Author/s:
Wang, Q;Chen, GQ;Kentish, SE

Title:
Sorption and diffusion of organic acid ions in anion exchange membranes: Acetate and lactate ions as a case study

Date:
2020-11-15

Citation:
Wang, Q., Chen, G. Q. & Kentish, S. E. (2020). Sorption and diffusion of organic acid ions in anion exchange membranes: Acetate and lactate ions as a case study. Journal of Membrane Science, 614, https://doi.org/10.1016/j.memsci.2020.118534.

Persistent Link:
https://hdl.handle.net/11343/274933

Sorption and diffusion of organic acid ions in anion exchange membranes: Acetate and lactate ions as a case study

Q. Wang, G. Q. Chen, S. E. Kentish*

Department of Chemical Engineering, The University of Melbourne, Victoria 3010, Australia

*Corresponding author. Tel: +61 3 8344 6682; Fax: +61 3 8344 6682; E-mail: sandraek@unimelb.edu.au (S. E. Kentish).

Abstract:

In this study, the sorption behaviour and conductivity of two anion exchange membranes (AR103 and AR204) equilibrated with sodium acetate and sodium lactate solutions are studied across a range of concentrations and pH values. The results indicate that the dissociation equilibria of the organic acids differ between the membrane phase and the external solution. There are significant concentrations of the neutral organic acid in the membranes at pH 6.5 even though the dissociation is virtually complete in the external solution. The concentration of this neutral acid increases as the pH is lowered, leading to a reduction in membrane conductivity. The diffusion coefficients of acetate and lactate ions in these membranes are determined from conductivity data. The results show that these diffusion coefficients are relatively constant but decrease slightly with an increase of external solution concentration due to osmotic deswelling. The diffusion coefficient of the acetate anion decreases as the pH falls, possibly due to dimer formation. Models extended from Manning's condensation theory have been utilized in the prediction of the co-ion concentrations within the membrane and the diffusion coefficients of the lactate and acetate anions. There is an excellent agreement between the experimental values of these parameters and the model predictions for the sodium lactate system but the model is unable to accurately fit the sodium acetate data.

Keywords: Anion exchange membranes, Acetate ions, Lactate ions, Diffusion coefficients

1. Introduction:

Organic acids such as acetic acid and lactic acid are used broadly within the food and pharmaceutical industries as preservatives [1], chemical intermediates [2] and buffer media. In addition, due to their biodegradable properties, there is a growing demand for these compounds in the production of polymeric materials [3]. Generally, organic acids are produced commercially either by fermentation or chemical synthesis. The former approach is preferred in the food industry as many food regulations stipulate that acids used in foods must be of biological origin [4]. The development of effective separation steps for organic acid recovery plays an important role in many biochemical industries since the conventional fermentation processes produce a mixture of organic acids as well as calcium, ammonium, or sodium salts [5]. Membrane processes, especially diffusion dialysis (DD), conventional electrodialysis (ED) and electrodialysis with bipolar membranes (EDBM), are widely used in the production and recovery of these organic acids [4-8] as they operate continuously and virtually eliminate the waste produced by other processes. However, commercial applications of these processes are often affected by the ion selectivity, electrical resistance and manufacturing costs of the ion exchange membranes (IEMs). Thus, to obtain a process with high efficiency and low energy consumption, a fundamental understanding of ion sorption and transport in IEMs is necessary. A better knowledge of the influence of polymer structure on transport properties could further facilitate rational development of ion exchange membranes with improved properties.

Ion transport in ion-exchange dense polymer membranes is normally quantified by ion diffusion coefficients. A variety of experimental techniques based on the Nernst-Planck equation have been employed to measure the diffusion coefficients of inorganic ions in these membranes, including a Donnan dialysis method [9-12], radiotracer method [13, 14] and conductivity method [15-18]. The conductivity method is the most often used as diffusion coefficients measured in the presence of an external driving force are closer to the real operation of the membrane process.

For one-dimensional ion transport in a membrane, the molar flux of ion i through a membrane, J_i^m, can be described by the Nernst-Plank equation as Eq. 1:

$$J_i^m = -D_i^m\left[\frac{dC_i^m}{dx} + \frac{z_i F C_i^m}{RT}\frac{d\psi}{dx}\right] \tag{1}$$

where D_i^m and C_i^m are the ion diffusion coefficient and concentration in the membrane, respectively; z_i is the valence of the ion; T is absolute temperature, R and F are the ideal gas constant and Faraday's constant, respectively. ψ is the electric potential and x is the thickness of the membrane.

In typical electric field driven ion transport, the Fickian component of the driving force in Eq. 1 is minimal and the electric potential difference becomes the dominant driving force for ion transportation. Under this electric potential difference, cations migrate toward the cathode and anions move toward anode. The electric current density (I) is related to the ionic fluxes in the membrane via Eq. 2.

$$I = F \sum_i z_i J_i^m \tag{2}$$

Combining Eq 1 and Eq 2 yields Eq. 3.

$$I = -\frac{F^2}{RT} \sum_i z_i^2 C_i^m D_i^m \frac{d\psi}{dx} \tag{3}$$

The membrane ion conductivity (κ) is defined by Eq. 4:

$$\kappa = {-I}\Big/{\frac{d\psi}{dx}} \tag{4}$$

Combining Eq 3 and Eq 4 then yields

$$\kappa = \frac{F^2}{RT} \sum_i z_i^2 C_i^m D_i^m = \frac{F^2}{RT} \left(z_+^2 C_+^m D_+^m + z_-^2 C_-^m D_-^m \right) \tag{5}$$

Eq 5 gives the relationship between the individual ion diffusion coefficients ($D_+^m\ and\ D_-^m$) and the ionic conductivity of the membrane but this expression cannot be solved to yield the individual diffusion coefficients. Some researchers assume that the co-ion concentration (C_+^m) approaches zero [9, 18-20], as the Donnan potential repels these ions from the ion exchange membrane and this prevents the internal co-ion concentration from rising beyond an equilibrium value [21]. This allows the diffusion coefficients of the counter-ions (C_-^m) to be determined by Eq 5.

The strength of the Donnan potential depends on the counter-ion/co-ion concentration difference between the membrane and the external salt solution. For conventional membrane processes, the counter-ion concentration difference between the membrane and solution decreases with the increase of external solution concentration as the counter-ion concentrations in the membrane itself are relatively constant [22]. This results in a weaker Donnan potential and greater co-ion sorption in the membrane. Thus, for ion exchange membranes equilibrated with concentrated solutions, the co-ions in the membrane must also be considered. To solve this problem, Kamcev et al. (2018) developed a new procedure in which the individual ion diffusion coefficients are obtained from experimental ion sorption and membrane ionic conductivity results [16]. They also modified Manning's counter-ion condensation theory[23, 24], originally developed as a ''limiting law'' for polyelectrolyte solutions, by relaxing the assumption of immobile condensed counter-ions, then used this as a model for the prediction of counter-ion diffusion coefficients in the membrane [16]. The central parameter in the modified Manning model is the dimensionless linear charge density of a polyelectrolyte, ξ, which depends on the average distance between fixed charge groups on the polymer chain. For monovalent ions, condensation occurs if ξ is greater unity (see Supporting Information).

With only one additional adjustable parameter, the modified Manning condensation theory offers excellent agreement with counter-ion/co-ion diffusion coefficients calculated from experimental results in NaCl systems. It is also predicted that this model will be suitable for similar 1:1 inorganic salt systems.

However, it is less clear whether it would suitable for organic acid systems as the dissociation equilibria of the organic acid and its ions may affect their transport behaviour.

As there is a growing demand for organic acid production by electro-membrane processes, a fundamental understanding of organic ion transport in IEMs is necessary, especially the influence of polymer structure on the transport properties. To date, most research on ion transport in ion exchange membranes relates to inorganic ions, with very little information about organic acids. These are generally weak acids that at neutral and low pH are only partly dissociated, which makes their sorption equilibria more complex. In this study, the sorption behaviour of acetic acid (pKa 4.76) and lactic acid (pKa 3.86) in anion exchange membranes are experimentally studied and compared with the sodium chloride system. The individual diffusion coefficients for the acetate and lactate ions in the same anion exchange membranes are then measured by a conductivity method and fitted to the modified Manning model proposed by Kamcev et al [16] to verify whether it is applicable to organic acid systems.

