

## Stability of layer-by-layer nanofiltration membranes in highly saline streams

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### HIGHLIGHTS

- The fundamental understanding of salinity stability for LBL assembly is reviewed.
- Osmotic pressure and Le Chatelier's principle clarify the relation of overcompensation and salinity stability.
- The methods to enhance the salinity stability of LBL NF membranes are proposed.

### ARTICLE INFO

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### ABSTRACT

Layer-by-layer (LBL) assembly is an essential method for the preparation of nanofiltration (NF) membranes, offering tunable charge and pore size, high water permeability, and good anti-fouling properties, making them highly suitable for resource recovery, seawater desalination, and other fields. Despite their advantages, LBL NF membranes suffer from salinity instability, limiting their use in highly saline streams. This perspective review provides a summary of the fundamental physical and chemical principles of LBL assembly related to the salinity stability of LBL NF membranes. We critically analyze the driving force of LBL assembly, the binding strength of polyelectrolyte (PE) pairs, and the overcompensation of LBL membranes. We also discuss the factors affecting overcompensation level with respect to two different time scales. Furthermore, we examine the relationship between overcompensation level and salinity stability of LBL membranes, considering physical (osmotic pressure) and chemical (Le Chatelier's principle) aspects. Our analysis demonstrates that the salinity stability of LBL NF membranes in highly saline solutions can be improved by selecting PEs with stronger binding strength, increasing the overcompensation level, and chemical crosslinking. These methods not only enhance the salinity stability of LBL NF membranes but also offer greater potential for their future application in highly saline streams.

### 1. Introduction

NF is a pressure-driven membrane separation process with typical nanoscale pore sizes of 0.5–2.0 nm and operation pressure between reverse osmosis (RO) and ultrafiltration (UF) [1–6]. It has been widely used in solute-solvent and solute-solute separations, which covers applications for energy-efficient desalination and water purification [7,8], wastewater reuse [9], resource extraction [10–12], and organic solvent filtration [13]. Ideal NF membranes shall have high permeability and

high solute-solvent (or solute-solute) selectivity to improve process efficiency and product purity. Interfacial polymerization (IP), a method for producing commercial thin-film composite (TFC) NF membranes, has a great advantage in separation performance control [14–18]. Nevertheless, TFC membranes often have low permeability [19–22] and high fouling tendency [23–25]; the use of organic solvent for the IP reaction also causes environmental concerns [26,27]. Many other synthesis methods, including phase inversion [28], surface coating [29], spraying [30], surface grafting [31], solvent activation [32], have also

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been reported. Nevertheless, these methods are complex and thus difficult to be scaled up, and the membrane separation performance is generally poor [33].

Layer-by-layer (LBL) assembly is an emerging technology to prepare NF membranes, by alternately depositing water-based cationic and anionic polyelectrolytes (PEs) on support substrates [34]. Fig. 1a shows a schematic diagram of the LBL assembly [35]. A membrane substrate is immersed in polycation and polyanion solutions in an alternative manner to adsorb PEs, followed by rinsing with water to remove the excessive PEs and rearrange the adsorbed PE layers [35,36]. A polyanion coating coupled with a polycation coating results in a PE bilayer. Multiple bilayers can be assembled by repeating the alternative coating cycle. The use of water as the solvent for LBL technology avoids harmful organic solvents, making LBL a green and sustainable membrane fabrication process [10,25,37–39]. In LBL, both cationic and anionic PEs carry linear long chains, resulting in intrinsic interconnected nanochannels for selective water transport with high permeability [34]. The wide selection of PEs could facilitate fine-tuning charges and pore size in the nanochannels for ion selective permeation [40]. In addition, LBL NF membranes often exhibit strong antifouling characteristics mainly due to two reasons: 1) membrane surface is hydrophilic [41,42]; 2) the electrostatic repulsion between the membrane surface and contaminants with the same charge hinders the adsorption of foulants [43,44]. LBL NF membranes could also show strong antibiofouling performance mainly due to strong binding between its multifunctional groups and nanomaterials [45]. Versatility of LBL NF membranes attributes great promise for their wider applications.

Despite their obvious advantages, LBL NF membranes have a major

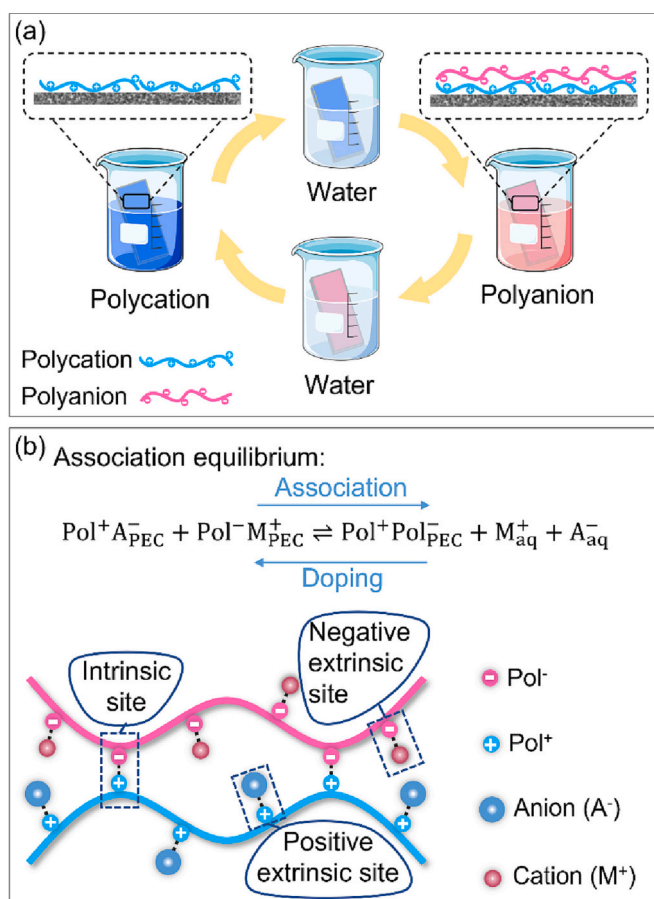


Fig. 1. Scheme of (a) LBL assembly to prepare nanofiltration membranes [35]; (b) The association equilibrium of PEC, with the right direction showing ‘association’ and left direction showing ‘doping’, and a scheme of intrinsic and extrinsic sites in PEC [46].

disadvantage of membrane instability when treating highly saline feed streams (e.g., for seawater pretreatment or source recovery from salt lakes). Typically, the polyelectrolyte complexes (PECs) formed in LBL assembly are regulated by electrostatic interaction between the anionic and cationic PEs and often do not involve strong chemical bonds. At high salinity, PECs tend to dissociate due to the competition between salt ions and paired PE units for the same site [45,47]. Many studies have shown impaired performance for LBL NF membranes in highly saline solutions. For instance, a study reported that the rejection of  $Mg^{2+}$  decreased from 90 % to 77 % under the influence of high salinity when increasing  $Mg^{2+}$  concentration from 5 mM to 500 mM [48]. Significant salt leakage of the LBL membrane was observed in forward osmosis using 0.5 M  $MgCl_2$  as draw solution [49]. Some studies suggested that crosslinking of LBL membranes could potentially improve their stability in saline solutions [25,50]. Nevertheless, up to date, there is no systematic review addressing this critical challenge of LBL NF membranes.

