

The role of membrane ξ -potential in solute rejection by low-pressure reverse osmosis membrane

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Abstract A new generation of reverse osmosis membranes, low-pressure reverse osmosis (LPRO) membranes, have been developed for operation under very low pressure (below 0.5 MPa). LPRO membranes have received attention especially for their application in the field of water and wastewater treatment, to provide a high water flux at low operating pressure while maintaining very good rejection levels of salts and organics. Our previous work on LPRO has shown that the rejection of some inorganic salts and organic compounds depends appreciably on the pH of the bulk solution, probably because LPRO membranes can have an electric charge. In this study we investigated experimentally the effectiveness of different LPRO membranes in separating inorganic salts and organic compounds from a bulk solution with different pH conditions. We also tried to measure membrane ξ -potential by using a streaming potential method. The results indicated that the membrane ξ -potential as well as the ion size or molecular weight of organics can be considered key factors in the rejection of ionic salts and dissociated organic compounds including pesticides and endocrine disruptors.

Keywords Dissociation constant; low pressure reverse osmosis (LPRO) membrane; membrane separation; membrane ξ -potential; streaming potential method

Introduction

The natural water system, including sources of drinking water, has been contaminated by various kinds of recalcitrant or hazardous substances such as pesticides, endocrine-disrupting chemicals and toxic inorganics. Many populated areas are facing water scarcity due to qualitative and quantitative deterioration of water sources. Membrane technology has been developed for desalination, removal of pollutants from water and wastewater, and recovery of water from effluent. Even conventional reverse osmosis (RO) membranes might be suitable for removing almost all pollutants. The use of RO systems, however, has been limited because they require high operating pressure, which entails high energy consumption. The introduction of low pressure reverse osmosis (LPRO) membranes would help membrane technology become more affordable and cost effective.

In previous work, we reported that the rejection of organic compounds by LPRO membranes is controlled mainly by molecular weight (Ozaki *et al.*, 2000, 2002). However, the rejection of dissociated chemicals depends also on the pH of the bulk solution and on the dissociation constant, indicating that the membrane potential also may be a main factor in this rejection.

It is well known that the membrane potential reflects its electric charge, which is induced by the dissociation of membrane surface components. The degree of dissociation depends on the pH of the bulk solution. For example, although the cellulose acetate RO membrane is called a non-charged membrane, the membrane actually has a slightly

negative charge. Ikawa *et al.* (1975) reported that the 6-nylon membrane, also classified as a non-charged membrane, was charged negatively in an acidic and neutral aqueous solution, charged positively in an alkaline aqueous solution, and had zero point of charge (zpc) at a certain pH. The composite membrane, which has been used frequently of late, is said to be charged negatively in a neutral or alkaline aqueous solution and charged positively in a comparatively strong acidic aqueous solution.

Information about the membrane potential should help clarify the mechanism underlying solute separation by the membrane. Such information has been scarce because the membrane potential is more difficult to measure than the potentials of other materials. In general, the potential of a material surface is indicated by ξ -potential measured in an electrolyte solution. The membrane can be measured by several methods: electrophoresis, streaming potential, electrometric titration, and other methods. The streaming potential method is the most adequate for measuring the membrane ξ -potential because it is the only method that does not require cutting of the membrane.

The objectives of this paper are to study the rejection of inorganic salts and organic