2. Experimental

2.1 Materials

Commercially available strongly basic anion exchange membranes (AEMs) (AR103-QDP and AR204-SZRA, GE Power and Water) were used in this study. These membranes were chosen as their behaviour with inorganic ions has already been well studied and because their chemical structure is known[22, 25, 26]. As shown in Kamcev et al., [25, 26], both membranes have quaternary ammonium fixed charge groups, but these are attached to styrenic groups in AR 103 and acrylic groups in AR204. Other relevant membrane properties are recorded in Table 1. All experimental results are reported on the basis of litres of ion exchange polymer. As reported by Kamcev et al [16, 26], these materials have a composite structure, which incorporates a hydrophobic, highly porous fabric support to enhance membrane mechanical properties. In this article, we refer to the combination of the anion-exchange polymer and the fabric backing as a composite membrane. The information on these backing materials and the method used for subtracting the effects of backing materials, using the method reported by Galizia et al.[27], are presented in the Supporting Information. All composite membrane samples were pre-soaked in a 1 M NaCl solution for 48 hours to ensure uniform counter-ion composition (Cl^-) and to remove any residual solvent. Membranes were then soaked in deionized water to remove the mobile ions. The external deionized water was replaced every 24 hours until the conductivity of the external deionized water was less than 5 μs/m (around ten times).

It should be noted that the water used here for desorption may have contained some bicarbonate anions and hydrogen cations due to atmospheric equilibration with CO_2. However, Kamcev et al. [28] indicate that this will affect desorption results only when the external solution concentration is less than 0.1M, which is not the case in this work.

Table 1. Properties of the Anion-exchange Polymer Used for This Study

Sample	Reported IEC [(meq/g (dry polymer)]^a	$C_A^{m,p}$[mol fixed charge groups/L (swollen polymer)]^b	$C_A^{m,w}$[mol fixed charge groups/L (water sorbed)]^b	Pure water uptake, w_u [g (water)/g (dry polymer)]^b	Water volume fraction, ϕ^w [L (water)/L (swollen polymer)]^b	ξ[22]
AR103	2.2 (min)	1.36 ± 0.02	3.40± 0.08	0.62 ± 0.02	0.40± 0.01	2.21
AR204	2.4 (min)	1.39 ± 0.02	2.46± 0.04	0.95 ± 0.06	0.57± 0.02	2.52

a. Values are reported by manufacturer. b. Data reported for membranes transferred to Cl^- form by 1 M NaCl then equilibrated with deionized water until the conductivity of the external deionized water was less than 5 μs/m).

Sodium chloride (NaCl, 99.7%) and sodium hydroxide (NaOH, 99.5%) were procured from Chem-supply Australia. Lactic acid (assay>85%), acetic acid (assay>97%), sodium iodide (99.0%) and sulphuric acid (95%~98%) were purchased from Ajax Fine Chem. Analytical standard of lactic acid (99.0%) and Acetic acid solution (0.5 M) for HPLC purchased from Sigma-Aldrich was used to confirm the concentration of the aforementioned lactic acid (assay>85%) and acetic acid (assay>97%) solutions. Purified water (13.2 MΩ cm, Millipore) was used for preparing all solutions used in this work.

2.2 Analysis

The concentration of organic acid was determined using high-performance liquid chromatography (HPLC) with a UV–Vis detector at a wavelength of 220 nm and 285 nm wavelengths, in which an Aminex HPX-87H ion exclusion column (BIO-RAD) was used with a mobile phase of 0.009 N H_2SO_4 at 0.6 ml/min and 60 °C [29]. The lactic acid and acetic acid concentration as supplied was confirmed using analytical standards with the measured concentrations shown in Table 2.

Table 2. The measured concentrations of lactic acid and acetic acid used in making up solutions

	Mol/kg	Wt%
Lactic Acid	10.34 ± 0.10	93.1
Acetic Acid	16.7 ± 0.5	99.9

The concentration of co-ions (sodium ions) were determined using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-OES 720ES, Varian).

2.3 Water uptake and water volume fraction

Circular composite membrane samples (∅ = 32 mm) were equilibrated in salt solutions (NaCl or HLa/HAc + NaOH solutions) of desired concentration and pH, with the external solution again replaced

5 times after equilibration for 24 hours. These membranes were then wiped gently (Kimtech wipes) to obtain their wet mass (m_w), thickness and diameter. The membranes were then dried in a vacuum oven at 50 ℃ until their weight stabilised (3 days) and the dry mass (m_d) then recorded. Water uptake (g water/g dry polymer) can be calculated as:

$$W_u = \frac{m_w - m_d}{m_d - m_b} \tag{6}$$

where m_b is the mass of the backing material. For circular composite membrane samples with a diameter of 32 mm, the volume (V_b) and mass (m_b) of backing material is given in Table 3.

Table 3. Volume (V_b) and mass (m_b) of backing for circular ion exchange membrane samples (diameter = 32 mm)

Membrane	Mass (g)	Volume (×10^{-4} L)
AR103	0.125	1.32
AR204	0.144	1.26

The water volume fraction (L water/ L swollen polymer) can be calculated as:

$$\phi^w = \frac{V_w}{V_m - V_b} \tag{7}$$

where V_w is the volume of water which is estimated by the weight of water ($m_w - m_d$), given a density of 1 g/cm^3. V_b is the volume of the backing material (Table 3) and V_m is the volume of the swollen composite membrane. Thus, the relationship between the molar concentration of ions in the swollen polymer ($C_i^{m,p}$) and per unit of liquid sorbed in the composite membrane ($C_i^{m,w}$) is shown as follows:

$$C_i^{m,w} = \frac{C_i^{m,p}}{\phi_w} \tag{8}$$

2.5 Anion/cation sorption measurement

Following the pre-soaking and water washing steps described above, the size (diameter, thickness and weight) of swollen composite AEMs were recorded to estimate the number of fixed charges (N_f) in each sample base on Equation 9:

$$N_f = (V_{m1} - V_b) \times C_A^{m,p} (mol/L\, polymer) \tag{9}$$

where V_{m1} is the volume of the swollen composite membrane sample (Cl$^-$ form) and V_b is the volume of backing material. The $C_A^{m,p}$ is the fixed charge concentration of swollen polymer shown in Table 1.

The composite membranes were then immersed in 80 ml of the desired salt solution for 24 hours. The solution was then replaced and soaked in a fresh solution for a further 24 hours. In total, the external solutions were replaced 5 times to ensure that equilibrium had been reached. These membranes were then wiped gently (Kimtech wipes) and the thickness and diameter measured to calculate the volume of the swollen composite membrane after equilibrium (V_m, Ac$^-$/La$^-$ form). The fixed charge concentration ($C_{fix}^{m,p}$, mol/ L swollen polymer) after equilibration in the desired salt solution can be estimated as

$$C_{fix}^{m,p} = \frac{N_f}{V_m - V_b} \tag{10}$$

For co-ion concentration measurement, the equilibrated membranes were transferred to 20 mL of water for 24 hours. Again, the solution was then replaced and soaked again for 24 hours, until a total of 2 soaking periods had occurred. The concentration of co-ions (C_d^+, sodium ions) in the desorption solution (volume V_d) were determined using ICP-OES. The co-ion concentration in the swollen polymer ($C_+^{m,p}$, mol/L swollen polymer) can then be calculated as

$$C_+^{m,p} = \frac{C_d^+ \times V_d}{V_m - V_b} \tag{11}$$

As lactic acid and acetic acid are weak acids, the total acid released from the membranes includes neutral molecules which cannot be recognized as counter-ions. Thus, the concentration of counter-ion ($C_-^{m,p}$, acetate/lactate ions) in the polymer here is calculated as the concentration of fixed charges ($C_{fix}^{m,p}$) plus the concentration of co-ions ($C_+^{m,p}$).

