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Effect of ion composition on nanofiltration rejection for desalination pretreatment

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ABSTRACT

This experiment investigated and explains the rejection of calcium and magnesium ions and conductivity under the influence of the coexisting ions. Nanofiltration (NF) membranes have been used as pressure-driven type of cross-flow system in water treatment. The evolution of flux and rejection was followed in time during 2 h. For analysis and comparison, the values after 1 h of filtration were used. The NF membranes used in this study were thin film composite NF membranes NE90 (Woojing, Korea). The experiment indicated that Donnan exclusion had strong effect with cation when operated at low flux. However, the overall ion rejection, which was conducted by conductivity value, was high due to influence of dielectric phenomenon. For anion, electric repulsion between the NF membrane and chloride was high enough to push calcium and magnesium ions through the membrane by Donnan exclusion phenomenon. Chloride ion had stronger effect on the rejection of magnesium ion than the calcium ion. The results indicate that the electrostatic repulsion between the other anions (nitrate, sulfate, and bicarbonate ions) and the membranes seemed to be strong enough with the low concentration, but vice versa at high concentration.

Keywords: Desalination; Nanofiltration; Pretreatment; Ion composition; Coexistingion

1. Introduction

Desalination of seawater or brackish ground water or river water for a public potable water supply is increasingly being considered or adopted around the world. An inherent problem of desalination processes is scaling since it leads to precipitation on the desalination equipment. This problem increases operation and maintenance cost as well as high-energy requirement. Nanofiltration (NF) membrane has recently been employed as a pretreatment for desalination processes to overcome scaling problem [2–4,12,13]. NF pretreatment for thermal processes, such as multistage flash, makes it possible to operate at high distillation temperatures of (120–160 °C) with high recovery rate and without chemical addition. This process significantly improves the quality of permeate from reverse osmosis (RO) membrane [3]. An NF membrane is a type of pressure-driven membrane that its properties fall between ultrafiltration (UF) and RO membrane. The benefit of NF is easy for operation reliability and low-energy consumption as well as high efficiency of pollutant removal [1]. This helps in minimizing scale

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formation on equipment of RO and thermal desalination processes. Therefore, NF membrane has attracted interest worldwide for pretreatment of desalination processes. A recent comprehensive review on the use of NF membrane in water treatment has been presented elsewhere [15].

NF is a membrane filtration process widely used for separating multivalent solutes from univalent salts. It is a potential and pressure-driven membrane separation process that has been widely used in the treatment of water desalination and also water softening applications [5]. Multivalent solutes are removed through mechanisms including size exclusion, adsorption, charge repulsion, and hindered transports [9]. The rejection of ions by NF membranes might be explained by the combination of theories such as charge shielding, Donnan exclusion, dielectric effect, and degree of hydration [17]. However, several details must be clarified in order to predict the performance of the NF membrane in removal of the ions from feed water. This experiment investigated and explained the rejection of calcium and magnesium ions under the influence of the coexisting ions, mainly by electrostatic interaction.

2. Theory

The rejection of ions by nanomembranes might be explained by the combination of theories such as charge shielding, Donnan exclusion, dielectric effect, and degree of hydration. Charge shielding is phenomenon counterion shields on the membrane surface triggering repulsion interaction between shielding charge and co-ion in solution [18]. Donnan exclusion is phenomenon which is interaction between ion in solute and ion on membrane surface. The Donnan exclusion involves in ion rejection, ion rejection increase with the increasing co-ion charge and a decrease with the increasing counterion charge. Counterion can attach and diffuse through membrane surface [10]. Dielectric effect is the combination of phenomenon of charge shielding and Donnan exclusion. Two phenomenons occur via dielectric effect. First, the shielding counterion on membrane surface making polarization charge locates in boundary layer. This polarization charge has repulsion force with co-ion bringing about increase in rejection of co-ion. Second, the counterion, which adsorbs on membrane surface and also in side membrane sheet due to Donnan exclusion, is high enough to have repulsion interaction with the counterion (same sign with them) (Saliha et al., 2009). This results in increase in rejection of counterion. Degree of hydration takes charge of rejection of SO_4^{2-}, NO_3^-, and HCO_3^-. Degree of hydration is about amount of water molecules attracted to the molecules. The molecules having high degree of hydration will have low rejection and no effect on flux changing.

