Separation of Small Organic Ions from Salts by Ion-Exchange Membrane in Electrodialysis

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Electrodialysis (ED) can be applied in the food and fermentation industry for separating inorganic salts and organic ions from other fractions. However, the separation efficiency for small organic ions should be understood in detail. In this article, the membrane selectivity and transport mechanism of small organic ions from mixed salts by ion-exchange membranes are theoretically and experimentally investigated. First of all, the influence of current density on the solute flux (organic ions and inorganic ions) and on membrane selectivity (between organic ions and inorganic ions and between different organic ions) in ED has been studied. The selectivity was shown to be influenced by changing the applied current density. It was observed that separation of inorganic ions from organic solutes was feasible, but the selectivity was dependent on the size, charge, and functional groups of the organic ions. Furthermore, results imply that binary organic anions with larger molar mass (>130, i.e., aspartate and tartrate) can be adsorbed onto the membrane free volume and hence form a charged double layer, which affects membrane selectivity. Finally, competition between small organic and inorganic ions is discussed by comparison of the concentration profiles and current efficiencies of the different anions. © 2010 American Institute of Chemical Engineers *AIChE J,* 57: 2070–2078, 2011

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Introduction

Electrodialysis (ED) is widely applied in desalination, water and wastewater treatment, food, pharmaceutical, and other industrial applications for salts, acids, and organic compounds separation and products purification.[1–15] In these processes, organic compounds may either be a product or a waste fraction. In this context, a study on transport of charged organic compounds in ED is essential.

Fatty acids can be obtained from fermentation broths for the food and pharmaceutical industry. In this area, both ED with bipolar membranes (EDBMs) and conventional ED have great advantages, which have been reported in various publications.[16–18] Novalic et al.[16] investigated the recovery of high-molecular-weight organic acids (defined as $\geq$200 g mol^{-1}) by a combination of a conventional ED and a two compartments system with bipolar and cation-exchange membranes.

By optimization of current density and pH, small and larger amino acids can be successfully separated from protein hydrolysates by ion-exchange membranes in ED. Sandeaux et al.[19] suggested a procedure to separate amino acids from protein hydrolysates in an efficient way: first, a mixture of amino acids from hydrolyzed protein was neutralized and decolorized; then, demineralization by ED was performed to separate neutral amino acids molecules from the salts; finally, by adjusting pH, different amino acids can be fractionated from the mixture.

Membrane fouling, scaling, and poisoning are main bottlenecks in ED applications. Kim et al.[20] and Lee et al.[21] studied fouling of ion-exchange membranes by natural organic matter (NOM) during river water desalination in ED. Results indicate that hydrophobic NOM with high molecular weight is adsorbed on the membrane surface and causes fouling of anion-exchange membranes. NOM adsorption is influenced by both pH and ion strength, i.e., lower pH and higher ion strength can reduce fouling.[20,21] Both size and charge affect NOM transport in ED.

Small organic acids (carboxylic acids, amino acids, and some unsaturated fatty acids, with a MW below 200 g mol^{-1}) can be found in secondary sewage effluents, fermentation products, and other industrial streams.[1–3,19,22] Compared with high-molecular-weight organic compounds, small charged organic compounds are easier to migrate through ion-exchange membrane in ED and cause less fouling. Kelman and Grieves[23] reported temporary fouling of ion-exchange membranes by valerate during ED, and no fouling was observed for other smaller carboxylic acids in ED.

Small organic acids are more difficult to be fractionated and to be separated from inorganic ions by ED, which is due to their similar size and charge(s). However, systematic studies are needed to understand transport mechanisms of small organic ions during desalination and purification in industrial processes.

Moon et al.[22] investigated a mixture of acetic, formic, lactic, and succinic acids and observed that molar concentration, ionic charge, molecular weight, degree of ionization, and ionic equivalent conductivity and type of anion-exchange membrane can affect the separation of the organic ions.

Separation of different inorganic anions can be a good reference for discussing mechanisms for separation between small organic anions (OAs) and inorganic anions. Sata et al.[24,25] studied the separation of various anions from chloride and found that the hydrophilicity of an ion-exchange membrane affects the separation efficiency of hydrated anions, i.e., in case weakly basic anion-exchange groups are introduced in (on) the membranes, the membrane hydrophilicity will decrease, which causes more hydrophobic anions, i.e., nitrate and bromide, to penetrate faster through the anion-exchange membranes, compared with sulfate and fluoride. Monovalent and divalent anion separation mechanisms have been discussed widely[24,26–31] for both laboratory study and industrial application. Selectivity between monovalent and multivalent anions can be basically ascribed to size exclusion and charge repulsion/attraction. On the other hand, operation parameters are important in the mono- and multivalent ion-separation process. Current density, flow rate, and pH can influence permselectivity of ion-exchange membranes. Zhang et al.[31] reported that a decrease in current density increased the selectivity of both standard and monovalent selective anion-exchange membranes when they experimented on the synthetic RO concentrates from a food industry with PC-SK, PC-SA, and PC-MVA (PCA-Polymerchemie Altmeier GmbH, Germany) ion-exchange membranes. It was also reported that ion competition takes an important role on ion selectivity in ED process on mixed salts solutions.[31]

A limited number of studies on expatiating separation mechanisms between small organic ions and inorganic ions in the mixed solution were published. Kelman and Grieves[23] and Grieves et al.[32] discussed transport of short-chain monocarboxylic organic acids with chloride and sulfate salts by ED. It was shown that at 95% dissociation, transport of formate, acetate, and propionate was faster than for butyrate and valerate.

