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Electrolyte dialysis using charge-mosaic membranes

David L. Grzenia[a], Akira Yamauchi[b], S. Ranil Wickramasinghe[a]*

[a]*Department of Chemical and Biological Engineering, Colorado State University, Fort Collins, CO 80523, USA*
Tel. +1 970 491 5522; Fax: +1 970 491 7369; email: wickram@engr.colostate.edu
[b]*Kyushu University, 2-41-18 Mizutani, Higashi-ku, Fukuoka 813-0041, Japan*

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ABSTRACT

Charge-mosaic membranes represent a subset of bipolar membranes. They contain anion- and cation-permeable domains. Anions and cations can pass through the membrane without violation of microscopic electrical neutrality. Consequently, much higher rates of transport of electrolytes compared to non-electrolytes of the same size are obtained. The ability of charge-mosaic membranes to separate low molecular weight electrolytes from non-electolytes of similar size could lead to applications such as desalination of amino acids and other organic species. Here we have determined rates of $CoCl_2$ (2:1 electrolyte), $CuSO_4$ (2:2 electrolyte), $NiSO_4$ (2:2 electrolyte), and $NiCl_2$ (2:1 electrolyte) transport through a charge-mosaic membrane made of microspheres under dialysis conditions. The results are compared to literature values for transport of KCl, a monovalent 1:1 electrolyte. Our results indicate that the mass flux of salt is the same for all four salts and for KCl. In all cases negative osmosis is observed where the volume of the dialysate increases. At the same initial dialysand salt concentration, the volume of the dialysate compartment increased more rapidly for divalent 2:1 electrolytes compared to monovalent 1:1 and divalent 2:2 electrolytes tested here. The results highlight the effect of electrolyte charge on permeability for charge-mosaic membranes.

Keywords: Charge-mosaic membranes; De-salting; Dialysis; Electrolytes; Transport rates

1. Introduction

Electrodialysis is a membrane-based separation process that finds numerous industrial applications. Monopolar (cation and anion) or bipolar membranes consisting of both positively and negatively charged layers placed next to each other [1,2] have been used. Monopolar membranes have been used for applications such as demineralization of whey [3,4] and organic acids [5], separation of amino acids [6], blood treatments [7], wine stabilization [8] and fruit juice deacidification [9]. Bipolar membranes have been used for the production of mineral and organic acids [1] and the separation of proteins [10].

Here we focus on the use of charge-mosaic membranes, a subset of bipolar membranes. These membranes, which were first proposed by Sollner [11], consist of cation- and anion-permeable domains. These domains are arranged in a three-dimensional mosaic such that the anion- and cation-exchange domains are linked from one membrane surface to the other. If the electrolyte concentration on either side of the membrane is different, anions and cations can flow through their respective paths without violation of microscopic electrical neutrality. Thus, unlike monopolar membranes, charge-mosaic membranes have high permeabilities for electrolytes as they contain pathways for the transport of cations and anions [12]. In fact, charge-mosaic membranes display salt permeabilities orders of magnitude greater than the permeability for non-electrolytes of comparable size [13].

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*Corresponding author.

Thus, while a sized-based separation process such as nanofiltration may be used to reject large multivalent ions from aqueous solutions containing smaller electrolytes, charge-mosaic membranes hold the potential to concentrate aqueous streams containing small organic molecules while removing electrolytes of similar size that may be present [14]. In particular, charge-mosaic membranes may be used to de-salt and concentrate solutions of small non-electrolytes [15].

Numerous investigators have studied charge-mosaic membranes. Ishizu et al. [16] have investigated the transport of organic and inorganic solutes through charge-mosaic membranes. They found that the transport of KCl was about 20 times greater than glucose and sucrose. Hirahara et al. [17], on the other hand, observed that the permeabilities of monovalent ions such as KCl, NaCl, HCl and NaOH are about 50–200 times those of glucose and sucrose.

