SOLUBLE AND INSOLUBLE POLYELECTROLYTE COMPLEXES

A Thesis in
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by
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Abstract

The addition of near equimolar amounts of poly(diallyldimethylammonium chloride) to poly(isobutylene-alt-maleate sodium), and vice-versa, results in formation of a polyelectrolyte complex that precipitates from solution as a liquid coacervate containing roughly 70 wt. % water. Zeta-potential and viscosity titrations conclude that these polyelectrolyte complex coacervates are nearly charge-neutral, with similar stoichiometry regardless of the order of addition and that our coacervates carry a weak net negative charge. Swelling and rheological properties of the coacervates are studied at different salt concentrations in the surrounding solution. The enhanced swelling observed at high salt concentration suggests these coacervates behave like polyampholyte gels, with salt screening charge attractions. However, the stronger swelling at very low salt concentrations suggests the coacervates also act like polyelectrolyte gels, owing to their weak net charge. Linear viscoelastic oscillatory shear measurements indicate that the coacervates are viscoelastic liquids and that increasing ionic strength of the medium weakens the electrostatic interactions holding the polyelectrolyte network together, lowering the relaxation time and viscosity. We use the time-salt superposition idea recently proposed by Spruijt, et al. to access timescale ranges otherwise inaccessible, by constructing master curves for these soft materials. The effect of polyanion chain length is studied with similar
swelling observed for all molecular weights, as functions of ionic strength. Linear viscoelastic measurements reveal that polyelectrolyte complexes constructed from higher molecular weight polyelectrolytes maintain constant crosslink density, but have more bridging between the polyelectrolytes, slowing their relaxation. This behavior can be described by a model, derived from the Yukawa potential for ion interactions that are screened by salt, imparting a salt concentration dependence to the relaxation times of the coacervate. Although swelling increases by a factor of 2.6 when salt concentration is changed from supernatant ($c_s = 0.09$ M) to the highest salt concentration studied ($c_s = 1.3$ M) our model ignores that concentration change and describes the relaxation time only in terms of ion interaction energetics. Fitting the model to the data suggests two results: 1) There are $N = 5.5$ associations that must be simultaneously broken for relaxation of chain segments; roughly corresponding to the number of positive or negative charges in one Kuhn monomer of each polyelectrolyte. 2) The degree of polymerization dependence of the relaxation time is $n^{1.9}$ which suggests the terminal relaxation of Rouse-like, evaluated from four polyanion Mw = 6, 65, 165 and 320 kg/mol.
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This thesis would not have been possible without the guidance, support, instructions, and patience of my supervisor Dr. Ralph H. Colby. I thank him for accepting me as his student under special circumstances, and giving me the opportunity to pursue my graduate studies.
Coacervates are formed when oppositely charged polyelectrolytes in aqueous solution spontaneously interact to form polyelectrolyte complexes. These ionically crosslinked macro-ion rich materials are entropically driven by the release of counterions and energetically driven by electrostatic attractions between oppositely charged repeat units.[5] Formation of polyelectrolyte complex coacervates is not only possible with oppositely charged polyelectrolytes but also with other oppositely charged species, such as proteins[6], micelles[7], and dendrimers[8]. These soft materials exhibit unique chemical, physical, and electrical properties compared to other conventional gel networks. The understanding of these ionically bound materials is essential and has gained interest in biological systems.[9] These polyion complexes have been found to be good replacements for collagen, which is a connective tissue, due to their high porosity for body fluids.[10] In addition, it has been shown that animal internal systems accept these materials without evident irritation or infection surrounding the tissue adhering material. Potential applications include drug and gene delivery, microcapsules, and connective structures between bones.[10–13]

Coacervates can also be utilized in modern devices such as dialysis membranes, battery separators, and environmental sensors. Neutral polyelectrolyte complex membranes have shown to be useful in the desalination of sea water due to reverse
osmosis capability. Dialysis and ultrafiltration are also possible for purifying or concentrating solutions containing colloids. These techniques are possible because of the coacervate’s high porosity allowing high permeability of water, electrolytes, and water soluble solutes; while being impermeable to high molecular weight macromolecules and large colloidal particles. Significant interest has been shown in using these membranes as hemodialyzers (artificial kidneys) and hemooxygenators (artificial lungs).[10] In addition, polyelectrolyte complexes can function as separators in batteries. The dense microstructure of these coacervate gels hinders electrical transport of all ions except the smallest species (hydrogen and hydroxyl ions). Thus unwanted interelectrode transfer is minimized.[10] Finally, coacervates can serve as humidity detectors, thanks to the sensitivity of dielectric constant to moisture. These sensors detect humidity through the change in resistance, capacitance, and impedance with relative humidity.[10]

It was initially suggested that polyelectrolyte complexes form a ladder network model, due to the initial rod-like structure of both extended polyelectrolyte chains that zipper together due to electrostatic attractions.[14] However, rheological measurements have shown that in fact polyelectrolyte complexes rather form randomly interlinked system known as the scrambled egg model.[10] The charge repulsion that stretches polyelectrolytes in solution is compensated (and screened) by the oppositely charged polyanion, relaxing the stretched conformation in the coacervate.
Figure 1.1. Coacervate formation in aqueous solution between polycation and polyanion. The resulting polyelectrolyte complexes form a random ionic network described by the scrambled egg model.

The resulting material is an ionically crosslinked network, in which both polyelectrolytes are homogeneously distributed in the coacervate, with near stoichiometric balance and random walk conformations.[10] At near zero net charge, polyelectrolyte complexes are classified as polyampholytes due to having both anion and cation units. Thus, they adopt polyampholyte characteristics and are fairly simple to form compared to conventional synthetic polyampholytes. As seen in the scrambled egg conformation of Figure 1.1, the fact that positive charges are on one chain and negative charges are on another is immaterial, as the properties will be dominated by interactions between opposite charges and the connected nature of polymer chains. The electrostatic interactions in the gel\(^1\) are correlated so that each charge is compensated by opposite charge. Thus long range repulsions are screened by the presence of the opposite charges.[16] It is important to note that after coacervate formation is complete, a large number of clusters are formed carrying local patches with a net charge. These excess charges are mediated by oppositely charged clusters interacting with each other, which explains the macroscopic aggregation behavior shown schematically in Figure 1.1.[17]

As polyanion solution is slowly added to a high molecular weight polycation

\(^1\)Despite being viscoelastic liquids, these coacervates are grouped in the broad classification of gel. [15]
solution, the coacervate that forms adopts different net charges at different poly-electrolyte ratios, influencing its properties. Adding the first few drops of polyanion results in the negatively charged chains interacting with polycations in solution, forming non-stoichiometrically balanced soluble polyelectrolyte complexes. In this state each complex is still positively charged, due to the excess of uncomplexed positive sites remaining, as shown in Figure 1.2 at left.

Figure 1.2. Addition of polyanion to an excess higher molecular weight polycation solution. Positive charges are compensated by oppositely charged polyelectrolytes as more polyanion is added, until the system reaches a stoichiometrically balanced state. Further addition causes the polyanions to rearrange to incorporate excess negatively charged chains to decrease the Coulomb self-energy.

Further polyanion addition to the non-stoichiometric polyelectrolyte complexes will eventually cause the system to reach an isoelectric point where the coacervates have no net charge. Dropping all the soluble complexes out of solution to achieve a zero zeta-potential is very difficult and needs extreme precision to be attained, which will discussed in further detail in Section 2.3.1 using zeta-potential measurements. Ideally, every positive unit on the polycation is compensated by a polyanion unit at the isoelectric point. In reality however, perfect pairing between the oppositely charged polyelectrolyte is not expected, due to structural (charge spacing and distributions) and chain flexibility differences. Therefore, not all charged units on polyelectrolytes are accessible for electrostatic compensation, owing to steric hindrance and topological constraints within the scrambled egg model. Conse-
sequently, uncomplexed moieties in the polyelectrolyte complexes remain forming charged loops and tails.[1, 18] This causes the net charge to slightly deviate from neutrality.[12] Additional polyanion molecules added to the neutral complex will cause the polyanions in the complex to rearrange so the newly added chains can be incorporated.[1] Finally, after the complex gets saturated with polyanion the newly arrived negative polyelectrolyte chains will remain in solution.