Although transport of small organic ions has already been studied, fractionation of mixtures and separation of organic ions from inorganic salts is not yet understood in detail. Transport mechanisms are still to be investigated and systematically discussed. This article describes an experimental and modeling approach to provide a fundamental understanding of separation of organic ions with ED.

Theory

Mass transport modeling of the anions

The concentration of ion A in the diluate solution circuit (in a recirculation mode) can be expressed by the ratio of the total mass of ion A (m_A) to the total volume of the diluate solution circuit. After a period of time t, concentration of ion A in the diluate circuit (c_A^d (t)) can be calculated as follows:

$$c_\mathrm{A}^\mathrm{d}(t) = \frac{m_{\mathrm{A},0}^\mathrm{d} - \int_0^t J_\mathrm{A} A_{\mathrm{tot-A}}^\mathrm{m} dt}{V_0^\mathrm{d} - \int_0^t J_\mathrm{w} A_{\mathrm{tot}}^\mathrm{m} dt}$$

$$\text{with } J_\mathrm{A} = \frac{dm_\mathrm{A}}{A_{\mathrm{tot-A}}^\mathrm{m} dt} \text{ and } J_\mathrm{w} = \frac{dV}{A_{\mathrm{tot}}^\mathrm{m} dt}, \quad (1)$$

where $m_{\mathrm{A},0}^\mathrm{d}$ is the initial mass of ion A, V_0^d is the initial volume of the diluate circuit, J_A and J_w are mass flux of ion A and the water (solvent) flux through the membranes, $A_{\mathrm{tot-A}}^\mathrm{m}$ is the total active surface area of the ion-exchange membrane for ion A transport, and $A_{\mathrm{tot}}^{\mathrm{m}}$ is the total active surface area of the cation- and anion-exchange membranes in the ED stack.[33]

Because of the relatively low concentration of salts in target water (around 30 meq L^{-1}), osmosis and electroosmosis can be disregarded, i.e., water transport ($J_{\mathrm{w}}A_{\mathrm{tot}}^{\mathrm{m}}$) is negligible. Thus, the concentration of ion A in diluate compartment after time t can be expressed as follows:

$$c_{\mathrm{A}}^{\mathrm{d}}(t) = \frac{m_{\mathrm{A}}^{\mathrm{d}} - \Delta m_{\mathrm{A}}(t)}{V_0^{\mathrm{d}}}. \tag{2}$$

Thus, the transported ion mass during time period t can be calculated as follows:

$$\Delta m_{\mathrm{A}}(t) = m_{\mathrm{A}}^{\mathrm{d}} - c_{\mathrm{A}}^{\mathrm{d}}(t)\, V_0^{\mathrm{d}}. \tag{3}$$

The current efficiency (CE) of ion A is defined as the ratio of the electrical charge "consumed" by ion A to the total electrical current charge. Assuming the applied current constant, the CE of ion A (η_{A}) can be calculated as follows:

$$\eta_{\mathrm{A}} = \frac{z\frac{\Delta m_{\mathrm{A}}(t)}{M_{\mathrm{A}}}F}{It} \times 100\ (\%), \tag{4}$$

where $\Delta m_{\mathrm{A}}\ (t)$ can be calculated from Eq. 3, M_{A} is molar mass of ion A, F is the Faraday constant, I is the applied current, and t is the time period.

Selective permeability, separation factor, and separation efficiency

Ion-exchange membranes may offer a possibility to selectively permeate different ions under a certain electrical potential. This is usually called membrane selective permeability.[34] Previous studies have shown that the membrane selective permeability ($T_{\mathrm{B}}^{\mathrm{A}}$) is dominated by the distribution coefficient ($K_{\mathrm{B}}^{\mathrm{A}}$) and the mobility ratio ($\frac{\bar{u}_{\mathrm{A}}}{\bar{u}_{\mathrm{B}}}$) of the two ions through the ion-exchange membrane. Thus, the selective permeability $T_{\mathrm{B}}^{\mathrm{A}}$ can be expressed by the following equation:

$$T_{\mathrm{B}}^{\mathrm{A}} = (z_{\mathrm{A}}\bar{u}_{\mathrm{A}}/z_{\mathrm{B}}\bar{u}_{\mathrm{B}})K_{\mathrm{B}}^{\mathrm{A}} \ \text{ with } \ K_{\mathrm{B}}^{\mathrm{A}} = \frac{c_{\mathrm{A}}^{\mathrm{m}}/c_{\mathrm{B}}^{\mathrm{m}}}{c_{\mathrm{A}}^{\mathrm{w}}/c_{\mathrm{B}}^{\mathrm{w}}} \tag{5}$$

where z_{A}, z_{B}; $\bar{u}_{\mathrm{A}}$, $\bar{u}_{\mathrm{B}}$; $c_{\mathrm{A}}^{\mathrm{m}}$, $c_{\mathrm{B}}^{\mathrm{m}}$; and $c_{\mathrm{A}}^{\mathrm{w}}$, $c_{\mathrm{B}}^{\mathrm{w}}$ refer to charge, electrochemical mobility, ion concentration in the membrane, and ion concentration in water, respectively.

