



Water electro-transport with hydrated cations in electrodialysis



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HIGHLIGHTS

- Water transport rate model was established for electrodialysis.
- A novel advice was installed to record minor volumetric change online.
- Cations with different charges were used for investigating the water transport.
- Chelates can reduce water electro-osmosis.

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ABSTRACT

Electrodialysis (ED), an efficient, low energy consumption and environmentally friendly separation and desalination technology, has attracted great attentions. Due to a drawback in water transport mechanism from the dilute stream to the concentrate one, its applications are limited, especially on the concentrating or desalinating seawater/brackish water, biological products-contained streams. In this work, the relationship between water transport rate (WTR) and ion species in ED was firstly studied by using ion exchange membranes with different ion exchange capacities (IECs). A mathematical model based on Nernst–Planck equation was established to further associate WTR with IECs, membrane matrix backbone materials, bulk solution concentration, electrolyte type, etc. The results indicate that WTR during ED is a very significant phenomenon and cannot be ignored. To mitigate this effect, attention should be paid to the modification of membrane matrix materials and the selection of suitable IEC or functional groups or the introduction of ligands to obtain a win–win coupling of high desalination ability and low WTR.

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1. Introduction

Electrodialysis (ED) is a useful electro-membrane process for the purification and demineralization of electrolytic solutions, e.g. seawater/brackish water desalination to produce freshwater [1–4], treatment of concentrated brine [5–9], separation of multi-amino acid mixture from solvents [10,11], re-concentration of useful resources such as phosphorus/heavy metals [12,13] and some others [14]. It allows for recycling inorganic ions and reusing freshwater to avoid the discharge of dilute solution in the waste which is a disadvantage to the environment.

As inherent great desalination superiority, ED has brought great interest. However, when being used for concentrating dilute solution, there always exists water transport from the dilute compartment to the concentrate one. This water transport between adjacent compartments would significantly affect process efficiency. For example, this water transport will decrease the water recovery rate for the desalination

of seawater/brackish water. There are series of works taking water transportations into considerations during ED [15–19]. However, few have concerned with a mathematical model or experiment investigation for the water transport.

Generally speaking, there are two ways for water transport across an ion exchange membrane in ED. One is the osmotic water transfer due to concentration/osmotic pressure difference and the other is electro-osmotic water transport that resulted from the migration of hydrated ions under the gradient of electrochemical potential. Based on previous investigations, the latter is the dominant [5,20,21].

In this work, water transport will be investigated through ion exchange membranes during the ED process. On the one hand, based on the mechanism of electro-osmosis induced water transport; a mathematical model was derived from a hypothesized capillary across ion exchange membrane and the Nernst–Planck equation to describe the effect of supporting electrolytes, ion exchange membranes, etc. on water transport rate (WTR) in ED. On the other hand, a set-up was designed and installed to precisely measure *minute*-volume change between compartments in the ED stack. A series of cations with different valence and hydrated numbers will be used to investigate actual

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water transport through ion exchange membranes and in turn demonstrate the deriving mathematical model.

2. Experiment setup and materials

2.1. Materials

2.1.1. Membranes

The used membranes were Neosepta AMX (AEM, Tokuyama Co., Japan), Neosepta CMX (CEM, Tokuyama Co., Japan), LabA (AEM, Hefei Chemjoy Polymer Materials Co., Ltd.), and LabC (CEM, Hefei Chemjoy Polymer Materials Co., Ltd.). CMX and AMX are homogenous membranes with sulfuric acid and quaternary amine groups as fixed charge respectively; they were produced from the cross-linked styrene-divinylbenzene (PS-DVB) copolymer and reinforced by polyvinyl chloride (PVC) fibers. LabC and LabA membranes are also homogenous membranes with the same sulfonic acid and quaternary amine groups; LabC membranes were produced from the polymerization of sodium *p*-styrenesulfonate (SSS) in a poly(vinylidene difluoride) (PVDF)/N,N-Dimethylformamide (DMF) solution while LabA membranes were manufactured from the polymerization of VBC in PVDF/DMF solution, and then quaternized by TMA. Specifically, a series of LabC membranes with different IECs of 0.62 (defined as LabC-1), 1.42 (defined as LabC-2) and 1.81 (defined as LabC-3) were used to investigate the influence of functional group density for cation exchange membranes on WTR.

