Experimental report

22/09/2022

Proposal:	**EASY-1045**	**Council:**	4/2021
Title:	Influence of the polymer concentration and ionic strength on the fine structure of coacervates		
Research area:	Chemistry		

This proposal is a new proposal

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Experimental team:	
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Samples: polyacrylic acid/Poly(diallyldimethylammonium chloride)

Instrument	Requested days	Allocated days	From	To
D22	4	4	04/10/2021	05/10/2021

Abstract:

Under defined conditions, the complexation of polyelectrolytes leads to a liquid-liquid phase separation where a polymer-rich dense phase (coacervate) is in equilibrium with a polymer-poor phase (supernatant). The structure of a coacervate is between a concentrated polymer solution and a gel. The structure factor is typically fitted by the Ornstein Zernike function affording the mesh size. When the polymer is too high, the coacervate cannot form due to the too high ionic strength in the medium. This is referred at the self-suppressed coacervate. We recently put in evidence a linear decrease of the density of the coacervate phase as function of the polymer concentration until reaching the self-suppressed state. It is hypothesized that the mesh size should also vary as function of the polymer concentration. In this experiment we would like to study not only the role of the polymer concentration but also the ionic strength and the temperature on the mesh size of the coacervate and self-suppressed states phases.

Impact of the initial polyelectrolyte concentration on the local structure of a complex coacervate phase.

In order then to evaluate more directly the static local structure of the network, small angle neutron scattering measurements (SANS – D22 ILL) were performed on each coacervate & self-suppressed phase. PE solutions were prepared in full D_2O as well and pD was adjusted with NaOD prior to complexation.

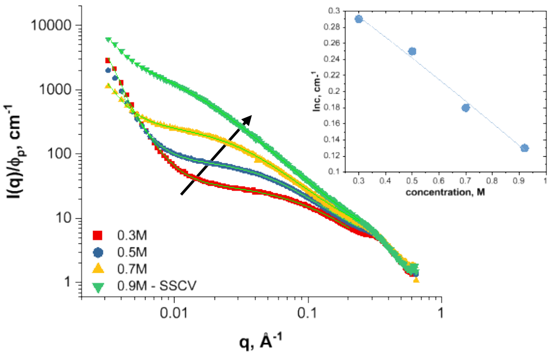

Figure 1. (a) Small angle neutron scatting (SANS) signature of the different coacervate phases measured at ILL on D22 in D_2O. The solid lines are an *Ornstein–Zernike (OZ)-Debye-Bueche (DB)* fit to the data (see below). **(b)** Incoherent scattered intensity (background) taken at high q before any correction.

We can see from **Figure 1** (insert) that the incoherent scattering taken at high q decreases linearly as the concentration of PE solution increases. This effect is due to the decreasing presence of hydrogen (H) atoms in both PEs and thus emphasizes once again that the polymer content (or density) of the coacervate decreases linearly with PE concentration. Furthermore, **Figure 1 (a)** clearly shows that the SANS signature varies significantly within each phase, suggesting that the local structure also varies with concentration. A result that may not be obvious to interpret without DLS results. In the medium and high q region, it is easy to imagine that the PE chains overlap in the complex coacervate phase, like neutral polymers in a semi-dilute solution. In this case, the semi-dilute polymer solution at equilibrium follows the Ornstein-Zernike (OZ) structure factor accounting for the concentration fluctuations at high q.