3. Materials and methods

A laboratory-scale cross-flow NF membrane was used in the experiment (Fig. 1). Raw water was fed into the filtration module by gear pump. The filtration experiments were carried out with a commercial nanofiltration unit on cross-flow module. In all experiments, transmembrane pressure (TMP) was 0.8 MPa at room temperature. A high cross-flow velocity of 1.5 L/min was applied in order to minimize concentration polarization. The membrane surface area was 0.005 m^2. The evolution of flux and rejection was followed in time during 2 h. For analysis and comparison, the values after 1 h of filtration were used.

The NF membranes used in this study were thin film composite NF membranes NE90 (Woojing, Korea). The membrane material was meta-phenylene-diamine with MWCO of 210–310 Da, zeta potential at pH 7 was −38.7 mV, contact angle was 41.5 ± 3.7 (°), and roughness was 48 nm.

4. Results and discussion

4.1. Membrane permeability

To calculate membrane permeability, water was subjected to permeation under different operating pressure as shown in Fig. 2. It is observed that NF membrane exhibited almost linear relationship

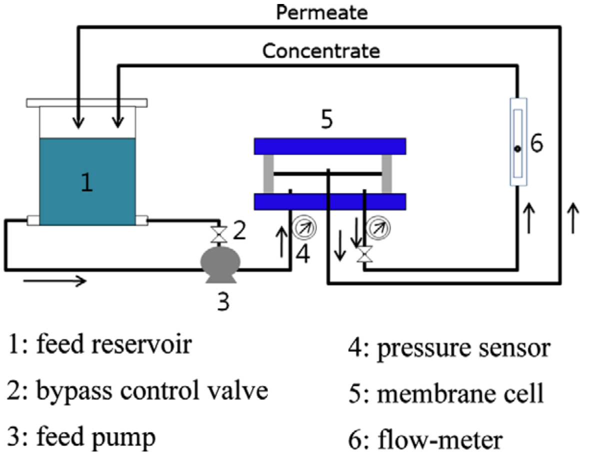

Fig. 1. Schematic of laboratory-scale cross-flow NF membrane system.

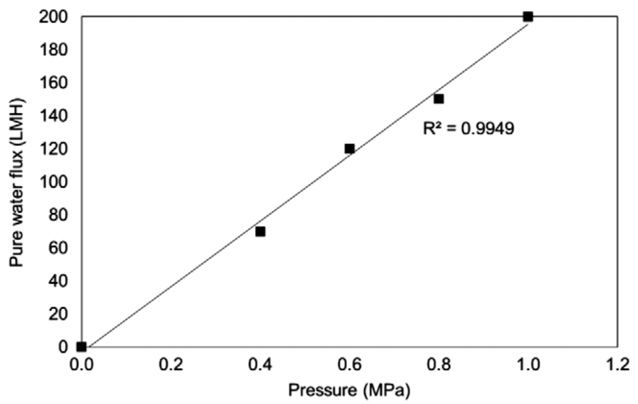

Fig. 2. Pure water flux as a function of pressure for NE90 membrane.

between flux and the TMP with R^2 value of 0.9949 at pH 7 and temperature of 20°C.

4.2. Effect of cation

Fig. 3 shows permeate flux of membrane with the variation of potassium and sodium ion concentration in feed water. The result shows that increasing of potassium ion concentration results in slight decrease of flux. On the other hand, the increasing of sodium ion concentration results in fast decrease of flux. Moreover, NF membrane flux in the presence of ionic solution also depends on pH of solute due to the association and dissociation of functional groups on the membrane surface as a result of changing membrane charge and consequently influencing flux characteristic [7]. However, in this study, effect of pH was not observed, thus the experiment was conducted at neutral pH to observe only effect of coexisting ion on calcium and magnesium flux and rejection.