Coacervates constructed from hydrophilic polyelectrolytes have the texture of a soft gel, composed of polyelectrolyte complexes and water. The polyions have been found to be insoluble in common low polarity solvents. These gels are typically composed of 5-40 wt. % polyelectrolyte complexes and 95-60 wt. % water depending on the relative humidity of the surroundings, molar mixing ratio, hydrophobicity of the neutral portions of each polyelectrolyte, and the salt concentration during coacervate formation.[6, 12, 19–21] Coacervate behavior also change with pH of the solution, where the pH dependence varies between different polyelectrolyte complexes types.[22] Our coacervates are around 33% polyelectrolyte complex and 67% water, when immersed in the supernatant (0.09 M). The ionic network is held together by electrostatic attractions which result in a collapsed globule structure.[23] Competition between short range attraction and long range repulsion determines their physical properties and water content.[24–27] At stoichiometric balance, polyelectrolyte complexes have equal amounts of positively and negatively charged monomers, forming a macroscopic reversible gel with zero net charge. In reality, polyelectrolyte complexes carry a slight net charge which induces macroscopic repulsions within the coacervate, exhibiting weak polyelectrolyte behavior.[17, 28] Zeta-potential titrations and swelling measurements allowed us to deduce qualitatively the degree of excess charge and the sign of the net charge of our coacervates.

Polyelectrolyte complexes significantly far from the stoichiometric point stay in solution due to their net charge, and are called soluble non-stoichiometric poly-
electrolyte complexes. These soluble polyions form an opaque solution that in some respects resembles both polyelectrolyte and polyampholyte solutions with a significant net charge.[29] Zhang & Shklovskii plotted a phase diagram, Figure 1.3, of these coacervates at different polyelectrolyte ratios.[1]

Here $x$ is the polycation to polyanion charge ratio, $L$ is the length of the polyelectrolyte chains, and $r_s$ is the Debye length. As oppositely charged polyelectrolytes are mixed together they form polyelectrolyte complexes, which adopt different structures at different $x$ values. At low and high $x$ values, the predominant charged polyelectrolyte stays with an extended conformation in solution, where at $0<x<x_c$ there is excess polyanion charge, whereas there is excess polycation charge for $x_d<x<x_m$. Further addition of polyelectrolyte moves the system closer to stoichiometric balance, from either side of the diagram, to form net-neutral polyelectrolyte complexes that precipitate to form the coacervate. The remaining

**Figure 1.3.** Phase diagram of polyelectrolyte complexes at different ratio of polycation and polyanion represented by $x$. The vertical axis $L/r_s$, is the ratio of the contour length of polyelectrolyte to the Debye screening radius. Spheres represent condensate of nearly neutralized polyelectrolyte complexes. Blue/red stretched rectangles are negatively/positively charged polyelectrolyte complexes, respectively. Tadpoles have neutral head and charged tail, existing as soluble polyelectrolyte complexes. Adapted from Zhang & Shklovskii. [1]
excess polyelectrolytes either stay in solution at low Debye lengths (inter-complex disproportionation) [30] or are part of a neutral head, called tadpole (intra-complex disproportionation)[1], at high Debye lengths (from $x_c$ to $x_t$ or $x_d$ to $x_t'$). Tadpoles are formed when part of a polyelectrolyte chain is neutralized (insoluble neutral head) and the remaining monomers in the chain are partially complexed (soluble tail), shown in Figure 1.4.[1]

![Figure 1.4](image)

**Figure 1.4.** Types of polyelectrolyte complex at different charge fractions. a) Soluble complexes that carry a strong charge; b) tadpole, where part of the polyelectrolyte is neutral and the remainder remains soluble; c) neutral coacervate that drops out of solution. Adapted from Zhang & Shklovskii. [1]

The shielding effect that occurs at high salt concentrations prevents the attachment
of the tail due to the salt ions screening it from the neutral head, thus allowing the charged tail to remain in solution. The formation of tadpoles is less likely when the size between the oppositely charged polyelectrolytes is significantly different, whereas when both polycation and polyanion have approximately the same chain lengths, tadpole formation is more likely. Finally, as $x$ gets closer to 1, larger amounts of polyelectrolyte participate in formation of coacervate until polyelectrolyte chains are depleted from solution. Solutions with higher ionic strength broaden the neutral complex phase, which means that the coacervates carry a partial net charge that is stabilized by salt screening. Going to yet higher salt concentrations, not shown in Figure 1.3, will prevent formation of coacervates due to fully screening electrostatic attractions.

Properties of polyelectrolyte complexes depend on the charge density, molecular weight, and position of ionic sites within the polyelectrolyte chains; as well as on the chemical environment such as pH, temperature, and salt concentration.[5] Increasing temperature has shown an increase in polyelectrolyte diffusion due to lower ionic crosslink association life time. Changes in temperature have shown no evidence of any thermal transition.[12] Salt screens the Coulomb interactions, softening polycation/polyanion interactions. The swelling observed as salt is added is governed by the extent of electrostatic interactions in the polyelectrolyte complexes, and not by the microstructure of the gels. This phenomena is caused by the small Debye lengths that screen short-range electrostatic attraction.[31] Coacervates formed from weakly charged polyelectrolytes swell less at high ionic strength than those formed from more strongly charged polyelectrolytes. Balanced polyelectrolyte complexes collapse in low ionic strength solutions and expand at high salt concentrations, which is classic polyampholyte behavior.
Figure 1.5. Swelling at different salt concentrations. a) Polyelectrolyte is characterized by chain contraction due to the repulsive screening at higher salt concentrations. b) Polyampholyte behavior occurs when salt ions cause increase in chain dimensions, due to the screening of attractive electrostatic interactions. c) Polyelectrolyte complexes are described as polyampholyte gels with a net charge, showing characteristics of both polyelectrolytes (low salt concentration) and polyampholytes (high salt concentration).

Many polyelectrolyte complexes are polyampholyte gels carrying a slight net charge, behaving as a polyelectrolyte (low ionic strength) and as a polyampholyte (high ionic strength). At low salt concentration, the coacervate swelling is governed by osmotic pressure, induced by the trapped counterions inside the gel network. The extent of swelling at low salt concentration depends on the net charge, fewer uncomplexed sites means that there are fewer trapped counterions and therefore smaller osmotic pressure. Electrostatic interaction screening starts taking effect at higher salt concentration. Long range electrostatic repulsions are initially screened due to the large Debye length, which will cause slight shrinking in the gel. Further
increase in salt concentration (smaller Debye length) will eventually screen short
range electrostatic attraction between the oppositely charged polyelectrolytes, re-
resulting in polyelectrolyte complexes swelling. At high ionic strength, the swelling
ratios of coacervates with different net charges converge to the same value.[3] This
is due to the fact that at high salt concentrations nearly all electrostatic attractions
are screened and the swelling ratio variation between polyelectrolyte complexes is
very small. At very high salt concentrations (>1.9 M) the coacervate dissolves
back into solution.[3]

This swelling behavior of polyampholyte gels has also been explained and mod-
eled using excluded volume by Higgs and Joanny.[16] polyelectrolyte complexes in
low ionic strength solution are analogous to regular polymers in poor solvent, where
attractive interactions dominate and the excluded volume is negative. Slightly
charged coacervates go through a minimum excluded volume which is the point
where the system shifts from having polyelectrolyte to polyampholyte character-
istics and has the smallest swelling. Minimum excluded volume depends on the
extent of trapped counterions in the coacervates. High salt concentrations, after
minimum excluded volume, are equivalent to good solvent, where the excluded vol-
ume of the network gel turns positive. This dependence can be modeled through
the following:[16]

\[ \nu = -\pi (f \cdot l_B)^2 r_D + 4\pi \cdot l_B \cdot \Delta f^2 \cdot r_D^2 \]  

(1.1)

Where \( f = f^+ + f^- \) is the total charge fraction of monomers, \( \Delta f = f^+ - f^- \) is
the charge carried by the coacervate. The parameters \( l_B \) and \( r_D \), the Bjerrum and
Debye lengths, depend on the solvent dielectric constant, respectively. The Debye
length also has an inverse salt concentration dependence. Both values are given
by the following equations (derivation Appendix A):

\[ l_B = \frac{e^2}{4\pi \cdot \epsilon \cdot \epsilon_0 \cdot kT} \]  

(1.2)
\[ r_D = \sqrt{\frac{1}{8\pi \cdot l_B \cdot C_s \cdot N_A}} \]  

The first term in Equation 1.1 described the polyampholyte behavior which depends on the fraction of monomers that are electrostatically attracted. The second term describes the repulsive interaction screening of polyelectrolytes and is characterized by the fraction of uncomplexed charges in the system (net charge). It also depends on Debye length squared, making it more dominant at low salt concentration. When \( f^+ = f^- \) and \( \Delta f \) is equal to zero then a system is described as a polyampholyte. On the other hand, when \( f = \Delta f \) then the system behaves like a polyelectrolyte. Our complex coacervates are in between these two behaviors with closer tendency to polyampholytes.

