



Role of coexistence of negative and positive membrane surface charges in electrostatic effect for salt rejection by nanofiltration

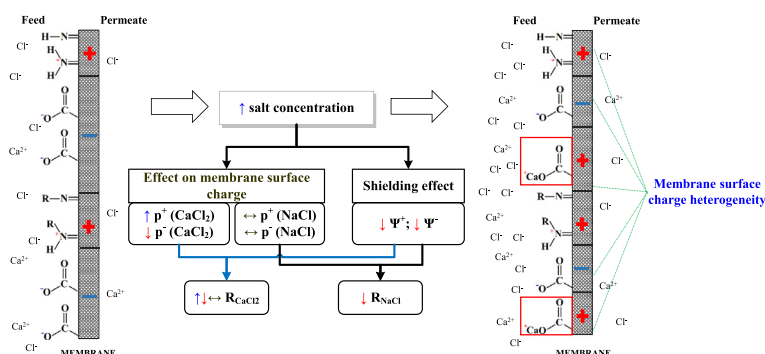
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GRAPHICAL ABSTRACT



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ABSTRACT

Electrostatic effect is a primary mechanism for nanofiltration (NF) in rejecting mineral ions in water. In this study, efforts were devoted to understand the change of membrane surface charges by pH-titrating synthesized poly(piperazine-amide) material in the presence of NaCl or CaCl₂ of different concentrations. It revealed that the membrane surface charges were resulted from dissociation and protonation of functional groups when in contact with NaCl solution, and additionally from specific complexation of calcium ions by acidic groups when in contact with CaCl₂ solution. Viewing the membrane with a uniform surface potential could not well explain the rejection behavior for CaCl₂-containing solutions. We proposed to treat the membrane surface as a mixed collection of positively and negatively charged regions, with these regions able to reject ions relatively separately. Increasing calcium ion concentration in the feed water could increase the proportion of positively charged regions. The enhanced shielding on positively-charged regions could reduce the rejection of calcium ions while that on negatively-charged regions could increase the rejection. This study could act to initiate further studies on the roles and importance of the coexistence of negative and positive charges at membrane surface in electrostatic effect on salt rejection.

1. Introduction

Nanofiltration (NF) is a membrane technology lying between

ultrafiltration and reverse osmosis (RO) which can selectively remove many types of dissolved matter from the feed water while possessing a relatively high water permeability [1,2]. The most common

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applications of NF technology are water softening [3], removal of natural organic matter [4], and decontamination of arsenic [5], heavy metals [6] and trace organic compounds [7]. Notwithstanding these applications, NF is a complex process which is yet not well understood. Mechanistic studies are still required for a deeper understanding and a better exploitation of the NF technology.

NF membranes have a relatively large molecular weight cut-off (from ~200 to ~500 Da) and as such the steric effect is not as strong as that by reverse osmosis membranes. In addition, NF membranes feature a plentiful of charges on the surface when in contact with water [8,9]. The membrane surface charges can arise from a number of mechanisms. While the dissociation of surface acidic groups and physical adsorption of anions lead to the formation of negative charges, protonation of surface alkaline groups, physical adsorption of cations and chemical binding of cations result in the formation of positive charges on membrane surface [10–13]. The water pH has a great effect on membrane surface charges in that pH can affect not only the dissociation/protonation of membrane surface functional groups but also the chemical binding of ions by these groups. In addition, ionic strength can also have a substantial influence on surface charge by changing the acidity/basicity of the surface functional groups and by establishing new equilibrating concentrations for surface adsorption and complexation [14–16]. The membrane surface charge endows NF membranes with a characteristic rejection mechanism by the electrostatic effect [17,18]. Variation of the membrane surface charge density can probably also change the membrane “pore” size and therefore the strength of steric effect on solute rejection [19].

The strength of electrostatic effect is widely indicated by the magnitude of zeta potential [20–22]. Most commercial NF membranes have a negative zeta potential at neutral pH, because on the surfaces negative charges dominate over positive charges. The conditions which have effects on surface charges can affect the zeta potential. In addition, ionic strength can have a great effect on zeta potential by the so-called shielding effect; an increased ionic strength usually leads to a reduced zeta potential but can rarely change its sign (e.g. from negative to positive) [19,23,24]. In comparison, a few studies [25,26] were devoted to determine the membrane surface potential from the measured surface charge density according to the classical Gouy–Chapman theory [27]. The membrane surface potential would be more appropriate to indicate the strength of electrostatic effect.