Fig. 4 shows calcium ion, magnesium ion, and conductivity rejection of NE90 membrane with the effect of potassium ion in feed water. The result shows that increasing ion concentration results in decrease of conductivity rejection. And the rejection was increased again at final potassium ion concentration. The decline of calcium ion and magnesium ion rejection in the case of sodium ion might be caused by low permeate flux (Fig. 3). The calcium ion and magnesium ion could easily diffuse through membrane surface. Since at the same pressure (1.0 MPa), the adsorption capacity of cation on negative membrane surface is the same the experiment had low flux results even at high

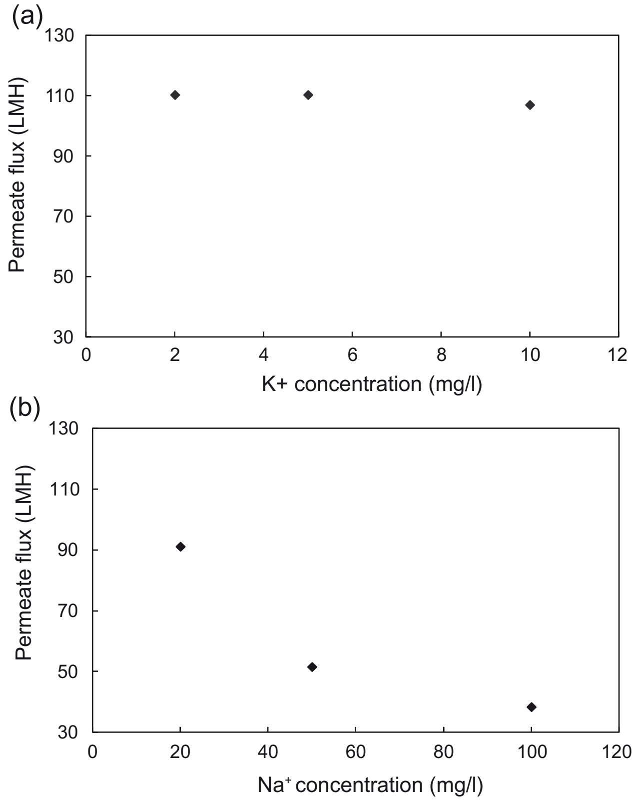

Fig. 3. Permeate flux with the variation K^+ (a) and Na^+ (b) of NE90 operated with TMP of 1.0 MPa and cross-flow velocity of 1.5 L/min.

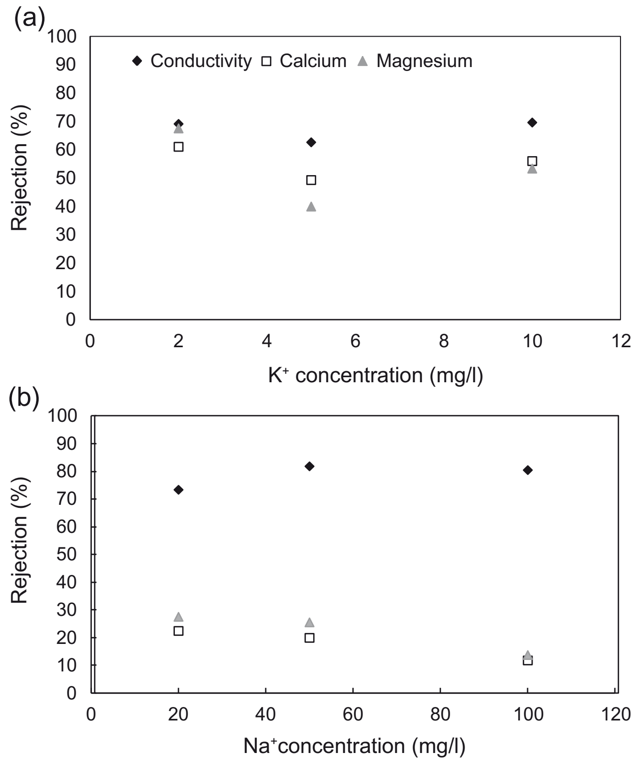

Fig. 4. Rejection with the variation K^+ (a) and Na^+ (b) ion of NE90 operated with TMP of 1.0 MPa and cross-flow velocity of 1.5 L/min.

diffusion capacity of cation through negative membrane surface. However, the overall ion rejection (conductivity) was increased because there was high rejection of anion due to dielectric phenomenon.

