Experimental report

13/02/2017

Proposal:	**9-11-1806**	**Council:**	4/2016

Title: Complexation of oppositely chargedpolyelectrolytes monitored under near-equilibrium conditions through a desalting transition pathway

Research area: Soft condensed matter

This proposal is a continuation of 9-11-1765

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Samples:
Sodium polyacrylate
polydiallyldimethylammonium chloride
Poly(sodium 4-styrenesulfonate)
Polyethylenimine

Instrument	Requested days	Allocated days	From	To
D22	3	3	23/09/2016	26/09/2016

Abstract:

We would like to shed some light on the electrostatic assembly mechanism and morphological signature(s) at the nm scale in pseudo-equilibrium conditions of model oppositely charged polyelectrolytes by combining the unique potential of SANS with a dialysis set-up allowing a fine tuning of the magnitude of the interaction and the reaction time through a slow desalting transition pathway. The monitoring of the inner structure of two well-known (PDADMAC/PANa and PEI/PSSNa) systems will be investigate as a function of the molar and the molecular weight charge ratios and the ionic strength difference.

Is the formulation of colloids and macromolecules that easy? Can we fully control and predict out-of-equilibrium assemblies? A central question for academic laboratories and industries where formulation is a key step; and surprisingly scarcely investigated in the literature. In particular, although an extensive body of research has been devoted to the vibrant domain of polyelectrolytes complexes (PECs) during the last decade, a complete understanding of the mechanism controlling the formation of such PECs in solutions and at an interface is still lacking. No systematic studies that couple morphology, thermodynamics and formulation pathway have been carried out on these electrostatic complexes. We have started recently to tackle this issue and shown that the formulation pathway *or the ways the various components come into intimate contact* strongly influence the final morphology and properties of such complexes.

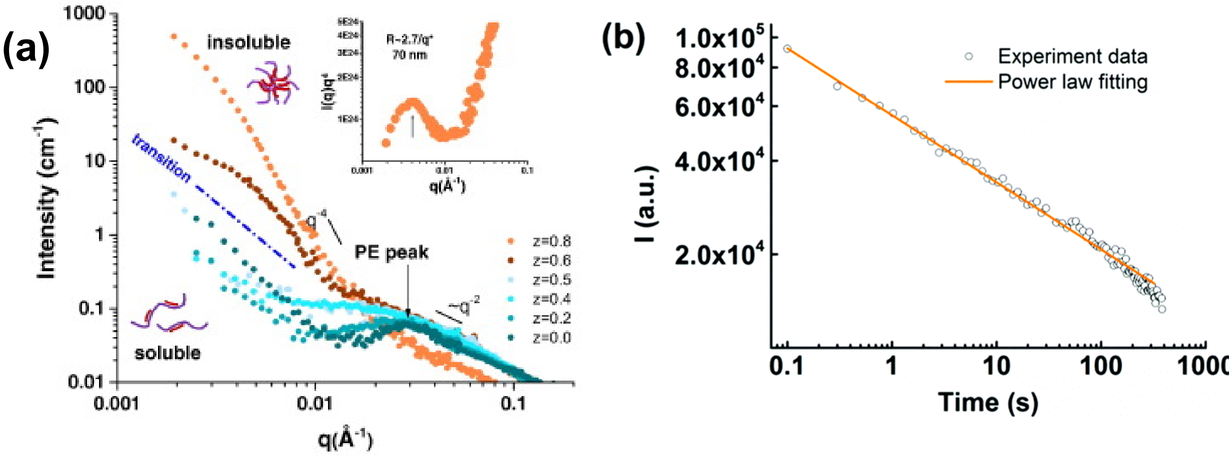

Figure 1. SANS I-q *profile* of poly(diallyldimethyl ammonium chloride)/sodium poly(acrylate) ($PDADMAC_{45k}/PANa_{2k}$) complexes at pH 10 without added salt made by direct mixing using a Stopped-Flow mixing device. (a) PECs prepared at various Z ratios out of the beam highlighting the transition at $z = 0.6$ from soluble to insoluble PECs forming dense spherical nanoparticles (R~70), (b) Intensity count versus decay time in the low q range (0.0025–0.056 Å^{-1}) highlighting the fast complexation kinetics of coacervation at stoichiometry (Z=1.1). ILL D22 & LLB PAXY. [1-2]

