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1 **Advanced electrokinetic characterization of layer-by-layer assembled polyelectrolyte**
2 **membranes: consideration and use of the electrokinetic leakage phenomenon**

3
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10
11
12 **Abstract**

13 The sensitivity of zeta potential to the sign of the surface charge of membranes makes it an
14 interesting parameter for the characterization of layer-by-layer (LbL) modified polyelectrolytes
15 membranes. However, during tangential electrokinetic measurements, a non-negligible
16 parasitic phenomenon referred to as “electrokinetic leakage” may occur. If not taken into
17 account, this phenomenon can lead to dramatic quantitative and qualitative errors, especially
18 when it comes to characterize the surface charge of layer-by-layer assembled polyelectrolyte
19 membranes. In this work, we show that it can lead to substantial errors when interpreting
20 experimental data, including misinterpreting the sign of the membrane surface charge density.
21 An advanced protocol based on the measurement of the streaming current by varying the
22 spacing between the two samples needed for the measurements allows to (i) correct the raw
23 data for the electrokinetic leakage phenomenon and thus to correctly and accurately determine
24 the zeta potential of the membrane surface and (ii) to detect whether polyelectrolytes are
25 deposited only on the membrane surface or whether they can also penetrate into the membrane
26 pores. The approach followed and the conclusions drawn in this study can be straightforwardly
27 applied to any kind of membrane functionalization.

28
29
30 Keywords: Tangential streaming current, zeta potential, electrokinetic leakage, layer-by-layer
31 modification, polyelectrolyte membranes.

1. Introduction

Zeta potential is a widely-used indicator providing insight on materials surface charge [1]. Its determination is valuable for membrane separations, to understand fouling [2–9], ageing [10–13] and rejection mechanisms [14,15]. It is therefore crucial to use characterisation techniques and develop optimised experimental protocols to determine the zeta potential of membranes reliably and accurately.

The zeta potential, as a surface charge indicator, is particularly useful for the characterization of layer-by-layer (LbL) modified membranes [16–20]. Its sensitivity to the surface charge sign makes it reliable to characterize the successively deposited layers of anionic and cationic polyelectrolytes. Layer-by-layer deposition of polyelectrolytes is a frequently used method to control electrostatic interactions, to understand the membrane fouling mechanisms [21] and to tune membrane separation performances [22]. Zeta potential cannot be measured directly and can only be calculated from experimentally measurable electrokinetic quantities such as the streaming potential or the streaming current [23–29]. Electrokinetic measurements are most often carried out in tangential mode in which an electrolyte solution is put in motion by a hydrostatic pressure gradient. Because of the tangential motion, this technique is aimed at providing information about the electrical properties of the outer surface of the membrane (skin layer).

However, it has been shown that a part of the streaming current generated by the hydrostatic pressure gradient is likely to flow through the porous layer(s) underneath the membrane surface [27]. This parasitic phenomenon can be taken into account by adding a contribution to the classical Smoluchowski equation as first proposed by Yaroshchuk and Luxbacher (2010) [27] and subsequently applied in a few studies [2,30,31].

In this study, we functionalized different types of membranes with polyelectrolytes with the aim of (i) showing that failure to take into account the electrokinetic leakage phenomenon could lead not only to significant quantitative errors in assessing the membrane surface zeta potential but also to qualitative errors when interpreting the experimental data and (ii) giving evidence that the parasitic contribution brought by the electrokinetic leakage phenomenon can also be used to obtain valuable complementary information on the phenomena occurring inside the pores of the modified membranes. The choice to focus this study on LbL assembled polyelectrolyte membranes was motivated by the inversion of sign of the surface charge expected when alternating layers of polycations and polyanions, but the conclusions drawn from this work can be generalised to any type of membrane functionalization.

2. Theoretical background

In order to achieve electrokinetic measurements, most often two flat membrane samples are placed facing each other and separated by a distance h_{ch} (gap height, Figure 1). The channel thus formed between the samples is filled with an electrolyte solution, which is further put into motion thanks to a pressure gradient. The solution therefore moves tangentially to the charged surfaces of the samples, carrying ions towards the low-pressure side [27,31]. As the solution contains an excess of counterions (to balance the surface charge of the samples), an electric current, called streaming current (I_s), is generated. If the thickness of the channel formed between the samples is much larger than the Debye length of the solution, the zeta potential (ζ) of the membrane surface can be calculated from streaming current measurements with the classical Smoluchowski equation (when applied to tangential electrokinetic measurements, it implicitly assumes dense and non-conducting samples):

$$I_s = \frac{Wh_{ch}\varepsilon_0\varepsilon_r\Delta P}{\eta L}\zeta \quad (1)$$

with,

W : channel width

L : channel length

ε_0 : vacuum permittivity

ε_r : dielectric constant

η : viscosity

ΔP : pressure difference

It has been demonstrated that for porous membranes the classical Smoluchowski approach may break down [27] if a part of the streaming current is likely to flow through the porous layer(s) underneath the membrane surface (Figure 1). This parasitic phenomenon has been called electrokinetic leakage [2]. Describing the sample/channel/sample system as a parallel electrical circuit, Yaroshchuk and Luxbacher [27] derived the following equation as an alternative to the classical Smoluchowski equation (which implicitly assumes that the experimentally measured streaming current (I_s) does not flow elsewhere than in the channel formed by the two samples of membranes):

$$I_s = I_s^{ch} + 2I_s^{pore} = \frac{Wh_{ch}\epsilon_0\epsilon_r\Delta P}{\eta L}\zeta_{surf} + \frac{2Wh_{mb}^{eff}\epsilon_0\epsilon_r\Delta P}{\eta L}\zeta_{pore} \quad (2)$$

with,

I_s^{ch} : part of the streaming current circulating in the channel (i.e. along the membranes surfaces; see Fig. 1)

I_s^{pore} : part of the streaming current circulating in each sample (the term $2I_s^{pore}$ represents the electrokinetic leakage)

h_{mb}^{eff} : effective thickness in which the electrokinetic leakage occurs

ζ_{surf} : zeta potential of the membrane external surface

ζ_{pore} : zeta potential of the membrane pores.