4.3. Effect of anion ion

Fig. 5 shows permeate flux of NF membrane with the variation of chloride, nitrate, sulfate, and bicarbonate ion concentration in feed water. The results indicated that electric repulsion between the NF membrane and chloride ion was high, so that it could push calcium and magnesium ions pass through the NF membrane. The influencing phenomenon was expected to be Donnan exclusion. It seems that chloride ion had stronger effect on magnesium than calcium ion. In the case of the other anions, electrostatic repulsion between the ions and the membrane was high enough to push the cations through membrane at low concentration which was mainly influenced by Donnan exclusion. However, at high anion concentration the opposite trend occurred because as expected at high anion concentration the electrostatic repulsion was overcome by the deposition of the cations on the membrane surface. It attributes to the simultaneous decrease of cations deposition caused by less electrostatic repulsion between the anions and the membrane, and as a result higher flux was observed.

Fig. 6 shows calcium ion, magnesium ion, and conductivity rejection with the effect of chloride, nitrate, sulfate, and bicarbonate ion in feed water. The result shows that increased anion concentration caused a decrease in calcium ion and magnesium ion rejection. This may be due to the effect of ion deposition on membrane surface in the initial making rejection drop due to diffusion of calcium ion and magnesium ion. It seemed that anions force calcium ion and magnesium ion pass through membrane and it had strong effect on magnesium ion than calcium ion. It seemed that bicarbonate ion forces calcium ion and magnesium ion pass through membrane and it had strong effect on calcium ion than magnesium ion.

From the above results, the rejection of calcium ions was found to be higher than that of magnesium ion. This may be explained by the smaller ionic radius of magnesium, the value is around 0.16 nm. The pore size of NE90 is around 210–310 Da (around 0.10–0.15 nm) which divalent ions cannot pass through via sieve effect. The transport phenomenon of divalent ions depends on interaction of solute, solvent, and membrane charge due to charge effect. It is an energy called "solvation energy" that involves different types of intermolecular interactions: hydrogen bonding, ion-dipole, and dipole-dipole attractions or van der Waals