The polyelectrolyte complex morphology has been suggested to follow the “scrambled egg” model, where oppositely charged polyelectrolyte chains randomly bond.[14] This results in an ionically crosslinked system where each polyelectrolyte chain is attached to multiple oppositely charged chains. Positive and negative polyelectrolytes are randomly arranged in the complex, which develops some short-range correlations due to like charged chains avoiding each other.[1] The mechanical properties of the coacervates are determined by the chain dynamics, network structure, and the stoichiometry of polyelectrolyte complexes. Linear viscoelastic (LVE) oscillatory shear measurements allow the understanding of the mechanical properties of these soft reversible gels, and how the system responds to different salt concentrations and molecular weights, as well as determination of the association lifetime of the ionic crosslinks. This lifetime depends on the activation energy required to rearrange cation-anion associations, defined as the dissociation and reformation of two ion pairs at different positions on the polyelectrolyte chain. Therefore, polyelectrolyte complexes have the ability to restore their network by rearranging their ionic-crosslinks after a stress has been applied. Conventional polymers with a network structure on the other hand, will restore their original
dimensions after a stress has been applied. Chains are more mobile at higher salt concentrations, because salt screening the electrostatic attractions lowers the association lifetime. The viscoelasticity observed in this system obeys time-salt superposition,[32] which allows us to access time-scales otherwise inaccessible due to physical and instrumental limitations. Salt screening lowers the association energy and the association lifetime, which sets the time scale for the viscoelastic transition from elastic character at high frequencies (low salt) to viscous character at low frequencies (high salt). Varying the molecular weight of the polyelectrolyte in polyelectrolyte complexes keeps constant crosslink network density, due to the equal extent of positive/negative electrostatic interactions. However, polyelectrolytes with larger molecular weight have greater amount of bridging between the oppositely charged polyelectrolytes.

When polyelectrolytes are in aqueous solution, they are surrounded by their respective counterions due to the electrostatic interactions forming a double layer. Coacervate formation is thermodynamically more favorable compared to the polyelectrolytes initial state because restricted counterions have more translational freedom and thus higher entropy.[5] During complexation, polyelectrolyte chains go from being strongly stretched in solution to forming a liquid sediment with random walk conformation, hence polyelectrolytes lose translational entropy and gaining conformational entropy.[2] Counterion translational entropy is the most dominant factor, followed by conformational entropy of the polyelectrolytes. The translational entropy of polyelectrolyte has a small effect and is insignificant compared to the other two entropy terms. Therefore, the overall entropy term can be defined by the following equation:

$$\Delta S = \Delta S_{\text{counterions}} + \Delta S_{\text{conformational}}$$

(1.4)

The entropy of complexation depends on the ionic strength of the surrounding solution. At low salt concentrations, counterion induced entropy is large due to
the fact that the difference in ion concentration between the double layer and the surrounding solution is very high. Conformational entropy is also at its maximum at low ionic strength, due to polyelectrolyte chains going from being highly extended to having random walk conformation in the coacervate phase. Increasing the ionic strength of the solution reduces the translational entropy of counterions until $\Delta S \rightarrow 0$, due to the lower concentration difference between the double layer and the solution. In addition, a solution with high salt concentration screens the electrostatic repulsions of a high stretched polyelectrolyte chain, allowing it to relax. Therefore, the conformational entropy of polyelectrolytes during complexation is also dampened, however, $\Delta S$ remains positive.

The process of forming polyelectrolyte complexes can be either exothermic or endothermic depending on the ionic strength of the surrounding solution. The free energy of complexation ($\Delta F$) of the system is given by two terms, the Coulomb energy ($\Delta E$) and entropic contribution of counterion release ($-T \Delta S$), giving the following equation:

$$\Delta F = \Delta E - T\Delta S$$  \hspace{1cm} (1.5)

Complexation of polyelectrolyte complexes is favorable when $\Delta E < 0$ and $\Delta S > 0$. As the salt concentration is increased the entropic contribution will decrease, which is less favorable for polyelectrolyte complex formation. The free energy, sum counterion entropy term and electrostatic contribution of the polyelectrolyte chains,[33] changes during complexation and also depends on salt concentration. At low ionic strengths, polyelectrolyte complexes form tight ion pairing between the opposite charged macromolecules, while the counterion concentration in the double layer is dilute. As a result, a large decrease in electrostatic energy arises, making complexation an exothermic process. At higher salt concentration, the Debye length gets smaller and the counterions in the double layer are more compact. In addition complexes have weaker binding interactions between the oppositely charged
chains, due to electrostatic screening. Therefore, the increase in energy to release an ion is not compensated by the decrease in binding energy from the formed coacervate. These phenomena are confirmed by Schaaf et al. calorimetric data measurements.\[34\]

**Figure 1.6.** Salt concentration dependence of the energetic and entropic parts of the free energy of polyelectrolyte complex formation. $\Delta E$ corresponds to the Coulomb energy of the whole system, $\Delta F$ the free energy of complexation, and $T\Delta S$ is the entropic contribution from counterion release. Adapted from Gucht et al. \[2\]

These behaviors are depicted as a function of salt concentration in Figure 1.6.\[2\] At low ionic strengths the polyelectrolyte complex formation is exothermic, due to the counterions high entropy gain and macro-molecules electrostatic energy decrease. At higher salt concentrations, the entropy gain decreases and the electrostatic energy weakens, resulting in an endothermic process. The exact ionic strength at which the crossover occurs varies between polyelectrolytes, depending on their properties. Eventually at very high salt concentration, the free energy of complexation becomes positive which prevents the formation of complexes due to the high screening effect. \[2\]
Coacervates also change in opaqueness at different salt concentrations. At low ionic strength, in deionized water, polyelectrolyte complexes are slightly turbid and at high salt concentrations they turn clear. These changes are due to polyelectrolyte complexes phase separating, revealing the formation of micron size droplets in the system.[3] Frozen domains may be possible for more hydrophobic polyelectrolytes that form coacervates with 40 ± 20 wt. % water that have a Tg above room temperature. During the preparation of these gels, large spatial fluctuations in net charge spontaneously form. Thus, polyelectrolyte complexes that are placed in low ionic strength solution create frozen domains with different net charge values. These spatial concentration fluctuations exhibit a micro-aggregated structure, where domains carry net charge (polyelectrolyte) and other have zero net charge (polyampholyte), causing the high turbidity in the system.[35]

Figure 1.7. Internal structure of polyelectrolyte complexes with slight net charge. At low salt concentrations, oppositely charged chains form complexes, and strands with excess charge are strongly stretched. This causes the formation of charged domains making the gel look turbid. Increasing the salt concentration makes the network neutral and appear clear. Adapted from Nisato et al. [3]

At higher salt concentration screening dominates, and the entropic term of the counterions (first term in Equation 1.4) decreases nearly to zero and the system behaves like a neutral system. The evenly distributed charge, as seen in Figure
1.7, decreases the phase domain size and makes the coacervates appear clear.[3]
Chapter 2

Non-Stoichiometric Soluble Polyelectrolyte Complexes

2.1 Introduction

Complete coacervate formation is preceded by the formation of non-stoichiometric soluble polyelectrolyte complexes, which are present in the supernatant. Soluble complexes have interesting properties that depend on the composition of polyanion and polycation in solution. Colloidal formation occurs due to the large amount of uncomplexed polyelectrolytes, creating an opaque solution. The number of polyelectrolytes in solution is at its maximum, milky white solution, about halfway to reaching a 1:1 polyanion/polycation charge ratio, explained further in Section 2.3.2. Approaching stoichiometric balance will result in all soluble complexes dropping out of solution and forming a liquid sediment (neutral polyelectrolyte complex coacervate) in a clear solution containing NaCl ions. This resembles a phase transition at the isoelectric point occurring at a precise polycation fraction $X$, as shown in Figure 1.3. In this chapter we will discuss how the zeta-potential and viscosity of the supernatant depend on amounts of positive and negative charges in solution. Zeta-potential (also known as electrokinetic potential) is a property that depends on the suspended colloids in solution. Solutions with excess polycation or polyan-
ion will exhibit a positive or negative zeta-potential, respectively. Particles with large excess charge in solution will tend to repel each other and the soluble polyelectrolyte complexes with the same sign charge similar repel each other. On the other hand, particles that don’t exhibit any force that prevent polyelectrolytes from coming together are net-neutral and have a zero zeta-potential, this state is known as the isoelectric point.

The viscosity of the supernatant also depends on concentration. As the concentration of soluble complexes in the solution increases, the viscosity increases. The entanglements and bridging that arise at higher concentrations causes further increase in viscosity, and the viscosity only decreases after the soluble complexes start to drop out of solution to form the coacervates.

