Heterogeneity of Polyelectrolyte Diffusion in Polyelectrolyte-Protein Coacervates: A $^1$H Pulsed Field Gradient NMR Study

A.R. Menjoge, S. Vasenkov (University of Florida, Chemical Engineering)

Introduction

Polyelectrolyte-Protein coacervation is of interest for applications such as micro-encapsulation of active food components, active drug ingredients or enzymes because properties of protein such as enzymatic activity, ligand binding, or helical content undergo little or no change upon coacervation. Here we report results of Pulsed Field Gradient (PFG) NMR studies of nanoscale diffusion in coacervates formed from a homogeneous globular protein (Bovine Serum Albumin) and poly(diallyldimethylammoniumchloride), a narrow weight distribution cationic polymer (polyelectrolyte).

Application of high gradient strengths (up to 30 T/m) allowed observation of polyelectrolyte diffusion in coacervates on length scale as small as ca. 100 nm and larger. Diffusion properties were studied for coacervates formed at different pH and ionic strengths i.e. under conditions of varying protein-polyelectrolyte interaction energy.

Experimental

Diffusion experiments were conducted using the 750 MHz wide bore Bruker Biospin spectrometer located at the AMRIS facility on the University of Florida campus. High (up to 30 T/m) magnetic field gradients were generated using diff60 diffusion probe and GRATE60 amplifier (Bruker Biospin). Diffusion measurements were performed for a broad range of diffusion times (between around 30 and 200 ms) using the PFG NMR stimulated echo sequence. PFG NMR attenuation curves were obtained by measuring the signal intensity as a function of the amplitude of the magnetic field gradients ($g$) while keeping all other parameters of the stimulated echo sequence the same.

Results and Discussion

Measured PFG NMR attenuation curves showed a deviation from the mono-exponential behavior for all studied coacervate samples. Such deviation indicates that there are different ensembles of polyelectrolyte, which are characterized by different effective diffusivities. The existence of these ensembles and the pattern of their changes with increasing diffusion time support the hypothesis about the existence of submicrometer-sized dense domains that are suspended in a continuous dilute phase. The polyelectrolyte ensemble with the smallest diffusivity is attributed to normal self-diffusion in dilute domains representing ca. 85% of the coacervate volume, while the ensembles with large effective diffusivities are tentatively assigned to polyelectrolyte transport arising from concentration gradient-driven flows in dilute domains. Such flows are believed to occur due to constant break up and formation of dense domains. These results are in a qualitative agreement with the recent data obtained by dynamic light scattering (DSL), fluorescence recovery after photobleaching (FRAP) and rheology.

Conclusions

PFG NMR diffusion studies of polyelectrolyte in several coacervate samples reveal the existence of diffusion heterogeneity for polyelectrolyte on length scales from ca. 1000 nm down to 100 nm. Such studies become possible due to the application of PFG NMR with high (up to 30 T/m) magnetic field gradients.

References