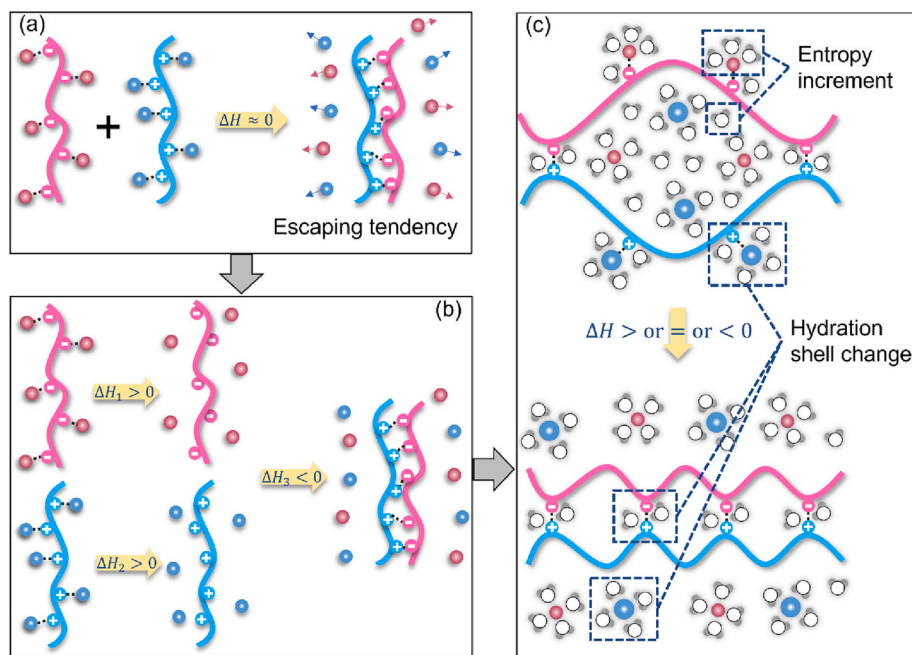
In this critical review, we first summarize the state-of-the-art fundamental understanding of the chemical and physical basis for LBL assembly in correlation to stability in high salinity streams. The thermodynamics of LBL assembly, including the driving force, binding strength, and overcompensation are critically analyzed. Approaches for enhancing the stability of LBL NF membranes in highly saline solution are introduced to provide scientific and technical guidance for the application of LBL NF membranes under high salinity environment. Future aspects of LBL membranes in saline feed highlight the potentials of LBL NF membranes in various applications.

## 2. Fundamentals of LBL assembly

### 2.1. Driving force for PE association

The LBL separation layer, or the PEC, is formed spontaneously with the ‘association’ of polyanion ( $Pol^-$ ) and polycation ( $Pol^+$ ) (Fig. 1b) [47]. The PEC ‘association’ can be reversed, a process known as ‘doping’, to result in  $Pol^+A^-$  and  $Pol^-M^+$  as salt concentration increases [51]. There is a competitive relationship between the association of PE pairs and the association of PE and counterions [47]. When the concentration of counterions increases, it is beneficial to the competition of counterions. Counterions tend to bind to PEs and destroy PE pairs. This behavior is called ‘doping’. All PE pairs ( $Pol^+Pol^-$ ) are termed intrinsic sites, while the PE units associated with a counterion ( $Pol^+A^-$  and  $Pol^-M^+$ ) are called extrinsic sites [46,52,53]. The electroneutrality in PEC is balanced by the PE pairs and PE/ion pairs. Research on the driving force of LBL assembly has been an enduring topic. There are two main controversial driving forces of assembly: 1) the electrostatic interaction between opposite charges of PEs; 2) the entropy increase caused by the release of counterions and water molecules. The cartoons in Fig. 2 present the three typical historical stages of the driving force of LBL assembly:

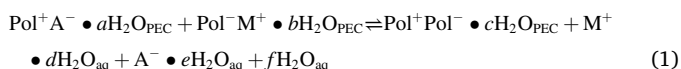
- (1) In 1960s, limited by the minimal detecting threshold of thermal analytical instrument, no heat was detected upon PE association. Thus, electrostatic interaction was ruled out as the main driving force of assembly [54]. In addition, the absence of counterions was observed in PEC [55]:  $Cl^-$  in the liquid supernatant after poly-(vinylbenzyltrimethylammonium chloride) (PVBTAC) and excess sodium poly(styrenesulfonate) (PSSNa) reaction were titrated by  $Ag^+$ , and it was found that all  $Cl^-$  were released into the solution. Therefore, it had been speculated that counterions were shaken off and the entropy of the system increased when cationic and anionic PEs assembled, as shown in Fig. 2a. The entropy increment contributes to a negative free energy, and the main driving force for assembly was considered as ‘escaping tendency’ of counterions [54].
- (2) In 1990, heat signatures in poly(trimethylammonium-2-ethyl methacrylate) chloride (PTMAC)/PSS association were detected



**Fig. 2.** Evolution of understanding the driving force of PEC association: (a) The escaping tendency was the main driving force of LBL assembly [54]; (b) Enthalpy change was detected, and electrostatic interaction was believed to be the main driving force [56,57]; (c) Most of the free energy of PE complexation is contributed by entropy change from released counterions and water molecules, and the small enthalpy change is due to the hydration shell change [47].

by a C-80 Calvet microcalorimeter with the precision  $\pm 0.1\%$  [56,57]. The experimental results indicated convincing evidence of electrostatic interaction. Thus, enthalpy instead of entropy change has been proposed as the main driving force showing in Fig. 2b [56,58–63].

- (3) However, enthalpy as the driving force was not yet the ending of the understanding. Fu et al. [47] measured PEC association constant  $K_a$  obtained from salt doping experiments, and then substitute into  $\Delta G^0 = -RT \ln K_a$  to evaluate the free energy of association. The enthalpy change upon PE association was determined by isothermal calorimetry and entropy increase was calculated from  $\Delta G^0 = \Delta H^0 - T\Delta S^0$ . It was found that PE assembly could be exothermal, endothermal and athermal, which contributes only a small part of the free energy; 90%–100% of the free energy of PE complexation was contributed by entropy change from released counterions and water molecules upon assembly. They also tested hydrogen bond change by Raman spectroscopy, and the small enthalpy change during PE association was verified to derive from net changes in hydration shells around the PE repeat units and the counterions, as shown in Fig. 2c ‘hydration shell change’ and Eq. (1) which shows the change in hydration water molecule [64], rather than the electrostatic interaction between charged substances.



According to the latest research, entropy increase by releasing small ions and water molecules is the main driving force of PE association. The hydrophobic PEs that tend to release water molecules and the hydrated salt ions that are tightly wrapped by the hydration layer and thus difficult to bind to PE can enhance the stability of PEC in highly saline solution [65]. Quantification of the Gibbs free energy of PEC association using different PEs or salts in Sections 2.2 and 2.3 is a more intuitive manifestation of PEC salinity stability.

## 2.2. Binding strength of PE pairs

The binding strength of PE pairs is determined by the Gibbs free energy of PEC association, which can reflect the difficulty of ion doping in salt solution. PEC is sensitive to the salt in the bulk solution [53,66–68]. Adding salt tends to break the binding of  $\text{Pol}^+ \text{Pol}^-$ , converting them to  $\text{Pol}^+ \text{A}^-$  and  $\text{Pol}^- \text{M}^+$ , and water and ions are introduced consequently [67], whereas association occurs when the salt concentration declines [66,67]. Doping in highly saline solution leads to reduction in intrinsic compensation, resulting to loosen LBL separation layer, and declined ion separation performance. The PE pair with greater binding strength is more resistant to salt doping, and thus the prepared LBL NF membrane is more stable in highly saline solution. Therefore, the binding strength of PE pairs is an important parameter for the stability of LBL NF membranes in high salinity environment.

Binding strength of PE pairs can be quantified experimentally and used as a reference for the selection of PE pairs for LBL NF membrane preparation. Fu et al. [69] studied the binding strength of different PE pairs by measuring the association constant  $K_a$  of Eq. (1). The Gibbs free energy of a series of associated PE pairs are listed in Table 1. PVA and PSS has the strongest binding strength, followed by PAH and PSS. A ranking of the binding strength of individual PE is given in Fig. 3: PSS >

**Table 1**  
Gibbs free energy of PE association [69].

$\Delta G_a^0$ (kJ mol <sup>-1</sup> )	PSS	PVS	PAMPS	PAA
PDDP	0.57	–	–2.70	–
PVTA	–0.97	–1.52	1.40	–
PDADMA	–2.19	–	3.14	6.03
PAH	–6.34	–3.50	–3.36	–2.30
PVA	–7.10	–2.18	–	–

Note: Polycations: PAH (poly(allylamine)); PDADMA (poly(diallyldimethylammonium)); PDDP (poly(*N,N*-dimethyl-3,5-dimethylene piperidinium)); PVA (poly(vinylamine)); PVTA (poly(vinylbenzyltrimethylammonium)). Poly anions: PAA (poly(acrylic acid)); PAMPS (poly(acrylamido-2-methylpropanesulfonate)); PVS (poly(vinylsulfonate)); PSS poly(styrenesulfonate). Polyethylene mine (PEI) is also a common polycation, but the Gibbs free energy about PEI association is not available.