For the measurement of total Ac/La (neutral HAc/HLa plus Ac$^-$/La$^-$ adsorbed in the membrane), the equilibrated composite membranes were transferred to 50 mL 0.03 M H_2SO_4 solution for 24 hours (twice). The total Ac/La adsorption ($C_d^{Total\ Ac/La}$) released to the external solution was then determined using high-performance liquid chromatography (HPLC). Then the total acid concentration ($C_{Total\ Ac/La}^{m,p}$, mol/L swollen polymer) can be calculated as

$$C_{Total\ Ac/La}^{m,p} = \frac{C_d^{Total\ Ac/La} \times V_d}{V_m - V_b} \tag{12}$$

Those concentrations ($C_{fix}^{m,p}$, $C_+^{m,p}$ and $C_{Total\ Ac/La}^{m,p}$) with unit mol/L swollen polymer can be transferred to concentrations ($C_{fix}^{m,w}$, $C_+^{m,w}$ and $C_{Total\ Ac/La}^{m,w}$) with unit mol/L water sorbed by Eq 8.

2.6 Conductivity measurement

The membrane resistance was measured for membranes submerged in solutions of acetic acid/lactic acid with various pH values (adjusted by NaOH). The electrical resistance of the composite membranes was measured by direct current measurements using a four-compartment cell with a four-electrode configuration (see Fig. S1 in Supplementary material) at constant temperature (25±1 °C). Two Pt electrodes were used as reference electrodes, while the working and counter electrodes were expanded metal. Two Luggin capillaries were used to minimize the distance (6 mm) between the reference electrodes and the membrane surface. The outer diameter of the capillary tip was 4 mm, which was small enough compared to the distance between the reference electrode and membrane surface to minimize artifacts caused by shielding of the current [30]. The capillaries were open to, and filled with, the same solution as the test cell. The resistance was found by determining the relationship between applied current density and voltage drop. To subtract the resistance of the solution between the tips of the voltage measuring capillaries, two runs were performed, one with the membrane ($\mathrm{R_{s+m}}$) between two capillaries and one without (blank run, $\mathrm{R_s}$). The composite membrane resistance, $\mathrm{R_m}$, was obtained by subtracting the solution resistance, $\mathrm{R_s}$, from the $\mathrm{R_{s+m}}$. The electrical conductivity is then obtained using the following formula:

$$k = \frac{x}{R_m \times S} \tag{13}$$

where R_m, is the composite membrane resistance; S is the cross-section area and x is the thickness of the membrane.

All experimental results are reported on the basis of ion exchange polymer, the method for subtracting the effect of the backing materials on membrane conductivity is presented in the Supplementary Information.

2.7 Data analysis

Unless otherwise stated, all experiments were repeated in triplicate to determine the percentage error, as two standard deviations either side of the mean.

The external NaLa/NaAc solutions were prepared by adding the required amount of neutral organic acid and then adjusting the pH using NaOH. In a NaLa/NaAc solution with a pH value of 6.5, less than 2% of the acid is undissociated (0.2% of the lactic acid and 1.8% of the acetic acid). This means that the measured molar Ac/La concentration and the measured Na molar concentration should be close to identical. However, an error of 10% was observed due to the error between different instruments (HPLC vs ICP). At lower pH values, it is not possible to use HPLC analysis for the quantification of NaLa/NaAc in these external solutions due to the formation of the neutral acid. Hence to maintain a consistency in the data, all the external NaLa/NaAc concentrations in this paper are based on the sodium concentration regardless of pH. For data focused on the total Ac/La concentration inclusive of the neutral acid species, an error bar of 10% is included due to the error between HPLC and ICP.

Activity coefficients in the external solution were determined from the Pitzer model (See Supplementary Information).

3. Results and discussion

3.1 Ion sorption

Membrane water uptake is a key membrane property that influences ion transport in water swollen membranes. The water uptake of a membrane can be affected by its polymer properties and the composition of the external solutions. AR204 uptakes more water than AR103, but as noted by Kamcev et al. [25], it is difficult to relate this to the chemical structure as the degree of crosslinking is unknown. When submerged in NaAc/NaLa solutions of increasing concentration, the water uptake of both AR103 and AR204 slightly decreased due to osmotic deswelling [31] (Figure 1), which is similar to the trend when using NaCl as external solutions [25]. At the same concentration, membranes submerged in NaAc had a higher water uptake than those equilibrated with NaLA indicating that the lactate anion is more hydrophobic. Kamcev et al. [25] record similar water uptakes for the same membranes equilibrated in NaCl.

The composite membrane balanced with sodium lactate (AR204, Ac^{-} form ~0.65 mm) is thicker than that balanced with sodium acetate (AR204 ~0.63 mm) which is thicker again than that balanced with chloride (~0.60 mm, AR204, Cl^{-} form), even though the water uptake does not follow this trend. This may be due to the difference in counter-ion size, as the Stokes radius of Cl^{-} (0.121 nm) [32, 33] < Ac^{-} (0.194 nm) [34] <La^{-} (0.231 nm) [32].

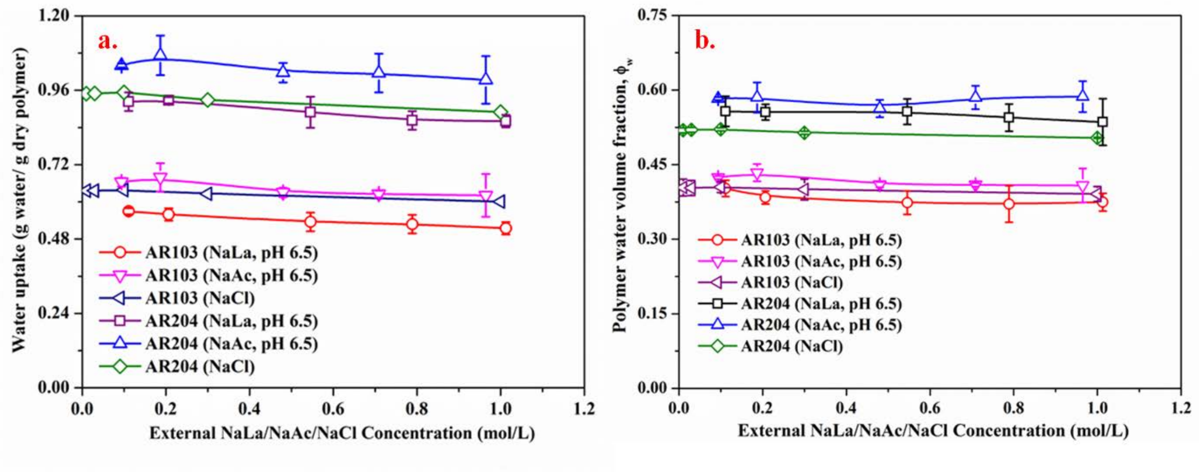

Figure 1. (a) Water uptake and (b) volume fraction of water sorbed in the polymer as a function of external sodium lactate (NaLa), sodium acetate (NaAc) and sodium chloride (NaCl) concentration. The water uptake [25] and water volume fraction [26] of the membranes in NaCl solutions are from the literature.

Due to the different water contents, the fixed charge concentration (based on water sorbed or based on the swollen polymer) after equilibration in different solutions also changes (Table 4). However, it is noteworthy that the values based on the swollen polymer are identical within error for both polymers

AR103 and AR204. The counter-ion concentration is calculated as the fixed charge plus co-ion concentration, so varies with each sample.

Table 4. Estimated fixed charge concentration in the membrane when equilibrated with NaAc/NaLa/NaCl solutions (averaged over the concentration range 0.1-0.9 mol/L)

Membrane / External solution	AR103		AR204	
	mol/L water sorbed	mol/L swollen polymer	mol/L water sorbed	mol/L swollen polymer
Sodium Acetate (NaAc)	3.13 ± 0.12	1.31 ± 0.01	2.28 ± 0.01	1.31 ± 0.01
Sodium Lactate (NaLa)	3.41 ± 0.10	1.29 ± 0.03	2.40 ± 0.04	1.29 ± 0.03
Sodium Chloride (NaCl)	3.40 ± 0.08	1.36 ± 0.02	2.46 ± 0.04	1.39 ± 0.02

As shown in Figure 2, the membrane co-ion concentration increases with an increase of external NaAc/NaLa solution concentration, due to weaker Donnan exclusion. Similar results are also observed in the NaCl system [22, 35].

