## 2.10 Layer-by-Layer modification of multibore membranes

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**Shortened Summary:** The Layer-by-Layer (LbL) technology offers the possibility to modify ultrafiltration membranes in a way that certain retentions for dissolved substances, such as sulfate, DOC or trace substances are possible. Depending on the polyelectrolyte coating of the membrane, not only the performance parameters but also certain membrane properties change. In order to understand these changes and to gain an understanding of the altered retention mechanisms in the modified membranes, polymeric membranes were investigated in this work with respect to their optimal coating, membrane properties and solute retention behaviour. After initial tests, two polyether sulfone ultrafiltration membranes were found to be suitable for LbL modification, a flat sheet membrane and a multicapillary membrane. When coated with the polyelectrolytes poly-(diallyldimethylammonium chloride) (PDADMAC) and poly (sodium 4-styrenesulfonate) (PSS), it became clear that the number of bilayers (DL) deposited and the additional ionic strength in the coating solution were the dominant factors during coating. Coating at 0.1 mol/L NaCl additional ionic strength and a layer number of 8 DL resulted in 70% sulfate retention for both membranes, with the flat sheet membrane having a slightly higher permeability of 15.6 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$ compared to the capillary membrane. Additionally, a stable backwash for the multicapillary membrane could be achieved when coated under pressure (1 bar).
After single layer coating, the so-called odd-even effect was observed, in which the coatings terminated with the polyanion exhibited higher retention and slightly lower permeability than the coatings terminated with the polycation, suggesting that the charge of the top polyelectrolyte has an influence on the separation behaviour of the LbL membranes. This effect could be confirmed by zeta potential measurements. The separation limit of the membrane, the so-called molecular weight cut-off (MWCO) was found to be between 300 and 400 Da after coating with 8 DL, which corresponds to the MWCO of nanofiltration membranes. Despite this low MWCO, no retention comparable to NF membranes could be achieved for sulfate. Further studies on ion retention showed that size exclusion was initially the dominant factor, caused by the reduction in pore size due to the polyelectrolyte coating. From the results of this work, it can be concluded that increased solute retention is possible by LbL modification of flat and multicapillary membranes. The retention mechanisms here are similarly complex to those of NF membranes, which LbL membranes resemble not only in separation behavior but also in many membrane properties.

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