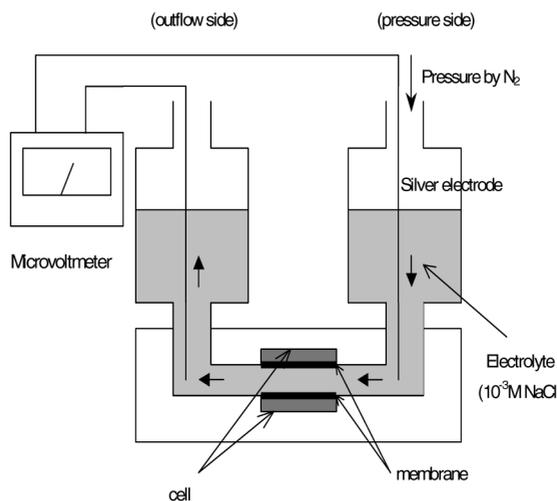


Figure 1 Schematic diagram of the streaming potential method experimental set up

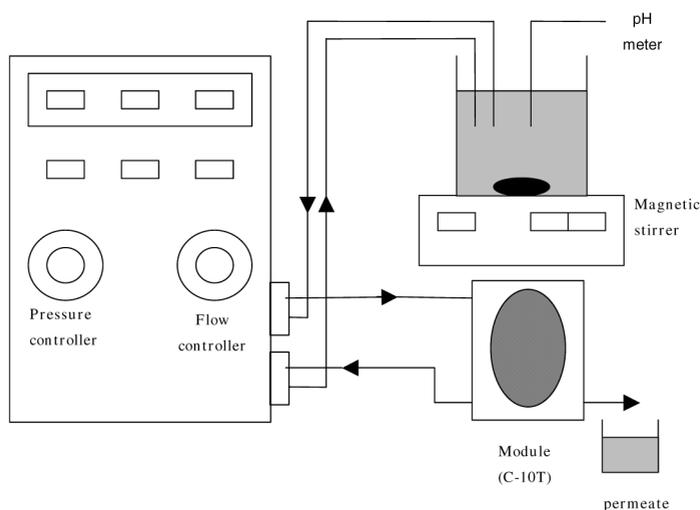


Figure 2 Schematic diagram of the membrane separation experimental set up

compounds by using LPRO membranes and to measure the ξ -potentials of the membranes used, in order to investigate the roles of those potentials in the rejection of solutes.

Materials and methods

Measurement of ξ -potential using the streaming potential method

A schematic diagram of the apparatus for measuring the membrane ξ -potential is shown in Figure 1. In this device, a micro-voltmeter detected the potential difference across each end of the silver chloride electrodes in the cell with the membrane, in which the electrolyte (10^{-3} M NaCl solution) was streamed by using pressurized N_2 gas. The cell was made of quartz glass, and the size of cell was 21 mm width and 41 mm length. The surface of the membrane mentioned below was exposed to the electrolyte. The electrolyte used in this research was 10^{-3} M NaCl solution, because this is the solution used to test membrane efficiency. The pH of the electrolyte solution was adjusted by 1 M HCl and NaOH solutions.

The membrane ξ -potential (ξ) was calculated by the following equation according to the Helmholtz-Smoluchowski formula:

$$\xi = 1.06 \times 10^5 \times (1/\rho) \times (E/P)$$

where ρ is the specific resistance of the solution and E/P is the gradient of potential difference to operating pressure.

Membranes

Four flat sheet membranes, manufactured by the Nitto Denko Corp., Japan (ES20, NTR-729HF, NTR-759HR and LF10), were used in this study. The characteristics of the membrane are listed in Table 1.

The NTR-759HR is an aromatic polyamide composite membrane categorized as an RO membrane. Under the optimum operating pressure of 1.0–2.0 MPa, this membrane exhibits flux higher than that of the conventional asymmetric RO membrane because of the thinness of its skin layer and its ionic character. The NTR-729HF is a conventional nanofiltration (NF) membrane whose surface layer material is a polyvinyl alcohol. The ES20 membrane, a multi-layer thin film composite of aromatic polyamide with a rough surface configuration, is a representative LPRO membrane and is called an ultra low pressure reverse osmosis (ULPRO) membrane. This membrane requires less than half of the operating pressure that most commonly available aromatic polyamide composite RO membranes require, and it gives higher solute rejection than the NTR-729HF of a conventional LPRO membrane. The LF10 is designed to minimize the adsorption of organic and inorganic foulants onto the membrane surface, which is characterized by a rough configuration and low electric charge.

Table 1 Summary of membranes used in laboratory-scale experiments

Characteristics	Membrane			
	LF10	ES20	NTR-759HR	NTR-729HF
Classification	ULPRO	ULPRO	(LP)RO	NF
surface area (cm ²)	60	60	32	60
Materials	Polyvinyl aromatic & polyamide alcohol	Aromatic polyamide	Aromatic polyamide	Polyvinyl alcohol
Feed pressure range (kgf/cm ²)	10–20	5–10	10–20	10–20
Reference 0.05% NaCl rejection (%)	99.8	99.7	99.6	94.0

