Supporting Information to Modelling and predicting the interactions between oppositely and variously charged polyelectrolytes by frontal analysis continuous capillary electrophoresis

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1. The influence of the co-pressure on the migration times of PLL

In order to quantify the free PLL chains in the PLL-PAMAMPS mixtures, various co-pressures were tested to ensure the entrance of free PLL chains in the capillary while avoiding the entrance of free PAMAMPS chains and PEC (see Figure S1). As can be seen in Figure S1, a high co-pressure of 20 mbar causes a rapid detection of the PEC. When a moderate co-pressure (10 or 15 mbar) was applied, a small plateau corresponding to free PLL chains was detected, but the width of this plateau was too small and these pressure values were not selected. A co-pressure of 5 mbars was more suitable with an analysis time of 18 minutes.

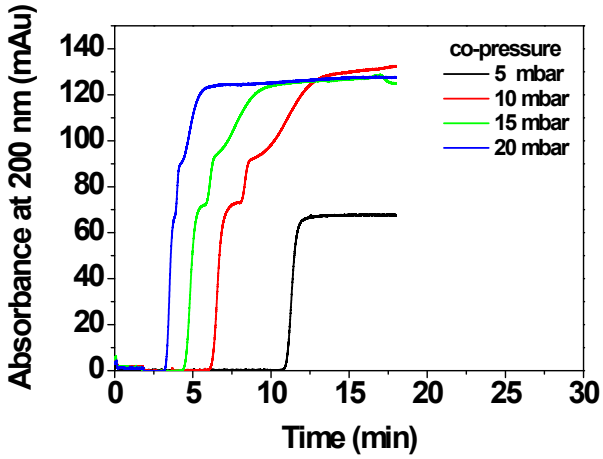

Figure S1. Electropherograms obtained by FACCE for PLL-PAMAMPS 100% mixtures for different co-pressures. Experimental conditions: PDADMAC coated capillary 33.5 cm (8 cm to the detector) × 50µm i.d. Electrolyte: 12mM Tris, 10m M HCl, 1090 mM NaCl, pH 7.4. Applied voltage: 1 kV. The initial PLL and PAMAMPS 100% concentrations in the mixtures were respectively 1 g/L and 1.14 g/L.

2. Preparation of PEC mixtures

The concentrations of the oppositely charged polyelectrolytes for the preparation of PLL-PAMAMPS mixtures as well as the investigated ionic strengths are summarised in Table S1.

3. Isotherms of adsorption

The influence of the ionic strength and the chemical charge density on the thermodynamic parameters on the interactions between PLL and PAMAMPS was studied by plotting 20 isotherms of adsorption displayed in Figure S**2** to Figure S**6** with the non-linear curve fitting allowing the determination of the binding site constants and the chain stoichiometries.