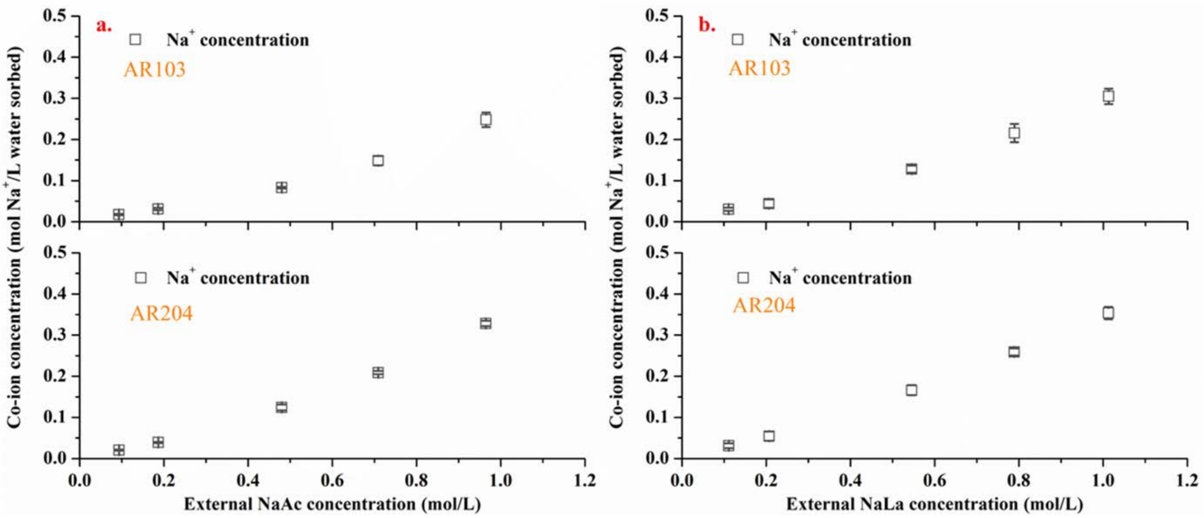

Figure 2. Co-ion (Na$^+$) concentration in different membranes when equilibrated with (a) NaAc and (b) NaLa at pH 6.5.

In ion exchange membranes, the number of counter-ions is equal to the number of co-ions plus the number of fixed charge groups because of the electroneutrality requirement [25]. As shown in Figure 3, there is a slight increase in the Ac$^-$ or La$^-$ concentrations with increasing external solution concentration, due to an increasing number of co-ions. In both AR103 and AR204, the concentration of total Ac or La released from the membranes is greater than the ion (Ac^- or La^-) concentration in the membrane (co-ion concentration plus fixed charge concentration). This is due to the presence of neutral HAc/HLa within the membrane. Within experimental error, the concentration of neutral acetic acid may be consistent with that expected in the external solution (i.e 1.8% based on the pKa). However, it is clear that the dissociation equilibria for the lactate system is different within the membrane than in the bulk solution (Figure S4), where only 0.2% is expected to be in the neutral form.

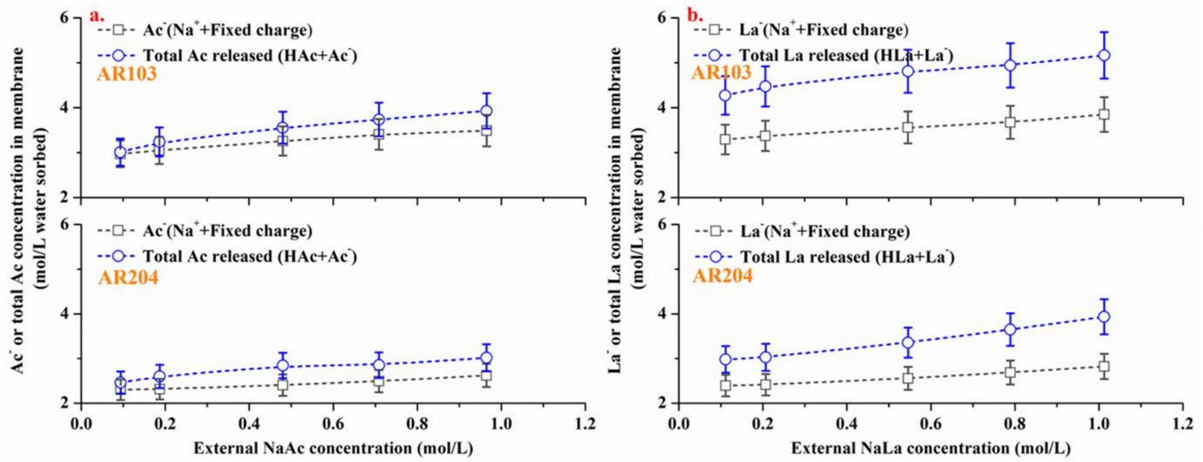

Figure 3. Molar concentration of counter-ions obtained from a charge balance (circles) and total Ac or La released (squares) for (a) for NaAc and (b) NaLa in AR103 and AR204. The counter-ion concentration, C_-^m, is equal to the sum of the measured fixed charge group concentration, C_A^m (shown in Table 4), plus the measured co-ion concentration, C_+^m (shown in Figure 2), in the membrane. The error (10%) between different instruments (HPLC/ICP/IC) is taken into account in the error bars shown.

Weak acids dissociate more readily at high pH, so for solutions with the same concentration, a lower pH corresponds to a lower ionic concentration (Figure 4). This explains the increasing proportion of the neutral species in the membrane as the pH falls, as indicated by the widening gap between the curves in Figure 4. When the pH value is less than 4 for HAc (pKa 4.76), some of the Cl^- in the membrane cannot be replaced due to the limited number of organic anions in the external solution. Conversely, for the HLa system (Figure 4 (b)), there is no Cl^- remaining within the polymer after equilibrium because HLa has a lower pKa (3.86) value.

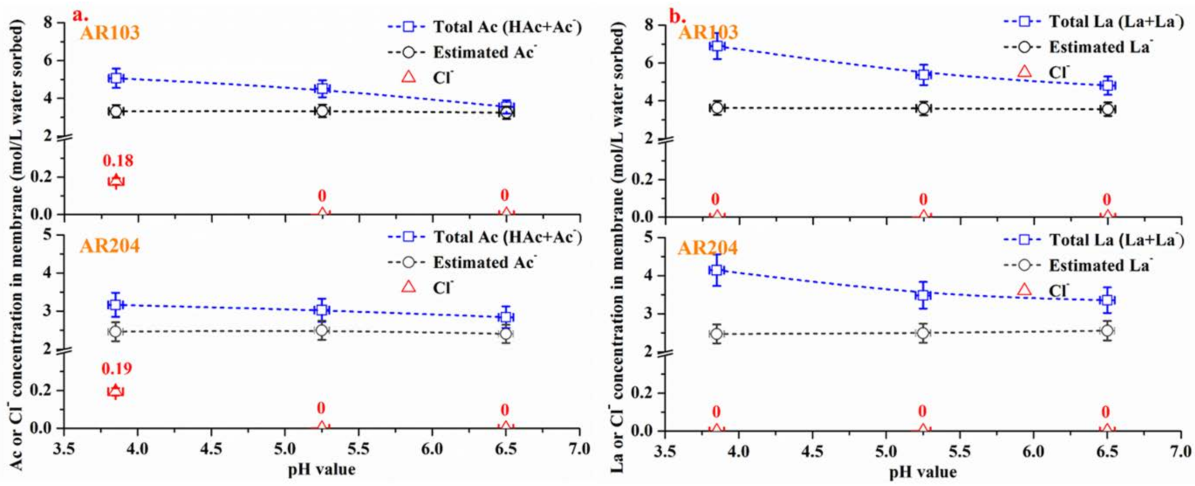

Figure 4. Molar concentration of the counter-ions and total Ac/LA in AR103 and AR204 (a) for 0.40 M HAc and (b) for 0.55 M HLa solutions across a range of pH values (adjusted by NaOH). The triangle is the Cl^- concentration present in the membrane after equilibration. The dissociated acetate/lactate concentration in the membrane is estimated as $C_{fix}^{m,w} + C_{s}^{m,w} - C_{Cl^-}^{m,w}$. The error (10%) between different instruments (HPLC/ICP/IC) is taken into account in the error bars shown.

