

# Extrinsic compensation: key component for separation of Layer-by-layer Nanofiltration membranes

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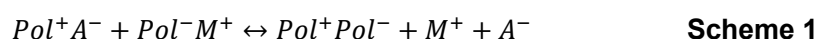
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## ABSTRACT

Layer-by-layer self-assembly nanofiltration membranes involve alternative exposure of support to either cationic or anionic polyelectrolytes (PEs), resulting in a polyelectrolyte multilayers (PEMs) of a controllable thickness as the separation layer [1]. The formation of PEMs is driven by entropy increase during the pairing of oppositely charged polyelectrolytes as shown in **Scheme 1** [2]. The charge compensation occurs: a positive charge in polycation is balanced by a negative charge in polyanion, called **intrinsic compensation** as  $Pol^+Pol^-$ ; if the charges in PEs are balanced by small counterions, i.e.,  $Pol^+A^-$ , it is called **extrinsic compensation**. During assembly, excessive polycations are always observed within PEMs; leading to free cationic groups not paired with anionic groups. This is named **overcompensation**. In this paper, we intend to analyze the impact of overcompensation on the unique separation behavior of LBL nanofiltration membranes in high salinity feed streams.



We highlighted extrinsic compensation as an important factor in determining the rejection of multivalent ions of LBL membranes in saline solutions (seawater and salt lake brine). A poly(styrene sulfonate) (PSS) / poly(allylamine) (PAH) LBL hollow fiber with PAH overcompensation was utilized as a model [3-5]. Extrinsic compensation of anions increases the adsorptive permeance and reduces the rejection of adsorbed anions; this consequently alters the original characteristics of the separation layer, thus affecting the separation behavior of other ions via the Donnan effect.

A similar mechanistic model is applicable for other types of affinity interaction of non-ionic matters, such as micropollutants, to the membrane materials. This nonionic affinity interaction falls into an extended extrinsic compensation category which affects the rejection behavior of the LBL membrane in a similar pattern. Further experimental evidence is imperative to scientifically prove our concept and we expect the present model would expand the fundamental understanding of the affinity effect in the separation of nanofiltration membranes.

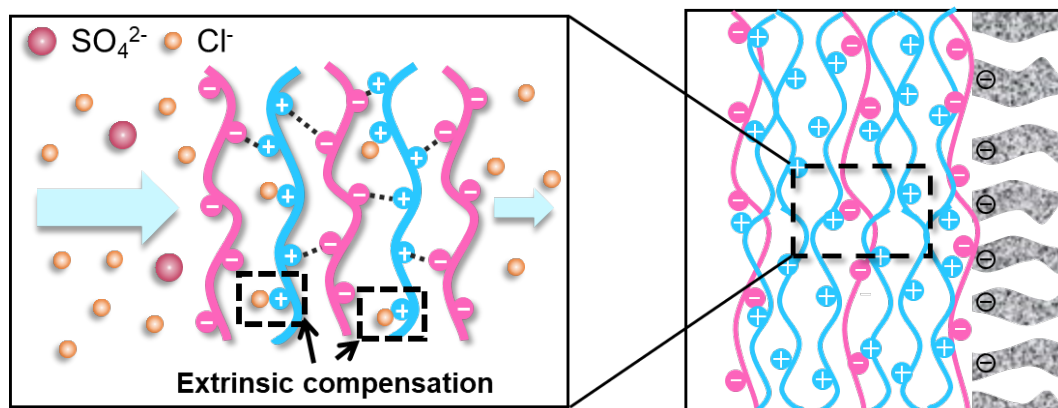


Fig1. Schematic diagram of extrinsic compensation mechanism in the PSS/PAH LBL membrane. The graph shows  $\text{Cl}^-$  preferentially diffuses across the membrane and  $\text{SO}_4^{2-}$  ions were rejected.

## KEYWORDS

Nanofiltration; Layer-by-layer; Extrinsic compensation; Seawater; Salt lake brine.

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