Source: Nitto Denko Report

Membrane separation

Two types of laboratory-scale experimental setup were used for the membrane tests: a continuous type and a batch type. Figure 2 shows a schematic diagram of a continuous-type test unit. Each membrane was supplied in flat sheet form and mounted in the cross-flow module (C10-T). The membrane module was 110 mm wide, 210 mm long, and 82 mm high. The effective membrane surface area of the module was 60 cm², with 46 mm width and 180 mm length. A magnetic gear pump with a standard operating flow rate, 0.5–1.5 L/min, was used to operate the system at 0.4 MPa. The setup equipped with C10-T was used mainly for evaluating the performance of LPRO membranes in separating organic compounds and NaCl. All the organic solutes used in the experiment are listed in Table 2 along with their molecular weights and dissociation constants. The initial concentration of the solutes was 10 mg/L. In the case of slightly soluble organic compounds, such as pentachlorophenol, sodium salts of organic compounds were dissolved directly in double-distilled water. The rejection was measured under different pH values adjusted by HCl and NaOH solutions. Membrane efficiency was tested by sodium chloride at a concentration of 100 mg/L.

The batch-type test unit (c-70B) consists of a pressure cylinder, which used nitrogen gas to create high transmembrane pressure across a flat sheet membrane, and a test cell with an effective volume of 0.38 L and the effective membrane surface area of 32 cm². The cell was equipped with a magnetic stirrer inside to avoid concentration polarization. The test cell was used for the separation of boric acid using the NTR-759HR membrane at a transmembrane pressure of 0.6 MPa. The solution pH was adjusted initially to a fixed value.

Analysis

The concentrations of boron and sodium were analysed by a high-frequency plasma radiation analyser (ICPS-4960, Shimadzu), and chloride ion was analysed by an IONPAC AS4A ion chromatographer (Dionex). Chlorophenols, nitrophenols, and MCPA were analysed by a diode array UV spectrophotometer (HP 89532A) at 220nm. A total organic carbon (TOC) analyser (model TOC-500A, Shimadzu) was used for the other organic compounds. Permeate samples were taken every 30 minutes for the measurement of permeate flux and concentration. The feed concentration was measured at the middle of every 30 minute interval. The rejection R(%) was calculated by the following expression on each sample taken after the permeate became stable:

Table 2 Organic compounds used in this study

Compound name	Formula	Molecular weight	Dissociation constant(pKa)
Acetic Acid	CH ₃ COOH	60	4.7
Urea	(NH ₂) ₂ CO	60	–
Aniline	C ₆ H ₇ N	93	4.7
p-Nitrophenol*	C ₆ H ₄ O ₃ NNa	161	7.1
2,4-Dichlorophenol	C ₆ H ₄ O ₅ Cl ₂	163	7.9
2,4-Dinitrophenol	C ₆ H ₄ O ₅ N ₂	184	4.1
Methyl Alcohol	C ₂ H ₅ OH	46	–
Ethylene Glycol	HOCH ₂ CH ₂ OH	62	–
Benzyl Alcohol	C ₆ H ₅ CH ₂ OH	108	–
Glucose	C ₆ H ₁₂ O ₆	180	–
2,4,5-Trichlorophenol*	C ₆ H ₂ Cl ₃ ONa	219	6.7
Pentachlorophenol*	C ₆ OCl ₅ Na	288	4.7
MCPA	C ₉ H ₉ O ₃ Cl	200	3.1
Bisphenol A	C ₁₅ H ₁₆ O ₂	228	9.59~10.56
17-β estradiol	C ₁₈ H ₂₄ O ₂	272	10.08

* Sodium salt

$$R = (1 - C/C_0) \times 100 (\%)$$

where C and C_0 are the concentrations (mg/L) for the permeate and the feed solution, respectively.

Results and discussion

ξ -potential of the membrane

Figure 3 shows the dependency of ξ -potentials of four membranes on pH by using 10^{-3} M NaCl for the electrolyte. For all membranes, the ξ -potential showed positive values under the strong acidic condition. Those potentials were found to decrease sharply from positive to negative values as pH increased, and further decreased gradually in the neutral and alkaline regions.

Table 3 shows the zpc values of membranes interpolated on the basis of the results of the results shown in Figure 3. The zpc values ranged from pH 2.66 to 3.74. This indicates that the electric property of the membrane changes dramatically depending on the pH.