2.2 Experimental Procedure

2.2.1 Materials

Poly(diallyldimethylammonium chloride) (PDADMAC) with Mw = 400-500 kg/mol and poly(isobutylene-alt-maleate sodium) (IBMA-Na) with different molecular weights (320, 165, 65, and 6 kg/mol), with structures shown in Figure 2.1, were chosen for the formation of polyelectrolyte complexes.

![Molecular structure of: a) IBMA-Na and b) PDADMAC](image)

*Figure 2.1. Molecular structure of: a) IBMA-Na and b) PDADMAC*

PDADMAC was readily available, purchased from Sigma Aldrich, and only required dialysis for purification (see Section 3.2.1). Maleic anhydride/isobutylene
copolymers were purchased from Kuraray Co., Ltd. (Kuraray America, Inc., NY). IBMA-Na with molecular weights 165, 65, and 6 kg/mol were already hydrolyzed, dialyzed, and freeze dried (Eastman Kodak Company).[4] Maleic anhydride copolymer with 320 kg/mol molecular weight was dissolved in deionized water, and hydrolyzed for 24 hours at 50°C with the addition of excess NaOH and was finally dialyzed. The degree of sodium counterions ($\alpha_{IBMA-Na}$) shown in Table 2.1 were obtained measuring the pH of the polyanion solutions with a concentration of 5.00 mg/mL. Using The following equation and figure from Sauvage et al. paper, [4] the $\alpha_{IBMA-Na}$ values were calculated:

$$pK_{app} = pH - \log\left(\frac{\alpha_{IBMA-Na}}{1 - \alpha_{IBMA-Na}}\right)$$  \hspace{1cm} (2.1)

![Figure 2.2. $pK_{app}$ as a function of $\alpha$ for IBMA-Na. Adapted from Sauvage et al. [4]](image-url)
2.2.2 Zeta-Potential

Zeta-potential titration was used to study the soluble complexes at different polycation/polyanion fractions to determine the isoelectric point. Soluble samples with different positive charge fractions (from 0 to 1) were separately prepared in 20 mL vials. For all the different samples, PDADMAC and all IBMA-Na molecular weights had a concentration of 4 weight % and 5 weight %, respectively. One polyelectrolyte was slowly added, using a pipette, into a vial containing the oppositely charged polyelectrolyte to ensure the system had enough time to mix. In addition, VWR Vortex Analog Mixer was used during coacervation to ensure proper mixing of the polyelectrolytes. Polyelectrolyte complex samples with different charge fractions were prepared using both polyelectrolytes as titrants.

\[
X \equiv \frac{m_{\text{PDADMAC}} \cdot \alpha_{\text{PDADMAC}}}{M_{\text{w}_{\text{PDADMAC}}}} + 2 \frac{m_{\text{IBMA-Na}} \cdot \alpha_{\text{IBMA-Na}}}{M_{\text{w}_{\text{IBMA-Na}}}}
\]

\[
X \equiv f^+
\]  

(2.2)

\(X\) is the charge fraction of positively charged units (equivalent to \(f^+\) given by Higgs and Joanny), \(m\) is the mass, and \(M_w\) is the molecular weight of a repeat unit of the polyelectrolytes. It was assumed that PDADMAC’s repeat units were all quaternized amines, making \(\alpha_{\text{PDADMAC}}\) equal to 1. Around 1.6 mL supernatant, composed of non-stoichiometric soluble polyelectrolyte complexes and sodium chloride ions, was placed in cuvette using 800 \(\mu\)L pipette. Subsequently, the cuvette was placed into Brookhaven ZetaPALS, and the required data was inputted into the computer software (temperature, solvent type, etc.). Obtained data allowed us to find the fractions where the solution has a near zero net charge (isoelectric point).
2.2.3 Supernatant Viscosity

Samples were prepared in the same manner to zeta-potential samples. Contraves Low Shear 30 Viscometer was used to find the viscosities of all samples. The bottom cup, specific for Contraves, was filled up with around 2-3 mL of supernatant. Temperature was controlled at 25 °C using a circulating water bath. The inner bob was slowly descended into the bottom cup, while making sure the walls don’t come into contact. Before starting a run, the torque was zeroed for all the 5 sensitivity modes. For very viscous solutions sensitive mode 5 was used to get the measured torque value in the range of 40 - 80, and lower viscosity samples were set accordingly to lower modes. Multiple shear rates were studied for each supernatant and the viscosity was observed to be Newtonian and averaged.

2.3 Results and Discussion

Before analyzing the isoelectric point, it is important to distinguish the extent of neutralization with sodium counterions on the different IBMA-Na molecular weights. The degree of sodium counterion ($\alpha_{IBMA-Na}$) in IBMA-Na polyanion was obtained using Figure 6b in Sauvage et al. by measuring the pH (see pH titrations in Appendix E). [4] The extent of neutralization is given by,

$$\alpha = \frac{[COO^-]}{[COOH + COO^-]} \quad (2.3)$$

and the results of the degree of neutralization are listed in Table 2.1, obtained from Equation 2.1 and the titration curve of Figure 2.2.
Table 2.1. pH of individual IBMA-Na molecular weights dissolved in deionized ultra pure water and their corresponding degree of neutralization value ($\alpha_{IBMA-Na}$), in addition to the polydispersity index.

<table>
<thead>
<tr>
<th>IBMA-Na Molecular Weight (kg/mol)</th>
<th>pH</th>
<th>$\alpha_{IBMA-Na}$</th>
<th>Mw/Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>8.537</td>
<td>0.75</td>
<td>1.75</td>
</tr>
<tr>
<td>65</td>
<td>9.443</td>
<td>0.85</td>
<td>2.60</td>
</tr>
<tr>
<td>165</td>
<td>9.105</td>
<td>0.83</td>
<td>3.04</td>
</tr>
<tr>
<td>320</td>
<td>8.680</td>
<td>0.77</td>
<td>2.40</td>
</tr>
</tbody>
</table>

Isoelectric point is independent of molecular weight and thus should always have the same composition, however this assumes that all used IBMA-Na’s have the same neutralization with sodium counterions.[17] Since different $\alpha_{IBMA-Na}$ values were obtained, with no general molecular weight trend, this means that the isoelectric point is independent of the IBMA-Na molecular weight.

2.3.1 Zeta-Potential

Determining the isoelectric point is important to understand the net charge of the coacervates. The zero volt potential point in zeta-potential titrations, shown in Figure 2.3, determines the charge fraction of the coacervate.
Figure 2.3. Zeta-Potential values of non-stoichiometric soluble polyelectrolyte complexes in the supernatant, as a function of positive charge fractions with different IBMA-Na molecular weights. Using (a) PDADMAC and (b) IBMA-Na as titrant.
Figure 2.3 shows the zeta-potential data collected for polyelectrolyte complexes using different IBMA-Na molecular weights. The zeta-potential of the solution changes steadily during the addition polyelectrolyte, and changes more quickly near stoichiometric balance. Forming coacervates exactly at the isoelectric point is therefore very difficult due to the abrupt transition. Further addition of polyelectrolyte into a solution that has reached its isoelectric point, has a continuous effect on the coacervate in which the zeta-potential of the solution continues to change in a weak manner (more in Section 2.3.2). To determine the fraction of the isoelectric point, we connected the two data points closest to neutrality and found the 0 mV intercept (fitting of equations can be seen in Appendix C). The polyelectrolyte complex compositions at the isoelectric point are summarized in Table 2.2.

Table 2.2. Fraction of positively charged units \((X)\) in the coacervate at the isoelectric point for different IBMA-Na molecular weights using zeta-potential measurements of the supernatant.

<table>
<thead>
<tr>
<th>IBMA-Na Molecular Weight (kg/mol)</th>
<th>(X)</th>
<th>PDADMAC Titrant</th>
<th>IBMA-Na Titrant</th>
<th>(\alpha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.44</td>
<td>0.46</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>0.47</td>
<td>0.52</td>
<td>0.85</td>
<td></td>
</tr>
<tr>
<td>165</td>
<td>0.41</td>
<td>0.42</td>
<td>0.83</td>
<td></td>
</tr>
<tr>
<td>320</td>
<td>0.39</td>
<td>0.40</td>
<td>0.77</td>
<td></td>
</tr>
</tbody>
</table>

Due to the varying \(\alpha\) on the different IBMA-Na molecular weight chains, different charge fractions were obtained during coacervation. IBMA-Na with a higher \(\alpha\) value requires larger amount of PDADMAC to neutralize and thus has a higher \(X\) value at the isoelectric point. Theoretically, if \(X\) is equal to 0.5 the coacervate has a zero net-charge and there are no uncomplexed sites. Values below 0.5 imply that the system has an overall negative charge and values above 0.5 produce coacervates with a net positive charge. This deviation could originate from differences in the
flexibility of the chain or effective size of the monomer group along the polymer backbone.[36] Table 2.2 indicates that the polyelectrolyte complexes formed all carry a slight excess negative charge.