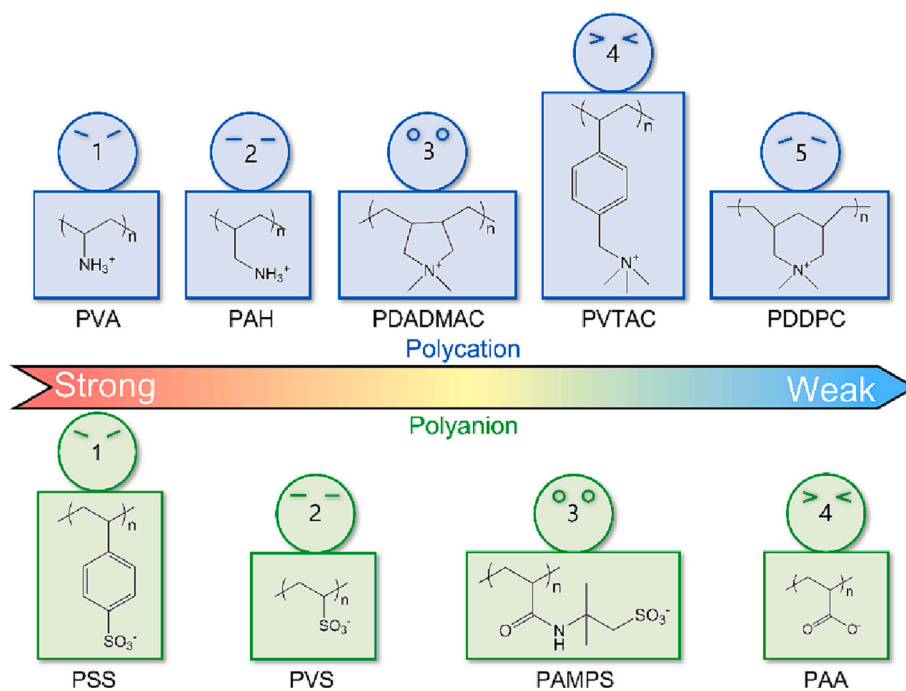


Fig. 3. Scheme of binding strength of PE pairs [69], adapted with permission from ref. [69]. Copyright 2017 American Chemical Society.

PVS > PAMPS > PAA for polyanions, PVA  $\approx$  PAH > PDADMA > PVTAC > PDDPC for polycations. The chemical structure of the PEs determines the binding strength. The binding of carboxylate is generally weaker than that of sulfonate, and the binding of primary amine is stronger than that of quaternary ammonium. Hydrophobic PEs normally have high binding strength. In addition, the binding of aromatic sulfonates was stronger than aliphatic sulfonates, because of the additional interaction between cation and  $\pi$  bond [69]. Due to the presence of resonant  $\pi$  electrons, the aromatic groups can be an electron-donating ligand to bind a positively charged species with empty orbitals through coordination bonds

[70–72]. Selection of PEs with higher binding strength should be beneficial to stability of LBL NF membranes in highly saline solutions. Therefore, PE pairs of PVA/PSS and PAH/PSS are favorable for LBL membrane preparation, while PDADMA/PAA, PDADMA/PAMPS, PVTAC/PAMPS and PDDPC/PSS are not recommended.

### 2.3. Counterions and binding strength

The other factor affecting the stability of PECs are the counterions. The capability of the counterions to associate with the charges in the

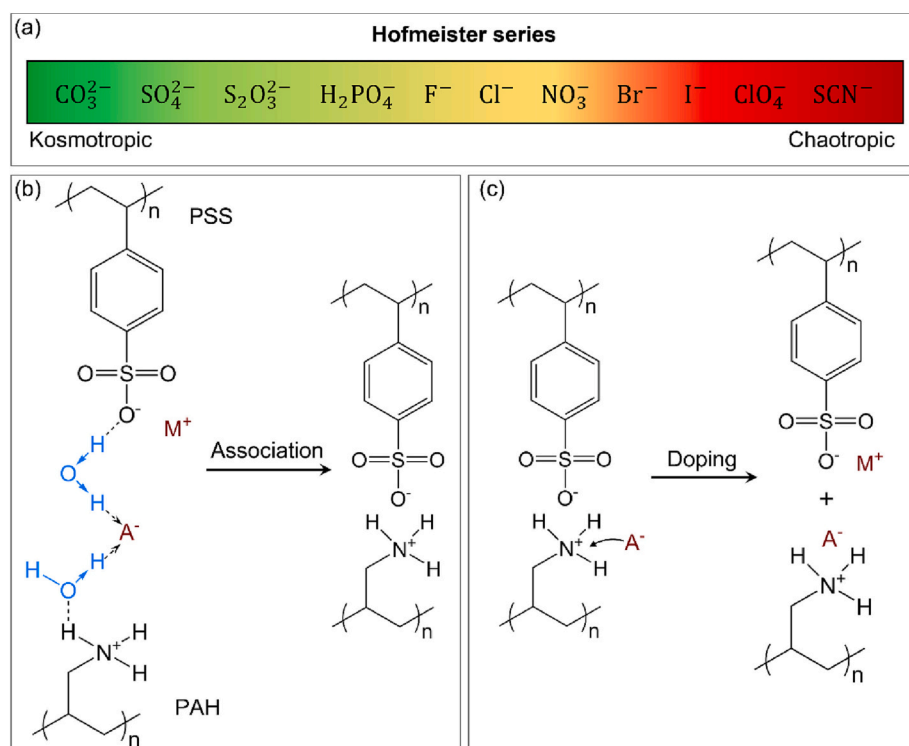


Fig. 4. (a) Hofmeister series. (b) Hydrogen bonds in the hydrated layer of charged groups in PSS and PAH are polarized by kosmotropic ions, followed by dissociation. The hydration layer is destroyed, and PSS and PAH associate. (c) Direct binding of bare chaotropic anions to PAH in PEC. Weakly hydrated anions with high  $K_{\text{dop}}$  can bind directly to positively charged groups in polymers [77], so the bare chaotropic anions can easily attack the binding sites in PEC, leading to dissociation.  $\text{M}^+$ : cation;  $\text{A}^-$ : anion.

polycations or polyanions is crucial as demonstrated in an empirical description of the ability of anions to ‘salting out’ proteins from aqueous solutions, in a Hofmeister series as shown in Fig. 4a [73]. Not surprisingly, it was found that this empirical rule was also applicable in PEC doping [65,74]. It was found that the difference of cations in the Hofmeister series is much smaller, so anions are generally discussed [75]. The ions in Hofmeister series (Fig. 4a) are categorized into kosmotropic and chaotropic ions in line with their water affinity. The kosmotropic ions at the left are characterized by ‘making’ water structure, which are tightly bound to adjacent water molecules due to small size and high charge density. The chaotropic ions at the right are characterized by ‘breaking’ water structure [76]. Because of large size and low charge density, their binding strength with water is lower than that between the water molecules and bulk water. Therefore, water molecules are more inclined to return to bulk water [64,76,77].