Another way of expressing membrane selectivity is using separation factors, as proposed and calculated in literature.[1,21,23,24,33] Those calculations can be derived and concluded as follows:

$$\alpha_{\mathrm{B}}^{\mathrm{A}}(t) = \frac{1 - (c_{\mathrm{A}}(t)/c_{\mathrm{A}}(0))}{1 - (c_{\mathrm{B}}(t)/c_{\mathrm{B}}(0))}, \tag{6}$$

where, $\alpha_{\mathrm{B}}^{\mathrm{A}}$ is the separation factor, and $c_{\mathrm{A}}\ (0)$, $c_{\mathrm{B}}\ (0)$, $c_{\mathrm{A}}\ (t)$, and $c_{\mathrm{B}}\ (t)$ refer to the concentration of ion A (B) in the diluate at time 0 and t, respectively.

However, separation factors are difficult to compare when complex mixtures with different ions are investigated in ED. Thus, another method for calculating the membrane selectivity was suggested by Van der Bruggen et al.[26] In this method, the selectivity (separation efficiency, S) between component A and B is evaluated as follows:

$$S_{\mathrm{B}}^{\mathrm{A}}(t) = \frac{(c_{\mathrm{A}}(t)/c_{\mathrm{A}}(0)) - (c_{\mathrm{B}}(t)/c_{\mathrm{B}}(0))}{(1 - c_{\mathrm{A}}(t)/c_{\mathrm{A}}(0)) + (1 - (c_{\mathrm{B}}(t)/c_{\mathrm{B}}(0))}. \tag{7}$$

The range of $S_{\mathrm{B}}^{\mathrm{A}}$ is from -1 to 1. If ion A is assumed to transport slower than ion B, the $S_{\mathrm{B}}^{\mathrm{A}}$ value is between 0 and 1; if ion B is transported slower, then the $S_{\mathrm{B}}^{\mathrm{A}}$ is between -1 and 0.

Materials and Methods

Electrodialysis equipment, membranes, and feed waters

A Berghof BEL-500 ED laboratory-scale ED apparatus was used in all experiments. The setup consisted of three separated circuits with three vessels for the diluate, the concentrate, and the electrolyte rinsing solution. The ED stack consisted of five cell pairs with one extra cation-exchange membrane added between the anolyte solution chamber and the first concentrate compartment to ensure that no anion was transported to the anolyte. Thus, in total, five pieces of anion-exchange membranes and seven pieces of cation-exchange membranes were used. The schematic diagram of the stack configuration is shown in Figure 1.

PC-SK standard cation-exchange membranes and PC-SA standard anion-exchange membranes (PCA-Polymerchemie Altmeier GmbH, Germany) were installed in the stack. The PC-SK membrane (thickness 130 μm) has an ion-exchange capacity of around 1 meq g^{-1} and contains $-\mathrm{SO_3Na}$ functional groups. For the PC-SA membrane (thickness 90–130 μm), the ion-exchange capacity is about 1.5 meq g^{-1}. This membrane contains $-\mathrm{NR_4Cl}$ functional groups. Permselectivity of the membranes is higher than 93–96% (information given by the supplier). For each membrane, the active surface area is 0.0058 m^2 (58 cm^2), and the flow channel width between two membranes is 0.5 mm.

The synthetic feed solution was made by AR grade chemicals, which include: NaCl 7.63 mmol L^{-1}, $\mathrm{MgSO_4}$ 4.46 mmol L^{-1}, $\mathrm{NaNO_3}$ 0.31 mmol L^{-1}, $\mathrm{NaHCO_3}$ 8.20 mmol L^{-1}, $\mathrm{Na_2HPO_4}$ 0.44 mmol L^{-1}, and, as outlined in the different experiments, 120 mg L^{-1} (measured as TOC) of organic ion (formate, acetate, propionate, butyrate, tartrate, or aspartate, respectively).

Information (MW, pK_{a} value,[35] and the ion net charge at pH 8.5) on the inorganic and organic ions used in the experiments is shown in Table 1. A pH of 8.5 was selected because this value allows a clear interpretation of transport of organic ions based on their speciation as a function of pH. Before the experiments, the pH was corrected by NaOH to 8.5 and was kept constant during the experiments.

During the experiments, the volume of diluate, concentrate, and electrode rinsing solutions was 4 L. As initial concentrate and diluate, the same solution was used. As an electrode rinsing solutions, 0.1 M $\mathrm{Na_2SO_4}$ was used. The initial current was 0.25 or 0.5 A. The applied current was kept constant during the experiment until the voltage over the stack reached a value of 15 V. The current was then reduced stepwise (steps of 0.05 or 0.1 A) so that the voltage never exceeded 15 V. The flow rates of diluate, concentrate, and electrode rinsing solutions were all 80 L h^{-1}.