![Graph](image)

**Figure 2.4.** Charge fraction in polyelectrolyte complex over sodium counterion fraction in IBMA-Na as a function of the polyanion’s molecular weight.

To study the influence of molecular weight on the isoelectric point, first, all four $X$ values were normalized by dividing by $\alpha$. This aids in eliminating the difference in sodium counterion content between the polyanion molecular weights. Lower molecular weight polyanion illustrate higher $X/\alpha$ values compared to large molecular weight. Large polyelectrolyte chains are more restricted in their movement, creating topological constraints and restricting the system from rearranging.[37, 38] Polyelectrolyte macromolecules do not have the fundamental feature of chain sections crossing one other.[23, 39] This forbidden self-crossing is more significant in higher molecular weight polyelectrolytes and therefore a large amount of repeat units remain inaccessible for neutralization, thus having a lower $X/\alpha$ value. From Figure 2.4 one can infer that IBMA-Na 165K has the largest amount of uncom-
plexed anions, followed by IBMA-Na 320K, 65K, and 6K. Hence, the molecular weight dependence applies to our system roughly, except that IBMA-Na 165K is further away from neutrality. The expected $X/\alpha$ for IBMA-Na 165K is around 0.55

### 2.3.2 Viscosity

Supernatant viscosity measurements can also determine the isoelectric point, which may verify the values obtained through zeta-potential measurements. Viscosity of soluble complexes depends on the concentration, where higher concentrations in the supernatant have higher viscosities. Figure 2.5 below shows the specific viscosity values obtained at different positive charge fractions.
Figure 2.5. Specific Viscosity measurements of non-stoichiometric soluble polyelectrolyte complexes at different positive charge fraction. Using PDADMAC (filled symbols) and IBMA-Na (empty symbols) as titrants. ★ symbol in each graph indicates the minimum specific viscosity.

The general trend among the different molecular weights reveals a minimum around the 0.5 charge fraction, which is the region that corresponds to the formation of neutral coacervates. This decrease in viscosity of the supernatant indicates that the closer the system reaches stoichiometric balance, the smaller the concentration of soluble complexes. Measurements of pure IBMA-Na ($X=1$) show that higher molecular weight polyanion have higher viscosities. These results are expected because higher molecular weight polyelectrolyte has lower overlap concentration, consequently having higher viscosities. The charge fraction region between pure polyelectrolyte solution and neutral coacervate show the highest viscosity values,
due to the fact that the concentration in this range is very high.

Initially, the system starts forming soluble complexes with some degree of bridging after mixing the first drops of PDADMAC, as a consequence the viscosity starts to increase. After the viscosity reaches a peak, i.e. the point with maximum concentration, further addition forms neutral coacervates that settle as sediment. The viscosity keeps decreasing until everything drops out of solution to form a liquid sediment (the coacervate) and the solution is free of any soluble complexes. This implies that the lowest viscosity corresponds to the isoelectric point, which can be established from the specific viscosity as it reaches zero. Charge fractions at the isoelectric point calculated using specific viscosity are the following:

\textbf{Table 2.3.} Fraction of positively charged units ($X$) in coacervates at the isoelectric point for different IBMA-Na molecular weights from the minimum in specific viscosity.

<table>
<thead>
<tr>
<th>Molecular Weight (kg/mol)</th>
<th>IBMA-Na Titrant</th>
<th>PDADMAC Titrant</th>
<th>IBMA-Na Titrant</th>
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<tr>
<td>6</td>
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<tr>
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<td>0.41</td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td>320</td>
<td>0.37</td>
<td>0.37</td>
<td></td>
</tr>
</tbody>
</table>

The charge fractions retrieved using specific viscosity are similar to the ones obtained through zeta-potential as shown in Figure 2.6.
Figure 2.6. Comparing X fraction at the isoelectric point using zeta potential and specific viscosity technique. ■ Symbol shows PDADMAC as titrant, and ● shows IBMA-Na as titrant.

Few fractions show a larger difference, which is due to the subtle region near the isoelectric point, as stated earlier, and thus measuring the viscosity at that state is a challenging task. Therefore, it can be presumed that the charge fractions obtained from zeta-potential measurements are more reliable and closer to the true value. Isoelectric point fractions obtained through pH titrations are shown in Table E.1, however the X values have shown to be further away from the true value.

Soluble non-stoichiometric polyelectrolyte complexes have shown a difference in viscosities when comparing a state of excess PDADMAC to excess IBMA-Na. The viscosity of soluble complexes depends on the molecular weight of the excess polyelectrolyte. Polyelectrolytes with smaller molecular weight exhibit larger viscosities. Since IBMA-Na has smaller molecular weight compared to PDADMAC, soluble complexes have a more viscous solution when the polyanion is in excess, as seen in Figure 2.5.
Figure 2.7. (a) Soluble polyelectrolyte complexes with excess small molecular weight polyanion enhances bridging between oppositely charged polyelectrolyte creating a more viscous solution. (b) Excess high molecular weight polycation behaves similarly to regular polycation solution however with reduced charge, and thus polyelectrolyte repulsion prevents bridging.

When soluble polyelectrolyte complexes have excess small molecular weight polyanion, the system is equivalent to polycation chains that carry an excess negative net charge. In Figure 2.7 a, the small polyanions promote higher degree of bridging between the polycation chains and thus induce higher supernatant viscosities. On the other hand, soluble complexes with excess polycation behave similarly to the regular polycation solution, however, with reduced positive net charge. The schematic in Figure 2.7 b shows that the system does not promote bridging between the oppositely charge polyelectrolytes, and thus would not show an increase in viscosity. In fact, the system decreases in viscosity in the region of excess polycation, which is due to the fact that the neutral polyelectrolyte complexes drop
out of solution. This suggests that the formation of net neutral coacervates occurs at an earlier stage when polycations are in excess compared to when polyanions are in excess. This affect however applies much stronger for the high molecular weight polyanions (320K, 165K, and 65K) and weakly for the very small molecular weights (6K). The smallest polyanion molecular weight, IBMA-Na 6K, has given comparatively very small viscosity values compared to the other three molecular weights. Under a certain molecular weight polyelectrolytes do not induce the same degree of bridging and the regular polyelectrolyte solution has a relatively low viscosity.

Figure 2.5 also shows that net neutral coacervates at the isoelectric point return to being non-stoichiometric soluble complexes after mixing additional polyelectrolyte solution, as shown in Figure 1.2. The increase in viscosity indicates that newly added polyelectrolytes cause the polyelectrolytes in the coacervate to redissolve. Interestingly, the viscosities obtained after the isoelectric point behave in a similar fashion to the viscosities obtained before the isoelectric point with the opposite titrant. This concludes that the viscosity of the supernatant is just a function of charge fraction $X$ and molecular weight $M$, regardless of the polyelectrolyte being titrated.
3.1 Introduction

Coacervate characteristics are influenced by the properties of the polyelectrolytes it’s composed of and its surrounding chemical environment. We have studied these behaviors by varying the polyelectrolyte molecular weight and ionic strength of the solution. Salt ions in solution have a significant affect on the relaxation dynamics of clusters of ionic bonds.[40–42] Changing the molecular weight of polyelectrolytes participating in coacervation alters the degree of bridging between the polycation and polyanion in the coacervate. Longer polyelectrolyte chains have larger number of charged repeat units per chain, allowing it to ionically bond to more oppositely charged polyelectrolytes strands, thus raising the modulus. However, longer polyelectrolytes are more restricted in their movement during coacervate formation, creating topological constraints and delaying ionic sites from rearranging. Thus, a significant amount of repeat units may remain uncomplexed and inaccessible for neutralization. The electrostatic interaction between the oppositely charged polyelectrolytes is described by the Coulomb energy (derived in Appendix A):
\[ E = \frac{-e^2}{4\pi \cdot \epsilon \cdot \epsilon_0 \cdot r} = \frac{l_B}{r} kT \]  

(3.1)

Where \( e \) is the elementary charge of the ions, \( r \) is the separation between the ions, \( \epsilon \) is the dielectric constant, and \( \epsilon_0 \) is the vacuum permittivity. The final result in Equation 3.1 is written in terms of the Bjerrum length defined in Equation 1.2.

