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## Study on ion separation by bipolar membranes in reverse osmosis

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### Summary

Nanofiltration (NF) membranes, which have molecular weight cut-off between conventional reverse osmosis and ultrafiltration membranes, have separation mechanism based on charged effect because of their surface charge. Bipolar membranes which consists of two layers having fixed positive and negative charge in series, can be prepared on the NF membranes. It has been verified experimentally that bipolar reverse membranes are effective to separate ions according to their valence types. The selectivity is thought to be affected by charge structural parameters such as thickness of each layer and the charge density.

The purpose of the present study is to discuss theoretically the separation ability of a bipolar membranes in reverse osmosis to improve the separation performance. Furthermore, inorganic NF membranes were prepared for finally developing inorganic bipolar membrane.

The extended Nernst-Planck equation including the contribution of volume flux to salt permeation is used as the basic equation to describe the transport through bipolar membranes in reverse osmosis, together with electroneutrality, Donnan equilibrium and reverse osmosis conditions. By model calculation of single-electrolyte solutions, monopolar membranes show high rejection for electrolytes having divalent cations; that is, a negatively charged membrane rejects sodium sulfate much more than other electrolytes such as sodium chloride and magnesium chloride, while a positively charged membrane rejects magnesium chloride more than sodium sulfate. On the other hand, bipolar membranes reject electrolytes having divalent ions for both cation and anions more than mono-monovalent electrolytes; both sodium sulfate and magnesium chloride are rejected more than mono-monovalent electrolytes such as sodium chloride. Calculation of ion rejection in mixed electrolytes reveals that a bipolar membrane effectively separates ions according to their valences; divalent ions are rejected more than monovalent ones in mixtures.

Porous silica-zirconia membranes were prepared by coating  $\alpha$ -alumina tubes with silica-zirconia sols which were controlled to have various particle size ranging from 100 to 10 nm. The membrane pore diameter was estimated to be less than 1 nm based on the dynamic permeation method of wet air. Streaming potential measurements of KCl solution at various pH showed that the iso-electric point of the obtained silica-zirconia membrane was around pH 4; Permeation experiments of various kinds of electrolytes at pH 5 where the membrane was negatively charged, show that sodium sulfate having sulfate ion of divalent anion rejected more than nickel nitrate having nickel ion of divalent cation. The rejection of sodium chlorides was in-between. Rejection decreased with an increase in feed concentration, and increased with an increase in applied pressure. Rejection of sodium sulfate was more than 98 % for the feed concentration ranging from 1 to 10 mol m<sup>-3</sup>, and was almost in the same order of commercial polymeric NFs of negative charge.