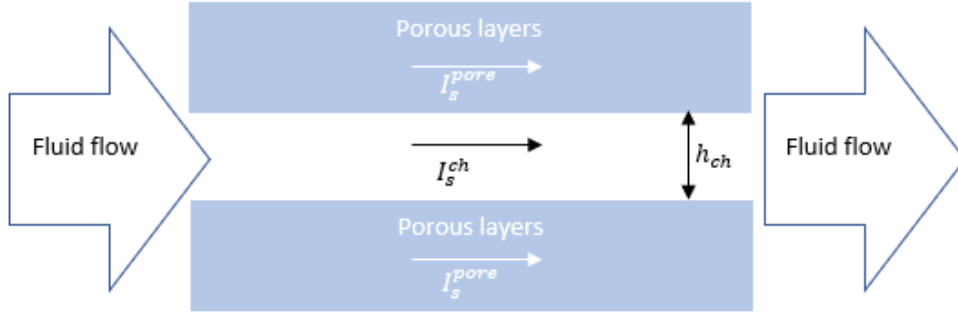


Figure 1: Possible pathways of the streaming current. The total streaming current I_s measured by an electrokinetic analyzer is equal to $I_s^{ch} + 2I_s^{pore}$.

According to Eq. 2, the surface zeta potential (ζ_{surf}) can be determined by measuring the streaming current for different channel heights (h_{ch}). Indeed, by plotting the streaming current coefficient ($I_s/\Delta P$) as a function of h_{ch} , Eq. (2) predicts a linear variation and shows that ζ_{surf} can be obtained from the slope. As for ζ_{pore} , it can be inferred from the y-intercept provided that the effective height where the electrokinetic leakage occurs (h_{mb}^{eff}) is known, which requires measuring the electric conductance (G_{cell}) at different channel heights [27]:

$$G_{cell} = \frac{W}{L}(h_{ch}\lambda_0 + 2h_{mb}^{eff}\lambda_{mb}) \quad (3)$$

with,

126 λ_0 : bulk conductivity

127 λ_{mb} : conductivity in the membrane pores

128

129 Eq. 3 can be further simplified if the membrane pores are much larger than the Debye length of
130 the solution by assuming $\lambda_0 \approx \lambda_{mb}$. It should be noted, however, that in the case of pore size
131 comparable to or smaller than the Debye length, this approximation would only lead to the
132 determination of effective zeta potentials inside pores.

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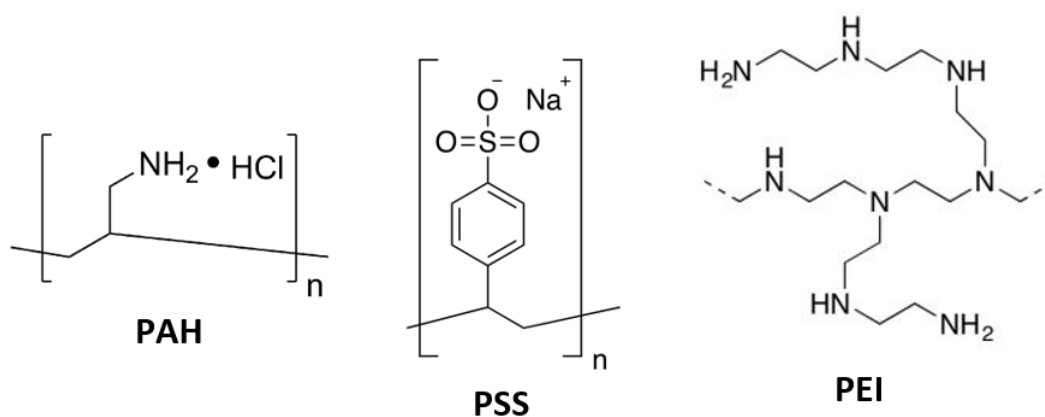
135 3. Experimental section

136

137 3.1 Chemicals

138 Poly(allylamine hydrochloride) (PAH; MW 15,000 g/mol), branched poly(ethyleneimine)
139 (PEI; MW 800 g/mol) and poly(4-styrene sulfonic acid) solution (PSS; MW 75,000 g/mol;
140 18wt.% in H₂O) were purchased from Sigma-Aldrich. Their chemical structures are shown in
141 Figure 2.

142 For the electrokinetic measurements and membrane modification, KCl (Fisher Scientific) and
143 NaCl (Sigma-Aldrich) solutions were prepared with deionised water (resistivity: 18 M Ω .cm).
144 The pH of electrolyte solutions was adjusted with HCl (Sigma-Aldrich) and KOH solutions
145 (Fisher Chemical).



146

147 **Figure 2:** Chemical structure of the polyelectrolytes used in this work.

148

149

150 3.2 Membranes

151 Three flat-sheet membranes were used as substrates for polyelectrolyte deposition: NF270
152 nanofiltration semi-aromatic polyamide membrane (FilmTecTM) with a molecular weight cut-

153 off (MWCO) of 400 Da, a regenerated cellulose (RC) microfiltration membrane (Sartorius)
 154 with an average pore diameter of 0.45 μm , and a polyvinyl chloride-silica (PVC-SiO₂) mixed
 155 matrix membrane (Amer Sil) with a 0.50 \pm 0.01 mm average thickness (Mitutoyo micrometer)
 156 and a bimodal pore structure (small pores in the range 0.02-0.1 μm , and larger ones between 1
 157 and 2 μm [32–34]).

158

159 3.3 Layer-by-layer modification

160 The unmodified membranes were cut and fixed onto rectangular sample holders (L = 2 cm; W
 161 = 1 cm) using double-sided adhesive tape. Three different polyelectrolyte solutions containing
 162 0.01 M NaCl were prepared for layer-by-layer surface modification (Table 1). First, the
 163 membrane sample was gently rinsed with deionised water for 1 min. The NF270, RC and PVC-
 164 SiO₂ membranes were then soaked in the PEI solution for 30, 15 and 1 min, respectively. The
 165 membranes were then rinsed again for 1 min. After the PEI deposition, one PSS/PAH bilayer
 166 was deposited on the membrane surface. The samples were contacted with the polyelectrolyte
 167 solution for 1 min, and then rinsed for 1 min. The pH of deposition of PEI and PSS (strong PE)
 168 solutions were not adjusted. For the PAH solution, the deposition pH was set to 3.7 to insure a
 169 full ionization of PAH chains [14].

170

171 **Table 1:** Polyelectrolyte type, pH and composition of the solutions used for LbL assembly.

Solution	pH	Polyelectrolyte concentration (M) [35]	NaCl concentration (M) [14,36]
PEI (+)	11.0	6.67×10^{-3}	0.01
PAH (+)	3.7	1.43×10^{-5}	0.01
PSS (-)	2.6	1.43×10^{-5}	0.01

172

173 3.4 Electrokinetic measurements

174 Electrokinetic measurements were conducted with a SurPass electrokinetic analyser (Anton
 175 Paar GmbH, Graz, Austria) equipped with an adjustable-gap cell. The streaming current was
 176 measured with Ag/AgCl electrodes by applying pressure ramps of 0.3 bar and periodically
 177 alternating the flow direction to limit electrode polarization. Electric conductance
 178 measurements were performed in alternative current mode under no flow conditions [37].