The actual performance, electrolyte and non-electrolyte transport rates and selectivity of a charge-mosaic membrane depends on three groups of variables: membrane properties, feed properties and operating conditions. Higa et al. [18] compared permeation rates for different charge-mosaic membranes. They indicate the importance of membrane properties (e.g. morphology, structure, thickness) on performance. Ishizu et al. [16] indicate the importance of solution properties (such as pH) on performance. For example, amino acid permeability is lowest when the solution pH equals the amino acid isoelectric point. Weinstein et al. [13] identify four regimes of operations: membrane control, solution control, co-ion leakage control and polarization control, indicting the importance of operating conditions such as applied pressure on membrane performance.

In this work we have investigated the performance of charge-mosaic membranes under dialysis conditions in the absence of an applied pressure drop. Charge-mosaic membranes prepared using microspheres were used [19–21]. We have extended the results obtained by previous investigators by studying transport rates of divalent 2:2 and 2:1 electrolytes. The experimental results obtained here are compared to literature data for the transport of KCl, a monovalent 1:1 electrolyte. Our results indicate the effect of electrolyte charge and the stoichiometry of the salt on membrane permeability. The results highlight the potential uses of charge mosaic membranes for desalting aqueous streams containing low molecular weight non-electrolyte products.

2. Experimental

Charged-mosaic membranes were donated from Dainichiseika Color & Chemical Industry (Tokyo, Japan). Takizawa et al. [22] provide a detailed description of the formation of these membranes. Four salts, $CoCl_2$, $CuSO_4$, $NiSO_4$, and $NiCl_2$, were purchased from Mallinckrodt Baker (Paris, KY) and used without further purification. The salts were dissolved in DI water.

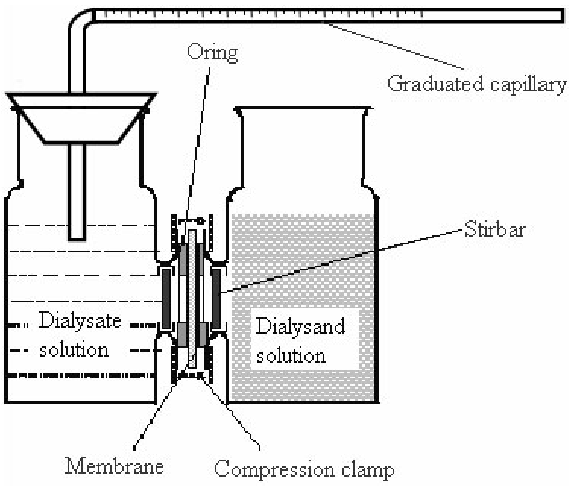

Fig. 1. Schematic representation of the diffusion cell. The graduated capillary was used to measure change in volume of dialysate with time. The graduated capillary was removed when determining the change in metal ion concentration in the dialsyate with time.

Fig. 1 gives a schematic representation of the diffusion cell used in these experiments for measurement of volume and concentration change. The experimental set-up consisted of two glass cells, the volume of each cell being 20 ml. Each glass cell contained a magnetic stir bar which was placed directly in front of the membrane. The effective membrane area was 3.14 cm^2. The membrane was fixed with two O-rings clamped between two cells to avoid leakage of solution.

Before the experiment, each membrane was immersed in DI water for 24 h. Various concentrations of the metal salts, $CoCl_2$, $CuSO_4$, $NiSO_4$, and $NiCl_2$, in the range 0.2 to 1 M were prepared. Dialysand (metal salt in DI water) and dialysate (DI water) were added simultaneously to the right- and left-hand glass cells at the commencement of the experiment. Experiments were run for up to 10 h.

The change in metal salt concentration in the dialysate compartment was determined by removing 600 μL from the dialysate at various times and measuring the absorbance at 600 nm for $CoCl_2$, $NiSO_4$, and $NiCl_2$ and 280 nm for $CuSO_4$ using a spectrophotometer. For a few experiments the salt concentration in the dialysand was also measured. Comparing the salt concentration in the dialysand and dialysate the mass balance on salt could be closed to within 10%. All measurements were taken in triplicate. All experiments were conducted in duplicate. The change in volume of the dialysate with time was measured using a graduated capillary (see Fig. 1).