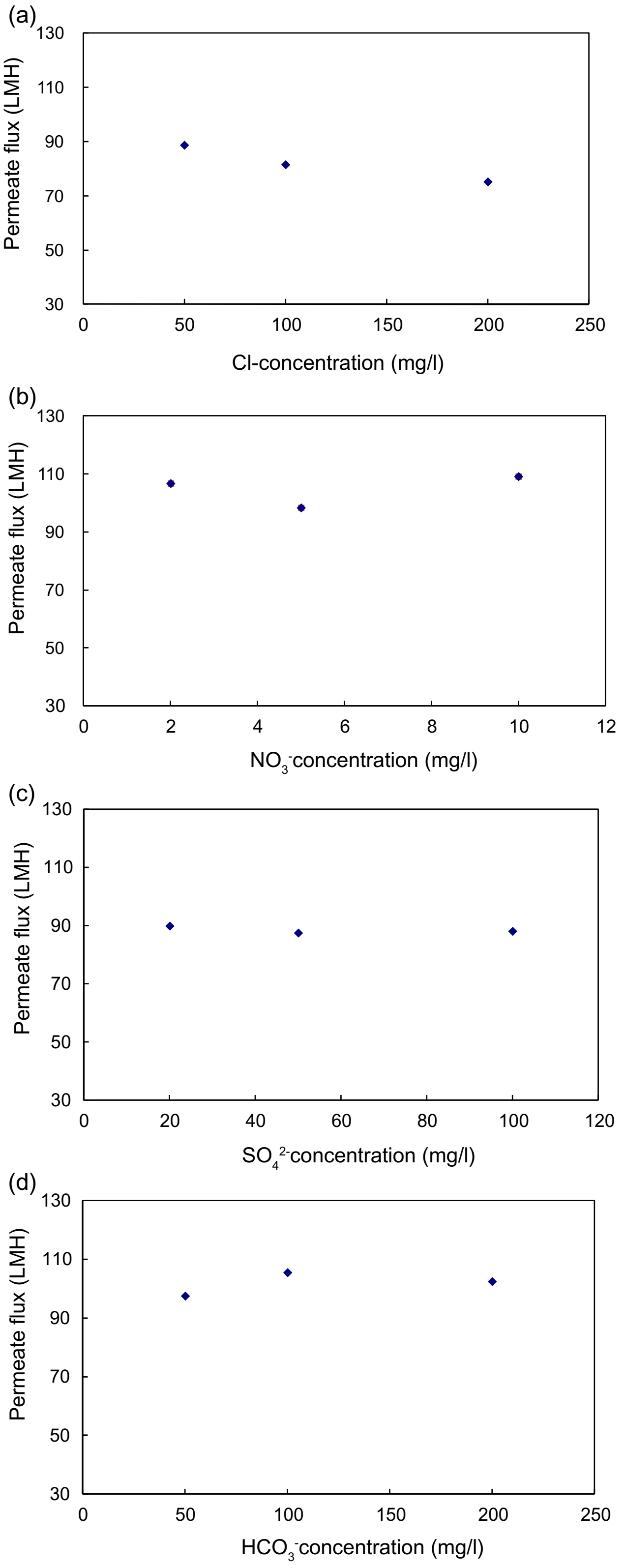

Fig. 5. Permeate flux with the variation Cl^{-}, NO_3, SO_4^2, and HCO_3 of NE90 operated with TMP of 1.0 MPa and cross-flow velocity of 1.5 L/min.