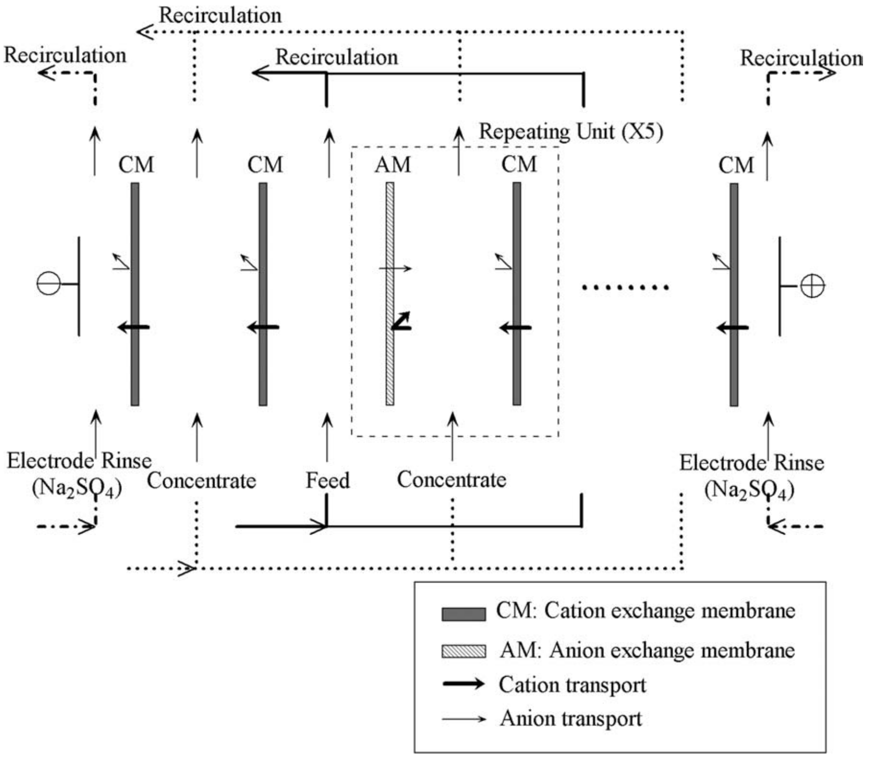

Figure 1. Schematic diagram of Berghof BEL-500 ED stack configuration.

Analytical methods

All chemicals in the experiments were analytical grade. Samples were collected every 30 min, and when current was lowered. The anion concentrations were measured by ion chromatography (DX-120 Ionchromatography with IONPAC AS12A Analytical Column, DIONEX, USA). The eluent contains 1.8 mmol L^{-1} $CO_3{}^{2-}$ and 0.2 mmol L^{-1} $HCO_3{}^{-}$.

The concentrations of bicarbonate and organic compounds were measured as ionic carbon and total organic carbon (TOC) using a TOC Analyzer (TOC 5000A TOC Analyzer and autosampler, Shimadzu, Japan).

Data analysis

All figures and tables refer to concentration changes in the diluate. The mass balances of the ions present in diluate and concentrate solution were verified. Data for concentrate and electrolyte will not be presented in this article.

The average separation efficiency $S(t)$ in a period of time t is calculated to express the selectivity of the membranes during the experiments by the following equation:

$$S(t) = \sum_j \frac{\Delta t_j \cdot S_j}{\sum_j \Delta t_j}, \tag{8}$$

where j is the sampling time, Δt_j is the time period between two samplings, S_j is the separation efficiency in the time interval between samples $j - 1$ and j, which can be calculated from Eq. 7.

Ion migration can be quantitatively expressed by means of CE, i.e., the fraction of the current that is used to transfer a certain ion. In this work, the average CE (η, %) of different anions is discussed. The average CE $\eta(t)$ during time period t is calculated by the following equation:

$$\eta(t) = \sum_j \frac{\Delta t_j \cdot \eta_j}{\sum_j \Delta t_j}, \tag{9}$$

Table 1. Information on the Inorganic and Organic Acids in the Experiments

		pK_a Value[35]	Net Charge at pH 8.5
Binary	Carbonic acid	pK_{a1}: 6.35, pK_{a2}: 10.33	−1
Ternary	Phosphoric acid	pK_{a1}: 2.15, pK_{a2}: 7.20, pK_{a3}: 12.35	−2
Unitary	Formic acid (MM = 46)	pK_a: 3.75	−1
	Acetic acid (MM = 60)	pK_a: 4.76	−1
	Propionic acid (MM = 74)	pK_a: 4.87	−1
	Butyric acid (MM = 88)	pK_a: 4.82	−1
Binary	Tartaric acid (MM = 150)	pK_{a1}: 3.04, pK_{a2}: 4.37	−2
Zwitterionic	Aspartic acid (MM = 133)	pK_{a1}: 1.89, pK_{a2}: 3.65, pK_{a3}: 9.60	−1

Table 2. Separation Efficiency of PC-SA Membrane to Different Anion Pairs With and Without Formate, Under Different Current Densities (i) at t = 150 min

Separation Efficiency	i = 86 A m^{-2} Salts	i = 86 A m^{-2} Salts + Formate	i = 43 A m^{-2} Salts	i = 43 A m^{-2} Salts + Formate
SO_4^{2-}/Cl^-	−0.01	−0.01	−0.15	−0.13
HPO_4^{2-}/Cl^-	0.04	0.06	0.32	0.34
HCO_3^-/Cl^-	0.05	0.03	0.23	0.37
HPO_4^{2-}/SO_4^{2-}	0.05	0.07	0.45	0.45
Formate/Cl^-		0.03		0.31
Formate/HCO_3^-		0.00		−0.06
Formate/SO_4^{2-}		0.04		0.43

where η_j is the CE of a certain ion in the time interval between samples $j - 1$ and j, which can be calculated from Eq. 4.