Anions have different effects on the PE pair due to the difference in the interaction with water in the hydrated layer - promoting PE association or dissociation. The distance that these ions can affect the surrounding water molecules is very small, approximately inside first hydration layer [78]. The numbers of water molecules in the first hydration layer of anions, named hydration numbers [79], are basically consistent with Hofmeister series comparing with Fig. 4a and Table 2. The more kosmotropic ions have larger hydration numbers, while the more chaotropic ions have lower hydration numbers. The interactions among ions, hydration waters and PEC are shown in Fig. 4b and Fig. 4c, taking PAH and PSS as an example. Strongly hydrated anions can destroy the hydrated shell of polar groups in polymer [77]. The water molecules in the hydration shell of charged groups in the PEs is polarized by kosmotropic anions through induction effect (Fig. 4b) [76,78]. Consequently, the hydrogen bonds combined with PEs are broken and water molecules are taken away, contributing to entropy increment. Meanwhile, the destruction of the hydration layer allows the opposite charged groups in the PEC to reach a sufficiently short distance to bind. Both entropy increase and destruction of the hydration layer promote the association of polyanions and polycations. Combined with the doping constant in Table 2, the kosmotropic ions have lower  $K_{dop}$ , which means it is more difficult for them to dope the PEC. On the contrary, weakly hydrated anions with high  $K_{dop}$  can bind directly to positively charged groups in polymers [77]. The bare chaotropic anions can easily attack the binding sites in PEC, leading to dissociation (Fig. 4c) [76,78]. Therefore, the chaotropic ions in the Hofmeister series dope PEC more easily [64], and the stability of the LBL NF membrane is reduced in the solution containing chaotropic ions. Considering the anions, LBL NF membranes are most probably stable in  $F^-/CH_3COO^-$  solution, but not in  $SCN^-/ClO_4^-$  solution at high concentration.

## 2.4. Overcompensation and salinity stability

### 2.4.1. LBL assembly occurs due to overcompensation

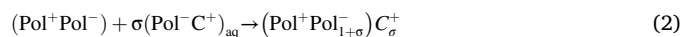
Polyanion and polycation in PEC is often assumed to be 1:1 (stoichiometric) [80], but in reality, there is usually an excess of one type of PE during PEC buildup [35,81,82], called overcompensation or

**Table 2**

Hydration Numbers of different anions in water [65] and doping constants ( $K_{dop}$ ) in PDADMA/PSS extruded PEC in NaA solution [64]. Doping constant is the equilibrium constant of doping reaction.

Anion ( $A^-$ )	Hydration number	$K_{dop}$
$SCN^-$	1.7	3.2
$ClO_4^-$	1.4	2.4
$I^-$	1.6	1
$Br^-$	1.9	0.42
$NO_3^-$	2	0.41
$Cl^-$	2	0.3
$ClO_3^-$	-	0.18
$CH_3COO^-$	-	0.02
$F^-$	2.7	0.008

overcharging as shown in Fig. 5a [46,83]. Overcompensation is represented by [84]:



where  $\sigma$  is overcompensation level.  $\sigma$  is defined as:

$$\sigma = \frac{[Pol^-]}{[Pol^+]} - 1 \quad (3)$$

This section outlines the impact of overcompensation upon PE assembly on the salinity stability of LBL membranes. Due to the strong interaction between the PEs, as well as the PEs and the charged surface, the PEs do not accumulate randomly, but deposit with a fixed sequence [85]. Overcompensation occurs due to correlation between PEs, forming an arrangement similar to Wigner crystals [85,86]. The deep understanding about how the correlation determines overcompensation exceeds the scope of this perspective. Upon each newly assembly of PE pairs, overcompensation of the last PE occurs. This is the core feature for assembly of the next oppositely charged PE [35].

The process of overcompensation is not only the excessive adsorption of PE with opposite charge on PEC surface, but also the PE adsorbed on the surface diffuses into the PEC through site diffusion [84]. Site diffusion (Fig. 5b) of PEs is at least 2 orders of magnitude faster than polymer diffusion, since only localized rearrangements of PEs with few kinetic restrictions were needed to propagate the charge when a polymer touched the film surface, leading to multilayer growth. Additional PEs could be added to the film through slight perturbation, and the PE chains did not need to transmit at the film level through PEC. If time is sufficient, overcompensated PE can diffuse throughout the whole PEC. More information about site diffusion is shown in supporting information (SI, S1).

The PEs in the solution are continuously adsorbed on the PEC surface and diffuse into the PEC. There is a relationship between the length of site diffusion path,  $\Delta$  (cm), and assembly time,  $t$  (s), defined as  $\Delta = \sqrt{2Dt}$ , where  $D$  is site diffusion coefficient ( $cm^2/s$ ) [84]. When the site diffusion path is shorter than the film thickness, the PEs are unable to diffuse to the whole PEC (Fig. 5c). Overcompensation level is affected by time and diffusion coefficient, controlled by kinetics [84]. When the site diffusion path is longer than the film thickness within assembly time  $t$ , the overcompensation reaches equilibrium, which is controlled by thermodynamics (Fig. 5c) [84]. It often takes several hours for PEC of several hundred nanometer thickness to reach overcompensation equilibrium, while only a few minutes is allowed for each layer in PEC assembly experiment [84,88,89]. Therefore, we need to consider two timescales which affect the state of overcompensation: a short time scale of a few minutes and a long time scale of a few hours.

On a short time scale of a few minutes, the overcompensation is far from equilibrium [46]. The overcompensation level is determined by adsorption of PE from the solution, PE diffusion coefficient in PEC and time [90]. PE adsorption is related to PE concentration and salt concentration [91]. PE adsorption increases with PE concentration and then reaches the plateau [91]. For instance, PDADMAC adsorption was reported to reach the plateau at 7 mg/L PDADMAC [91], normally lower than the PE concentration in LBL NF membrane preparation [25,92–94]. Higher ionic strength is found to be favored for PE adsorption [91]. The diffusion coefficient is affected by the type and concentration of salt [84]. The more chaotropic salt or higher concentration are favorable for site diffusion [84]. Therefore, higher PE concentration when not reaching the platform, higher salt concentration, more chaotropic salt, and more time (at short time scale) contribute to higher overcompensation level.

On time scale of a few hours, overcompensation reaches thermodynamic equilibrium. Overcompensation level weakly correlates with the PE molecular weight, and is independent of PEC thickness, polymer concentration and salt concentration [46]. The weak dependence between PSS overcompensation and PSS molecular weight scales as

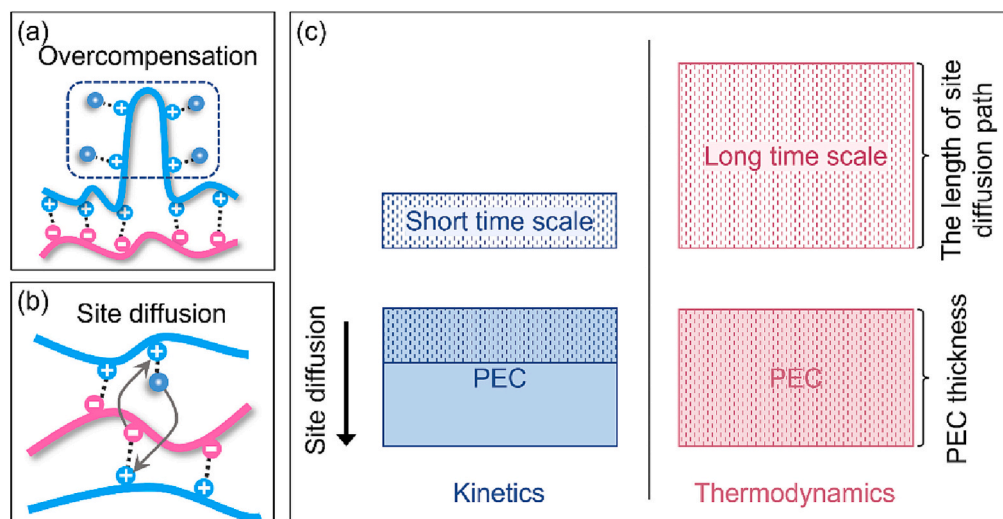


Fig. 5. Scheme diagram of (a) overcompensation of polycation [87] and (b) site diffusion [84]. (c) Overcompensation controlled by kinetics and thermodynamics. The dot-filled region represents the length of site diffusion path, and the solid-filled region represents PEC thickness. Kinetic control: When the assembly time is very short, the length of site diffusion path is possibly smaller than PEC thickness and thus the overcompensation region cannot cover the entire PEC [84]. Thermodynamic control: When the assembly time is very long, the length of site diffusion path is possibly longer than PEC thickness and the whole PEC reaches overcompensation equilibrium [84].