179 Before measurements, the membranes samples were soaked for at least 24 hours in a 10⁻³ M
 180 KCl solution. They were then attached to sample holders using double-sided adhesive tape (the
 181 sample support surface was gently wiped with a tissue paper to dry it sufficiently to ensure good

182 adhesion with the adhesive) and further inserted in the adjustable-gap cell. The KCl electrolyte
183 solution (500 mL) was circulated between the polyelectrolyte membrane samples for 2.5 hours
184 in order to remove the excess of loosely bound polyelectrolyte remaining on the surface after
185 layer-by-layer modification [22,38] and to obtain a stable signal. Electrokinetic measurements
186 were then performed at an average temperature of 22 ± 3 °C.

187 Each membrane was characterized according to two separate experimental protocols:

188 (i) The streaming current was measured for a fixed gap height and pH ranging from ~ 8
189 to ~ 3 (pH was adjusted by 0.05 M KOH and HCl solutions). Each time the pH was
190 changed, the solution was circulated for about 20 minutes to allow the new solution
191 to replace the previous one in the membrane pores and to equilibrate with the pore
192 surface, before performing streaming current measurements. The zeta potential was
193 further determined from the Smoluchowski equation (Eq. 1) and is denoted as
194 apparent zeta potential in the following. This protocol is hereafter referred to as
195 standard approach.

196 (ii) The streaming current and the electric cell conductance were measured at a fixed
197 pH value for various gap heights ranging from ~ 100 μm to ~ 40 μm . The zeta
198 potential was further determined by plotting the experimental streaming current
199 coefficient ($I_s/\Delta P$) and making use of Eq. 2. This protocol is hereafter referred to as
200 advanced protocol.

201

202 The gap height (h_{ch}) was calculated from the hydrodynamic flow rate thanks to the Hagen-
203 Poiseuille relation for parallelepipedic channels (Eq. 4), neglecting the contribution of the
204 membrane pores to the total hydrodynamic volume flow rate (Q_v):

205

$$206 \quad h_{ch} = \sqrt[3]{\frac{12\eta L Q_v}{W \Delta P}} \quad (4)$$

207

208 **4. Results and discussion**

209

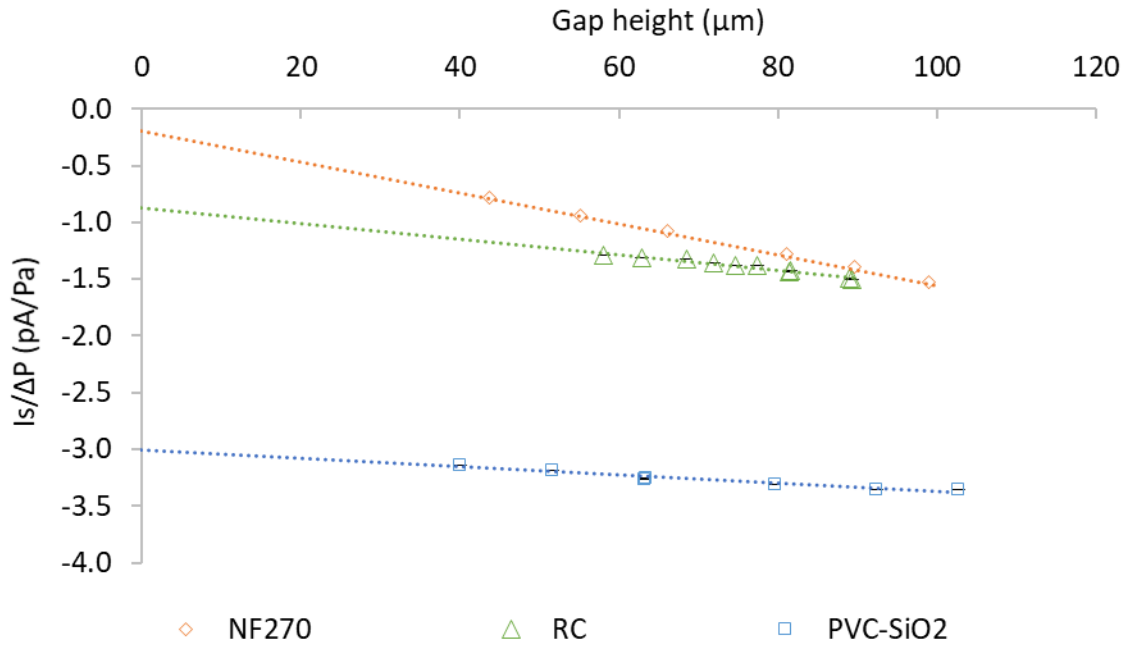
210 *4.1 Importance of the electrokinetic leakage phenomenon for the different membranes*

211 Figure 3 shows the experimental streaming current coefficient ($I_s/\Delta P$) measured at various
212 channel heights for the three membranes under consideration.

213 As expected from Eq. 2, the streaming current coefficient varies linearly with the gap height for
214 all three membranes. Negative slopes were obtained, meaning that the surface zeta-potentials
215 of the unmodified membranes were negative (according to Eq. 2). Extrapolation of
216 experimental data at zero gap height leads to non-zero values, which means that a non-zero
217 current circulated through the membrane samples during measurements. The value of the
218 electrokinetic leakage is therefore given by the value of the y-intercept. It depends on the
219 structural properties (thickness, porosity, tortuosity) and surface chemistry
220 (hydrophobicity/hydrophilicity, surface charge density) of the membrane but also on the
221 geometry of the measuring cell as the sample cross-section may be more or less exposed to the
222 hydrodynamic flow depending on the design of the measuring cell [31]. Considering arbitrarily
223 the streaming current coefficient measured for a gap height of 100 μm as a reference value, the
224 contribution of the electrokinetic leakage to the total measured current was found relatively
225 negligible (about 10%) for the NF270 nanofiltration membrane, much larger (41%) for the
226 microfiltration RC membrane and quite dominant (90%) for the thick and coarse-porous PVC-
227 SiO_2 membrane.