2.1.2. Supporting solutions

A series of ions such as Li^+ , Na^+ , K^+ , NH_4^+ , Cu^{2+} , Al^{3+} , Cl^- and SO_4^{2-} were used as supporting electrolytes and water transport carriers that circulate through concentrate and dilute compartment of the ED stack. Especially, two kinds of Cu^{2+} based chelate ions with ligand of NH_3 and Pyridine (Py), $\text{Cu}(\text{NH}_3)_x(\text{H}_2\text{O})_y^{2+}$ and $\text{Cu}(\text{Py})_p(\text{H}_2\text{O})_q^{2+}$, were used to investigate the effect of the ligand on water transport. These two complex ions were synthesized by the stoichiometrically adding of 25%–28% ammonia water and 99% Pyridine into Cu^{2+} solution, respectively. The concentrations for mono-valent, bi-valent and tri-valent cations are 0.6 mol L^{-1} , 0.3 mol L^{-1} and 0.2 mol L^{-1} , respectively. The main properties of the membranes and the physicochemical properties of cations were listed in Tables 1 and 2, respectively. Deionized water from reverse osmosis device (conductivity of $3 \mu\text{s/cm}$) was used throughout the experiment. The used electrolyte solutions were prepared by dissolving analytical grade reagents in deionized water.

2.1.2.1. Operation mode. A constant current density of 40 mA cm^{-2} (0.28 A) was applied onto the ED stack to maintain a constant movement of cations through ion exchange membranes. The voltage drops of the ED stack in the function of time were recorded at every 5 min to evaluate the stack resistance. The temperature of each compartment changes in the range of $25\text{--}30 \text{ }^\circ\text{C}$. In each compartment, the solutions were circulated at flow rate of 200 mL min^{-1} with linear flow velocity of several centimeters per second. For the details of one unit of the ED stack, it has the following: (a) Plexiglas spacers (thickness of 10 mm) with circle flow channel (7.07 cm^2) at the middle, and Silica gel plates (1 mm) as the spacers between membranes and Plexiglas spacers to

maintain the leakproofness; (b) a cation exchange membrane and an anion exchange membrane whose properties were listed in Table 1; (c) the initial working volume of $40 \pm 5 \text{ mL}$ for dilute or concentrate compartment which has a little deviation for different operations, 200 mL of Na_2SO_4 (0.3 mol L^{-1}) for anode and cathode compartments. The cross-section drawn of the ED stack was illustrated in a flow chart of the ED system (see Fig. 1).

2.2. Devices

Water transport was monitored by a lab-designed/made setup. As shown in Fig. 1, it was composed of two dilute and two concentrate compartments divided by three cation-exchange membranes and two anion-exchange membranes. Effective area of each membrane is 7.07 cm^2 . Two electrodes were made of titanium coated with ruthenium. Na_2SO_4 (0.3 mol L^{-1}) was used as rising solution of electrodes. Since water decrease in the ED process is not obvious due to the small membrane area, the vessel is specially designed with a high precise pipette to record online small volume change of concentrate or dilute compartment at time *t*. The dilute and concentrate solutions were circulated by a peristaltic pump with two connected heads (BT600L-2*YZ15, Baoding Lead Fluid Technology Co., Ltd., China) to guarantee the same hydrodynamic condition in dilute and concentrate compartments. Thus there is no pressure difference between dilute and concentrate compartments.

Before the experiments, the solution in each compartment was circulated with a specially designed vessel for 10 min to remove the bubbles inside the ED stack. The net changes in water transport (ΔV) were averaged from volume change in both concentrate and dilute compartments.

3. Development of water transport model in ED

As will be experimentally shown later, WTR has a relationship with membrane IEC, feed type, feed concentration and current density, etc. A mathematical model should be established to explain water transport through an ion exchange membrane in ED operation. Due to many similarities between a charged membrane and a capillary column packed with small charged particles [29], a model of electro-osmosis flow of water in a charged capillary column was introduced here to simulate water transport. During the ED process, the counter-ions in a supporting solution transport through ion exchange membranes via the adjacent functional sites under the potential difference. Therefore, the space between functional sites can be assumed as capillary which allows the passing of ions. Fig. 2a–b illustrates that the ion transport mechanism through a cation exchange membrane which electro-osmosis induced water transport exists therein. The theoretical models are derived as follows.

Traditionally, ion exchange membranes are classified into anion exchange membranes and cation exchange membranes depending on the type of ionic groups attached to the membrane matrix. The functional group type and dispersion density are directly related to membrane properties such as permselectivity, area resistance, and desalination/re-concentration efficiency. To investigate water transport mechanism

Table 1

The fundamental information of the used membranes.

	AMX	CMX	LabC-3	LabC-2	LabC-1	LabA
IEC (ion exchange capacity)/mmol g^{-1}	1.25	1.62	1.81	1.42	0.62	1.6
Wu (water uptake)/%	16	18	74.1	58.2	21.0	48.5
Area resistance $\Omega \text{ cm}^2$	2.35	2.91	3.3	4.5	22.3	3.5
Transport number (%)	98	98	>90	95	98	98
Reinforcing	Yes	Yes	No	No	No	No
Membrane matrix	PS-DVB +PVC	PS-DVB +PVC	SSS-DVB +PVDF	SSS-DVB +PVDF	SSS-DVB +PVDF	PVC-DVB +PVDF
Functional group	$\text{R}_4\text{-N}^+$	R-SO_3^-	R-SO_3^-	R-SO_3^-	R-SO_3^-	$\text{R}_4\text{-N}^+$

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