The above understanding forms the fundamental basis of current NF theory. It was widely applied for the interpretation of the many experimental observations for both sole and mixed salt solutions. For example, NF membranes could remove the multivalent co-ions at a much higher rate than the monovalent co-ions from the same water (e.g. sulfate over chloride ions) [28–30]. It was primarily because of that the electrostatic repulsion was stronger for multivalent co-ions which were not favourable for their approaching to and transporting through the membrane. Experimental studies showed that the increase of NaCl concentration in the feed water could lead to a reduction of its rejection by NF membranes [31–33]. It was attributed to the enhanced shielding effect which might lead to the reduction of membrane surface potential and resultantly the electrostatic effect. Notwithstanding the above success, a number of other experimental observations could not be well explained by the current theory. One notable example is the rejection of CaCl_2 by negatively charged membranes. The rejection is expected to increase with increasing concentration, because the Donnan effect is suppressed which resultantly would not be favourable for the mass transport of calcium ions and as such favourable for their rejection. While some studies showed that the CaCl_2 rejection went through a maximum value with the increase of its concentration [34–36], a number of other studies showed that the rejection decreased continually as the concentration increased [15,30]. Another example is that while an NF membrane had a lower rejection of CaCl_2 than NaCl when sole salt solutions were used, the membrane could reject calcium ions at a higher rate than sodium ions when a mixed salt solution was used

[37–39].

This study was conducted mainly to reconcile the existing controversies with regard to the electrostatic effect on salt rejection by NF membranes. Considering that the electrostatic effect (particularly the Donnan effect) is actually dictated by the membrane surface potential, efforts were devoted to understand the surface charge nature and density as a function of the salt type and concentration in the feed water by employing the pH titration method [13]. Self-prepared poly(piperazine-amide) material was used to represent the active layer polymer on the top of NF membranes. A new conceptualization of the electrostatic effect mechanism was proposed, which takes account of the co-existence of negative and positive charges on membrane surface. It was believed that the negatively charged and positively charged regions have different local surface potentials, which can exert electrostatic effects somewhat independently.

2. Materials and methods

2.1. Salt rejection experiments

A commercial NF membrane (DF10, Origin Water, China) was used for the salt rejection experiments. Details of the bench-scale NF system could be found in our previous studies [7]. The membrane was cut into a number of rectangular coupons which could fit the filtration cells in size. All membrane coupons were soaked in deionized (DI) water (Milli-Q, Millipore, USA) for at least 24 h prior to use. The fresh membrane in filtration cells was first compacted by filtering DI water at 9 bar for 2 h and the feed tank was then filled with a NaCl solution, a CaCl_2 solution, or a mixed NaCl and CaCl_2 solution (Table S1). To investigate the concentration effect, the NaCl and CaCl_2 concentrations were varied from 1.5 to 10 mmol/L and from 0.5 to 3.33 mmol/L, respectively. All feed water was buffered to a pH value at 7.4 by dosing 0.1 mmol/L NaHCO_3 followed by adjustment using concentrated HCl or NaOH solution. Filtration was carried out at five respective pressures of 2, 3.5, 5, 6.5, and 8 bar. At each applied pressure, water flux and solute concentrations in both the feed and the permeate were determined after a stabilization time of 4 h. Throughout each NF operation, all concentrate and permeate streams were returned back to the feed tank, except samples used for solute concentration determination. Water temperature was controlled at $16 \pm 2^\circ\text{C}$.

2.2. Membrane characterization

The DF10 membrane was characterized for the cross-section morphology through TEM observation, the surface wettability by employing the sessile drop method, and the nominal “pore” size by determining the rejection of a neutral solute (glucose) followed by fitting the rejection data using a hindered transport model [17,18]. More details could be found in the Supplementary materials. The FTIR spectra of the membrane were measured by using an ATR-FTIR spectrometer (Bruker, Horiba, Germany) (Fig. S2). Due to the relatively deep penetration depth (> 300 nm) of infrared rays, both the relatively thick polysulfone layer and the relatively thin polyamide layer were sampled. However, a comparison with the FTIR spectra of the NF270 membrane [40] showed that the DF10 membrane also had the characteristic absorbance band for the semi-aromatic piperazine-amide at around $1630\text{--}1671\text{ cm}^{-1}$. It suggested that DF10 was a kind of modified semi-aromatic poly(piperazine-amide) membrane. The typical chemical structure of poly(piperazine-amide) is schematically shown in Fig. S3.

The zeta potential versus pH profiles of the DF10 membrane were measured by using a SurPASS Electrokinetic Analyzer (Anton Paar GmbH, Austria), on principle of streaming potential determination. For each measurement, two pieces of DF10 membrane ($20 \times 10\text{ mm}^2$), which had been soaked in experimental electrolyte solutions for at least 12 h, were precisely cut and installed in an adjustable gap cell of the SurPASS instrument, separated with a $\sim 100\text{ }\mu\text{m}$ gap. The maximum

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