$\sigma \sim M^{0.15}$ . PECs with different thicknesses can achieve the same overcompensation level when the time scale is sufficiently large (several hours for the PEC with hundreds of nanometers) [84]. Excessive PE extends to the entire PEC film until overcompensation equilibrium, thus independent of the film thickness. The overcompensation level is independent of PE concentration. Similarly, an independence of overcompensation equilibrium on NaCl concentration is reported [84]. Although salt concentration affects instantaneous adsorption, PEs diffuse into PEC and fresh PE chains continue to adsorb on the surface until overcompensation equilibrium. The overcompensation is faster at higher NaCl concentration, owing to higher apparent PE diffusion rate. The final overcompensation levels were the same at different NaCl concentration, although the time varies for overcompensation equilibrium. Additionally, high NaCl concentration (>2 M) would cause PEC erosion, leading to decreased apparent overcompensation level [84].

#### 2.4.2. Swelling and osmotic pressure

The rejection and selectivity of LBL NF membranes decrease due to PEC swelling. Water is the most effective swelling agent for PEC, with high polarity and small molecular volume. Swelling of the PE has three main origins as shown in Fig. 6a. Firstly, charged PE pairs tend to form at least one hydration layer [95]. Secondly, when the salt is doping, the water molecules and more salt aggregate in PEC [67,96]. Thirdly, the counterions in PECs produce osmotic pressure, resulting in water absorption [95].

Osmotic pressure has great impact on PEC behavior in salt solution [65]. It has been observed by many groups [65,75,97] that with the increase of salt concentration in bulk solution, water is withdrawn from the PEC at the concentration below 0.5 M and then absorbed into PEC at higher concentration. There are two explanations for this phenomenon: electrostatic screening [75] and osmotic pressure [65]. O'Neal et al. [75] explained that as follows: (i) in 0–0.001 M KBr, extrinsic sites in PEC repel each other due to low ionic strength, the chains straighten and PEC swells; (ii) in 0.01–0.5 M KBr, PEC contracts owing to charge screening at sufficient ionic strength; (iii) in 0.5–1.6 M KBr, PEC swells due to charge screening and doping. However, Schlenoff et al. [65] demonstrated that as salt concentration increases, PEC dehydration is caused by osmotic pressure rather than the charge screening. They proposed that when overcompensation occurs in PEC, the trapped counterions generate osmotic pressure, and PEC could dehydrate when the osmotic pressure of the bulk solution is greater than that of PEC [65,97]. To prove the effect of osmotic pressure, a solution with polyethylene glycol (PEG) with the same osmotic pressure as salt was attempted to eliminate the effect of charge screening. The same dehydrating behavior of PEC was observed [65].

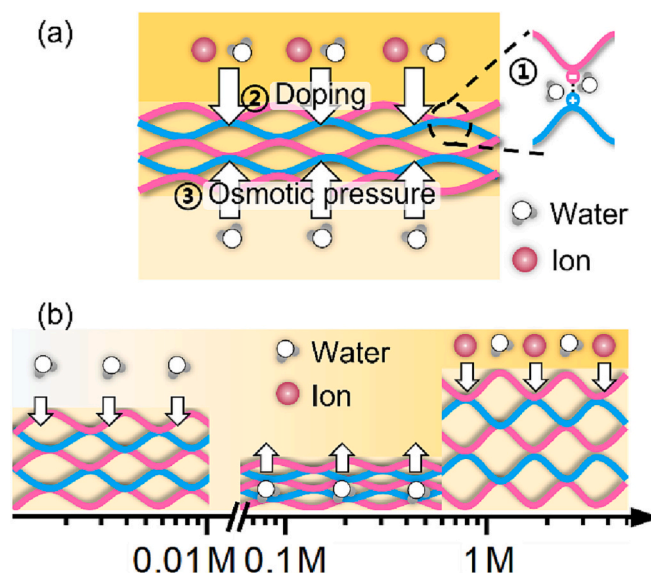


Fig. 6. (a) Three factors for PEC swelling. (b) Response of PEC to salt concentration: At very low salt concentrations, PEC swells when the osmotic pressure in PEC is higher than that in bulk solution; as the salt concentration increases, PEC is dehydrated when the osmotic pressure in PEC is lower than that in bulk solution; At even higher salt concentrations, ions from bulk solution enter the PEC to balance the osmotic pressure, bringing water into PEC, doping occurs and PEC swells.

Therefore, the osmotic pressure and doping can fully explain the change of PEC in saline solutions with the salt concentration from low to high as described in Fig. 6b. At low salt concentrations (< 0.01 M), PEC swells because of the relatively high osmotic pressure in PEC [95]. As the bulk salt concentration increases, the PEC dehydrates when the osmotic pressure of the bulk solution is greater than that inside the PEC. As the increase in the bulk salt concentration continues, the increment of external osmotic pressure overwhelms that of internal osmotic pressure due to PEC dehydration; thus external salt ions diffuse into PEC together with water molecules to establish the Donnan equilibrium between PEC and the bulk solution, balancing the osmotic pressure [67,98]. The PE pairs dissociate, owing to the salt ions, resulting in decreasing physical crosslinking, and thus more salt and water molecules penetrate into the PEC, finally leading to severe swelling [67,96].

We extrapolate that high overcompensation level increases stability

of the LBL NF membrane in highly saline solution. Overcompensation in LBL NF membranes generates excessive osmotic pressure, which can resist higher external osmotic pressure, and thus prevent the ions in the solution from entering the membrane to a certain extent [87]. Improving overcompensation level can shift the threshold of dehydration and doping to a higher salt concentration.

#### 2.4.3. Manipulate overcompensation and LBL salinity stability: Le Chatelier's principle

Aside from osmotic pressure, the shift of chemical equilibrium may also explain the effect of overcompensation on salinity stability of LBL NF membrane. For an overcompensated PEC system ( $\text{Pol}^+\text{Pol}_{\text{PEC}}^-$ ) as shown in Fig. 1b, there is a trend of chemical change from  $\text{Pol}^+\text{Pol}_{\text{PEC}}^-$  to  $\text{Pol}^+\text{A}_{\text{PEC}}^-$  and  $\text{Pol}^- \text{M}_{\text{PEC}}^+$ , upon contacting with a saline solution (MA). To stabilize the LBL NF membrane in highly saline solution, the formation of more  $\text{Pol}^+\text{Pol}_{\text{PEC}}^-$  is helpful. According to the well-known Le Chatelier's principle [99]:

“When a system at equilibrium disturbed, it tends to react in a way that relieves the effects of disturbances.”

The increase of one of the two items,  $\text{Pol}^+\text{A}_{\text{PEC}}^-$  or  $\text{Pol}^- \text{M}_{\text{PEC}}^+$  in Fig. 1b could drive the equilibrium to the right (association), which means higher overcompensation level could be favorable for LBL NF membranes in highly saline solution. More specifically, taking a stoichiometric PEC as an example, in the equilibrium equation in Fig. 1b, there is [69]:

$$K_{dop} = \frac{[\text{Pol}^+\text{A}_{\text{PEC}}^-][\text{Pol}^- \text{M}_{\text{PEC}}^+]}{[\text{Pol}^+\text{Pol}_{\text{PEC}}^-][\text{M}_{\text{aq}}^+][\text{A}_{\text{aq}}^-]} = \frac{y^2}{(1-y)a_{\text{MA}}^2} \quad (\text{at equilibrium}), \quad (4)$$

where  $y$  is doping level, and  $a_{\text{MA}}$  is the mean activity of salt ions of  $\text{M}^+$  and  $\text{A}^-$ . Doping level  $y$  is defined by the ratio of  $\text{Pol}^+\text{Pol}_{\text{PEC}}^-$  converted to  $\text{Pol}^+\text{A}_{\text{PEC}}^-$  and  $\text{Pol}^- \text{M}_{\text{PEC}}^+$ . When  $y \rightarrow 0$ , the PEC is completely intrinsic compensated. When  $y \rightarrow 1$ , the PEC is highly dissociated.