Results and Discussion

Influence of current density on membrane selectivity

Because of recirculation of diluate and concentrate during the experiments, the concentration of diluate decreased as a function of time. Thus, the limiting current can be reached under the experimental condition (as the ions were depleted). Based on the fact that at around 240–300 min the voltage reached the limiting voltage in all the experiments conducted in this investigation; therefore, the applied current had to be decreased to adapt the voltage operation under the limiting voltage. Operating below the limiting voltage can be ensured during $t = 150$ min in all of the experiments; thus, the results of the first 150 min were used to calculate the membrane selectivity. Membrane selectivity is represented by separation efficiency (S), which is calculated by Eq. 7.

Separation of formate from a mixture of ions (i.e., the synthetic feed, composition described in the Materials and Methods section) was observed at current densities of 43 and 86 A m^{-2} (i.e., applied current $I = 0.25$ A and 0.5 A), and the results are shown in Table 2. It can be seen that no selectivity was obtained at a current density of 86 A m^{-2}, as all the data are below ±0.10 under this condition. However, membrane selectivity was found at a current density of 43 A m^{-2} for all the anion pairs, except formate/HCO_3^-, and this regardless of the presence of formate. SO_4^{2-}/Cl^- shows a slightly reversed selectivity, which means that SO_4^{2-} moved slightly faster than Cl^-. A moderate selectivity was found for HPO_4^{2-}, HCO_3^-, and formate to chloride, i.e., the mentioned anions move moderately slower than chloride. No selectivity was found between formate and bicarbonate at either current density. The results imply that membrane selectivity can be achieved for PC-SA standard anion-exchange membrane when the current density is lowered, which is a confirmation of a previous study.[31]

Influence of molecule size on membrane selectivity

The separation efficiency of different OAs toward inorganic anions was studied at current density $i = 43$ A m^{-2}. Formate, acetate, propionate, and butyrate were chosen as they represent a homologous series of fatty acids with linear chain and a variable molar mass. Separation efficiencies are given in Table 3.

It can be seen from Table 3 that separation efficiencies between the OAs and chloride are 0.31, 0.58, 0.67, and 0.56 for formate, acetate, propionate, and butyrate, respectively. Thus, the separation efficiency increases with chain length. The same trend was also found for the separation efficiencies between the OAs and sulfate. Hence, it can be concluded that the membrane selectivity toward OAs increases with an increase of molar mass, or otherwise stated, with an increase of molecule size of the OAs. Acetate, propionate, and butyrate show a moderate to high (>0.60) selectivity toward sulfate. In all four experiments, the selectivity between sulfate and chloride is around −0.11, regardless of the presence of an organic component in the salt mixture.

Influence of functional groups on membrane selectivity

Butyrate, aspartate, and tartrate were selected to investigate the influence of functional groups on membrane selectivity. They have the same carbonic chain but different functional groups: butyric acid is a linear-chain fatty acid, tartrate acid is a binary organic acid with two extra hydroxyls, and aspartic acid is an amino acid that is a zwitterion with two carboxyl and one amido group.

As shown in Table 3, the separation efficiency (S) of butyrate to chloride and sulfate is 0.56 and 0.63, respectively, indicating that the organic acid is transported much slower than the smaller inorganic ions. The S values of aspartate to chloride and sulfate are both 0.34, which indicates that, relative to the transport of the inorganic ions, the transport of aspartate is faster than that of butyrate although both butyrate and aspartate have a net charge of −1 at pH 8.5. Apparently, the hydrophilic and zwitterionic head of the aspartate molecule facilitates membrane permeation. The S values of tartrate to chloride and sulfate are close to zero. Relative to sulfate and chloride, the transport of tartrate during ED is thus much faster than that of butyrate and aspartate and is of the same order of magnitude as that of sulfate and chloride. The combination of the facts that tartrate has a charge of −2 at pH 8.5 and that two hydrophilic hydroxyl groups are present may explain the good membrane permeability of tartrate. In Eq. 5, K represents the distribution coefficient of the ions between the solvent (water) and the membrane. If an OA has a higher hydrophilicity, the K value is higher, resulting in a higher selective permeability (T), i.e., a lower selectivity to inorganic anions.

It should be noted that the separation efficiency of sulfate/chloride changes to 0 and 0.09 in the experiment with

Table 3. Separation Efficiency of PC-SA Membrane to Inorganic and Organic Anions at the Presence of Different OA Under Current Density i = 43 A m^{-2} and the Voltage at t = 150 min

	SO_4^{2-}/Cl^-	OA/Cl^-	OA/SO_4^{2-}	Voltage (V)
Reference	−0.15	N/A	N/A	5.2
Salts + formate	−0.13	0.31	0.43	4.7
Salts + acetate	−0.11	0.58	0.65	4.5
Salts + propionate	−0.10	0.67	0.72	5.6
Salts + butyrate	−0.11	0.56	0.63	5.8
Salts + aspartate	0.00	0.34	0.34	14.1*
Salts + tartrate	0.09	0.02	−0.07	15.1

*Value measured after 120 min.