228 The contribution of the electrokinetic leakage to the measured current obviously depends on
229 the distance set between the samples, since the current flowing in the channel (I_s^{ch} ; see Figure
230 1) depends on h_{ch} , whereas the current flowing in the samples (I_s^{pore}) is independent of h_{ch} .
231 Consequently, when the electrokinetic leakage is not negligible, the value of the apparent zeta
232 potential deduced from the Smoluchowski equation (Eq. 1) is (i) incorrect and (ii) dependent
233 on the distance set between the membrane samples. It is illustrated in Figure 4 which shows the
234 pH dependence of the apparent zeta potential of the RC membrane for two different channel
235 heights ($103 \pm 2 \mu\text{m}$ and $58 \pm 2 \mu\text{m}$). It is found that the apparent zeta potential deduced from
236 the standard approach becomes more negative when decreasing the distance between samples
237 because the contribution of the electrokinetic leakage to the total current measured by the
238 electrokinetic analyzer increases with decreasing h_{ch} . We believe that the failure to account for
239 the electrokinetic leakage in streaming current and streaming potential measurements may
240 partly explain the significant discrepancies in zeta potentials reported in the literature for similar
241 membranes (as stated above, the magnitude of the electrokinetic leakage for a given membrane
242 depends on the type of measuring cell and thus on the electrokinetic analyzer).

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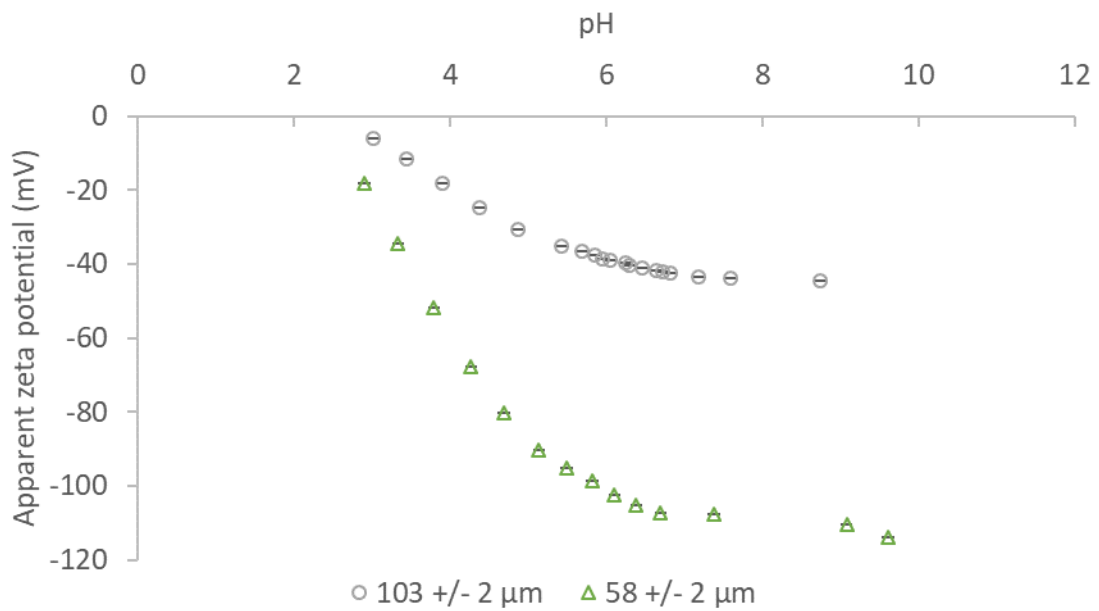


246

247 **Figure 3:** Streaming current coefficient ($I_s/\Delta P$) of the unmodified NF270, RC and PVC-SiO₂

248

membranes versus gap height; Solution: 0.001 M KCl at pH 5.60 ± 0.05 .



249

250 **Figure 4:** Apparent zeta potential of the RC unmodified membrane (determined from the

251 Smoluchowski equation) versus pH for two gap heights ($h_{ch} = 103 \pm 2 \mu\text{m}$ and $58 \pm 2 \mu\text{m}$);

252

Solution: 0.001 M KCl.

253

254 A simple method for checking whether a membrane is prone to electrokinetic leakage is to

255 perform two successive streaming current measurements, changing only the gap height between

256 the samples, and compare the values of the zeta potential obtained by the Smoluchowski

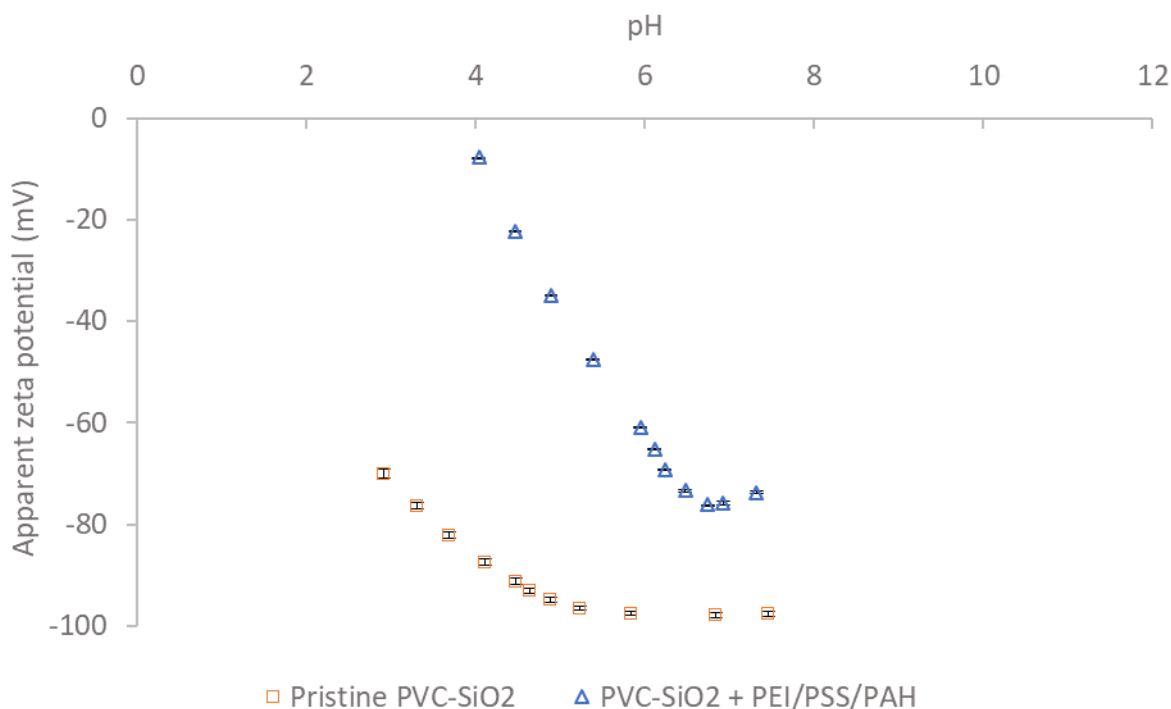
257 equation. Indeed, if different values are obtained, this means that electrokinetic leakage in the
258 membranes is not negligible and that a reliable and accurate determination of the zeta potential
259 requires following the advanced protocol and using Eq. 2.