Salt screening electrostatic interactions relies on the Debye screening length, shown in Equation 1.3. When coacervates are in low salt solution, the large Debye length screens only long range repulsive interactions. On the contrary, high ionic strength solutions with small Debye lengths screen short range attractions, consequently weakening ionic crosslinks and allowing an increase in polyelectrolyte diffusion and faster coacervate relaxation. This phenomenon can be modeled using the Yukawa potential; Coulomb energy with an exponential cutoff at the Debye length.

\[ E_a = kT l_B \sigma \cdot \exp\left(\frac{-\sigma}{r_D}\right) = kT l_B \sigma \cdot \exp\left(-\sigma \sqrt{8\pi \cdot l_B \cdot c_s \cdot N_A}\right) \]  

(3.2)

Where the Bjerrum length is 7.1 Å for water, \( N_A \) is Avogadro’s number, \( c_s \) is the solution’s molar salt concentration, and \( \sigma \) is the distance between two charges in a contact pair. The association lifetime \( \tau \) is thermally activated, with binding energy given by Equation 3.2, evaluated for the contact pair for ions of size \( \sigma \), taken here to be \( \sigma = 1 \) Å.

\[ \tau = \tau_0 \cdot \exp(N \cdot \frac{E_a}{kT}) \]
\[ \tau = \tau_0 \cdot \exp(N \cdot \frac{l_B}{\sigma} \cdot \exp(-\sigma \sqrt{8\pi \cdot l_B \cdot c_s \cdot N_A})) \]  

(3.3)

Here \( \tau_0 \) is a prefactor time scale that will be fitted to experimental data and is expected to depend on molecular weight. Constant \( N \) will be a fitting parameter and it signifies the number of associations that need to be broken to describe the
mobility of the chains.[43, 44] Taking $N = 1$ and expanding the interior exponential in Equation 3.2 for large Debye Length (i.e. low salt concentrations) gives the equation derived by Spruijt et al.[32]

$$\tau \propto \tau_0 \cdot \exp\left(l_B\left(\frac{1}{\sigma} - \sqrt{8\pi \cdot l_B \cdot c_S \cdot N_A}\right)\right) \quad (3.4)$$

The activation process given in their paper is governed by the rearranging of ionic sites by the dissociation of ion pairs and reforming the ionic bond at different positions. [32]

Swelling of these gel-like coacervates depends on their net-charge and the ionic strength of the solution. Coacervates closer to neutrality experience stronger polyampholyte behavior, where the presence of salt causes the system to swell by screening electrostatic attractions. Coacervates with a net charge have a slight polyelectrolyte behavior. In a salt free solution, polyelectrolytes expand due to electrostatic repulsions along the chain, and the addition of salt screens these electrostatic repulsions causing the polyelectrolyte chain to contract. All swelling values are reported in term of mass, using the following equation:

$$Q[c_s] \cdot F_{PE} = \frac{m[c_s]}{m_{Dry}} \cdot \frac{m_{Dry}}{m[c_{Supernatant}]} = \frac{m[c_s]}{m[c_{Supernatant}]} \quad (3.5)$$

Where $Q[c_s]$ is the swelling ratio of the coacervate, and $F_{PE}$ is the mass fraction of polyanion and polycation chains in the coacervate gel surrounded by its supernatant. Therefore, the swelling depends on $m[c_s]$ and $m[c_{Supernatant}]$, the masses of the coacervate at a specific salt concentration ($c_s$) and immersed in the supernatant at 0.09 M, respectively. The salt concentration of the supernatant was calculated on the assumption that the polycation releases all its counterions with $\alpha_{PDADMAC} = 1$. The polycation is presumed to be the limiting factor in coacervate formation since the gel is negatively charged. Using the $X$ values in Table 2.2, it was calculated that 1 g PDADMAC (0.00619 mol) and 1.13 g IBMA-Na (0.00523
mol) released 0.00619 mol NaCl counterions. The total solvent volume (calculated using the concentrations in Section 3.2.2) for 1 g PDADMAC is 0.07 L.

\[
c_{\text{supernatant}} = \frac{\text{mol}_{\text{NaCl}}}{V_{\text{solvent}}} = \frac{0.00619 \text{ mol}}{0.07 \text{ L}} = 0.09 M\tag{3.6}
\]

3.2 Experimental Procedure

3.2.1 Dialysis

All polyelectrolytes were dialyzed prior to coacervate formation, to remove excess ions and unwanted particles. PDADMAC and IBMA-Na320K were purified in a 400 mL dialysis cell, purchased from Amicon, using deionized water obtained from EASYpure UV/UF. This process was run by applying 40 psi pressure from an Argon tank into the dialysis cell that contained a 30,000-Mw cut-off membrane. The flushed water that went through the membrane was replaced by deionized water from the storage chamber. Depending on the concentration of polyelectrolyte in the dialysis cell, we were able to flush around 1.5 L of deionized water in 2 days. Polyelectrolyte purity was monitored by measuring the conductivity of the flushed dialysate periodically and was stopped when the dialysate had a conductivity close to deionized water (1-2 µS/cm). Dialysis of a batch that contains around 6 g of PDADMAC or 2 g IBMA-Na 320K takes about 1 week.

3.2.2 Preparation of Polyelectrolyte Complexes

PDADMAC and all IBMA-Na molecular weights used during coacervation were solubilized in deionized water at a concentration of 4 weight % and 2.5 weight %, respectively. Coacervate formation was started by separately dissolving the polycation/polyanion in deionized water. One of the polyelectrolytes was dissolved into a 500 mL beaker with a magnetic stir bar for continuous mixing, this was
followed by slowly adding the oppositely charged polyelectrolyte using a pipette. During the dropwise addition, initially charged soluble complexes start forming until they neutralize and net neutral coacervates form, as shown in Figure 3.1. Polyelectrolyte complex formation can be varied by altering the order of addition or by adding different ratios of polycation/polyanion.

**Figure 3.1.** Progression of Coacervation. a) Initial polyelectrolyte complex formation, after adding a few drops of oppositely charged polyelectrolyte. b) At a stage with large amount of non-stoichiometric soluble polyelectrolyte complexes in solution, before reaching stoichiometric balance ($X \approx 0.35$). c) Further addition of polyelectrolyte will result in all soluble complexes dropping out of solution and forming a liquid sediment (the coacervate at $X \approx 0.45$).
3.2.3 Swelling Measurements

After coacervate formation, the polyelectrolyte complex was isolated, washed with deionized water and placed into separate tared 50 mL vials with different concentrations of NaCl (Aldrich) solution. All salt solutions were prepared in de-ionized water. The complexes were left to equilibrate in solution for 48 hours. Eventually the solution was poured out and the coacervates were weighed to determine their swelling value, as shown in Equation 3.5. All swelling fractions were taken with respect to the preparation state, the supernatant at 0.09 M. Subsequently the coacervates were dried to obtain the polyelectrolyte mass fraction. This was done by placing the vial that accommodates the swollen coacervate in the appropriate freeze drying glassware to remove the water for 24 hours. To remove any remaining traces of water, the polyelectrolyte complexes were placed in a vacuum oven at 75°C for approximately 48 hours.

3.2.4 Rheology

Mechanical frequency sweep tests were carried out on a RDSII, Rheometrics Inc. with parallel plate configuration. Polyelectrolyte complex samples were squeezed into a thin film using two flat surfaces and then shaped into the desired geometry by using circular shaped cutter. The resulting cylindrical shaped coacervate sample was placed onto the top plate and was left to relax and equilibrate before starting a run. Depending on the viscosity of the polyelectrolyte complexes, 25 mm or 50 mm diameter plates were used for LVE measurements. The bottom plate served as a cup containing around 20-30 mL (submerging the sample) of desired salt concentration solution to keep the polyelectrolyte complexes from drying out, see schematic in Figure 3.2. After the sandwiching the sample between the two plates, the cup was covered with parafilm, to reduce evaporation during the measurements.
Measurements were taken at room temperature at around 23°C. Frequency sweep tests on all polyelectrolyte complexes with different salt concentrations covered a range from 0.01 - 100 rad/sec. Strain amplitude was increased as frequency was lowered to maintain torque in the range $2 < \tau_{\text{torque}} < 30$ g-cm/s$^2$. Strain sweeps show that all measurements reported correspond to linear viscoelastic response.

### 3.2.5 DRS

Coacervates used in DRS measurements were washed in deionized water to remove any excess salt. This experiment was measured using a 15 mm bottom and 10 mm top brass plates. After polishing and cleaning the plates, about 0.3 g of coacervate was squeezed flat with a spatula onto the bottom plate. Three triangular 1.02 mm spacers were added on top of the polyelectrolyte complex, which was further squeezed with the top plate to reach the thickness of the spacers. This sandwiched coacervate was placed into a liquid cell along with approximately 10 drops of deionized water (avoiding the top plate getting submerged), to keep the system from drying out. The liquid cell was subsequently placed into Novocontrol Broadband Dielectric Spectrometer, and all the necessary information was inputted into the software (geometry, operating temperature, voltage, frequency range etc.).
Measurements were all run at 25°C and 0.2 V with a frequency ranging from $1 \times 10^7$ to $1 \times 10^{-2}$ Hz.