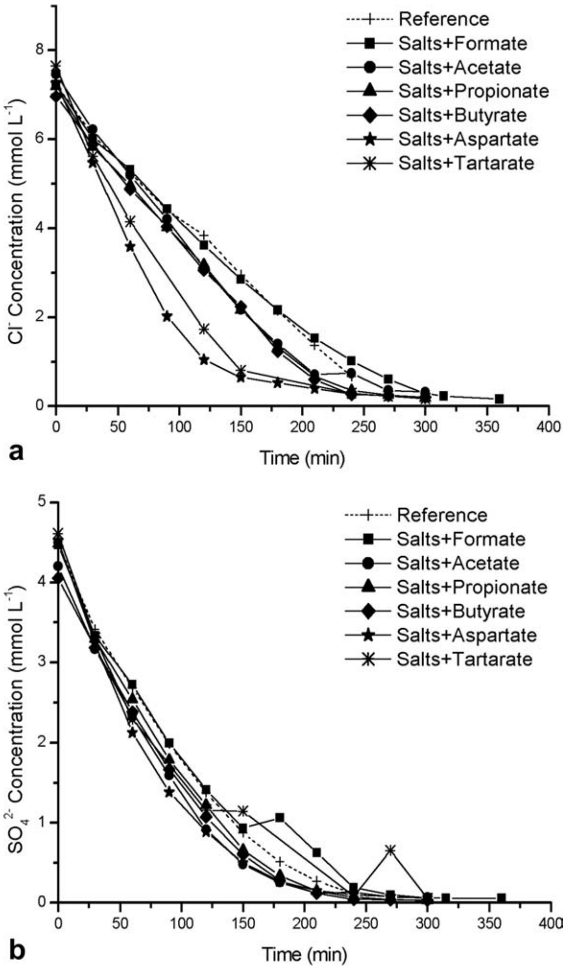

Figure 2. Concentration profiles of chloride (a) and sulfate (b) ions in different diluates as a function of time.

aspartate and tartrate, respectively. This probably can be explained by the phenomenon that organic ions adsorb and accumulate onto the membrane surface and change the electrochemical properties of the membrane. Kang et al.[36] evaluated the free volume (cavity) size of the cation-exchange membranes by chronopotentiometry and successive sorption experiments and investigated the electrodialytic separation of lysine-H$^+$ by self-made and commercial cation-exchange membranes. They reported that the counterions that are larger than the free volume size of the ion-exchange membrane accumulated on the membrane surface and formed a bipolar layer on the solution-membrane interface. This bipolar layer can significantly affect the membrane electrochemical properties: ion-exchangeable fractions in the free volume of the membranes decreased with an increase in the molecular weight of the counterion, when the molar mass was larger than $\sim$70.

On the basis of Kang et al.'s report, it is hypothesized that aspartate and tartrate (MM is 150 and 133, respectively) ionic sizes are comparable to the free volume size in the PC-SA anion-exchange membrane so that the membrane properties can be influenced. When an OA with counterionic functional groups (the counter ion is positive just like the fixed charges of the membrane) is adsorbed onto the membrane surface, a double-layer structure with a reduced negative charge can be formed, resulting from the repulsion of counterions, and this apparently reduces the permeability toward divalent ions. This phenomenon may also cause an increase of the operational voltage in the experiments with tartrate and aspartate in which the same constant current was used (0.25 A) to the other experiments. The voltage after 150 min during the experiments with the current fixed at 0.25 A is given in Table 3. Probably, this increase in voltage also caused the increase of the chloride ion flux in the aspartate and tartrate experiment, which is shown in Figure 2a. On the contrary, the sulfate ion flux was not increased with the higher voltage in the experiments with tartrate and aspartate as is shown in Figure 2b; apparently, the sulfate ion was repulsed by the electrical double layer (bipolar layer).

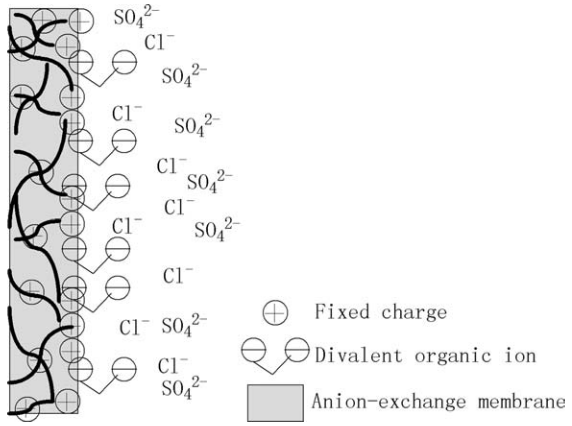

Figure 3. Schematic diagram of bipolar structure formation by divalent organic ions.

A schematic diagram is shown in Figure 3 to explain this phenomenon. This electrical double layer may interpret why the separation efficiency of sulfate/chloride converted from negative to positive when a larger OA with two carboxyl functional groups is present in the salt mixture.

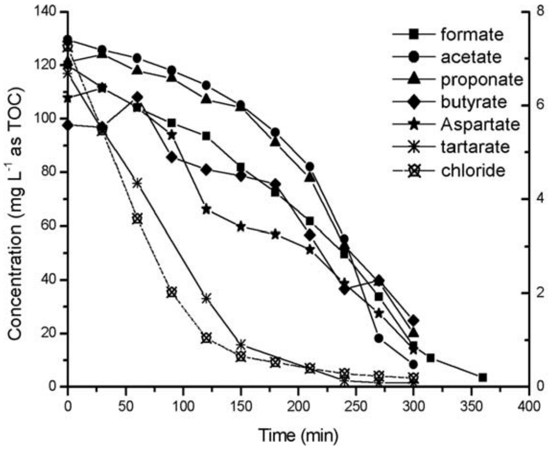

Figure 4. Concentration profiles of the organic anions and chloride (as a reference) in the diluate as a function of time.