260

261 4.2 Surface functionalization

262 Electrokinetic measurements were then conducted on unmodified and layer-by-layer modified
263 membranes. Figure 5 shows the pH dependence of the apparent zeta potential (calculated with
264 Eq. 1) of the unmodified and layer-by-layer modified PVC-SiO₂ membranes.

265 The apparent zeta potential was found less negative after membrane modification. For instance,
266 at pH 5.5, the apparent zeta potential increased from -89.8 mV for the unmodified membrane
267 to -49.4 mV for the PEI/PSS/PAH modified one. The conclusion that would be drawn by
268 following this standard approach is that the surface of the modified membrane remains
269 negatively charged, which is not expected for a cationic polyelectrolyte (PAH) terminated
270 membrane..



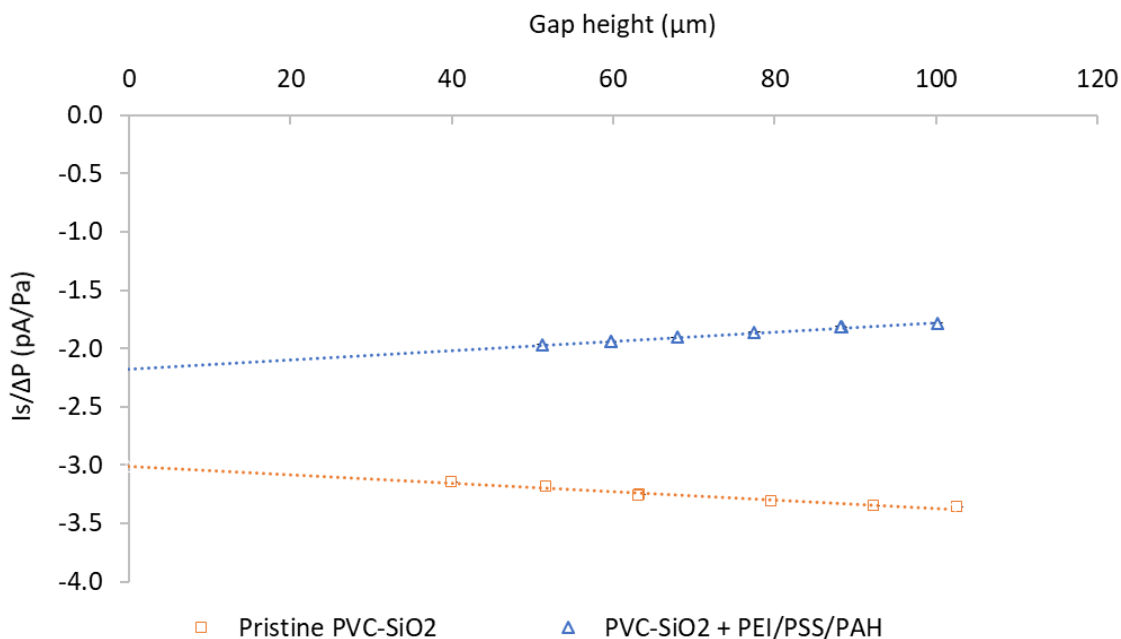
271

272 **Figure 5:** Apparent zeta potential of the unmodified and PEI/PSS/PAH modified PVC-SiO₂
273 membranes versus pH for $h_{ch} = 98 \pm 1 \mu\text{m}$; Solution: 0.001 M KCl.

274

275 However, Figure 6 provides evidence that the electrokinetic leakage phenomenon is actually
276 responsible for this apparent contradiction. Indeed, by plotting the streaming current coefficient
277 versus the gap height, a change in the sign of the slope is observed, from negative for the

278 unmodified membrane ($-3.38 \times 10^{-15} A.Pa^{-1}.\mu m^{-1}$) to positive for the PEI/PSS/PAH
 279 modified membrane ($+3.96 \times 10^{-15} A.Pa^{-1}.\mu m^{-1}$). As shown by Eq. 2, the slope has the
 280 same sign as the surface zeta potential. The advanced protocol thus makes it possible to
 281 highlight the positive surface charge density of the modified membrane terminated by the PAH
 282 layer.



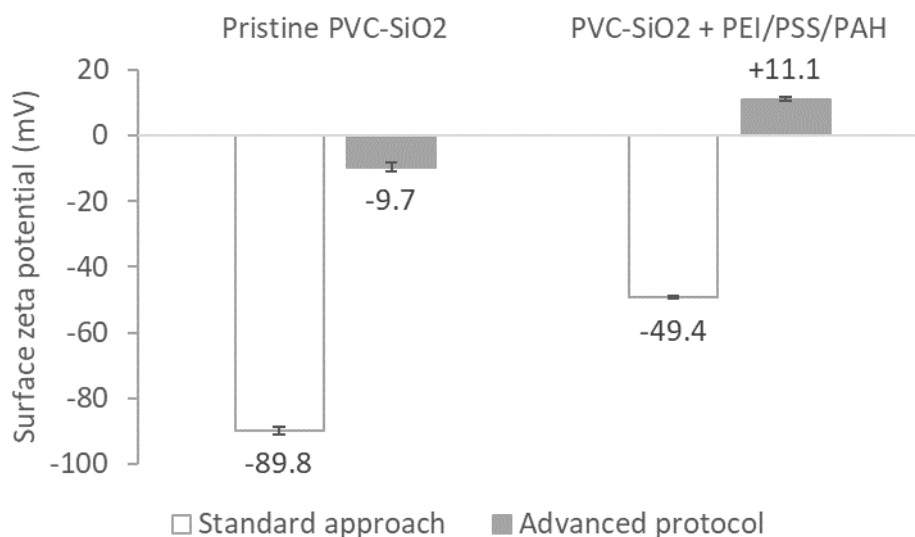
283
 284

285 **Figure 6:** Streaming current coefficient ($I_s/\Delta P$) of the unmodified and PEI/PSS/PAH
 286 modified PVC-SiO₂ membranes versus gap height; Solution: 0.001 M KCl at pH 5.60 ± 0.05 .

