

Regular Article

Effect of small molecules on the phase behavior and coacervation of aqueous solutions of poly(diallyldimethylammonium chloride) and poly(sodium 4-styrene sulfonate)

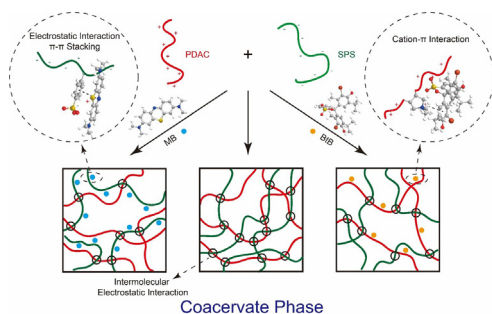
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GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: Complex coacervates are capable of easily partitioning solutes within them based on relative affinities of solute-water and solute-polyelectrolyte pairs, as the coacervate phase has low surface tension with water, facilitating the transport of small molecules into the coacervate phase. The uptake of small molecules is expected to influence the physicochemical properties of the complex coacervate, including the hydrophobicity within coacervate droplets, phase boundaries of coacervation and precipitation, solute uptake capacity, as well as the coacervate rheological properties.

Experiments: Phase behavior of aqueous solutions of poly(diallyldimethylammonium chloride) (PDAC) and poly(sodium 4-styrene sulfonate) (SPS) was investigated in the presence of various concentrations of two different dyes, positively charged methylene blue (MB) or non-charged bromothymol blue (BtB), using turbidity measurements. These materials were characterized with UV-vis spectroscopy, zeta potential measurements, isothermal titration calorimetry (ITC), fluorescence spectroscopy, and dynamic rheological measurements.

Findings: The presence of MB or BtB accelerates the coacervation process due to the increased hydrophobicity within coacervates by the addition of MB or BtB. The encapsulated MB or BtB tends to reduce the ionic crosslink density in the PDAC-SPS coacervates, resulting in a much weaker interconnecting network of the PDAC-SPS coacervates.

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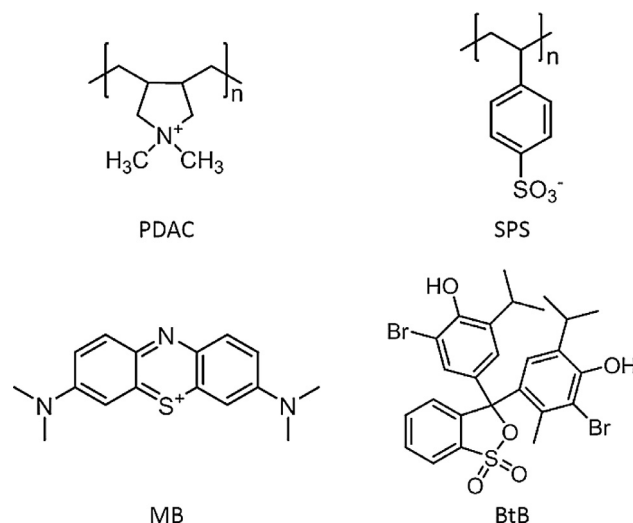
1. Introduction

It has been long known that the electrostatic interaction of oppositely charged polyelectrolytes can lead to the formation of soluble complexes, or to phase separation including liquid-liquid (coacervation) and liquid-solid (precipitation) separation, depending on factors such as charge density, ionic strength and polymer molecular weight [1–4]. When complex coacervation occurs, a dense polymer-rich phase (coacervate phase) and a very dilute polymer-deficient phase (aqueous phase), which exist in equilibrium, are formed [4–6]. The coacervation process is generally considered to be entropically driven by the release of small counter ions, producing dispersed polyelectrolyte-rich liquid coacervate droplets [4,5,7]. Complex coacervation has been applied in various fields, including pharmaceutical delivery and food industries as microencapsulates for drugs and flavors [8,9]. For example, chitosan-based coacervates have been investigated for the delivery of proteins and vaccines, which provides insight for the development of coacervates for delivery of protein biologics and vaccines [10]. Kohane et al. developed gelatin-gum Arabic complex coacervates for the encapsulation and thermally sensitive controlled release of flavor compounds, to improve the appeal of frozen baked foods upon heating [11].