Membrane separation

Inorganic materials. Figure 4 shows the pH dependence of boron rejection in the NTR-759HR membrane. The rejection was low at a low pH condition and increased as pH increased. It can be said in general that boron exists in boric acid when pH is low, and that the boric acid, in turn, dissociates into ionic form of $B(OH)_4^-$ as pH increases (Choi *et al.*, 1979; Adams, 1964; Greenwood, 1973). From the results shown in Figure 4, the surface of the NTR-759HR membrane was negatively charged in neutral and alkaline aqueous solutions. Therefore, the higher degree of boron rejection with pH could be due to mutual repulsion between the negatively charged membrane and $B(OH)_4^-$.

Figure 5 shows the rejection property of NaCl in the NTR-729HF membrane. The rejection of Na^+ and Cl^- decreased as feed pH increased, and then increased after a minimum point at pH 4 was reached. The pH that gave the lowest value was almost in accordance with the zpc value of the NTR-729HF membrane. Similar to the property of boron rejection, the

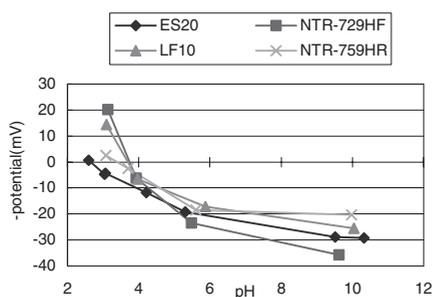


Figure 3 The effect of pH on ξ -potential of the membranes

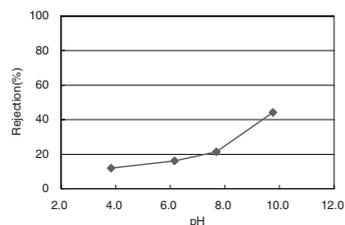


Figure 4 The effect of pH on rejection of boron (NTR-759HR)

Table 3 The zero-point of charge (zpc) of the membranes

Membrane	pH
ES20	2.66
NTR-729HF	3.74
LF10	3.70
NTR-759HR	3.39

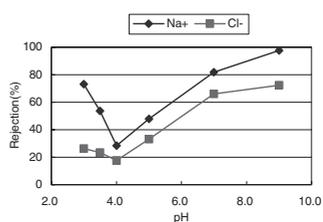


Figure 5 The effect of pH on rejection of NaCl (NTR-729HF)

mutual repulsion between the negatively charged membrane and the anion would increase the rejection of Cl^- when pH is in the region above the zpc value. Similarly, the higher rejection value of Na^+ could be explained from the mutual repulsion between the positively charged membrane and the cation. The rejection properties of Na^+ and Cl^- in the regions above and below the zpc value, respectively, could be attributed to the electroneutrality requirements on both sides of the membrane and to the Donnan potential. In addition, the ionized solutes could pass through the membrane easily if the membrane has no charge, because the repulsion between the membrane and the ions would be minimal.

The rejection of NaCl in the ES20 membrane was found to be around 99% regardless of pH. This means that the effects of membrane ξ -potential on electrolyte rejection would be dominant in a conventional LPRO membrane (NTR-729HF) rather than in an ULPRO membrane (ES20).

Organic compounds. Figure 6 shows the removal of acetic acid, aniline, and urea by ES20. The rejection of acetic acid increased with pH, whereas the rejection of aniline decreased with pH. The rejection of urea was almost constant. The rejection trends of urea and acetic acid with pH were quite different, although they have the same molecular weight (60). Urea cannot dissociate in the pH range of 3 to 9, but acetic acid can take on an anion form in the pH region above the pKa value (pH 4.7). Acetic acid and urea were rejected at the same level, around 34% at pH 3, where both compounds should be in an undissociated state. The rejection of acetic acid increased to 99.7% when pH was at least 5. These results indicate that molecular weight may be a main factor in the rejection of organic compounds at an undissociated state, and that the electrostatic repulsion between the negatively charged membrane and the acetic acid at the dissociated state may cause the overall rejection of acetic acid with pH. On the other hand, aniline was highly rejected at pH 3, where it may be dissociated in cationic form, because the pKa value is 4.7. The ES20 membrane has a slightly negative charge from the measurement of ξ -potential at pH 3. The high level of rejection may be due to the electrostatic interaction between ES20 and dissociated aniline. Figure 7 shows the rejection of p-nitrophenol, 2,4-dichlorophenol, and 2,4-dinitrophenol with pH. Their dissociation constants were 7.1, 7.9, and 4.1, respectively. The rejection of compounds increased with pH in the region above the pKa value, as seen in the rejection of acetic acid mentioned above. The results shown in Figures 6 and 7 suggest that the rejection of dissociated organic compounds with low molecular weight is significantly influenced not only by the positivity or negativity of the membrane ξ -potential, but also by its absolute value.