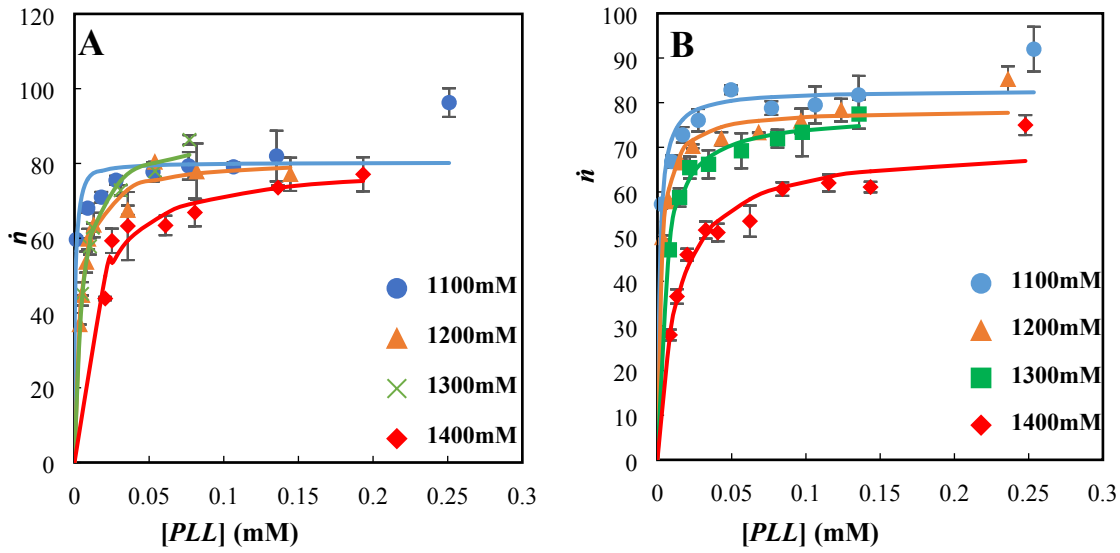

Figure S2. Isotherms of adsorption and non-linear curve fitting obtained for the interactions between PLL and PAMAMPS 100% at different ionic strengths as noticed on the graph and different orders of addition: PAMAMPS into PLL (A) PLL into PAMAMPS (B). Experimental conditions: PDADMAC coated capillary 33.5cm (8.5 cm to the detector) × 50 µm i.d. Background electrolyte: 12 mM Tris, 10 mM HCl and appropriate amount of NaCl, pH 7.4. Applied voltage: +1 kV with a co-hydrodynamic pressure of +5 mbar. Detection wavelength 200 nm. Samples were prepared in the background electrolyte by 50/50 v/v dilution of PAMAMPS and PLL solutions according to Table S1.

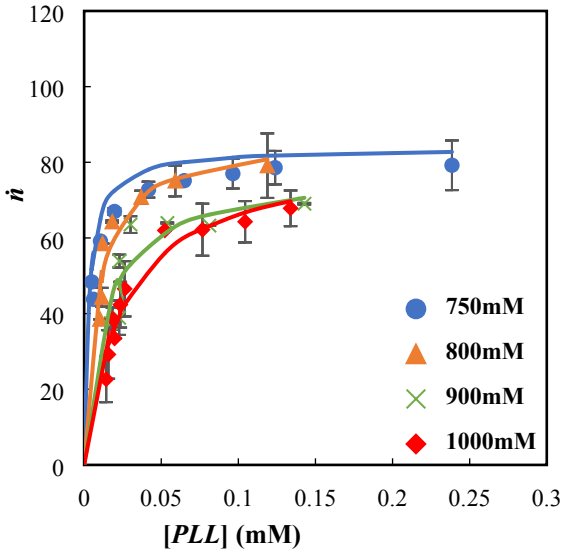

Figure S3. Isotherms of adsorption and non-linear curve fitting obtained for the interactions between PLL and PAMAMPS 70% at different ionic strengths as noticed on the graph. Experimental conditions were the same as in Figure S2.