287

288 Figure 7 shows the comparison of the zeta potentials determined at pH 5.60 for the unmodified
 289 and modified PVC-SiO₂ membranes following the standard approach and the advanced
 290 protocol (i.e. considering the electrokinetic leakage phenomenon). For the unmodified
 291 membrane, a 89% difference was observed between the surface zeta potentials determined from
 292 both protocols, which results from the strong electrokinetic leakage occurring through the PVC-
 293 SiO₂ membrane (see section 4.1). For the PEI/PSS/PAH modified membrane, the advanced
 294 protocol led a positive surface zeta potential of +11.1 mV (consistent with the cationic
 295 polyelectrolyte deposition on the membrane surface) while the standard approach led to a
 296 negative apparent zeta potential. The reason is that the positive streaming current generated
 297 along the membrane surface by the PAH layer is overcompensated by the negative current
 298 associated with the electrokinetic leakage occurring in the samples, so that the total current
 299 measured by the electrokinetic analyzer is negative, leading to a qualitatively wrong

300 interpretation when following the standard approach (based on the Smoluchowski equation) in
301 which the electrokinetic leakage is not subtracted from the total measured current.
302 These results demonstrate that not considering the electrokinetic leakage phenomenon can not
303 only induce quantitative errors on the value of the zeta potential but can also lead to a
304 qualitatively wrong interpretation of the raw experimental data.
305



306
307 **Figure 7:** Surface zeta potential of PVC-SiO₂ calculated with the standard approach and the
308 advanced protocol; Solution: 0.001 M KCl at pH 5.60 ± 0.05.

309
310 The same protocol was applied to the RC membrane, and led to similar results and conclusion
311 (see Figure S1 in the supporting information).

312
313 However, no significant difference was observed when comparing the standard approach and
314 the advanced protocol for the NF270 membrane (Figure 8). Indeed, both approaches led to
315 similar conclusions both quantitatively and qualitatively. Notably, the standard approach was
316 found able to highlight the positive charge density on the surface of the NF270 membrane after
317 PEI/PSS/PAH layer-by-layer modification. The reason for this is that the electrokinetic leakage
318 was found to be very low for the NF270 membrane (see section 4.1) and thus the standard
319 approach based on the Smoluchowski equation is reliable for this membrane.

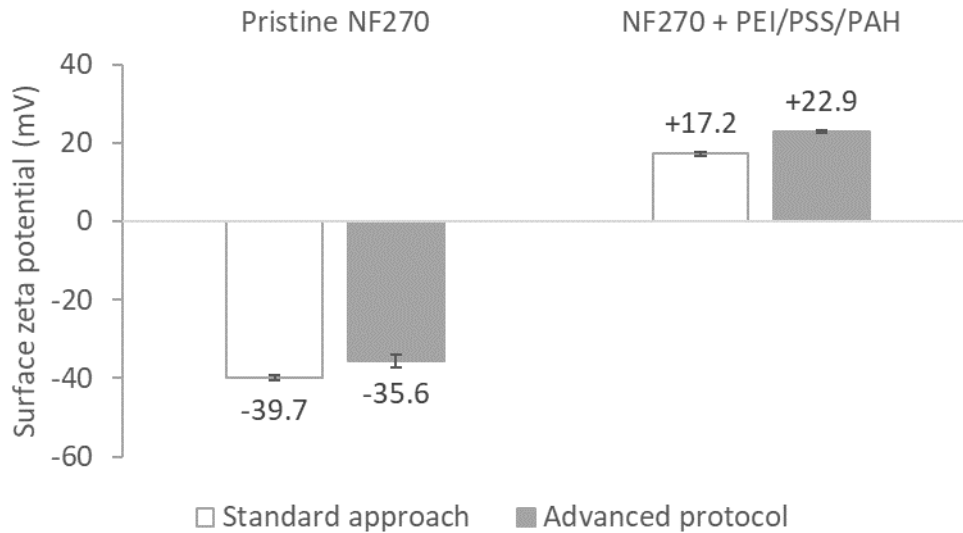


Figure 8: Surface zeta potential of the NF270 membrane calculated with the standard approach and the advanced protocol; Solution: 0.001 M KCl at pH 5.60 ± 0.05 .

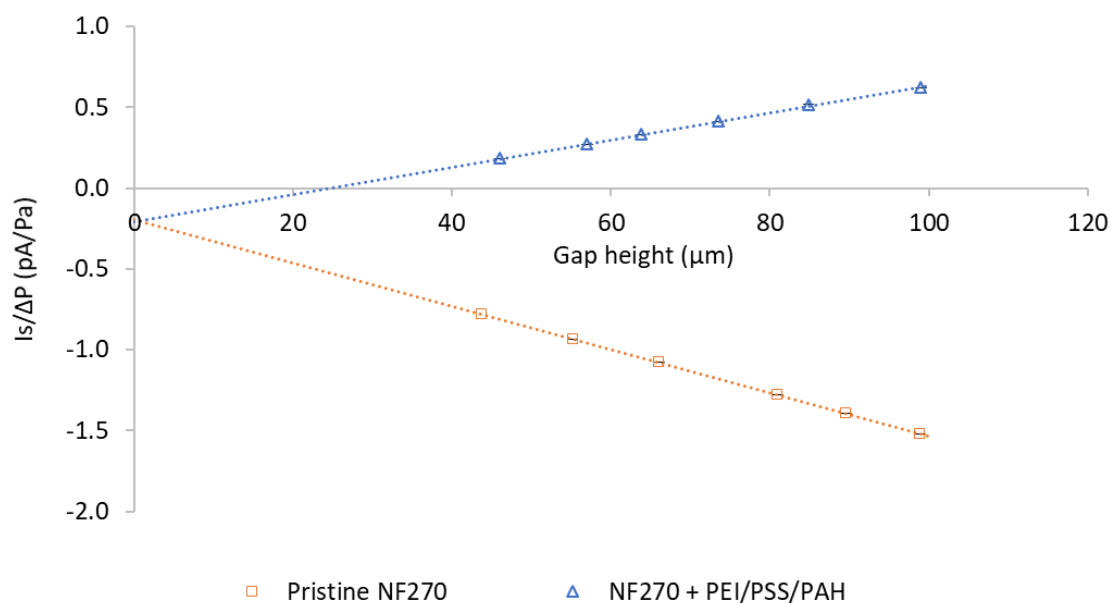
4.3 Extracting information from the electrokinetic leakage

So far, we have shown that the advanced protocol based on the measurement of the streaming current at different gap heights and Eq. 2 allows to correctly interpret the data of electrokinetic experiments and to determine a reliable value of the membrane surface zeta potential. In the last part of this work, we wished to demonstrate that the electrokinetic leakage phenomenon, considered up to this point as a signal interfering with the electrokinetic measurements, can be used to extract additional information on the membrane functionalization process.