Figure 8 shows the rejections of methyl alcohol, ethylene glycol, benzyl alcohol, and glucose. They are all undissociated organic compounds. This result shows that the rejection of undissociated compounds depends not on the ξ -potential but on the molecular weight. Our previous work has shown that the rejection of undissociated compounds with a molecular weight of less than around 150 is directly proportional to the molecular weight and molecular width (Ozaki *et al.*, 2002). Figure 9 shows the rejection levels of the following

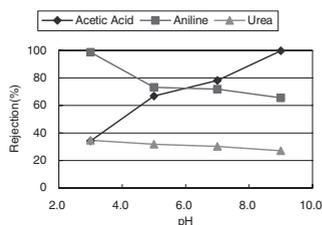


Figure 6 The rejection of acetic acid, aniline and urea (ES20)

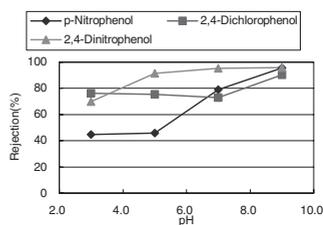


Figure 7 The rejection of dissociated organic compounds (ES20)

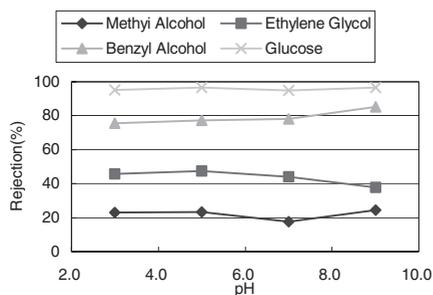


Figure 8 The rejection of undissociated organic compounds (ES20)

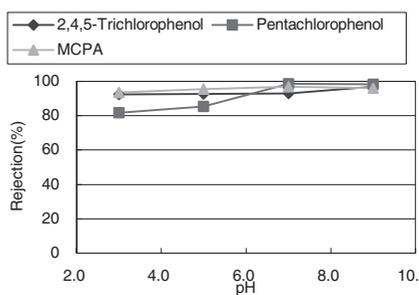


Figure 9 The rejection of dissociated organic compounds with high molecular weight (ES20)

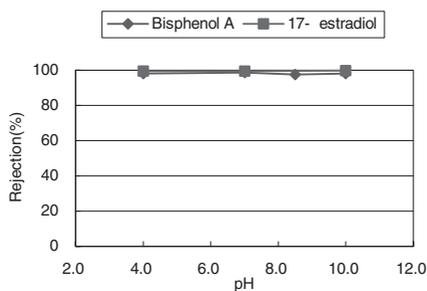


Figure 10 The rejection of endocrine disruptors (ES20)

dissociated organic compounds with pH: 2,4,5-trichlorophenol, pentachlorophenol, and MCPA. Although the rejection of pentachlorophenol showed a slight dependence on the pH of the aqueous solution, the rejection levels of other compounds were, on the whole, high regardless of the pH. This result shows that in the ULPRO separation of organic compounds with high molecular weight, molecular weight plays a more important role than membrane ξ -potential.

In recent years, some chemicals, such as bisphenol A in the water environment, have been reported to have the potential to interfere with the endocrine systems of the liver. These chemicals are called endocrine disruptors. Their removal is required in the water purification process. Figure 10 shows the rejection levels of two endocrine disruptors, bisphenol A and 17- β estradiol, by using ES20. As expected, the rejection levels did not show a dependence on pH, probably because they both have high molecular weight. Chemicals with low molecular weight, such as nonylphenol, may be dependent on solution pH and membrane ξ -potential.

Conclusions

1. The low pressure reverse osmosis membranes were positively charged under the strong acidic conditions and negatively charged under the weak acidic and alkaline conditions.
2. The zero point of charge (zpc) values of the LPRO membranes were found to be between 2.66 and 3.74, based on the streaming potential method of measurement.
3. The rejection levels of ionic organic salt and dissociated organic compounds with low molecular weight changed with pH, depending not only on the positivity or negativity of the membrane ξ -potential but also on the absolute ξ -potential value.
4. Organic compounds with high molecular weight, such as pentachlorophenol, showed high rejection levels regardless of the membrane ξ -potential.

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