3. Results and discussion

The variation of metal salt concentration in the dialysate compartment for the four metal salts is given in Figs. 2–5. As expected, the concentration of all four salts in the dialysate compartment increases with increasing time. Further the rate of increase in salt concentration in the dialysate compartment increases with increasing initial salt concentration in the dialysand compartment.

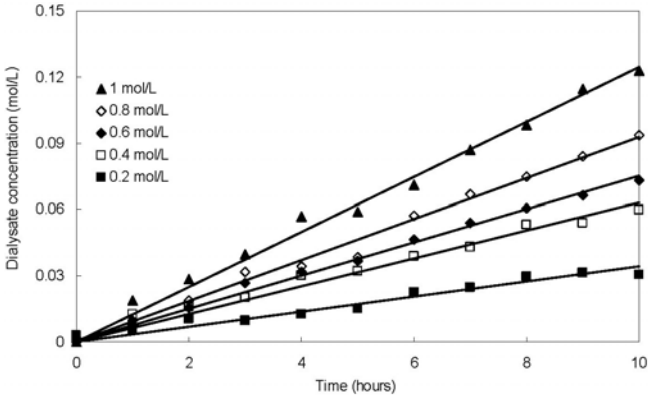

Fig. 2. Variation of $CoCl_2$ concentration in the dialysate as a function of time for various initial feed concentrations

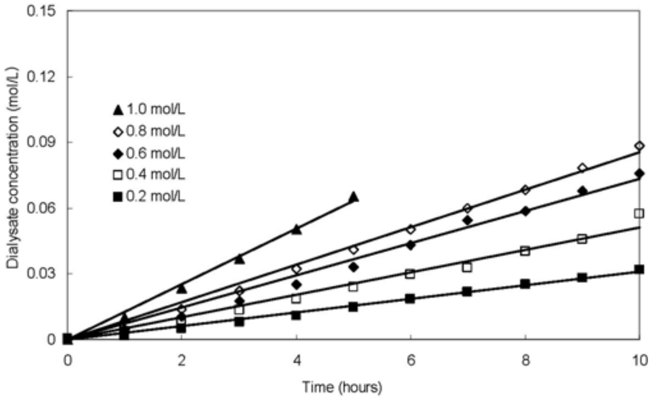

Fig. 3. Variation of $CuSO_4$ concentration in the dialysate as a function of time for various initial feed concentrations.

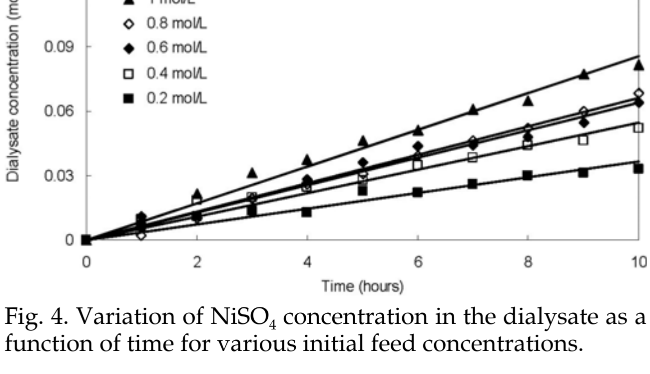

Fig. 4. Variation of $NiSO_4$ concentration in the dialysate as a function of time for various initial feed concentrations.

Fig. 6 gives the variation of volume flux as a function of time. If osmotic pressure difference between the dialysand and dialysate compartments were dominant, water transport would be from the dialysate to the dialysand compartment. However, in these experiments the volume of the dialysate compartment increased, indicating negative osmosis. Thus the volume flux is given as a negative value in Fig. 6. Further, Fig. 6 indicates that the water flux for a given dialysand salt concentration is the same for KCl and the divalent 2:2 electrolytes tested here. The water flux direction is the same but much greater for the 2:1 divalent electrolytes tested here.