Figure 9 shows the experimental streaming current coefficient ($I_s/\Delta P$) measured for the NF270 membrane at various channel heights, before and after PEI/PSS/PAH layer-by-layer modification. As stated above, the change in sign of the slope observed after modification of the membrane by PEI/PSS/PAH deposition indicates the reversal of the sign of the surface charge density (from negative to positive) and thus the successful membrane surface modification.

Figure 9 also shows that the y-intercept remained similar before and after PEI/PSS/PAH modification, which indicates that the electrokinetic leakage was not altered after the modification of the NF270 membrane. In other words, the polyelectrolytes were deposited onto the membrane surface without penetrating into the membrane. It is worth noting that this result can be interpreted in light of the concept of pore-dominated and layer-dominated regimes first introduced by de Groot et al. [39]. The pore-dominated regime occurs if the polyelectrolyte layers are formed inside the pores of the support. After the deposition of a certain number of

344 layers, a transition occurs leading to the layer-dominated regime where additional
 345 polyelectrolyte layers are formed on top of the support [40]. The results shown in Figure 9
 346 therefore demonstrate that, in the case of the NF270 membrane, the layer-dominated regime
 347 was reached from the first adsorbed layer (PEI) since the intensity of the electrokinetic leakage
 348 did not vary after polyelectrolyte adsorption. This result is consistent with the narrow pores of
 349 the NF270 nanofiltration membrane.
 350

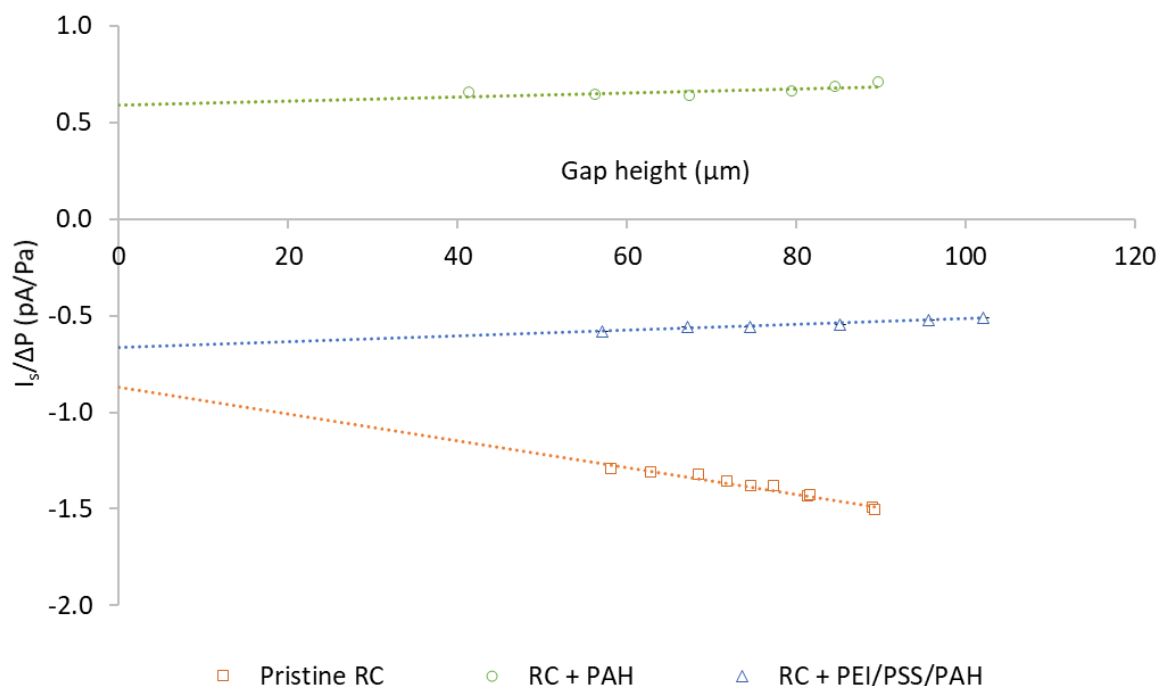


351 □ Pristine NF270 △ NF270 + PEI/PSS/PAH

352 **Figure 9:** Streaming current coefficient ($I_s/\Delta P$) of the unmodified and PEI/PSS/PAH
 353 modified NF270 membranes versus gap height; Solution: 0.001 M KCl at pH 5.60 ± 0.05 .
 354

355 Unlike the results obtained with the NF270 membrane, a decrease of about 25% in the
 356 electrokinetic leakage was observed after modification of the RC microfiltration membrane by
 357 PEI/PSS/PAH deposition (see Figure 10). The electrokinetic leakage alteration indicates that a
 358 certain amount of polyelectrolytes entered the RC membrane and adsorbed inside pores. Similar
 359 results were obtained with the PVC-SiO₂ membrane (see Figure 6). The fact that the intensity
 360 of the electrokinetic leakage varies after polyelectrolyte adsorption is the signature of the pore-
 361 dominated regime. Interestingly, the sign of the electrokinetic leakage remained negative after
 362 adsorption of the terminating polycation layer, which means that the polyelectrolytes deposited
 363 in the pores of the support did not cover all the porosity accessible to electrokinetic leakage.
 364 de Grooth et al. showed that the distinction between pore-dominated and layer-dominated
 365 regimes could be made on the basis of (i) the different mechanisms of membrane rejections, the
 366 rejections being mainly steric in the case of the pore-dominated regime and governed by