$S_{OZ}(q) = \frac{S_{OZ}(0)}{1+(q\xi)^m}$ with S(0) the structure factor extrapolated to q=0 (and related to the entanglement density and longitudinal osmotic modulus of the network) and ξ the correlation length or mesh size of the entangled network. The exponent m characterizes the polymer/solvent interaction and thus the underlying thermodynamics (m=2 for theta solvent or m=5/3 for good solvent). In addition, an excess of diffusion at low q is always present in PE solutions. This upturn has been attributed to local inhomogeneities several times larger than the radius of gyration of PEs in the solutions. We believe that these inhomogeneities actually originate from transient aggregates arising from dipole-dipole interactions and highlighted by Muthukumar in the dynamics of charged macromolecule solutions. It turns out that if the spatial scale of the concentration fluctuations due to the presence of these large transient inhomogeneities is large relative to the correlation length, then the two contributions can be summed and treated separately. The overall structure factor becomes

$S_{total}(q) = S_{OZ}(q) + \frac{S_{DB}(0)}{1+(q^2\zeta^2)^2}$ where the second term is the Debye–Bueche (DB) structure factor $S_{DB}(q)$ which accounts for the scattering by an inhomogeneous solid. $S_{DB}(0)$ is the extrapolated structure factor at q=0 and ζ represents the size of the inhomogeneities in the system. At low q, the DB contribution $S_{DB}(q) \sim 1/q^4$ dominates over that of the OZ, while at high q, where the DB scales as $S_{OZ}(q) \sim 1/q^2$ it is the reverse. The DB fit, however, should be taken with caution as a trend only because it is based on only a few low q data points and large errors are then possible. Indeed, **Figure 1** shows that the OZ-DB structure factor model accounts for the SANS data particularly well. We can see that the SANS correlation length ξ or the mesh size of the network increases with the PE concentration in agreement with DLS, density and polymer content data. The variation of the dynamic (DLS) and static (SANS) correlations length agree relatively well and scale with $\xi_H \sim (\varphi_{CCV})^{-\beta}$ (β ~ 3.2 and 2.7 for DLS and SANS respectively) (**Figure 2**). Hydrodynamic ξ_H values are, as expected, slightly higher than static values.

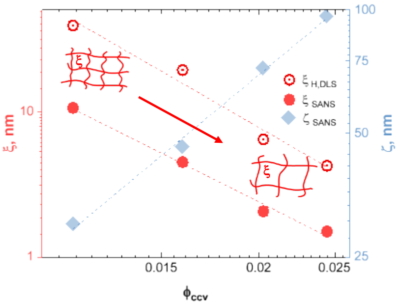

Figure 2. SANS and DLS correlation lengths ξ and SANS inhomogeneity sizes ζ as a function of the coacervate volume fraction φ_{CCV} prepared at different PE concentrations. Insert : Schematic representation of the network mesh size ξ.

At the same time, the size of the transient inhomogeneities ζ extracted from the OZ-DB fit decreases as the PE concentration increases (**Figure 2**). A somewhat expected result since the size of the transient inhomogeneities should intuitively be a function of the overall polymer concentration in the coacervate phase (dipole-dipole interactions increase with concentration). ζ increases then as expected while ξ decreases with the polymer volume fraction φ_{CCV} with a power-law variation. These results are entirely consistent with the TGA and density characterization of the coacervate and SSCV phases made previously. In summary, as the initial PE concentration increases, the interaction strength decreases, leading to a lower coacervate polymer content with a larger network mesh size (and lower transient inhomogeneities ζ). It should also be noted that the renormalized scattering intensity in the middle of the q range decreases with decreasing PE concentration, as shown in **Figure 1**. In this q-range the scattering intensity can be related to the osmotic compressibility $\left(\frac{\partial\pi}{\partial\phi}\right)^{-1}$ which is obtained by extrapolating the scattered intensity at zero angle $: I(q \rightarrow 0) = kT\phi^2\left(\frac{\partial\pi}{\partial\phi}\right)^{-1}$ The osmotic pressure of a polyelectrolyte solution in the absence of added salt is the sum of two contributions due to polymer chains on one hand and the counterions on the other. In practice, the osmotic pressure is governed by the counterions. Indeed, for a PE of DP 1000, the osmotic pressure due to counterions is 1000 times higher than the osmotic pressure arising from the PE chains if one assumes that counterions are not condensed. The decrease of $\left(\frac{\partial\pi}{\partial c}\right)^{-1}$ with PE concentration is then consistent with the formation of a coacervate phase of higher polymer concentration. In order to differentiate the contribution due to PE chains and counterions, the spectra were normalized by the polymer volume fraction in the coacervate. In **Figure 1**, we see an increase in the renormalized scattered intensity as the coacervate becomes lighter suggesting a decrease in the osmotic pressure. At this stage, this effect is not yet fully understood. However, it is conceivable that in such a dense coacervate phase, the high osmotic pressure (or low osmotic compressibility) is due to the small PANa (2k) chains and not necessarily to the counterions. Indeed, it is unlikely that the densest coacervate, formed by the strongest interaction, would have many free counter ions (and likely the reverse for the lightest). Furthermore, if we look more closely at very high q values (above 0.2 Å^{-1}), we observe a distinct correlation peak for each coacervate phase, which shifts (and flattens) to lower q with increasing PEs concentration (or decreasing φ_{CCV}) and, disappears in the SSCV single phase (**Figure 3**).