Solvent and electrolyte transport across a charge-mosaic membrane in the absence of an applied pressure drop are given by [19]:

$$J_v = -L_p \sigma_s \Delta \Pi_s \tag{1}$$

$$J_s = C_s (1 - \sigma_s) J_v + \omega_s \Delta \Pi_s \tag{2}$$

where J_v and J_s are the volume and solute fluxes, respectively, L_p is the water permeability, σ_s is the reflection coefficient, $\Delta\Pi_s$ is the osmotic pressure, C_s is the solute concentration, and ω_s is the permeability coefficient.

Fig. 6 indicates that J_v is negative. The osmotic pressure difference between the dialysand and dialysate compartments will lead to transport of water from the dialysate to the dialysand. Further, the membrane permeability, L_p, must be positive. Consequently, Fig. 6 indicates that σ_s, the reflection coefficient, must be negative. In an earlier study, Fukuda et al. [19] reported negative osmosis for dialysis of KCl using the same charge-mosaic membrane. They calculated negative reflection coefficients for KCl.

The direction of water flux will be determined by the sum of two competing effects. Due to the higher salt concentration in the dialsyand compartment, an osmotic pressure driving force will lead to water permeation from

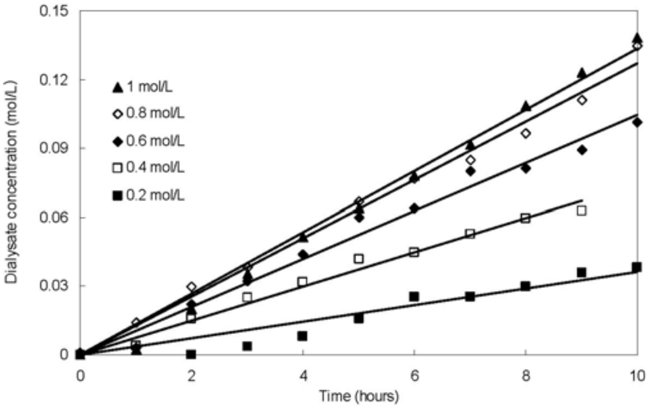

Fig. 5. Variation of $NiCl_2$ concentration in the dialysate as a function of time for various initial feed concentrations.

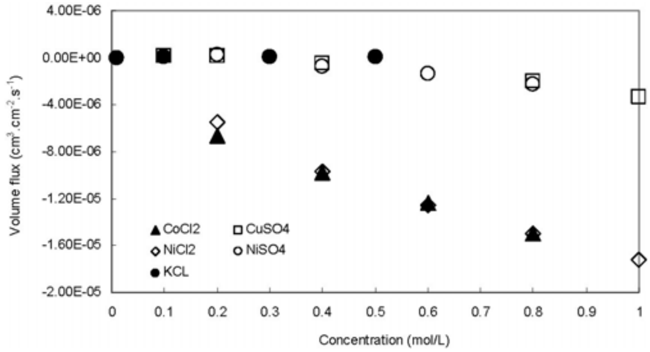

Fig. 6. Variation of volume flux as a function of time for $CoCl_2$, $CuSO_4$, $NiSO_4$, and $NiCl_2$ measured in this study. Variation of KCl flux reported by Yamauchi et al. [20] is also included.

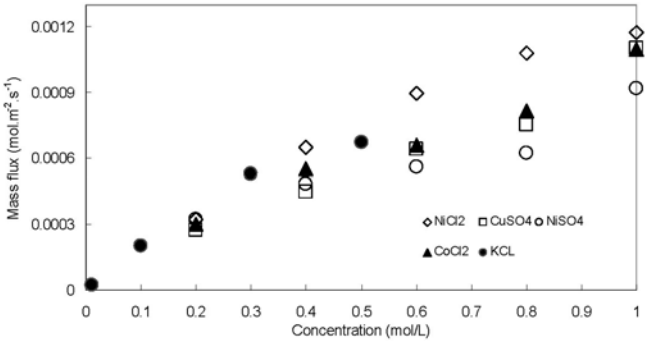

Fig. 7. Variation of mass flux as a function of concentration for $CoCl_2$, $CuSO_4$, $NiSO_4$, and $NiCl_2$, measured in this study. Variation of KCl flux reported by Yamauchi et al. [20] is also included.

the dialysate to the dialysand compartments. However, transport of the salt from the dialysand to the dialysate compartment will lead to co-transport of water. Our results for divalent 2:2 electrolytes are in agreement with previous observations for KCl and other monovalent 1:1 electrolytes. There is a small net water flux from the dialysand to the dialysate compartments.