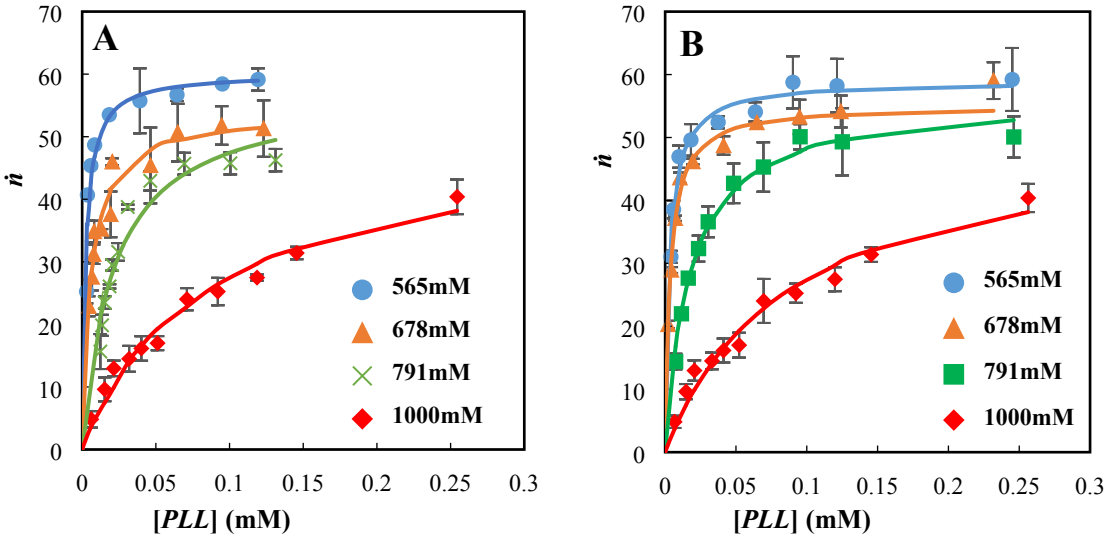

Figure S4. Isotherms of adsorption and non-linear curve fitting obtained for the interactions between PLL and PAMAMPS 55% at different ionic strengths as noticed on the graph and different orders of addition: PAMAMPS into PLL (A) PLL into PAMAMPS (B). Experimental conditions were the same as in Figure S2.

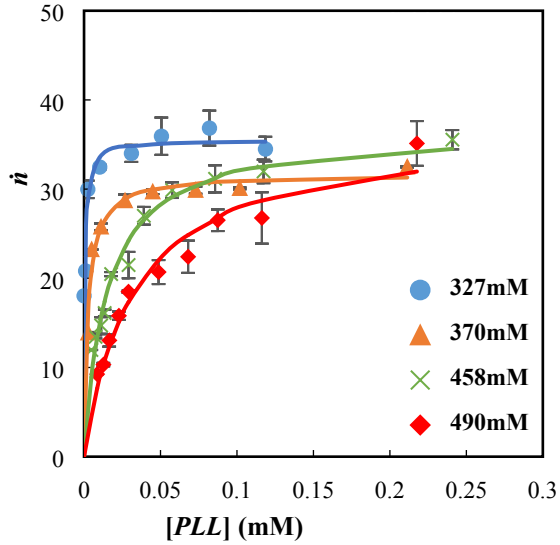

Figure S5. Isotherms of adsorption and non-linear curve fitting obtained for the interactions between PLL and PAMAMPS 30% at different ionic strengths as noticed on the graph. Experimental conditions were the same as in Figure S2.

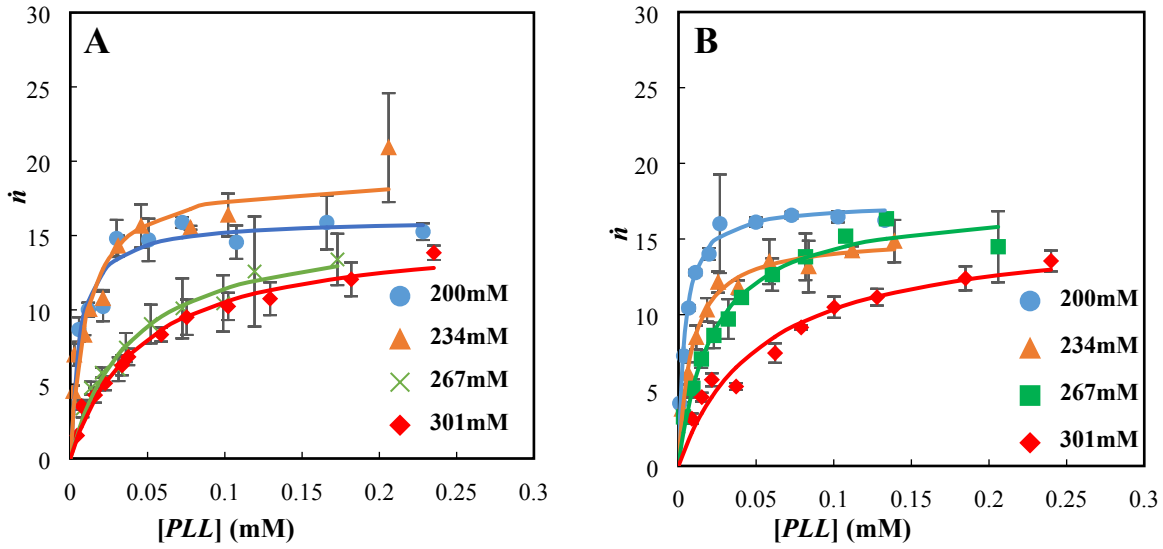

Figure S6. Isotherms of adsorption and non-linear curve fitting obtained for the interactions between PLL and PAMAMPS 15% at different ionic strengths as noticed on the graph and different orders of addition: PAMAMPS into PLL (A) PLL into PAMAMPS (B). Experimental conditions were the same as in Figure S2.