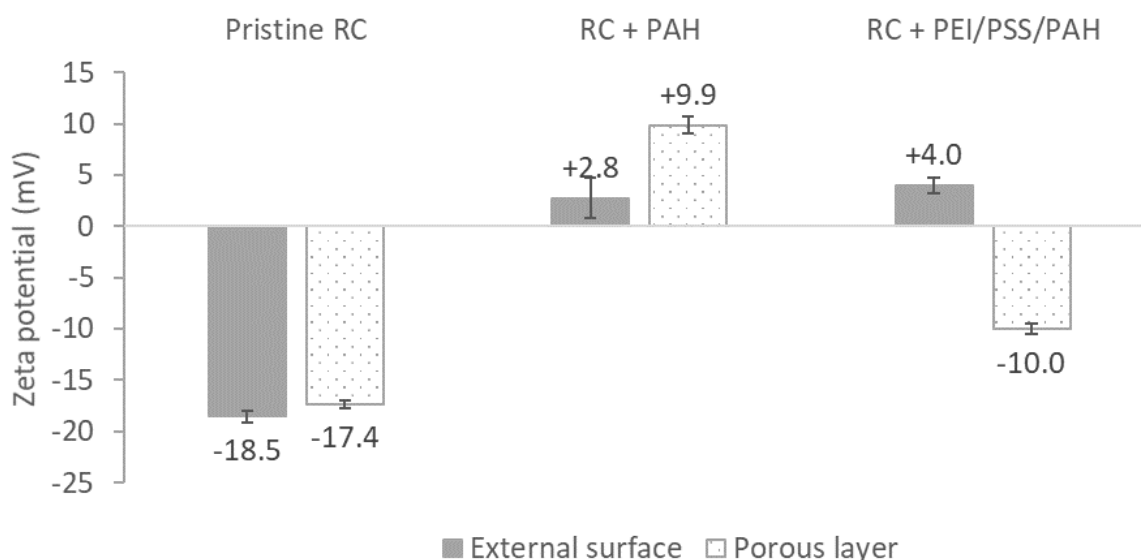
367 Donnan exclusion for the layer-dominated regime and (ii) the flip of the so-called odd-even
 368 effect on membrane permeability [39]. The advanced electrokinetic protocol used in the present
 369 work provides an alternative method since the pore-dominated regime can be associated with a
 370 variation of the electrokinetic leakage intensity with the number of deposited layers whereas an
 371 electrokinetic leakage independent of the number of deposited layers can be associated with the
 372 layer-dominated regime.
 373



374
 375 **Figure 10:** Streaming current coefficient ($I_s/\Delta P$) of the unmodified, PAH modified and
 376 PEI/PSS/PAH modified RC membranes versus gap height; Solution: 0.001 M KCl at pH 5.40
 377 ± 0.05 .
 378

379 As shown in Figure 10, the modification of the RC membrane by a single layer of PAH (without
 380 prior deposition of PEI and PSS) resulted in a change of sign of the electrokinetic leakage. This
 381 result indicates a significant adsorption of the polycation inside the RC membrane pores leading
 382 to charge inversion inside the pores. With the help of additional measurements of the cell
 383 electrical conductance versus the gap height and Eqs. 2 and 3 (using the approximation $\lambda_0 \approx$
 384 λ_{mb} in Eq. 3, which was reasonable since the pore size of the RC microfiltration membrane was
 385 much larger than the Debye length of the measurement solution, i.e. around 10 nm for a
 386 millimolar solution of a mono-monovalent electrolyte), the surface and inner zeta potentials
 387 (ζ_{surf} and ζ_{pore} , respectively) of the unmodified and modified RC membranes were determined

388 (Figure 11). As expected, similar values of ζ_{surf} and ζ_{pore} were obtained for the unmodified
 389 membrane. After modification, the surface zeta potential of the RC membrane increased from
 390 -18.5 mV to +2.8 mV and +4.0 mV (at pH = 5.40) for the two modified membranes terminated
 391 by a PAH layer. The impact of the PEI layer is highlighted by comparing ζ_{pore} for the
 392 membranes modified by PEI/PSS/PAH (-10.0 mV) and PAH only (+9.9 mV). It has been
 393 reported that branched PEI tends to form a web onto solid surfaces [41–43] and thus it hinders
 394 the subsequent penetration of PSS and PAH polyelectrolytes inside the RC membrane. These
 395 results suggest that the phenomenon of electrokinetic leakage could be an additional tool for
 396 providing insight into the complex mechanisms of deposition of polyelectrolyte layers in the
 397 membrane pores before reaching the layer-dominated regime [38].
 398



399
 400 **Figure 11:** External surface and pore surface zeta potentials of the unmodified, PAH and
 401 PEI/PSS/PAH modified RC membranes calculated with the advanced protocol; Solution:
 402 0.001 M KCl at pH 5.40 ± 0.05.
 403

404 As a final remark, it is worthwhile that LbL assembled polyelectrolyte membranes are often
 405 processed as hollow fiber membranes [39,44], where the common way to determine their zeta
 406 potential is to prepare a small module filled with a resin on the outside of the membrane so that
 407 the measuring solution cannot permeate the membrane. It must be stressed, however, that the
 408 use of such modules does not prevent the electrokinetic leakage through the membrane pores
 409 as demonstrated by Efligenir et al. [45]. It should be kept in mind, however, that the advanced
 410 protocol followed in the present study relies on a modification of the geometry of the channel

411 formed by the samples analyzed, which is not possible with a hollow fiber membrane since in
412 this case the channel geometry is fixed by the internal diameter of the membrane.

413

414 **5. Conclusion**

415 When tangential streaming current (or streaming potential) measurements are performed with
416 membranes, a part of the current measured by the electrokinetic analyzer may come from a
417 parasitic contribution occurring through the porosity of the membrane samples. This
418 phenomenon, known as electrokinetic leakage, can lead to misinterpretations of the
419 electrokinetic data. In this work, it was shown that the characterization by a standard approach
420 (i.e. based on the classical Smoluchowski equation) of layer-by-layer modified polyelectrolytes
421 membranes can be flawed not only quantitatively but also qualitatively if the phenomenon of
422 electrokinetic leakage is not considered in the interpretation of the raw data. A rigorous and
423 reliable characterization requires the use of an advanced characterization protocol based on the
424 measurement of the streaming current by varying the spacing between the two samples needed
425 for the measurements. This advanced protocol was applied to three types of membranes of
426 different nature and structure (a polyamide nanofiltration membrane and two macroporous
427 membranes, one made of regenerated cellulose and the other with a mixed PVC-SiO₂ matrix)
428 which were then modified with polyelectrolytes (PAH or PEI/PSS/PAH). It was shown that the
429 advanced protocol accounting for the electrokinetic leakage phenomenon allowed a reliable and
430 accurate characterization of the various membranes. Moreover, the analysis of the electrokinetic
431 leakage before and after membrane modification provided information on whether the
432 polyelectrolytes were deposited only on the membrane surface or whether they were able to
433 enter the membrane and adsorb onto its pores. Electrokinetic characterization rigorously
434 performed using the advanced protocol can thus not only demonstrate the success of membrane
435 surface modification but also provide insightful information on polyelectrolyte penetration. The
436 electrokinetic leakage phenomenon could also be used to monitor the transition between the so-
437 called pore-dominated and layer-dominated regimes as its intensity is expected to vary with the
438 number of polyelectrolytes layers in the pore-dominated regime, but be independent of the
439 number of deposited layers in the layer-dominated regime. Importantly, the conclusions drawn
440 from this work are not limited to LbL assembled polyelectrolyte membranes but can be
441 generalised to any type of membrane functionalization.

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