3.2 Ion conductivity of the anion-exchange polymers

With an increase in the external solution concentration of either NaLa or NaAc, the conductivity of the polymers remains relatively constant (Figure 5). The conductivity is a function of the co-ion and counter-ion concentrations and their diffusion coefficients in the polymer. The co-ion concentrations in the polymer increase slightly with the increase of external solution concentration (Figure 2). To counterbalance this, the diffusion coefficients of the ions in the polymer depends on the water content [36] and will decrease with ionic concentration due to osmotic deswelling [16] (Figure 1). It also should be mentioned that when the external concentrations increase, the concentration of neutral HAc/HLa in the polymer also increases (Figure 3), and this may also contribute to a decrease in polymer conductivity as the presence of the neutral HAc and HLa may block pathways through the polymer.

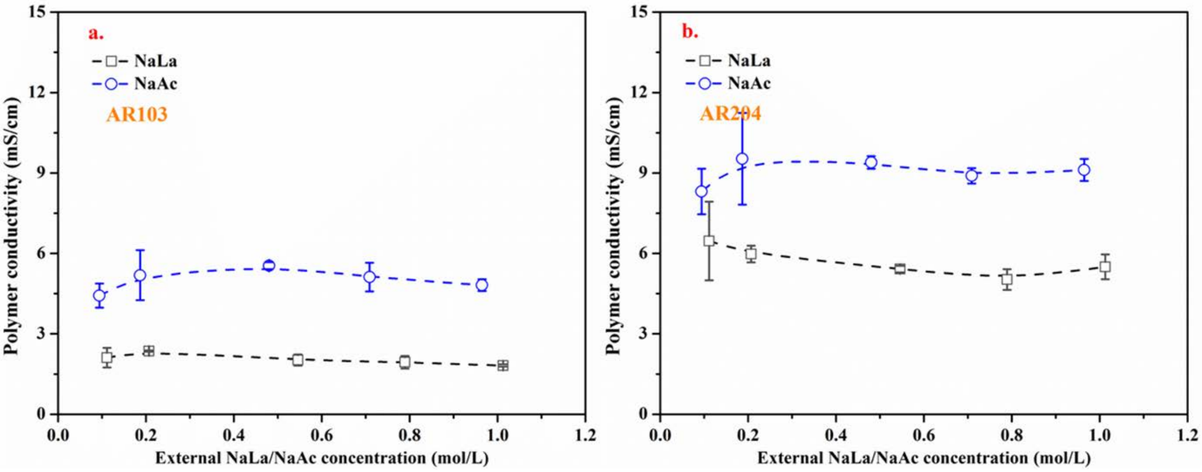

Figure 5. Ion conductivity of anion-exchange polymers in AR103 (a) and AR204 (b) as a function of external of sodium acetate/sodium lactate (pH 6.5) concentration, the solid line is drawn to guide the eye.

Membranes equilibrated at reduced pH were also tested. The conductivity of the polymers decreases with the decrease of pH (Figure 6). This reflects the increasing concentrations of neutral acid in the polymer as the pH falls, as with a lower pH, there is less HLa/HAc dissociated in the external solution which reduces ionic concentrations.

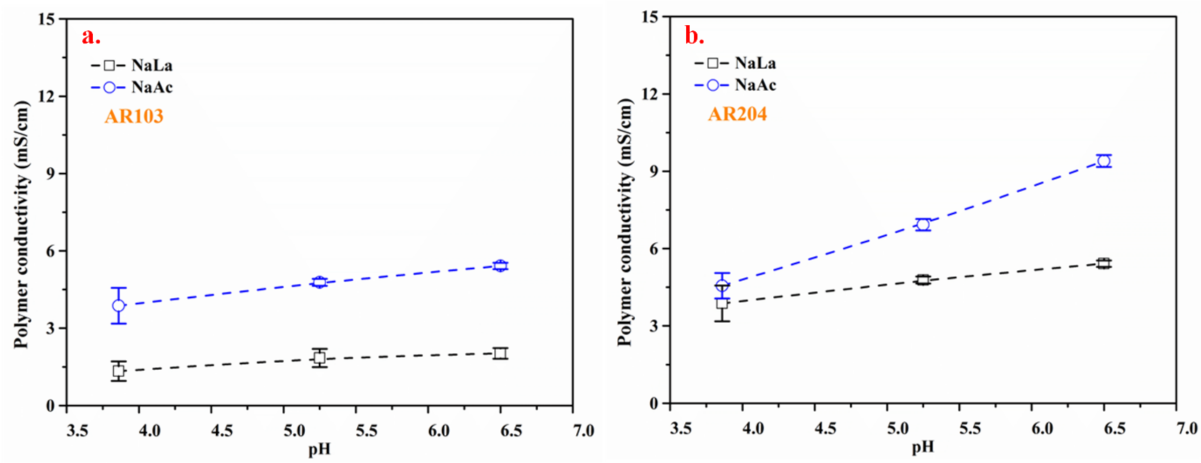

Figure 6. Ion conductivity of anion-exchange polymers in AR103 (a) and AR204 (b) as a function of the pH value of external sodium acetate/sodium solution, the solid line is drawn to guide the eye (La concentration: 0.48 mol/L, Ac concentration: 0.4 mol/L)

3.3 Experimental diffusion coefficients of La$^-$ and Ac$^-$

Combining the sorption data and polymer conductivity, the diffusion coefficients of ions in anion - exchange polymer can be calculated by Eq 5. As neutral HAc/HLa are not charged, they are not included in this calculation. The diffusion coefficient of Na$^+$ and Cl$^-$ in these polymers has been reported by Kamcev et al. [16] (Table 5) and these values are used directly in the calculations (Na$^+$ as co-ion and Cl$^-$ as a contributing counter-ion for the HAc + NaOH system at pH 3.86, see Figure 4). In the concentration range of this study (0.05 M ~0.9 M), these diffusion coefficients vary little (for example, the diffusion coefficient of Na$^+$ in AR103 (polymer) changes from 7.9 to 8.8 ×10^{-7} cm^2/s), so the values used are the average values across the range of 0.03 M to 1 M. The diffusion coefficients of acetate and lactate ions in anion-exchange polymers were then calculated by combining the sorption data (Figures 2, 3, 4), polymer conductivity (Figures 5, 6) and $D_{Na^+}^{m}$ and $D_{Cl^-}^{m}$ (Table 5). It should be noted that the diffusion coefficient calculated is based on the volume of swollen polymer, so the ion concentrations must be translated from mol/L water sorbed to mol/L swollen polymer via eq 8.

Table 5 Average values of $D_{Na^+}^{m}$ and $D_{Cl^-}^{m}$ reproduced from literature (×10^{-6} cm^2/s)

Membrane / Ions	AR103	AR204
Na$^+$	0.83	1.27
Cl$^-$	1.88	3.50

Note: external NaCl concentrations from 0.03 M to 1 M, reproduced from literature [16]

As shown in Figure 7, for the same membrane and at the same concentration, the diffusion coefficient of Ac$^-$ is higher than the value of La$^-$ and both are smaller than Cl$^-$ (Table 5). This can be explained by their Stokes radius, as Cl$^-$(0.121 nm) [32] <Ac$^-$ (0.194 nm) [34] <La$^-$ (0.231 nm) [32].The counter-ion (Ac$^-$ and La$^-$) diffusion coefficient is relatively constant over the range of external solution concentrations studied here. The slightly decrease at higher external concentrations is consistent with the decrease in polymer water content caused by osmotic deswelling (Figure 1).