Table S2. Concentrations of oppositely charged polyelectrolytes solutions for the preparation of PECs mixtures.

f **(%)**	***I*** **(M)**	**[*PAMAMPS*] stock solution (g/L)** *	**[*PLL*] stock solution (g/L)** *	**[*PLL*] diluted solutions (g/L)** *	**Volume of PAMAMPS stock solution in the mixtures (µL)**	**Volume of PLL diluted solutions in the mixtures (µL)**	**Final volume of the mixtures (µL)**
100	1.1	1.14	5	3 ; 2.5 ; 2 ; 1.6 ; 1.2 ; 1 ; 0.8 ; 0.6	100	100	200
	1.2			3 ; 2;1.6;1.2;0.8;0.7;0.6;0.5;0.4			
	1.3			2;1.6;1.2;0.8;0.7;0.5			
	1.4			4;3;2;1.6;1.2;1;0.8			
70	0.75	1.3	5	3; 2.5; 2; 1.6; 1.2; 1; 0.8; 0.7; 0.6	100	100	200
	0.8			3; 2; 1.6; 1.2; 1; 0.8; 0.7			
	0.9			3; 2; 1.6; 1.2; 1; 0.8; 0.7			
	1			3; 2.5; 2; 1.6;1; 0.9; 0.8; 0.7; 0.6; 0.5			
55	0.565	1.44	5	3; 2.5; 2; 1.6; 1.2; 1; 0.9; 0.8; 0.5	100	100	200
	0.678			3; 2.5; 2; 1.6; 1.2; 1; 0.9; 0.8; 0.7; 0.5			
	0.791			3; 2.5; 2; 1.6; 1.2; 1; 0.9; 0.8; 0.7; 0.6; 0.5			
	1			3; 2.5; 2; 1.6; 1.2; 1; 0.8; 0.6; 0.4; 0.2			
30	0.327	2	5	3; 2.5; 2; 1.6; 1.2; 1; 0.7; 0.6	100	100	200
	0.37			3; 2.5; 2; 1.6; 1.2; 1; 0.6			
	0.458			3; 2.5; 2; 1.6; 1.2; 1; 0.8; 0.7; 0.6; 0.5			
	0.49			3; 2.5; 2; 1.6; 1.2; 1; 0.8; 0.6; 0.4			
15	0.2	3.2	5	4; 3; 2.5; 2; 1.6; 1.2; 1; 0.8	100	100	200
	0.234			3; 2.5; 2; 1.6; 1.2; 1; 0.8; 0.6; 0.4			
	0.267			3; 2.5; 2; 1.6; 1.2; 1; 0.8; 0.6; 0.4			
	0.301			4; 3; 2.5; 2; 1.6; 1.2; 1; 0.8; 0.6; 0.4; 0.2			

(*) For each FACCE experiment, PAMAMPS and PLL stock solutions as well as PLL diluted solutions were prepared in the same Tris-HCl-NaCl buffer pH 7.4 (12 mM Tris, 10 mM HCl and appropriate amount of NaCl to adjust the ionic strength of the medium).

4. Prediction of the global constant of PLL-PAMAMPS 20% interactions

Table S3. Predictive and experimental values of the interaction parameters between PLL and PAMAMPS 20%.

		Predicted values			Experimental values			
I **(M)**	***log I***	***n*log *k*** [a]	n_{avg}	***k*** **$\times 10^6$ (M^{-1})**	***k*** **$\times 10^5$ (M^{-1})**	***n*** [a]	***n*log *k*** [a]	***relative difference*** **(%)** [b]
0.24	-0.61	142	22	4.85	3.96 ± 0.34	22.9 ± 0.2	128	10
0.37	-0.44	111		0.17	0.3 ±0.03	25.5 ± 0.9	114	3

([a]) *n* is the chain stoichiometry expressed in term of PLL chains bound per PAMAMPS chain.

([b]) $relative\,difference = \left| \frac{predicted\ n\log k - \exp erimental\ n\log k}{predicted\ n\log k} \right| \times 100$