Fig. 6 indicates that for 2:1 divalent electrolytes the water flux is much larger. According to solution chemistry [23], anions in aqueous solution attract water molecules loosely around themselves compared to cations. In other words, the shape of anions may be bulky in water. In the cases of $NiCl_2$ or $CoCl_2$, monovalent Cl ions may cause a slightly greater increase in the volume in the dialysate compartment compared to the $CuSO_4$ or $NiSO_4$ solutions. Therefore, the results in Fig. 6 would reflect qualitatively on the states of hydrated Cl ions. The higher permeability observed for 2:1 compared to 1:1 electrolytes is probably a result of the presence of two Cl ions rather than one and the interaction between the Cl ions and water molecules. The difference of 2:1 electrolytes and 2:2 electrolytes is of interest, but for quantitative elucidation further experimental inspection will be necessary.

The variation of mass flux for the electrolytes tested here as well as literature values for KCl [20] are given in Fig. 7. The mass flux for each salt was determined by dividing the gradient of the lines in Figs. 2–5 by the membrane surface area (3.14 cm^2) and multiplying the result by the volume of the dialysate compartment after accounting for any changes in the dialysate volume due to negative osmosis. As can be seen, within experimental error, the mass flux is the same for all the electrolytes. The mass flux may be predicted using Eq. (2). In comparing results for KCl and the 2:2 divalent electrolytes, the first term in Eq. (2), which represents the effect of water flux on electrolyte transport, will be the same. However, the permeability coefficient, ω_s, will also be the same, leading to the same mass flux for KCl and the 2:2 divalent electrolytes investigated here. This means that from a hydrodynamic aspect, transport rates of KCl and $CuSO_4$ are of the same order.

Fig. 7 also indicates that the mass flux for the 2:1 electrolytes is the same as the mass flux for the 1:1 electrolytes. Fig. 6 indicates that the value of the reflection coefficient for the 1:1 electrolytes will be less negative than for the 2:1 electrolytes. Thus the first term in Eq. (2) will be larger for the 2:1 electrolytes compared to the 1:1 electrolytes. However, the permeability coefficient will be larger for the 2:1 electrolytes, resulting in the same value for the mass flux for all four electrolytes tested here. This result would be attributed to the strong influence of the Cl^- ion in aqueous solutions [23].

The results obtained here extend previous literature data for the transport of 1:1 monovalent electrolytes through charge-mosaic membranes. Since transport rates for non-electrolytes are many order of magnitude lower, charge-mosaic membranes could be used to concentrate and de-salt aqueous streams containing small non-electrolyte species. Charge-mosaic membranes could find niche applications when desalting product species where product and salt to be removed are of similar size. For example, Linder and Kedem [14] indicate that removing sodium sulphate from industrial waste streams containing organics with molecular weights in the range 200–1000 Da is challenging using current nanofiltration membranes but may be possible using charge-mosaic membranes. Our results indicate that the water flux and therefore the efficiency of the separation for a given membrane will depend on the valency and stoichiometry of the electrolyte.

4. Conclusions

Transport of $CoCl_2$, $CuSO_4$, $NiSO_4$ and $NiCl_2$ through charge-mosaic membranes has been investigated. Our results indicate that the valency and stoichiometry of the electrolyte affect the water flux though the mass flux of the electrolyte was the same for the four electrolytes tested here. Our results add further support to the feasibility of using charge-mosaic membranes for desalination of aqueous streams containing small non-electrolyte species.

Acknowledgements

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