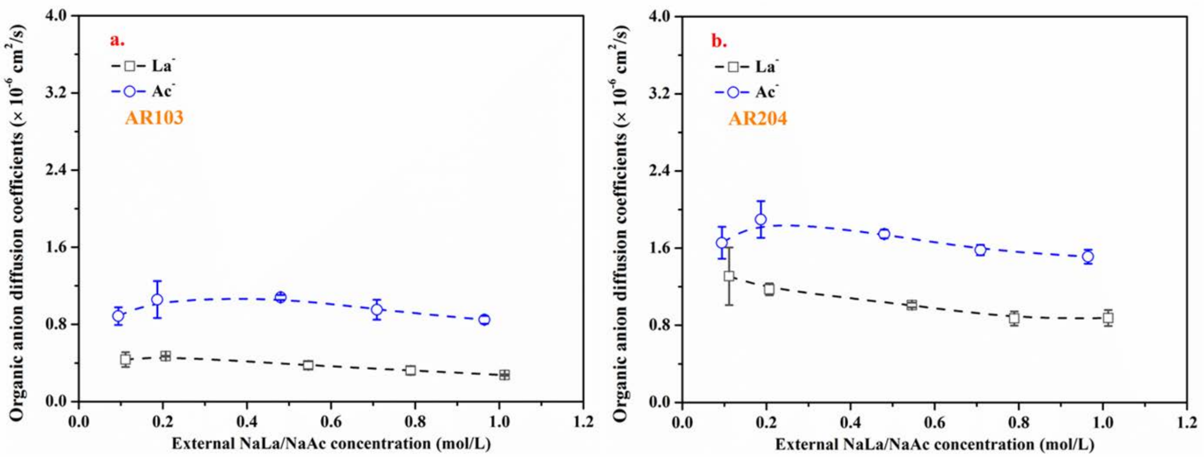

Figure 7. Diffusion coefficient of Ac$^-$/LA$^-$ in polymers of AR103 (a) and AR204 (b) as a function of the concentration of external NaAc/NaLa solution, the lines are drawn to guide the eye (pH 6.5).

As shown Figure 8, when decreasing the pH value of the external solutions, the diffusion coefficient of La$^-$ remains constant while the diffusion coefficient of Ac$^-$ decreases. This decline is difficult to explain, as it is the lactate system that has a much stronger increase in the neutral acid concentration within the membrane. One potential cause of the decline may be the formation of acetic acid dimers within the polymer structure at lower pH, as these are known to form in organic solvents [37, 38]. The larger molecular weight of these dimers would reduce the observed diffusion coefficient.

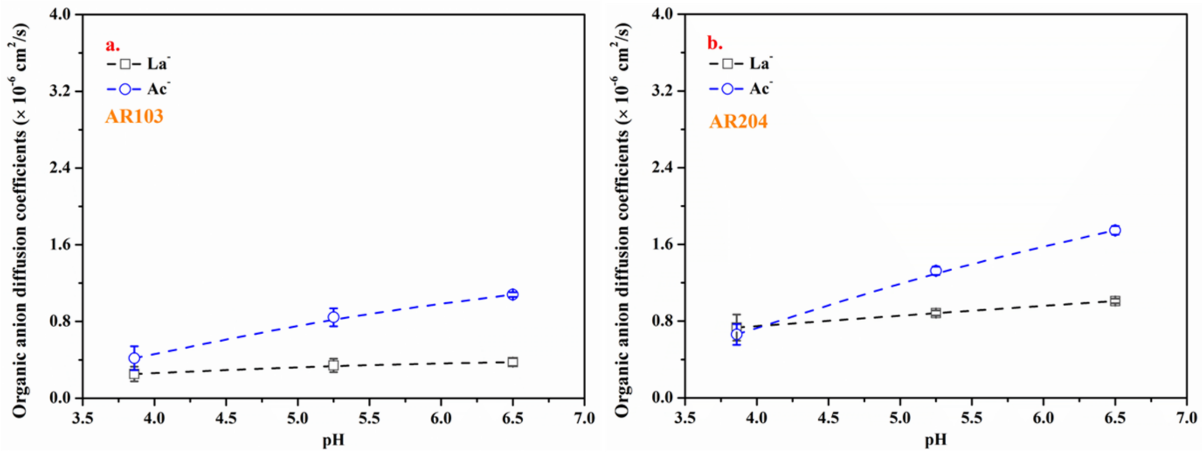

Figure 8. Diffusion coefficient of Ac$^-$ and La$^-$ in polymers of AR103 (a) and AR204 (b) as a function of the pH value of the external sodium acetate or sodium solution. The solid line is drawn to guide the eye (La concentration: 0.48 mol/L, Ac concentration: 0.40 mol/L)

3.4 Manning's counter-ion condensation theory

The data of membrane co-ion concentration can be fitted well to Eq S5 for the NaLa system using the same Manning parameters as determined by Kamcev et al. [22] for the NaCl system (AR204: $\xi = 2.52$, AR103: $\xi = 2.21$). As shown in Figure 9, a slightly better fit can be obtained if these values are reduced slightly (AR204: $\xi = 1.88 \pm 0.05$, AR103: $\xi = 1.88 \pm 0.07$). These changes might be explained by the extension of the polymer chains due to the larger size of the lactate ions and the corresponding decrease in fixed charge concentration (mol/L swollen polymer) shown in Table 2. The ξ value is inversely proportional to the distance between fixed charges on the polyelectrolyte chain (b, Eq. S1), so it would be expected to reduce as the polymer expands to accommodate these ions.

However, the values of ξ must be reduced significantly to obtain a reasonable fit for the NaAc system The new ξ values are below unity which means that there is no ion condensation occurring according to Manning's condensation theory [23, 25]. This is unrealistic. The discrepancy appears to relate to the significantly higher activity coefficients for sodium acetate (Figure S4) in the external phase relative to sodium lactate, as all other parameters are similar. It is unclear whether these higher activity coefficients in the external phase also relate to the formation of dimers.

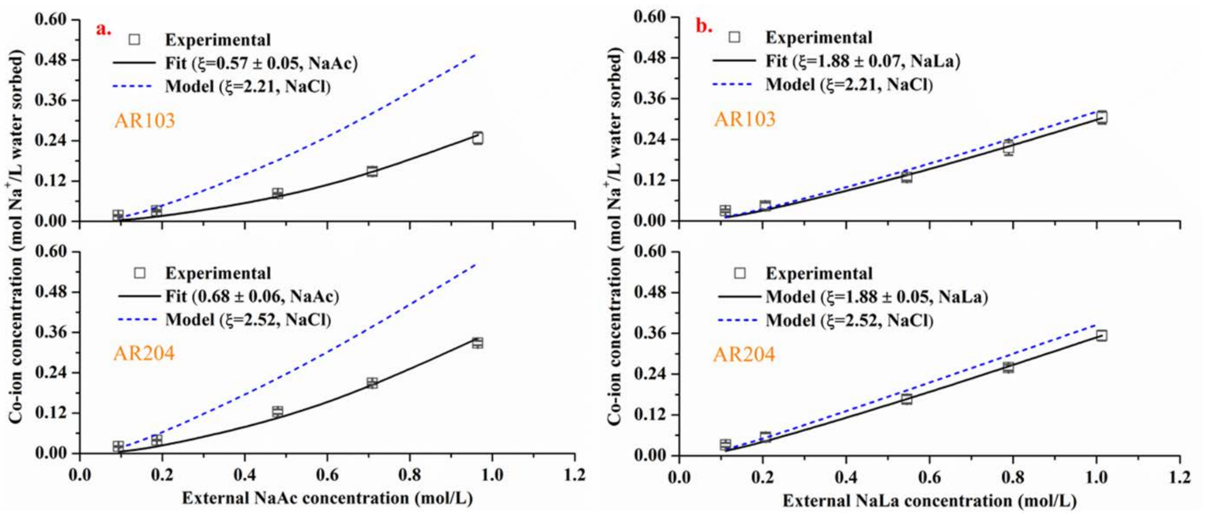

Figure 9. Co-ion (Na^+) concentration in different membranes when equilibrated with (a) NaAc or (b) NaLA at pH 6.5. The symbols represent experimental data, the dashed lines represent the fit to Eq. S5 using ξ values from Kamcev et al.; while the solid lines represent the fit to Eq. S2 ($\xi<1$) or Eq. S5 ($\xi>1$) with ξ as an adjustable parameter.

Eqs S3 – S8 were then used for the prediction of the diffusion coefficient of both La$^-$ and Ac$^-$ in the polymer with the ξ value fitted to experimental results for the NaLa system and for the NaAc system (Figure 9) and as reported in the literature. The variable α which accounts for the molecular architecture of the polymer and the structure of water within this was also calculated by fitting the model to experimental results. As shown in Figure 10, the diffusion coefficients of NaAc and NaLa are both predicted well by the model (Eq. S3 for $\xi < 1$, Eq. S6 for $\xi > 1$). For the NaLa system, the fitted constant values (α) are less than unity, as expected. Using the ξ value fitted by sorption experiments or as reported in the literature gives almost the same value for the constant, α.