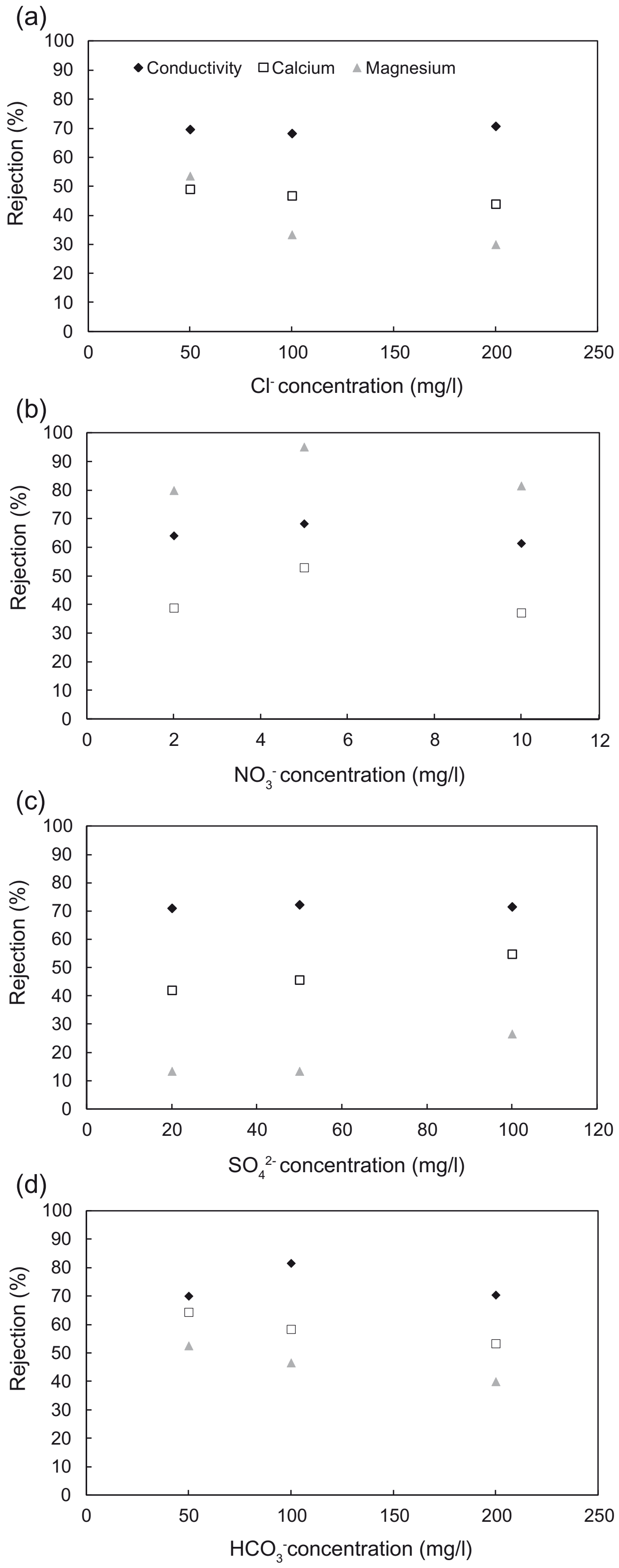

Fig. 6. Rejection with the variation Cl^- (a), NO_3 (b), SO_4^2 (c), and HCO_3 (d) ion of NE90 operated with TMP of 1.0 MPa and cross-flow velocity of 1.5 L/min.

forces [8]. The higher solvation energy of magnesium ion acts to augment their retention. The increase in rejection can be explained by the increase in the solvent flow, and as the transfer of solute does not increase well as solvent does, the solute is divided into a volume of more significant solvent. The permeate will be concentrated less and the rate of rejection will be more significant. Another explanation can also be given. For the charged membrane system, it was found that ionic molecules in boundary layer and surface charge density influence the characteristics of the ion concentration and distributions in the system [19]. When boundary charge was high, it had high potential for counterion to be adsorbed inside the pore and external bulk solution. Under the effect of pressure, there is a progressive accumulation of ions on the surface of the membrane due to drag force [20]. Therefore, the concentration polarization became high, which therefore establishes a gradient of concentration between the surface membrane and the feed solution. This difference in concentration induces a diffusional flow in the opposite direction of convective flow involving a reduction in transfer of the ions to the level of the membrane and thus more significant rejection.

At higher ion concentrations, the effect of steric hindrance can be negligible due to the shielding of charged solutes [11,14]. When NF membrane was placed in an ionic solution, due to association and dissociation of functional group on its surface, it leads to the formation of charges. The chemical and physical interactions exist, resulting in the adsorption of charges, since the counterions usually get adsorbed on the surface of membrane and co-ions are adsorbed onto the hydrophobic surface of the membrane. However, anion adsorption is more favorable due to its lower hydration radii compared to cations (Table 1).

The initial cationic deposition on membrane surface caused the rejection to drop due to diffusion of

Table 1
Atom properties

Atom	Charge	Ionic radii (nm)	Hydration radii (nm)
Calcium	+2	0.197	0.412
Magnesium	+2	0.160	0.428
Sodium	+1	0.186	0.358
Potassium	+1	0.213	0.331
Chlorine	−1	0.099	0.332
Nitrate	−1	0.148	0.335
Sodium	−2	0.177	0.379
Bicarbonate	−1	0.150	0.394

calcium ion and magnesium ion and also potassium ion through membrane surface. At high potassium ion concentration, there was high positive ion on membrane surface and also in membrane pore which created repulsion interaction between positive ion on membrane surface and solute (or called dielectric effect) causing increased rejection of calcium ion, magnesium ion, and conductivity (Fig. 6). Experimental data on rejection of calcium, magnesium, and conductivity with the variation of potassium ion in feed water are shown in Fig. 3. For Donnan effect, the negatively charged membrane tends to attract positively charged ions and vice versa. NF membrane in the presence of an ionic solution acquires charges due to the association and dissociation of functional groups on the membrane surface as a result of the ionization of functional groups on membrane surface. However, proper charge may be due to positive or negative charges on the functional group, which gives an approximate fixed charge. The physico-chemical interactions occur from the counterion adsorption of charges onto the membrane surface, due to the hydrophobic surface. However, anion adsorption is more favorable due to its lower hydration radii than the cations [16].