Ion transport competition between inorganic and organic anions

The change of the OA concentration in the diluate as a function of time is shown in Figure 4. It can be seen that three different types of concentration profiles can be distinguished:

(1) For acetate, propionate, and butyrate, the concentration of the organic ion decreased relatively slowly in the beginning (first 200 min) and then decreased faster until the end of the experiments.

(2) For formate and aspartate, the concentration of the organic ion decreased constantly.

(3) For tartrate, the concentration of the organic ion decreased faster in the beginning (first 150 min) and then decreased slower until the end of the experiment.

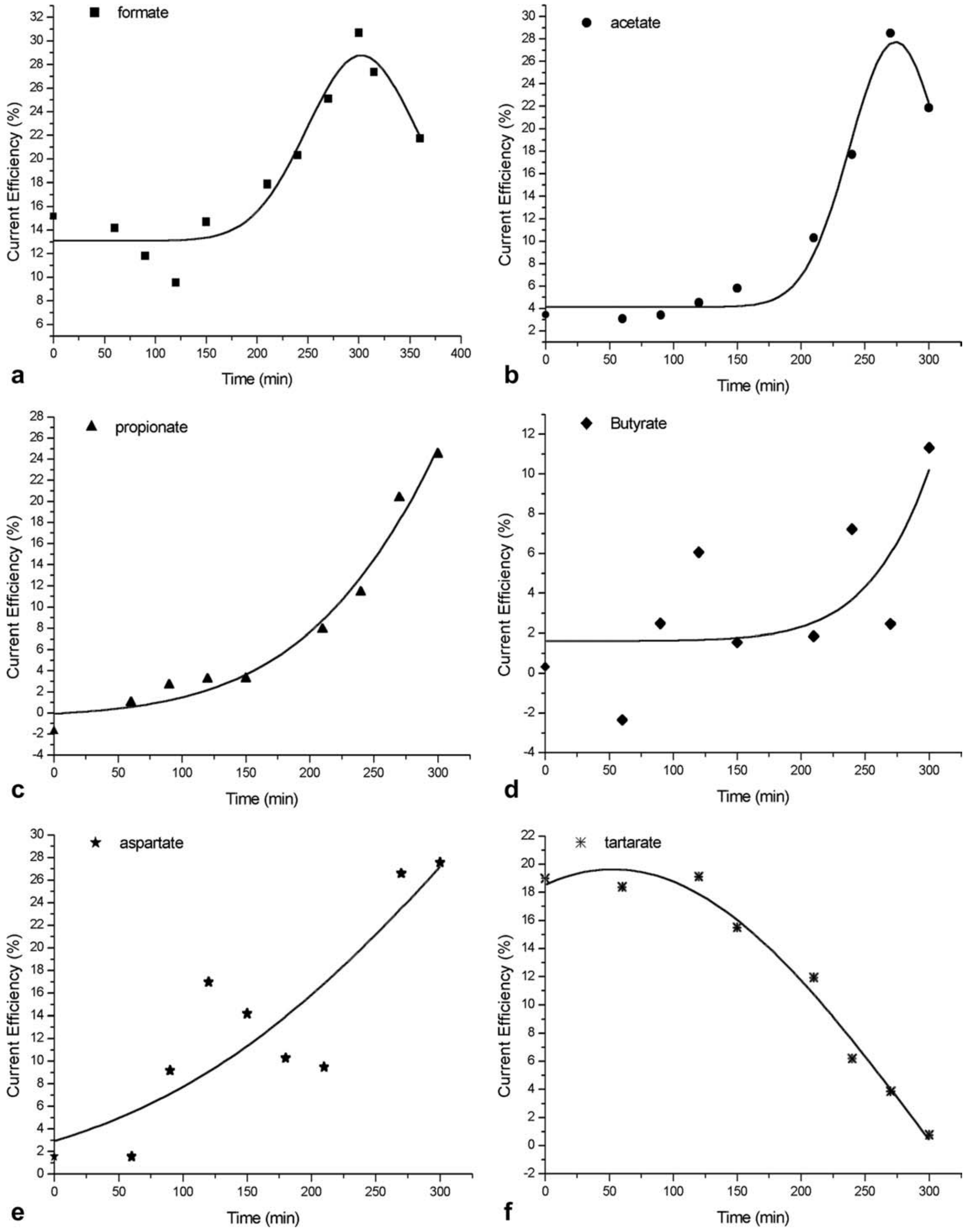

Figure 5. Current efficiency of the organic anions as a function of time.

(a) Formate, (b) acetate, (c) propionate, (d) butyrate, (e) aspartate, and (f) tartrate.