If the PEC is overcompensated by  $\sigma$ , taking polycation overcompensation as an example, the polycation and polyanion in the PEC are not at equilibrium; the state is represented by a reaction quotient  $Q_{dop}$ :

$$Q_{dop} = \frac{([\text{Pol}^+\text{A}_{\text{PEC}}^-] + \sigma)[\text{Pol}^- \text{M}_{\text{PEC}}^+]}{[\text{Pol}^+\text{Pol}_{\text{PEC}}^-][\text{M}_{\text{aq}}^+][\text{A}_{\text{aq}}^-]} = \frac{y(y + \sigma)}{(1-y)a_{\text{MA}}^2} > K_{dop}. \quad (5)$$

To achieve equilibrium, the reaction in Fig. 1b proceeds to the right, and polycation and polyanion tend to bind until

$$Q_{dop} = K_{dop}. \quad (6)$$

Fig. 7 illustrates the improvement of the salinity stability of PEC in salt solution by overcompensation. At the same doping level  $y = 0.1$ , the KBr solution activity of PEC with  $\sigma = 0\%$  is 0.38, while that of PEC with  $\sigma = 40\%$  is 0.85, more than the double of PEC with  $\sigma = 0\%$ . Therefore, higher overcompensation level is beneficial for LBL NF membrane stability in highly saline solution.

### 3. Stability of LBL NF membranes in highly saline solution

LBL NF membranes show excellent performance for ion separation, with high monovalent/divalent ion selectivity. Steric hindrance and Donnan exclusion are the main separation mechanisms [25,92,100–105]. The steric effect poses a high energy barrier, particularly for rigid pores with dimensions smaller than the bare size of the solute [12,106–109]. During the partitioning from bulk water into the confined environment of the membrane, solutes face an energy barrier due to steric hindrance as shown in Fig. 8a, which is imposed by their size and shape [12,110,111]. The effect of Donnan exclusion is to prevent almost all the co-ions (the ions with the same charge as the membrane) from entering the membrane, but to adsorb and transport the counterions [112,113]. When the LBL NF membrane is exposed to salt

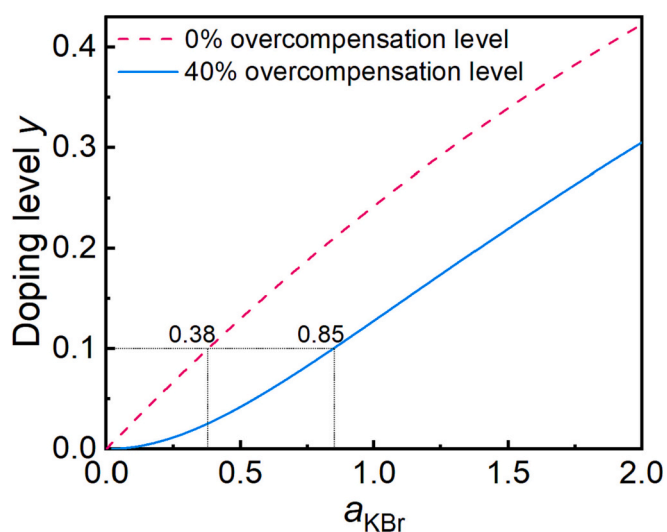


Fig. 7. Calculated changes of doping level  $y$  with KBr activity in PECs of different overcompensation, using Eq. (4) and (5). The  $K_{dop}$  used in calculation is from association constant of PAH/PSS ( $K_a = 12.92$ ) in literature [69].  $K_{dop} = 1/K_a$ , where the  $K_a$  is measured in KBr solution. Pink dash line is 0% overcompensation and blue solid line is 40%. The black dot line shows the different KBr activities corresponding to the two PECs at the same doping level ( $y = 0.1$ ). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

solution, the fixed charged groups in the membrane tend to exclude the co-ions, especially multivalent ions; the counterions can penetrate freely (Fig. 8b) [114,115]. In order to maintain the electroneutrality of feed and permeate solution, the counterions are also intercepted by the LBL membrane and salt rejection occurs [100]. Since the Donnan exclusion is much higher for multivalent ions than for monovalent ions, the LBL NF membrane can intercept multivalent ions but allow monovalent ions to pass through [116,117]. The rejection increases with the increasing co-ion valence and the ion permeation increases with the increasing counterion charge [118,119].

In a recent study, Dong et al. [25] proposed an extrinsic compensation mechanism for ion separation of LBL NF membranes, attributing to the attraction between anions and the PSS/PAH membrane with excessive PAH, as shown in Fig. 8c. The LBL NF membrane is charged due to overcompensation, which exists in the form of extrinsic sites. In ion separation, the extrinsic sites adsorb oppositely charged ions, shielding the spatial charge in the membrane. The charge screening leads to changes in the surface charge of the membrane, and thus affects the extent of the Donnan effect.

The performance of LBL NF membranes is impacted by high salinity via charge screening and membrane swelling. Cheng et al. [92] added NaCl in 5 mM  $\text{MgCl}_2$  to adjust the ionic strength and found that the  $\text{Mg}^{2+}$  rejection of PDADMAC/PSS membrane decreased sharply (from 60% to 20%) in the solution with higher ionic strength (from 50 mM to 500 mM NaCl), as shown in Fig. 9b. The reduced  $\text{Mg}^{2+}$  rejection is owing to invalidation of Donnan exclusion since the positive charge in the membrane is shielded by chloride ions at high ionic strength (Fig. 9a) [120]. Meanwhile, the membrane swelling in highly saline solution could be another reason for lower rejection of  $\text{Mg}^{2+}$  [121].  $\text{Pol}^+\text{Pol}_{\text{PEC}}^-$  tends to be doped by salt ions, following the equation in Fig. 1b [122] and the local folding of the PE chains occurs in high ionic strength [123], leading to large pore size and a loose PEC structure. The weak steric hindrance of the membrane results in low  $\text{Mg}^{2+}$  rejection. The swelling not only promotes salt permeation, but also increases water permeability by 30% ~50% at high ionic strength. It was also observed in Fig. 9c that the water permeability could recover to the initial value after rinsing the membrane completely with deionized (DI) water, suggesting

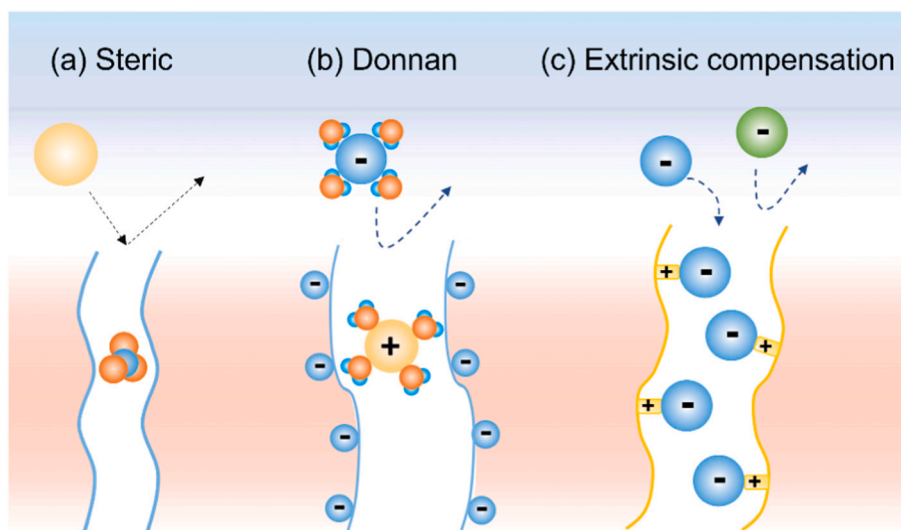


Fig. 8. Separation mechanisms of LBL membranes: (a) steric hindrance, (b) Donnan exclusion [12,111], (c) extrinsic compensation. Copyright 2021, Elsevier.