### 3.3 Results and Discussion

#### 3.3.1 Swelling

Swelling measurements allowed us to qualitatively infer the net-charge of each polyelectrolyte complex. Swelling observed in deionized water, the low salt limit, is a test which allows us to identify qualitatively how far the system is from net neutrality. Polyelectrolyte complexes that are further away from zero net charge show weak polyelectrolyte characteristics, whereas polyelectrolyte complexes very close to neutrality show polyampholyte behavior, observed in Figure 3.3. However, to normalize the swelling ratios of the coacervates it is important to eliminate the polymer mass fraction factor as shown in Equation 3.5. The polyelectrolyte mass fractions are given in Table 3.1.

**Table 3.1.** Mass fraction of polyelectrolyte ($F_{PE}$) in the coacervate surrounded by the surenatant with 0.09 M for different IBMA-Na molecular weights.

<table>
<thead>
<tr>
<th>IBMA-Na Molecular Weight (kg/mol)</th>
<th>$F_{PE}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.35</td>
</tr>
<tr>
<td>65</td>
<td>0.28</td>
</tr>
<tr>
<td>165</td>
<td>0.34</td>
</tr>
<tr>
<td>320</td>
<td>0.41</td>
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Table 3.2. Swelling ratio and normalized swelling ratio (Q·F) for different polyanion molecular weights at different salt concentrations.

<table>
<thead>
<tr>
<th>IBMA-Na Molecular Weight (kg/mol)</th>
<th>Salt Concentration (M)</th>
<th>Q</th>
<th>Q·F</th>
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<td>IBMA-Na Salt Molecular Weight (kg/mol)</td>
<td>Salt Concentration (M)</td>
<td>Q</td>
<td>Q·F</td>
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<td>1.3</td>
<td>6.22</td>
<td>2.55</td>
</tr>
</tbody>
</table>
Plotting these results gives the following figure.

![Figure 3.3. Swelling ratios of polyelectrolyte complexes prepared at their isoelectric point as a function of salt concentrations. All values are taken with respect to their initial state, which is the supernatant at 0.09 M NaCl.](image)

At the low salt concentration limit, pure deionized water with 0.00001 M salt concentration obtained through conductivity measurements, polyelectrolyte complex swelling is governed by the net charge. If a coacervate has net charge, counterion induced osmotic pressure will lead to the swelling of the system. Figure 3.3 shows that coacervates with high molecular weight are more likely to be non-stoichiometric, swelling getting as large as 1.48 times the mass of the gel surrounded by its supernatant. Long polyelectrolyte chains are more restricted by movement during coacervate formation, preventing the system from rearranging, and thus keeping a significant amount of polyelectrolyte repeat units inaccessible to be neutralized. Whereas, short polyelectrolyte chains can arrange themselves to minimize
the number of uncomplexed sites, therefore do not swell due to the lack of counterions in the coacervate. The general trend obtained through swelling measurements fully agrees with Figure 2.4. Both tests show that IBMA-Na 165K has highest degree of uncomplexed sites, followed by IBMA-Na 320K, 65K, and 6K. The tie between these two experiments is that coacervates with low $X/\alpha$ values have more trapped counterions and higher osmotic pressure with no salt present.

When the salt concentration reaches a specific value, the ions are at the transition from screening long range repulsions to screening short range attractions. The system’s swelling goes through a minimum, where it shifts from polyelectrolyte to polyampholyte behavior.[16]. The minimum swelling found for our coacervate occurs somewhere between 0.15 and 0.2 M NaCl, depending on the polyanion’s molecular weight. This salt concentration is equivalent to a Debye length of 7.9 Å, calculated using Equation 1.3. This transition is also described by Higgs and Joanny model (Equation 1.1), which also occurs when the excluded volume goes through a minimum. To approximately calculate $f^+$, we take the derivative of the excluded volume with respect to Debye Length, and set it to zero, giving the following:

$$\frac{\Delta f}{f} = \sqrt{\frac{l_B}{8 \cdot r_D}}$$

(3.7)

The Debye length ($r_D = 7.9$ Å) at minimum swelling results in $\frac{\Delta f}{f} = 0.34$. Assuming that $f$ is equal to 1, makes $\Delta f = 0.34$; allowing us to calculate $f^+$ and $f^-$. From zeta-potential measurements (Table 2.2) it was concluded that our coacervate have an excess negative charge, hence $f^- > f^+$. Therefore $f^+ = 0.33$ and $f^- = 0.67$. Comparing $f^+ = 0.33$ to $X$ (with an average value of 0.43), shows that there is a difference of about 0.1 positive charge fraction. This discrepancy is not understood but suggests the Higgs/Joanny model for polyampholytes may not apply to our coacervates.

Higher salt concentration, ranging from around 0.4 to 1.8 M NaCl, allows the
salt ions to screen ionic attraction between the oppositely charged polyelectrolytes without dissolving the gel. The damping of ionic crosslink interactions weakens the network stability, causing the system to swell. This polyampholyte effect is identical for most IBMA-Na molecular weight coacervates, as expected. However, IBMA-Na 65K illustrates highest swelling, suggesting that it has the largest amount of ionic interactions, perhaps related to its high $\alpha_{IBMA-Na}$ value. This concludes that the swelling observed at low salt concentration is due to the number of uncomplexed sites, and the swelling at high concentration is due to the number of complexed sites. Going to very high salt concentration, larger than approximately 1.8 M NaCl, a significant amount of electrostatic attractions get screened out and the coacervate is resolubilized. From Equation 3.2, $E_a/kT$ for a system with no salt equals to $l_B/\sigma = 7.1$. When the ionic strength of the solution is increased to 1.8 M NaCl, then $E_a/kT = 4.57$, showing nearly a 40 % decrease in energy. Therefore, coacervate formation process is reversible at high salt concentration, forcing the polyelectrolyte complexes to go back into solution. This phenomenon was our limiting factor in obtaining further swelling ratios measurements, especially for polyelectrolyte complexes with lower molecular weights.

### 3.3.2 Conductivity

The degree of excess charge in coacervates can be further studied using conductivity measurements from a Novocontrol Broadband Dielectric Spectrometer (see Appendix D). Measuring $\sigma'$ values as a function of frequency will give a good estimate of the amount of counterions trapped in the coacervate. Figure 3.4 shows the measured frequency dependence of conductivity.
Figure 3.4. Conductivity measurements as a function of frequency at 25 °C. Measurements were taken on coacervate with different IBMA-Na molecular weight that were washed off and equilibrated in deionized water.

The flat $\sigma'$ portion at high frequencies was the range of interest, which represents the conductivity of the counterions in the coacervates. Low frequencies are dictated mostly by electrode polarization, hence lowering the apparent conductivity. Some IBMA-Na coacervates don’t become flat at high frequencies, consequently their respective highest frequency value was used. Polyelectrolyte complexes that are closer to net-neutrality will show lower conductivity due to the fewer counterions trapped in the system. Coacervates that show higher swelling should theoretically also have higher $\sigma'$ values. Thus, when comparing conductivity, at high frequencies, with the swelling measurements, at low salt concentration (near 0 M), a similar trend should be noticed. Obtained conductivity values were converted to molar...
concentration for each molecular weight to determine the extent of uncomplexed sites.

Table 3.3. Conductivity of coacervate after exposure to deionized water and counterion concentration in coacervates at 25 °C.

<table>
<thead>
<tr>
<th>Molecular Weight (kg/mol)</th>
<th>Conductivity (S/cm)</th>
<th>Cl⁻ Concentration (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>$9.17 \times 10^{-5}$</td>
<td>0.058</td>
</tr>
<tr>
<td>65</td>
<td>$2.87 \times 10^{-5}$</td>
<td>0.018</td>
</tr>
<tr>
<td>165</td>
<td>$1.79 \times 10^{-3}$</td>
<td>1.15</td>
</tr>
<tr>
<td>320</td>
<td>$4.49 \times 10^{-4}$</td>
<td>0.286</td>
</tr>
</tbody>
</table>

Table 3.3 shows the conductivity and approximate Cl⁻ counterion concentration in polyelectrolyte complexes, where IBMA-Na 165K has the highest amount of counterions, thus generating the highest osmotic pressure. The comparison to swelling values agrees, where IBMA-Na 165K induces the most swelling followed by 320K, 6K and 65K. Hence, IBMA-Na 65K is the closest to being net-neutral and shows the strongest polyampholyte behavior as seen in Figure 3.3.