This can be rationalized by considering the competition between the *mixing time* and the *reaction time*. We have recently started to investigate at ILL the early stage complexation of different PEs with a stopped-flow set-up enabling very short mixing times (< 5 ms) (**Fig.1**). On the other side of the spectrum, we probe in the present work ***very long mixing times*** with the help of an online dialysis set-up (**Fig.2**) allowing a fine tuning of the magnitude of the interaction and the reaction time through ***a so-called slow desalting transition pathway*** where complexion occurs under pseudo-equilibrium. The desalting route involves the mixing of two oppositely charged PEs at a sufficiently high ionic strength to generate a so called *dormant solution* in which no interaction occurs due to charge screening. Then, a slow and controlled decrease of the ionic strength through dialysis against water triggers the complexation of PEs featured by a sharp transition from a non-clustered to a clustered state with a low polydispersity and polymorphism. Here, we have monitored in a continuous manner the different intermediate structures of the $PDADMAC_{45k}/PANa_{2k}$ system prepared at high salt concentration upon dialysis against water. The continuous decrease of the ionic strength within the cell was monitored through on line conductivity measurements in the reservoirs. The initial molar charge ratio Z (-/+) between the polyelectrolytes was also varied in order to study the complexation behavior under non-stoichiometry conditions. The low q range (0.003-0.065 Å^{-1}) was chosen to optimize the available experimental time.

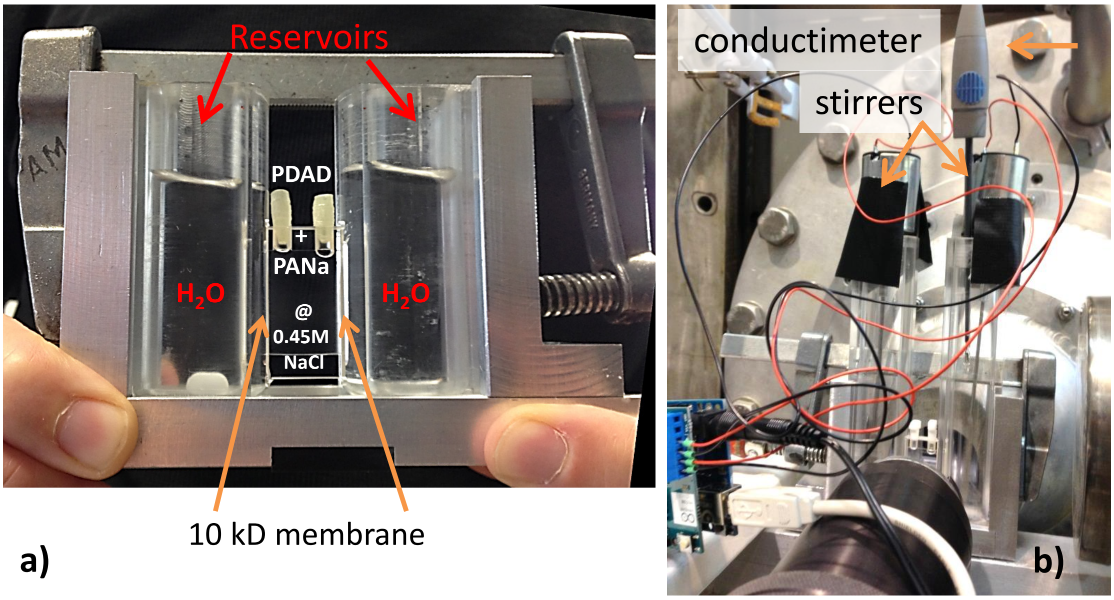

Figure 2. ***a)*** Pictures of the dialysis cell containing the dormant PE solution at a given Z sandwiched by two water reservoirs~~.~~ The membrane used in the present experiment has a 10kD mesh size. ***b)*** Dialysis cell under the neutron beam customized with a stirrer in each reservoir to insure a good homogenisation of the solution and a conductivity meter to monitor the ionic strength *vs* time.