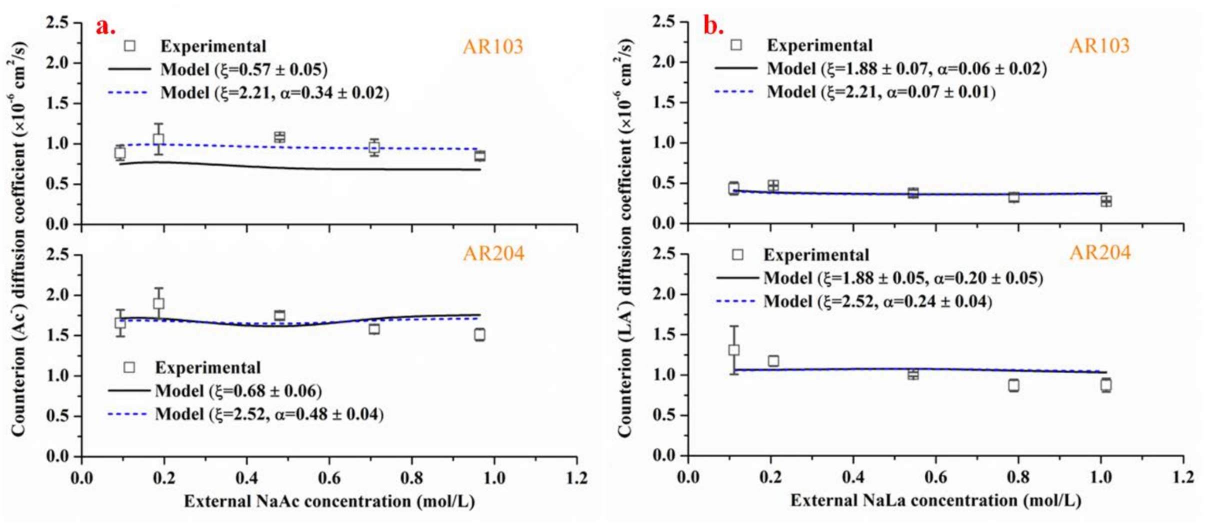

Figure 10 Experimental and model results of the diffusion coefficients of (a) Ac$^-$ and (b) La$^-$ as a function of the external concentration. The squares are the experimental data, the dashed line is the results predicted by Eq. S6 with ξ from the literature for an NaCl system [25], while the solid line is the results predicted by Eq. S3 ($\xi<1$) or Eq. S6 ($\xi>1$) with ξ predicted from Eq. S2 ($\xi<1$) or Eq. S5 ($\xi>1$)

The model predictions were then verified using the data at lower values of the pH of the external solutions. As shown in Figure 11, the agreement between modelling and experimental diffusion coefficients of NaLa system is reasonably good, indicating that the modified model proposed by Kamcev et al [16] can be used in NaLa system. However, the model is unable to predict the diffusion coefficient of the acetate ion in the polymers as the pH falls, regardless of the value of ξ used. As discussed above, this may relate to the formation of acetate dimers.

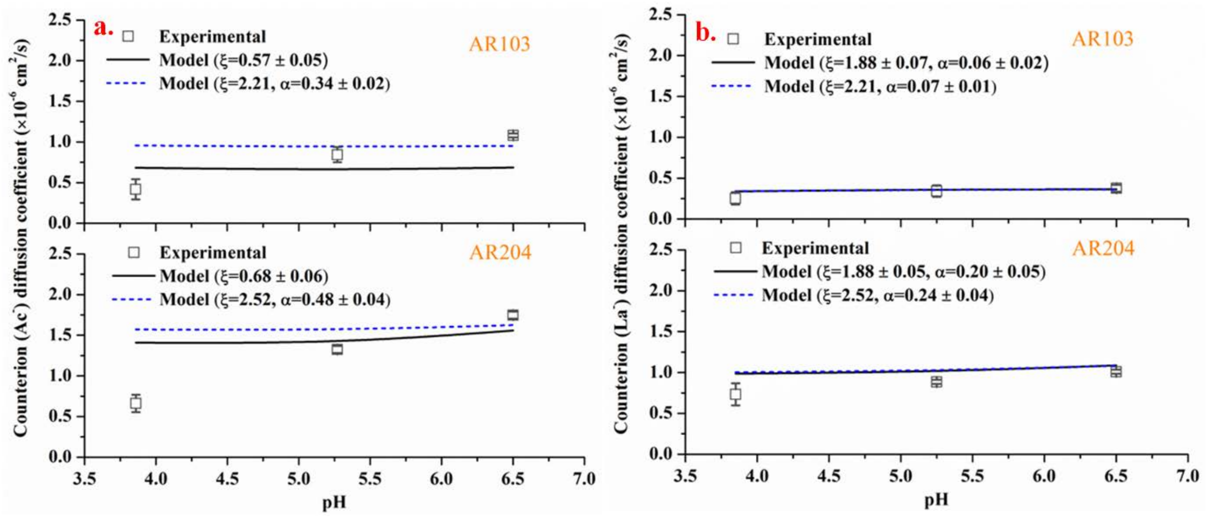

Figure 11 Experimental and model results of diffusion coefficients of (a) Ac$^-$ and (b) La$^-$ as a function of the pH value, black squares are the experimental values, dashed line is the results predicted by Eq. S6 with ξ from the literature for a NaCl system [25], while the solid line is the results predicted by model with ξ fitting by Eq. S2 (ξ<1) or Eq. S5 (ξ>1), (La concentration: 0.48 mol/L, Ac concentration: 0.4 mol/L)

4. Conclusion

Sorption experiments with organic acid salts (NaAc and NaLa) has shown that the dissociation behaviour of the organic acid can differ between the membrane phase and the bulk solution. Specifically, neutral lactic acid persists in significant quantities within the membrane phase at pH 6.5, whereas it is essentially absent from the bulk solution. The concentration of the neutral species increases as the pH is reduced below this value for both systems. In turn, this increasing concentration results in a fall in the polymer conductivity, possibly due to the neutral HAc and HLa blocking pathways through the polymer.

By combining the sorption data and conductivity of the polymers, the diffusion coefficients of acetate ions and lactate ions in two kinds of anion-exchange polymers (AR103 and AR204) are attained. In the range of experiments (0.06~0.9 M of external solution), the diffusion coefficients of both acetate ions or lactate ions are relatively constant (for AR103, Ac$^-$: ~0.9 ×10^{-6} cm^2/s, La$^-$: ~0.4 ×10^{-6} cm^2/s; for AR204, Ac$^-$: ~1.7 ×10^{-6} cm^2/s, La$^-$: ~1.1 ×10^{-6} cm^2/s) and slightly decrease with the increase of external solution concentration due to osmotic deswelling. The diffusion coefficient of Ac$^-$ is greater than the value for La$^-$ due to its smaller Stokes radius. When decreasing the pH value of the external solutions, the diffusion coefficient of La$^-$ remains constant while the diffusion coefficient of Ac- decreases. This decline may be caused by the formation of acetic acid dimers within the membrane structure at lower pH. The larger molecular weight of these dimer species would reduce the observed diffusion coefficient.

The sorption data of the NaLa system can fit well with the model using the Manning parameter (ξ) reported previously for the NaCl system. A better fit can be obtained if the ξ value is reduced slightly, which can be explained by the extension of the polymer chains due to the larger size of the lactate ions and the corresponding decrease in fixed charge concentration. The model can also be readily applied to determine the diffusion coefficient of the lactate anions, both at neutral pH and as this pH is reduced. However, the values of ξ must be reduced significantly (lower than the critical ξ value for 1:1 electrolytes) to obtain a reasonable fit for the NaAc system. This is unrealistic as the polymer structure will not change to this extent. Further, the Manning approach is unable to fit the diffusion coefficient data for this system. Hence for this organic acid, the modified Manning's condensation theory fails in its present form. This appears to relate to the higher activity coefficients for this species in the external solution.

