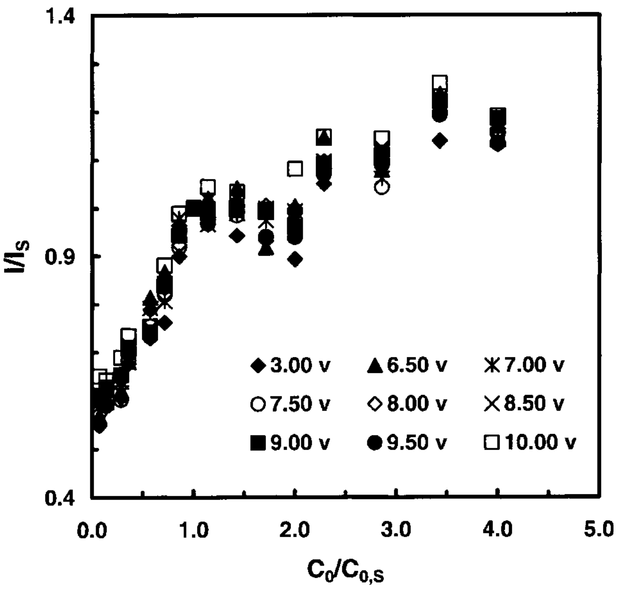


Figure 15. Scaling behavior of I vs. C_0 curves for KCl solution of Figure 14.

CONCLUSION

In the membrane electrodialysis process, when the rates of ion transport in the ion exchange membrane and in the electrolytic solution become comparable, it was found that there would be a processing limit because of the rate of ion exchange within the membrane. The experimental measurement of current vs. voltage of dilute solutions, such as KCl, NaCl, and LiCl, shows that for low electrical field ($0 < E < 100$ volt/m), a critical point was observed in the apparent conductance of the system with the increasing of initial ion concentration. These critical points occur at $C_{0,C} = 700$ ppm for Li^+; $C_{0,C} = 600$ ppm for Na^+; and $C_{0,C} = 350$ ppm for K^+. This indicates that there is an ion exchange limit within the membrane. The ion-exchange limit inside the membrane results from the capability of ion transport in the membrane being finite. And there will be ion accumulation inside the membrane near the surface where the number of ions entering the membrane is over its capacity to transport ions. Both the order of the critical point and the magnitude of the apparent conductance at the critical point indicate that the ion exchange limit is related to ion size. This experimental observation and the concept of ion exchange limit can provide a new understanding of membrane ion transport during estimation of separation efficiency of membrane electrodialysis process.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the IONICS Company at Watertown, Mass., for providing the ion exchange membranes used in this study. We would like also to thank Mr. Charles Cornwall and Mr. Barry King for their technical assistance during this study.

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Received July 2002
Revised October 2002