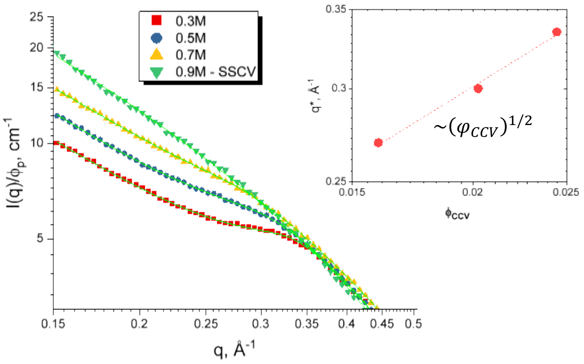

Figure 3. (a) High-q zoom of the SANS signature of the different coacervate and self-suppressed phases. The solid green lines are a fit to the data (see text). Insert : correlation length peak q* as a function of the coacervate volume fraction φ_{CCV}.

The scattering length density (ρ) of PDADMAC (~0.49.10^{6} Å^{-2}) is smaller than PANa (1.8.10^{-6} Å^{-2}), we then mostly see PDADMAC chains by SANS in D_2O (6.38.10^{6} Å^{-2}) as I(q)~ $\Delta\rho^2$. The observed peaks can then be assimilated to the polyelectrolyte peak seen for PDADMAC and PSSNa solutions at high concentration (>1M). In these individual PE solutions, the polyelectrolyte peak shifts to lower q values with increasing concentration, with a flattening of the peak due to an increase in ionic strength. We then can fit the SANS spectra of the different coacervate phases at high q (**Figure 3 a**) using the following equation

$S(q) = \frac{A}{q^n} + \frac{B}{(1+(|q-q^*|\varsigma)^m)} + bkg$ The first term describes the intensity rise, and the second term characterizes the local solvation properties and interactions around the polyelectrolyte chains. ς is the correlation length for the local solvation structure, and $q^*$the peak position. The correlation peak obtained at high q in the coacervate phase (**Figure 3**) is then a direct measure of the intensity of the electrostatic complexation between PDADMAC and PANa chains. In the densest phase, its intensity is the highest with a well-marked shape. As the density decreases while increasing the concentration of PE, it shifts to smaller values of q and disappears as the complexation in the self-suppressed single phase (SSCV) in which the ionic strength due to both free counterions is the greatest. We can see furthermore that the correlation peak q* scales as $\sim(\varphi_{CCV})^{1/2}$in the coacervate phase (**Figure 3 b**). For PDADMAC solutions, such scaling is found either in the case of semi-dilute solutions or in the highly concentrated regime (>1M in repeating units) which is consistent with a nematic order as shown by Rawiso's group although they could not observe it at the µm scale using optical microscopy. The polymer content within the densest coacervate is close to or greater than 1M in the PDADMAC monomers; a feature that perhaps suggests a nematic order. Further work is needed to fully address this issue