At low chloride concentration, adsorption at the membrane surface is negligible, whereas at higher concentrations, dielectric phenomenon occurs. Therefore, at high chloride concentration in feed, adsorption of chloride ions onto negatively charged membrane occurred [6], which agrees well with these results. However, chloride adsorption is prevalent on the membrane with respect to sodium adsorption, which is attributed to lower hydration radii of anions than cations. The cation is surrounded by water molecules with oxygen atoms approaching them, while anion is surrounded by water molecules with hydrogen atoms approaching them (Fig. 7). This experiment indicated that anion exhibited less effect on flux decline of negatively charged NF membrane due to its high degree of hydration. The electric repulsion between the NF membrane and chloride ion, nitrate ion and bicarbonate ion was so high that it could even force calcium ion and magnesium ion passing through the membrane. The experiment showed that when permeated calcium ion and magnesium ion cause a strong demand for anion permeation to meet the electroneutrality, it can be seen by decreasing of conductivity rejection together with calcium ion and magnesium ion rejection. The rejection rates of calcium ion and magnesium ion were similar.

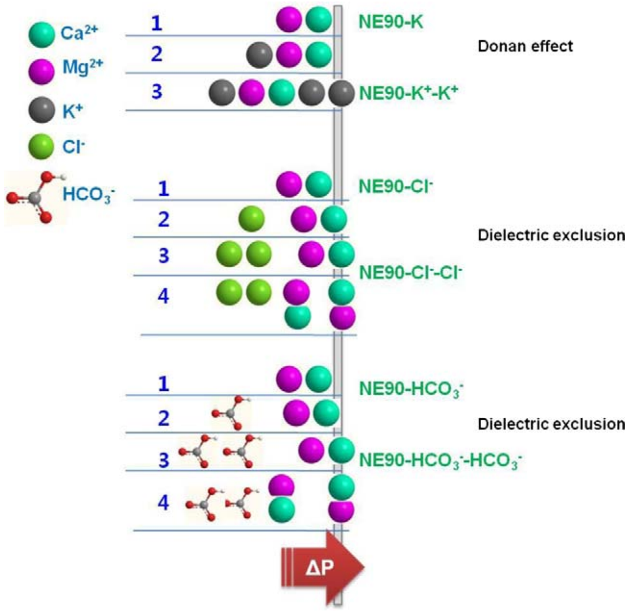

Fig. 7. Schematic sketch of interaction of cation and anion with membrane surface.

5. Conclusions

NF membrane desalination of seawater or brackish ground water or river water for a public potable water supply is a new promising technology which has been adopted around the world. This experiment investigated and explained the rejection of calcium and magnesium ions under the influence of the coexisting ions, mainly by electrostatic interaction. From the results, the study draws these conclusions:

- High concentration of cations may cause severe flux due to cation deposition on negative membrane surface via Donnan exclusion phenomenon. However, the overall ion rejection, which was observed through conductivity value, was high due to influence of dielectric phenomenon.
- With effect of chloride ion, flux, and rejection of the cations could be diminished as the effect of high electric repulsion between the NF membrane and chloride driving calcium and magnesium ions pass through the membrane through Donnan exclusion phenomenon. Chloride ion had stronger effect on magnesium than calcium ion.
- In the system having nitrate, sulfate, and bicarbonate ion as coexisting ion, it was found that the electrostatic repulsion between the other anions and the membranes seemed to be strong enough with the low concentration, but vice versa at high concentration. It can be mentioned that at high concentration of anions, flux, and rejection could be high owing to dielectric effect.

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