Five charge ratios Z (-/+) have been studied (0, 0.2, 0.5, 0.7, 1) corresponding to the different structures found in the PDADMAC/PANa system: from soluble complexes to coacervates through insoluble PEC nanoparticles. From light scattering experiments we know that the desalting transition for the current system occurs at 0.28M.[3]

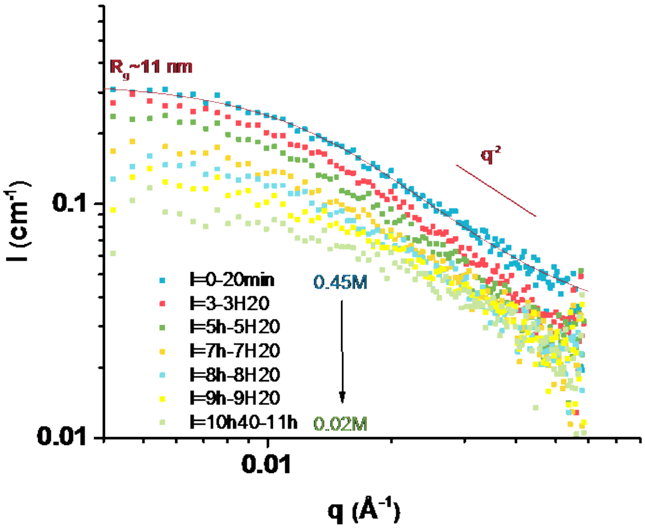

Figure 3. Neutron scattered intensity I(q) of the PDADMAC solution (Z=0) during the 11h dialysis. The red line is a simple Gaussian chain fit of the data giving rise to a Rg~10 nm. $I_{cell}(0)$=0.45M

In order to have a so called dormant PE system the initial solutions of PEs were prepared with 0.45M of NaCl to screen completely out the electrostatic interaction. Fig. 3 shows the dialysis performed on the $PDADMAC_{45k}$ stock solution alone (Z=0). In presence of 0.45M of salt, the PDADMAC behaves, as expected, as a Gaussian chain with a R_g ~12 nm. After more than 10h, the final ionic strength reached 0.22M which is not sufficient to see the polyelectrolyte peak (~0.03 Å^{-1}) present when no salt is added (see Fig 1.a).

Then, we illustrate the complexation occurring at Z=1 where the system is known to undergo a complex coacervation which corresponds to a liquid-liquid phase transition when oppositely charged PEs are mixed at charge stoichiometry. The speed of the dialysis (dI/dt) depends on the initial ionic strength difference between the cell and the reservoirs (ΔI). To insure a slow crossing of the desalting/coacervation transition, we performed the dialysis in two steps, by adjusting the ionic strength in the reservoir first at 0.17 M and then at 0 M (pure D_2O solution at pH=10). In such conditions the final ionic stregth in the cell was 0.025M.

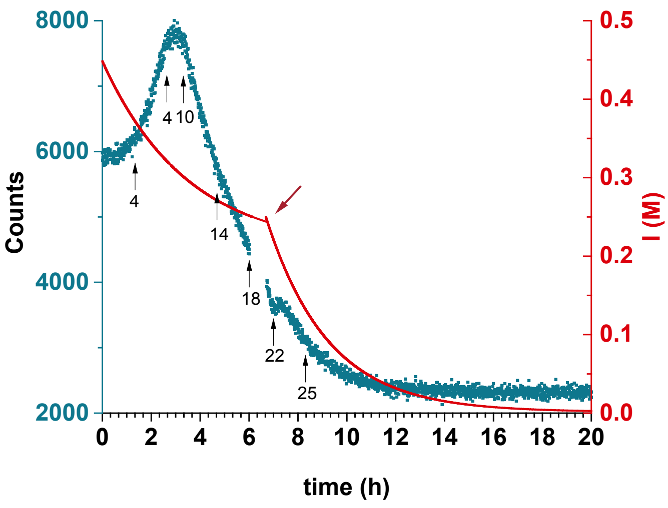

Figure 4. Overall neutron box count (L) and ionic strength $I_{Cell}(t)$ (R) as a function of the dialysis time. At the end of the first step (red arrow) the reservoirs were emptied and filled with a pure D_2O solution at pH=10). The black arrows indicate the position of the SANS curves in Fig.5.