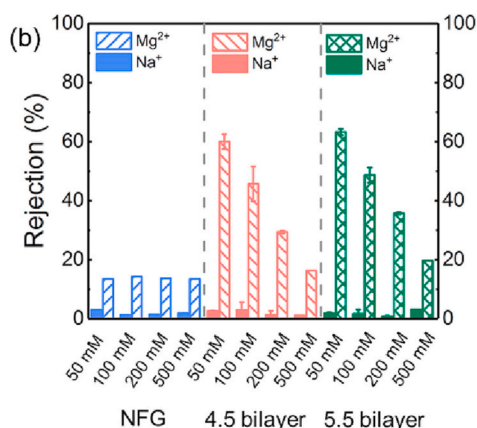
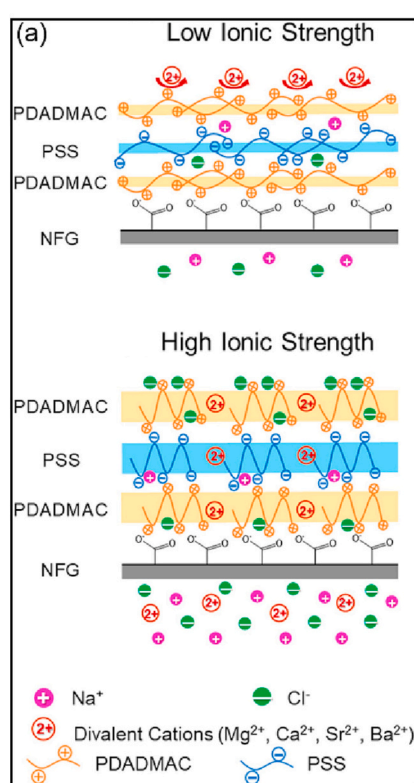
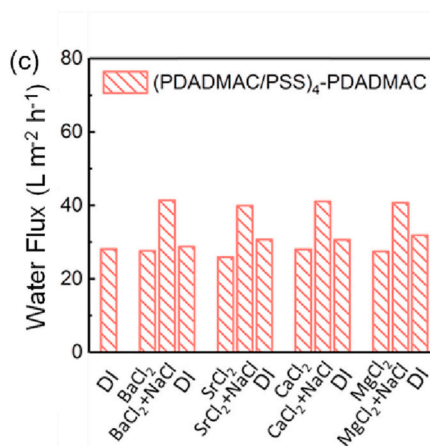


Fig. 9. (a) Scheme of the structure change of the PDADMAC/PSS membrane in highly saline solution. The membrane is thin and dense at low ionic strength but swelling and loose at high ionic strength. (b) Rejection of PDADMAC/PSS membranes in the mixed salt solution of 5 mM MgCl<sub>2</sub> and 50/100/200/500 mM NaCl. The rejection decreases as ionic strength increases. (c) Water flux of PDADMAC/PSS membranes before and after highly saline treatment (5 mM of each divalent salt and 500 mM NaCl) [92]. The flux increases at high ionic strength but recovers after the treatment. Copyright 2018, Elsevier.



that the effect of this ionic strength (500 mM NaCl) on PEM is reversible. De Groot et al. [124] also showed a permeability increase of 41 % for the PDADMAC/PSS membrane at the feed concentration from 0 to 1.5 M NaCl. More data from literature is listed in Table 3 to show the influence of ionic strength on rejection of LBL NF membranes in salt solution. In summary, the high ionic strength of the feed solution affects the ion separation performance of the LBL NF membrane from two aspects: (1) The surface charge of the LBL NF membranes is shielded and the Donnan effect fails; (2) The polyelectrolyte pairs partially dissociate, resulting in

larger pore size and membrane swelling.

At even higher salinity, i.e., a few molar, irreversible destruction occurs. The PEI-(PSS-PDADMAC)<sub>20</sub> film was prepared in 1 M NaCl and then immersed in 4 M NaCl solution [126]. In a few minutes, the film lost 45 % of its mass. For the PDADMAC/PSS multilayer, significant mass loss was observed in over 2 M NaCl solution, and 75 % at 5 M [127]. The PAH/PSS capsule was also found to shrink irreversibly in 3 M NaCl solution [122].

The advantages of high water flux, high separation efficiency,



**Table 3**  
Comparison of the rejection of LBL membranes in low and high salinity solution.

Membrane	Feed with low salinity	Rejection	Feed with high salinity	Rejection	
(PSS/PAH) <sub>2.5</sub>	500 ppm MgCl <sub>2</sub>	99.1 %	6000 ppm MgCl <sub>2</sub> and LiCl	96.2 % (MgCl <sub>2</sub> )	[10]
(PSS/PAH) <sub>4</sub>	100 ppm Na <sup>+</sup> (NaCl)	74 %	1000 ppm Na <sup>+</sup> (NaCl)	40 %	[125]
(PDADMAC/PSS) <sub>4</sub>	120 ppm Mg <sup>2+</sup> (MgSO <sub>4</sub> )	90 %	12,000 ppm Mg <sup>2+</sup> (MgSO <sub>4</sub> )	77 %	[48]
(PDADMAC/PSS) <sub>4,5</sub>	5 mM MgCl <sub>2</sub> and 50 mM NaCl	~60 %	5 mM MgCl <sub>2</sub> and 500 mM NaCl	~16 %	[92]
(PSS/PAH) <sub>2</sub>	1000 ppm MgCl <sub>2</sub>	98.1 %	10,000 ppm TDS	86.8 % (Mg <sup>2+</sup> )	[50]
(PSS/PAH) <sub>1.5-X</sub>	1000 ppm MgCl <sub>2</sub>	98.2 %	10,000 ppm TDS	96.2 % (Mg <sup>2+</sup> )	[50]
(PSS/PAH) <sub>2.5</sub>	500 ppm MgCl <sub>2</sub>	99.5 %	24,800 ppm TDS	~90 % (Mg <sup>2+</sup> )	[25]
(PSS/PAH) <sub>2.5-X</sub>	500 ppm MgCl <sub>2</sub>	~98 %	24,800 ppm TDS	~93 % (Mg <sup>2+</sup> )	[25]

Note: TDS: total dissolved salt; X: crosslinked.

environmental friendliness and easy regulation of the membrane structure endow LBL NF membranes great perspectives for selective ion separation in resource recovery, particularly from saline brines [12]. However, experimental evidence as well as the theoretical analysis seemingly pronounced a death penalty of LBL NF membranes in high salinity streams. With the increase of salt concentration, the separation layer of the LBL membrane swells due to the increase of doping level. The pore size of the membrane increases, followed with decreased performance. High binding strength corresponds to high stability and stable performance as salt concentration increases. The position of ions in the Hofmeister series has a great influence on LBL membrane stability: more chaotropic ions easily dope the LBL membrane, resulting in the more unstable performance. However, the oxidation state of metal ions in the solution has little effect on the membrane stability. Further improvement of the stability of the LBL NF membrane performance in high salinity is probably but facing great challenges.

#### 4. Recommendations for improving the LBL membrane stability in highly saline solution

It is urgently needed to improve the stability in highly saline streams. There are several options to constrain the swelling by harnessing the power of chemistry. Chemical crosslinking is a commonly used method to improve salinity stability of LBL NF membranes so far. Liu et al. [50] crosslinked (PSS/PAH)<sub>1.5</sub> with glutaraldehyde (GA). Compared to 2 bilayers of uncrosslinked PSS/PAH membrane with 86.8 % rejection of Mg<sup>2+</sup> in 10,000 ppm TDS, the rejection increased to 96.2 %, as shown in Table 3. The chemical crosslinking of PEs largely reduces swelling, but at a penalty of sacrificed water permeability [128,129]. Membrane surface charges are normally consumed during chemical crosslinking, and thus the Donnan exclusion effect is altered [25,50,130]. Crosslinking can be a direct reaction between PEs. For instance, amidization occurs between amino groups in PAH and carboxyl groups in polymethacrylic acid (PMAA) [131] or PAA [132,133] (Fig. 10a); the photo-crosslinking of PSS which has benzene ring occurs under ultraviolet (UV) irradiation (Fig. 10b) [134]. Crosslinking can also occur using GA as a crosslinking agent to react with amino [50,134–140] or hydroxyl [141] in PEs (Fig. 10c and Fig. 10d). Moreover, crosslinking can be achieved by modifying PEs with functional groups that can crosslink, such as benzophenone (Fig. 10e) [142,143], alkyne and azide functional groups (Fig. 10f) [144] and reactive silane groups (Fig. 10g) [131]. Versatility of crosslinking provides promise for a salinity stable LBL NF membrane.