These three types of concentration profiles can be explained by a transport competition phenomenon between the OA and the accompanying inorganic anions. From Table 3, it can be seen that separation efficiencies (*S*) of acetate, propionate, and butyrate are almost the same; all of the *S* values show a moderate to high selectivity (0.5–0.7) to chloride and sulfate. This means that chloride and sulfate ions are transported much faster than acetate, propionate, and butyrate. Thus, the concentration of acetate, propionate, and butyrate decreased slower in the beginning because of the fact that there were still inorganic ions present. However, under constant current conditions, OAs began to show higher fluxes when the inorganic anions were removed. Table 3 also shows that separation efficiencies of formate and aspartate are quite similar; a moderate selectivity (0.3–0.5) to the inorganic anions (chloride and sulfate) was reached. Therefore, the flux of formate and aspartate is relatively stable. Only the concentration profile of tartrate is of the third type. As discussed, no selectivity was found between tartrate and the inorganic anions (chloride and sulfate), as shown in Table 3. This is attributed to the net charge (-2) and the high hydrophilicity of the tartrate anion. It can also be seen from Figure 4 that the concentration profile of tartrate is very similar to that of chloride, which is an inorganic anion. It should be noted that dicarboxylic salts as aspartate and tartrate are known as chelators and may form larger organic–metallic ligands molecules. However, the stability constant of aspartate and tartrate to Mg^{2+} is low (the logarithm of the stability constant for aspartate–magnesium is 2.43 and is less than 2 for tartrate–magnesium),[37,38] and the effect of the electrical field to the chelation equilibrium is not clear yet. As shown in Figure 4, the organic–metallic ligands are not likely taking a role.

The ion competition between organic and inorganic anions can also be expressed using the current efficiencies (η, %) of the OAs as a function of time. The current efficiencies were calculated by Eq. 4. Figure 5 shows two types of CE profiles: the profile of tartrate vs. that of all other OAs. As described in the above sections, the PC-SA anion-exchange membrane cannot separate tartrate from the inorganic anions; thus, the CE of tartrate continuously decreased as a function of time (as shown in Figure 5f). However, as selectivity was found for the other OAs, the CE of the other OAs increased as a function of time, until the OA began to deplete (as shown in Figures 5a–e). On the other hand, both Figures 5a,b show a peak at 270–300 min, which attributes to the slower mobility compared with the inorganic ions (i.e., Cl^- and SO_4^{2-}). As the inorganic ions were depleted during the first 270 min., the CE of organic ions (formate or acetate) continuously increased and reached a peak after around 270–300 min. Then, the organic ion was also depleted, which resulted in the decrease of the CE curve. It should be mentioned that the CE curves of propionate, butyrate, and aspartate are expected to show similar trends as the CE curves of formate and acetate if the experiments would have continued longer. In the butyrate experiment, the CE only increased to 12% after 300 min, which shows that the ionic size of butyrate can significantly diminish its transport. On the other hand, a non-monotonic increase can be observed in curves (d) and (e). The scatter of curve (d) is due to a low CE of butyrate (0–8%) during the experiment compared with the CE of the other organics (0–25%), which is attributed to the low mobility of butyrate. However, the scatter of curve (e) is probably due to the occurrence of both negative and positive charges in the molecule which makes the relative mobility (to the inorganic ions) of aspartate more complicated; as described in the Materials and Methods, from 0 to 120 min 0.25 A was applied, and after 120 min 0.1 A was applied in the experiment, and this results in an increase of the CE of aspartate during 0–120 min and decreases–increases during 120–300 min.

Table 4. Summary of the Relative Mobility, Current Efficiency (CE) Trend, and the Organic Ion Characters Which Dominant the Result

	Relative Mobility*	Dominant Factor	CE Trend
Formate	–	Size	Increased up to 30% with peak
Acetate	– –	Size	Increased up to 30% with peak
Propionate	– –	Size	Increased up to 26%, no peak
Butyrate	– –	Size	Increased up to 12%, no peak
Aspartate	–	Size, functional group	Increased up to 30%, no peak
Tartrate	±	Charge, functional group	From 22% decreased to zero

*From weak to strong, the relative mobility between organic ion and inorganic ion is represented by "– –" (very weak), "–" (weak), and "±" (equal).

Table 4 summarizes the relative mobility (separation efficiency between the organic ion and the inorganic ions, as shown in Table 3), the CE of the organic ion (which reflects the organic ion and inorganic ions transport competition), and the organic ion characters (size, charge, and functional group) that probably affect the separation.

Conclusion

Membrane selectivity and transport mechanism of small organic ions from mixed salts by ion-exchange membranes in an ED stack were theoretically and experimentally investigated in this article. The separation efficiency was postulated to be more suitable than the separation factor to describe membrane selectivity for complex salts mixtures to be separated by ED membranes. It was experimentally shown that membrane selectivity can be influenced by changing the applied current density. Based on the model of ion transport, it was observed that membrane selectivity is dependent on the size, charge, and functional groups of the organic ions.

The results indicate that, on the one hand, it is observed that ionic size of butyrate can significantly affect the transport competition to the inorganic ions, which means that butyrate ionic size is close to free volume (cavity) size of PC-SA membrane. On the other hand, by comparing the separation efficiency of sulfate/chloride, the results imply that binary OAs with a larger molar mass (>100, i.e., aspartate and tartrate) can be adsorbed to the surface and the free volume of an anion-exchange membrane and form a charged double layer, which decreases the permeability of sulfate and results in an increase of the separation efficiency of sulfate to chloride. Finally, competition between the small organic ions and inorganic ions was discussed using a comparison of concentration profiles and CE of the different anions. Because of the hydrophilic functional groups of tartrate, the migration through the anion-exchange membrane is the fastest of all OAs considered, and the permeability is close to that of the inorganic anions. This indicates that an organic ion with a higher hydrophilicity (such as tartrate ion) is easier to pass through the free volume of PC-SA membrane. It is thus more difficult to separate tartrate than any of the other OAs considered by ED.

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