As the coacervate phase has low surface tension with water, it is capable of easily partitioning solutes within it based on relative affinities between the solute and the polyelectrolytes and water. For example, our previous study shows that complex coacervates formed with oppositely charged polyelectrolytes have the ability to efficiently sequester a cationic dye, methylene blue (MB), through both electrostatic and π - π interactions [12]. Another study on hydrogen-bonding complex coacervates reveals that with the specific hydrogen bonding interaction between the solutes and polymer, the uptake efficiency can be significantly increased. Additionally, by adjusting the hydrophobicity within coacervate droplets, the partition coefficient of solutes can be tuned [13]. These preliminary studies may give insight into better designing polymeric coacervate-based materials for drug delivery or personal care products.

It has been widely reported that the phase behavior of polyelectrolyte aqueous solutions is highly dependent on many factors, *i.e.*, molecular weight, polymer concentration, stoichiometry of the two interacting polyelectrolytes, ionic strength, charge density, as well as the temperature of the solution [1,14,15]. For instance, it was found that upon shortening the chain length of polyelectrolytes, or when there is a significant deviation of the stoichiometric polycation/polyanion ratio, the stability of the complex coacervate phase was decreased [1]. It has been reported that increases in salt concentration can lead to transitions from precipitates to coacervates and finally to polyelectrolyte solutions [1,16]. The precipitate-coacervate transition is regarded as the result of successive replacement of ion pairs between oppositely charged polyelectrolytes. Compared to the precipitate-coacervate transition, the coacervate-solution transition occurs at relatively high salt concentrations, where intermolecular electrostatic interactions have been significantly screened. However, there are few studies on how the sequestered solutes within coacervates would in turn impact the phase behavior and coacervation of aqueous polyelectrolyte systems.

This study provides a more complete understanding of phase behavior and complex coacervation of synthetic, strong polyelectrolytes in the presence of small molecules, using poly(diallyldimethylammonium chloride) (PDAC) as the polycation and poly(sodium 4-styrene sulfonate) (SPS) as the polyanion. The small molecules partitioned into the coacervate in this work are an aromatic cationic water-soluble dye (methylene blue or MB) as well as an aromatic non-ionic dye (bromothymol blue or BtB) into the



Scheme 1. Chemical structures of PDAC, SPS, MB and BtB.

PDAC-SPS coacervates was studied. These various molecules can be seen in Scheme 1. The influence of the small molecules on the phase boundaries was examined and explained with a number of techniques, including spectrofluorimetry isothermal titration calorimetry (ITC) and rheology to examine the interaction between the dyes and polyelectrolytes, as well as the influence of these dyes on the physical properties of the coacervate. Although works studying how to encapsulate small molecules into coacervates are represented in the literature, there are few if any reports showing how the presence of these small molecules impact phase boundaries or other transitions such as precipitation and rheological properties of the coacervates themselves.

2. Experimental section

2.1. Materials

Poly(diallyldimethylammonium chloride) (PDAC, $M_n = 16000$, $PDI = 1.4$), poly(sodium 4-styrene sulfonate) (SPS, $M_n = 13000$, $PDI = 1.6$), and MB, BtB and ANS dyes were purchased from Sigma-Aldrich. The molecular weight and polydispersity of PDAC and SPS were measured by aqueous gel permeation chromatography (GPC) using polyethylene oxide standards. Both the polycation PDAC and the polyanion SPS are strong polyelectrolytes and are insensitive to pH. All water was dispensed from a Milli-Q water system at a resistivity of 18.2 M Ω cm. All these materials were used as received without further purification.

2.2. Turbidity measurement

Turbidity was used to qualitatively measure the extent of coacervate formation as a function of PDAC/SPS stoichiometry (PDAC/SPS) at different total polyelectrolyte concentration, with the addition of various amounts of MB or BtB. The detailed information on the concentration of PDAC and SPS stock solutions with various concentrations of added MB or BtB, namely PDAC-MB and SPS-MB, or PDAC-BtB and SPS-BtB stock solutions, were listed in Tables S1 and S2. Turbidity measurements for the titration with the addition of MB were performed using a 2 cm path length fiber-optic colorimeter (Brinkmann PC 950) at a wavelength of 420 nm. Turbidity measurements for the titration with the addition of BtB were performed on an Agilent 8453 UV-vis Spectrophotometer at a wavelength of 600 nm, to avoid the absorbance of BtB at 420 nm.

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