In addition to chemical crosslinking, we also propose two approaches for the first time to improve the salinity stability of LBL NF membranes, according to the state-of-the-art experiments and theoretical understanding of the LBL NF membrane assembly:

- (i) Selecting PE pairs with strong binding strength, or PE pairs that can form hydrogen bonds for preparing LBL NF membranes with high salinity resistance. Redesign of the chemical structure of the PEs, either polycations or polyanions, by adding the noncovalent bonding of PEs upon assembly, i.e., hydrogen bonding and hydrophobic interaction, would presumably enhance the binding strength, as well as the salinity resistance [145].
- (ii) Increasing the internal osmotic pressure can improve the balance of external osmotic pressure and tolerate higher salt concentration. Therefore, it is recommended to enhance the overcompensation level for improve the salinity stability. Taking polycation overcompensation as an example, the chaotropic salts are suggested as the background salt for polycation in the LBL assembly; high background salt concentration, high polycation concentration and prolonged assembly time are also recommended to increase the overcompensation of polycations. As a consequence, the surface charge of the membrane increases, and the separation performance based on the Donnan exclusion is also enlarged.

#### 5. Conclusions

This review provides a comprehensive understanding of the chemical physical basis for LBL assembly in correlation to salinity stability. We clarified the strong correlation of the thermodynamics of LBL assembly, including the driving force, binding strength of PE and overcompensation to the LBL salinity stability. We propose two methods to enhance the salinity stability of LBL NF membranes, namely by selecting PE pairs with high binding strength and improving the overcompensation level.

The overcompensation level plays a significant role in the osmotic pressure of PECs, and a threshold salinity content exists for LBL NF membranes in general. However, they tend to exhibit relatively more stability in a kosmotropic salt solution. By increasing the overcompensation level, the internal osmotic pressure is raised, thereby increasing the threshold and improving the salinity stability of LBL NF membranes. According to Le Chatelier's principle, increasing the overcompensation level promotes the forward association of PECs and inhibits the reverse doping reaction. Additionally, we also discuss chemical crosslinking as a means to enhance the salinity stability of LBL NF membranes.

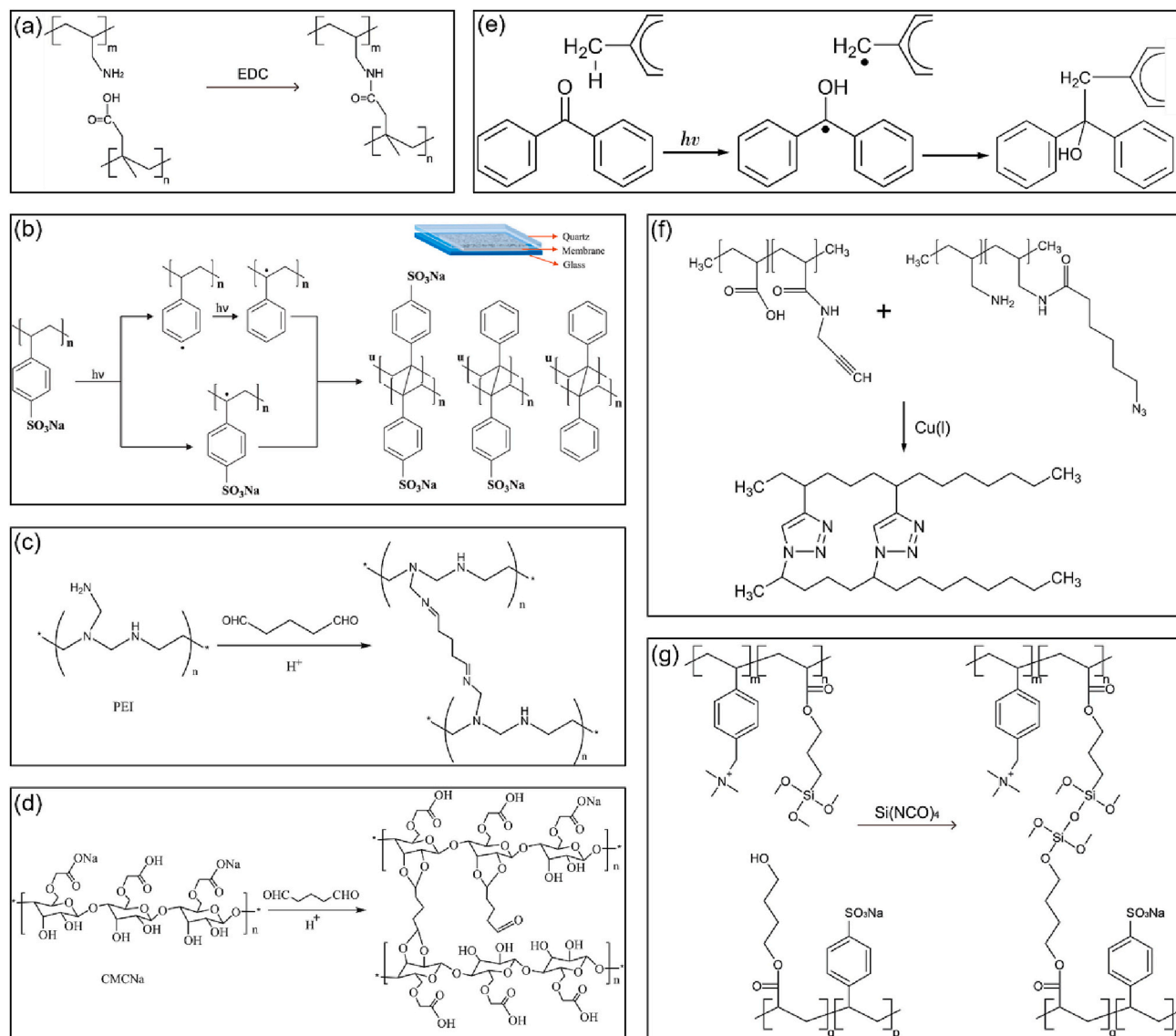
The salinity stability of LBL NF membranes has not been widely discussed in the literature. However, we believe that the issues raised in this paper would spark the interest of researchers, and further research will be necessary to confirm our understanding. Nonetheless, we expect that this paper will encourage more systematic research to be conducted in this area, which will eventually help set a clear boundary for the application of LBL nanofiltration membranes.

#### CRedit authorship contribution statement

**Jiarui Chen:** Conceptualization, Investigation, Visualization, Writing – original draft. **Shanshan Xu:** Writing – review & editing. **Chuyang Y. Tang:** Writing – review & editing. **Binjie Hu:** Supervision, Funding acquisition, Writing – review & editing. **Begum Tokay:** Supervision, Writing – review & editing. **Tao He:** Supervision, Funding acquisition, Writing – review & editing.

#### Declaration of competing interest

This is to declare that they have no known competing financial



**Fig. 10.** Crosslinking reactions: (a) Amide bond formation between PAH and PMAA [131]. Copyright 2013, Elsevier. (b) PSS photo-crosslinking under UV [134]. Copyright 2013, Elsevier. (c) Schiff base reaction between GA and PEI. GA acts as a crosslinker [141]. Copyright 2015, Elsevier. (d) Reaction between hydroxyl in sodium carboxymethyl cellulose (CMCNa) and carbonyl in crosslinker GA [141]. Copyright 2015, Elsevier. (e) Photo-crosslinking between benzophenone and organics [142].  $n-\pi^*$  transition caused by UV results in biradical for crosslinking [143]. (f) Alkyne-azide 'click' chemistry using a Cu(I)-catalyzed alkyne-azide cycloaddition (CuAAC) to form 1,2,3-triazole linkages [144]. (g) Siloxane bond formation [131]. Copyright 2013, Elsevier.

interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

No data was used for the research described in the article.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.desal.2023.116520>.

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