Acknowledgements

Q. Wang acknowledges the University of Melbourne for a Melbourne Research Scholarship.

References

[1] H. Eggensperger, K.-H. Diehl, P. Oltmanns, Preservatives and their use, in, Google Patents, 1997.
[2] W. Deng, Y. Wang, S. Zhang, K.M. Gupta, M.J. Hülsey, H. Asakura, L. Liu, Y. Han, E.M. Karp, G.T. Beckham, Catalytic amino acid production from biomass-derived intermediates, Proceedings of the National Academy of Sciences, 115 (2018) 5093-5098.
[3] P.A. Gunatillake, R. Adhikari, Biodegradable synthetic polymers for tissue engineering, Eur Cell Mater, 5 (2003) 1-16.
[4] Y. Wang, N. Zhang, C. Huang, T. Xu, Production of monoprotic, diprotic, and triprotic organic acids by using electrodialysis with bipolar membranes: Effect of cell configurations, Journal of membrane science, 385 (2011) 226-233.
[5] Y.H. Kim, S.H. Moon, Lactic acid recovery from fermentation broth using one‐stage electrodialysis, Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental & Clean Technology, 76 (2001) 169-178.
[6] X. Zhang, C. Li, X. Wang, Y. Wang, T. Xu, Recovery of hydrochloric acid from simulated chemosynthesis aluminum foils wastewater: an integration of diffusion dialysis and conventional electrodialysis, Journal of membrane science, 409 (2012) 257-263.
[7] C. Huang, T. Xu, Y. Zhang, Y. Xue, G. Chen, Application of electrodialysis to the production of organic acids: state-of-the-art and recent developments, Journal of membrane science, 288 (2007) 1-12.
[8] E. Molnár, M. Eszterle, K. Kiss, N. Nemestóthy, J. Fekete, K. Bélafi-Bakó, Utilization of electrodialysis for galacturonic acid recovery, Desalination, 241 (2009) 81-85.
[9] K. Sato, T. Yonemoto, T. Tadaki, The determination of diffusion coefficients of counter-ions in the ion-exchange membrane by means of batchwise Donnan dialytic experiments, Journal of membrane science, 53 (1990) 215-227.
[10] C.-C. Ho, D.-S. Jan, F.-N. Tsai, Membrane diffusion-controlled kinetics of ionic transport, Journal of membrane science, 81 (1993) 287-294.
[11] X. Tongwen, H. Binglin, A RAPID METHOD TO DETERMINE DIFFUSION COEFFICIENTS OF COUNTER—IONS IN AN lON—EXCHANGE MEMBRANE, Chinese J. of Chem. Eng, 5 (1997) 81-86.

[12] T.-C. Huang, P.-H. Lian, The interdiffusion of counterions in a cation-exchange membrane, Industrial & Engineering Chemistry Fundamentals, 18 (1979) 221-226.

[13] A. Goswami, A. Acharya, A. Pandey, Study of self-diffusion of monovalent and divalent cations in Nafion-117 ion-exchange membrane, The Journal of Physical Chemistry B, 105 (2001) 9196-9201.

[14] A.-L. Rollet, J.-P. Simonin, P. Turq, Study of self-diffusion of alkali metal cations inside a Nafion membrane, Physical Chemistry Chemical Physics, 2 (2000) 1029-1034.

[15] D.N. Amang, S. Alexandrova, P. Schaetzel, The determination of diffusion coefficients of counter ion in an ion exchange membrane using electrical conductivity measurement, Electrochimica acta, 48 (2003) 2563-2569.

[16] J. Kamcev, D.R. Paul, G.S. Manning, B.D. Freeman, Ion diffusion coefficients in ion exchange membranes: significance of counterion condensation, Macromolecules, 51 (2018) 5519-5529.

[17] T.W. Xu, Y. Li, L. Wu, W.H. Yang, A simple evaluation of microstructure and transport parameters of ion-exchange membranes from conductivity measurements, Separation and Purification Technology, 60 (2008) 73-80.

[18] A. Elattar, A. Elmidaoui, N. Pismenskaia, C. Gavach, G. Pourcelly, Comparison of transport properties of monovalent anions through anion-exchange membranes, Journal of Membrane Science, 143 (1998) 249-261.

[19] G. Pourcelly, P. Sistat, A. Chapotot, C. Gavach, V. Nikonenko, Self diffusion and conductivity in NafionR membranes in contact with NaCl+ CaCl2 solutions, Journal of membrane science, 110 (1996) 69-78.

[20] D. Nwal Amang, S. Alexandrova, P. Schaetzel, The determination of diffusion coefficients of counter ion in an ion exchange membrane using electrical conductivity measurement, Electrochimica Acta, 48 (2003) 2563-2569.

[21] F.G. Helfferich, Ion exchange, Courier Corporation, 1995.

[22] J. Kamcev, M. Galizia, F.M. Benedetti, E.-S. Jang, D.R. Paul, B.D. Freeman, G.S. Manning, Partitioning of mobile ions between ion exchange polymers and aqueous salt solutions: importance of counter-ion condensation, Physical Chemistry Chemical Physics, 18 (2016) 6021-6031.

[23] G.S. Manning, Limiting laws and counterion condensation in polyelectrolyte solutions I. Colligative properties, The journal of chemical Physics, 51 (1969) 924-933.

[24] G.S. Manning, Limiting laws and counterion condensation in polyelectrolyte solutions II. Self‐diffusion of the small ions, The Journal of Chemical Physics, 51 (1969) 934-938.

[25] J. Kamcev, D.R. Paul, B.D. Freeman, Ion activity coefficients in ion exchange polymers: Applicability of Manning's counterion condensation theory, Macromolecules, 48 (2015) 8011-8024.

[26] J. Kamcev, D.R. Paul, G.S. Manning, B.D. Freeman, Predicting salt permeability coefficients in highly swollen, highly charged ion exchange membranes, ACS applied materials & interfaces, 9 (2017) 4044-4056.

[27] M. Galizia, F.M. Benedetti, D.R. Paul, B.D. Freeman, Monovalent and divalent ion sorption in a cation exchange membrane based on cross-linked poly (p-styrene sulfonate-co-divinylbenzene), Journal of membrane science, 535 (2017) 132-142.

[28] J. Kamcev, E.-S. Jang, N. Yan, D.R. Paul, B.D. Freeman, Effect of ambient carbon dioxide on salt permeability and sorption measurements in ion-exchange membranes, Journal of Membrane Science, 479 (2015) 55-66.

[29] G.Q. Chen, F.I. Eschbach, M. Weeks, S.L. Gras, S.E. Kentish, Removal of lactic acid from acid whey using electrodialysis, Separation and Purification Technology, 158 (2016) 230-237.

[30] A.J. Bard, L.R. Faulkner, J. Leddy, C.G. Zoski, Electrochemical methods: fundamentals and applications, wiley New York, 1980.

[31] A.R. Khare, N.A. Peppas, Swelling/deswelling of anionic copolymer gels, Biomaterials, 16 (1995) 559-567.

[32] A. Bouchoux, H. Roux-de Balmann, F. Lutin, Nanofiltration of glucose and sodium lactate solutions: Variations of retention between single-and mixed-solute solutions, Journal of membrane science, 258 (2005) 123-132.

[33] E. Nightingale Jr, Phenomenological theory of ion solvation. Effective radii of hydrated ions, The Journal of Physical Chemistry, 63 (1959) 1381-1387.

[34] P. Banerjee, S. Yashonath, B. Bagchi, Rotation driven translational diffusion of polyatomic ions in water: A novel mechanism for breakdown of Stokes-Einstein relation, The Journal of chemical physics, 146 (2017) 164502.

[35] J. Kamcev, D.R. Paul, B.D. Freeman, Effect of fixed charge group concentration on equilibrium ion sorption in ion exchange membranes, Journal of Materials Chemistry A, 5 (2017) 4638-4650.

[36] J. Mackie, P. Meares, The diffusion of electrolytes in a cation-exchange resin membrane I. Theoretical, Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences, 232 (1955) 498-509.

[37] Y. Fujii, H. Yamada, M. Mizuta, Self-association of acetic acid in some organic solvents, The Journal of Physical Chemistry, 92 (1988) 6768-6772.

[38] G. Allen, E.F. Caldin, The association of carboxylic acids, Quarterly Reviews, Chemical Society, 7 (1953) 255-278.