As can be seen in Fig.4, the box count has a pronounced peak close to 0.28M where the desalting transition occurs.[3] Before the peak the interaction is progressively *turned back on* and consequently the complexation of the PEs. At the desalting transition, full coacervation occurs (Z=1)[1-2] generating µm size droplets that coarsen over a few hours and sediment down well in agreement with an overall count that slowly level-off. At the end, neutrons see likely the structure(s) present in the poor-polymer phase (in equilibrium with the much denser coacervate phase).

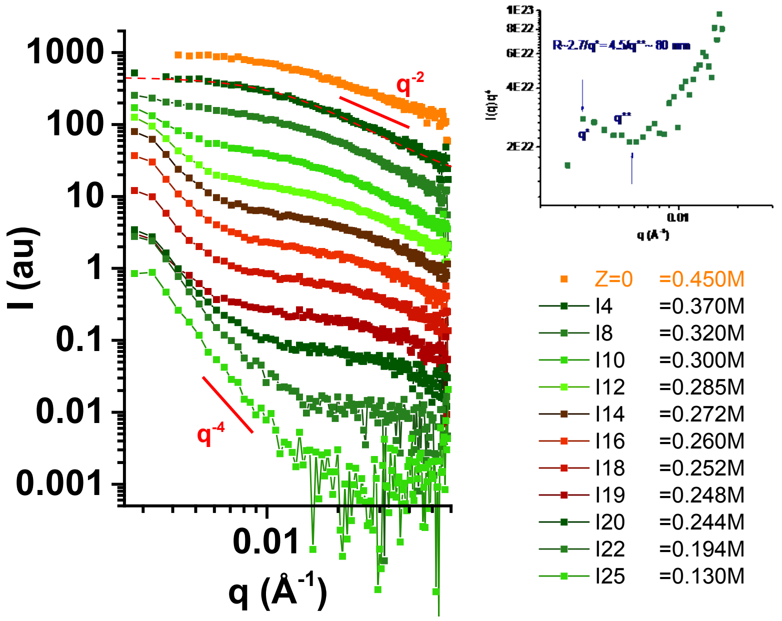

Figure 5. Neutron scattered intensity I(q) as function of the time/decreasing ionic strength during the dialysis performed at Z=1. The curves have been shifted vertically for clarity. The orange squares present the PDADMAC Gaussian chains at 0.45M (Fig 3.). Inset is the Porod representation $I(q)q^4$ *vs.*q of I22.

As can be seen in Fig. 5, the SANS curves monitored during the desalting experiment indicate a progressive transformation of Gaussian chains ($\sim q^{-2}$) in the dormant solution (0.45M) when PEs do not interact yet into larger and denser (q^{-4}) objects at the end of the dialysis where the ionic strength is lower (0.13M, I_{25} on Fig.4) and the interaction higher. Furthermore, the Porod representation suggests the presence of dense spherical complexes with sizes (R~70-80 nm) in full agreement with neutron (Fig.1) and light scattering experiments performed through direct mixing.

1. Early stage kinetics of polyelectrolyte complex coacervation monitored through stopped-flow light scattering. *Liu et al.* ***Soft Matter*** (2016), **12**, 9030-9038.
2. Structure, thermodynamic and kinetic signatures of a synthetic coacervating polyelectrolyte system. *Liu et al.* **Adv. Coll. Int. Sci.** (2017)**,** 239, 178-186.
3. Fine-tuning the assembly of highly stable oppositely charged cerium oxide NPs in solution and at interfaces. *Sekar et al.* ***Colloids Surf. A*** (2016), 500, 98–104.