### 3.3.3 Rheology

Viscoelasticity of coacervates exhibit reversible behavior compared to regular crosslinked polymers that have permanent crosslinks due to the nature of the bonds.[45, 46] The ionic linkages between polycations and polyanions in polyelectrolyte complexes can break and rearrange. This rearranging behavior allows the system to have a viscous behavior at lower frequencies. At higher frequencies the system is unable to relax, forming an elastic network with modulus $\sim 10^5$ Pa. The chain dynamics and degree of bridging in the coacervates determine the mechanical properties of the system, where low chain mobility and high extent of bridging give higher moduli. The addition of salt screens ionic linkages, increases polyelectrolyte chain
diffusion and lowers viscosity. At low salt concentrations polyelectrolyte complexes behave like soft elastomers, whereas at higher salt concentrations the complexes become more liquid like. All samples exhibit viscous character at low frequencies, with $G''$ larger than $G'$ meaning that these 'gels' are viscoelastic liquids. The salt ions lower the association energy and the association lifetime. This allowed us attain behaviors at different timescales otherwise inaccessible using solutions with different ionic strength using time-salt superposition.\cite{32} Rheology measurements at different salt concentrations, shown in Figures\ (3.5, 3.7, 3.9, 3.11), allowed the construction of master curves using horizontal frequency shift factors, with $\omega_{\text{shift}} = \beta \times \omega$, as seen in Figures\ (3.6, 3.8, 3.10, 3.12).\footnote{\textsc{ibma-Na 320K}} master curve was also vertically shifted using shift factor $a$ (see Section 3.3.3.1 for explanation).
Figure 3.5. Vertically shifted frequency sweep plots, for visual purposes, of PDADMAC+IBMA-Na 6K coacervates at different salt concentrations. Shift constants b: DIW=800, supernatant=200, 0.2 M NaCl=50, 0.3 M NaCl=10, 0.5 M NaCl=1.
Figure 3.6. Master curve of PDADMAC+IBMA-Na 6K coacervates using time-salt superposition with horizontal shift factors. □ Symbol indicates the storage modulus $G'$, and ◦ is the loss modulus $G''$. 
Figure 3.7. Vertically shifted frequency sweep plots, for visual purposes, of PDADMAC+IBMA-Na 65K coacervates at different salt concentrations. Shift constants $b$: DIW=1300, supernatant=300, 0.2 M NaCl=60, 0.3 M NaCl=10, 0.5 M NaCl=4.5, 0.7 M NaCl=4, 0.9 M NaCl=1.
Figure 3.8. Master curve of PDADMAC+IBMA-Na 65K coacervates using time-salt superposition with horizontal shift factors. □ Symbol indicates the storage modulus $G'$, and ○ is the loss modulus $G''$. 
Figure 3.9. Vertically shifted frequency sweep plots, for visual purposes, of PDADMAC+IBMA-Na 165K coacervates at different salt concentrations. Shift constants $b$: DIW=1300, supernatant=300, 0.2 M NaCl=60, 0.3 M NaCl=10, 0.5 M NaCl=4.5, 0.7 M NaCl=4, 0.9 M NaCl=1.
Figure 3.10. Master curve of PDADMAC+IBMA-Na 165K coacervates using time-salt superposition with horizontal shift factors. □ Symbol indicates the storage modulus $G'$, and ◦ is the loss modulus $G''$. 
Figure 3.11. Vertically shifted frequency sweep plots, for visual purposes, of PDADMAC+IBMA-Na 320K coacervates at different salt concentrations. Shift constants b: DIW=10000, supernatant=1800, 0.2 M NaCl=300, 0.3 M NaCl=100, 0.5 M NaCl=15, 0.7 M NaCl=7.5, 0.9 M NaCl=3, 1.1 M NaCl=1.5, 1.3 M NaCl=1.
Figure 3.12. Master curve of PDADMAC+IBMA-Na 320K coacervates using time-salt superposition with horizontal shift factors. □ Symbol indicates the storage modulus G’, and ○ is the loss modulus G”. Vertical shift constants a: DIW=1.3, supernatant=1, 0.2 M NaCl=1, 0.3 M NaCl=1.72, 0.5 M NaCl=1.4, 0.7 M NaCl=2.1, 0.9 M NaCl=1.7, 1.1 M NaCl=2.2, 1.3 M NaCl=2.6.
Using time-salt superposition allowed us to obtain master curves for coacervate’s dynamics over a range of eight decades in frequency. The lower frequency limiting factor was polyelectrolyte complexes reaching very low viscosity, resulting in noisy rheology measurements. Whereas, the upper limiting factor was rheometer reaching its maximum frequency accessible for the coacervates immersed in deionized water. Polyelectrolyte complexes mechanical properties are independent of their formation, because neither the order of addition nor the polycation/polyanion fraction had any effect on the rheology. This suggests that the crosslink density stays constant. Moreover, the modulus value where $G' = G''$ stays independent of salt concentrations. This salt independence suggests identical network structure with constant number of ionically bonded charged units.[45]

The time-salt superposition technique also allowed us to construct and compare master curves for all four IBMA-Na molecular weights, as seen in Figure 3.13.
Figure 3.13. Master curves constructed using time-salt superposition of coacervate samples with different polyanion molecular weight. (a) Storage modulus $G'$ and (b) loss modulus $G''$ at ambient temperature around $23 \, ^{\circ}C$. 
Polyelectrolyte complexes containing higher molecular weight polyanion exhibit higher storage and loss modulus, due to higher degree of bridging. This gives us the ability to control the network structure and relaxation time using molecular weight. The three graphs in Figure 3.13 overlap, excluding higher frequencies, when shifted horizontally suggesting the idea of time-molecular weight superposition. At high frequencies, polyelectrolyte complexes do not overlap very well due to counterion generated osmotic pressure. Upon swelling the network gets stretched, moving the junctions further apart. Stretching the network strands (R) has an effect on elasticity of the coacervates, consequently influencing the modulus. The modulus is inversely proportional to $R^2$, hence decreasing the modulus at high frequencies.[47] This implies that non-stoichiometric coacervates only differ in dynamics at high frequencies compared to neutral systems.

The point where the storage and loss modulus are equal was used as a reference point to compare the plots at different salt concentration, since no relaxation times were observed in the eight decades of frequency master curves. This point was calculated by taking only a few $G'$ and $G''$ values around the crossover point and fitting it to a 3rd degree polynomial. At first glance, frequency increases with increasing salt concentration due to the screening effect, seen in Figure 3.14. We were restricted to few points due to the instruments frequency limit at 100 rad/s.
Figure 3.14. Frequency of the $G'$ and $G''$ crossover point at different NaCl concentrations for coacervates with varying polyanion molecular weight.

Two behaviors are observed in Figure 3.14 as seen by the changing slope. In the range 0.00001 M till 0.10 M NaCl (first two points) the frequency dependence is different than the high salt concentration range. This difference is due to the polyelectrolyte and polyampholyte effects that are observed at the low and high frequencies, respectively. The change in slope that occurs between the salt concentrations 0.1 M and 0.2 M NaCl agrees with the behavior transition obtained through swelling measurements.
Table 3.4. \( \tau \) for different polyanion molecular weights at different salt concentrations.

<table>
<thead>
<tr>
<th>IBMA-Na Molecular Weight (kg/mol)</th>
<th>Salt Concentration (M)</th>
<th>( \tau ) (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.00001</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>0.09</td>
<td>0.046</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>0.011</td>
</tr>
<tr>
<td>65</td>
<td>0.00001</td>
<td>0.62</td>
</tr>
<tr>
<td></td>
<td>0.09</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>0.044</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.009</td>
</tr>
<tr>
<td>165</td>
<td>0.00001</td>
<td>4.17</td>
</tr>
<tr>
<td></td>
<td>0.09</td>
<td>1.58</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>1.33</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>0.021</td>
</tr>
<tr>
<td>320</td>
<td>0.00001</td>
<td>320.4</td>
</tr>
<tr>
<td></td>
<td>0.09</td>
<td>131.36</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>25.61</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>13.51</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>3.72</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>0.087</td>
</tr>
<tr>
<td></td>
<td>1.3</td>
<td>0.029</td>
</tr>
</tbody>
</table>

The reciprocal of the frequency data, shown in Table 3.4, were fitted to Equation 3.3, giving the following result:
Figure 3.15. Model comparison to experimental data of $G'$ and $G''$ crossover points for coacervates at different molecular weights.

The fitting of the four molecular weights shows a good fit at the high salt concentration range, where $\tau$ decreases with molecular weight and salt concentration. At low salt concentrations however, our model doesn’t fit very well due to the fact that it doesn’t describe the polyelectrolyte behavior that is seen in this range.

As stated in Section 3.1, constant $\sigma$ was set to 1 Å. Fitting parameter $N$ was calculated to be 5.5 which means that 5 to 6 ionic bonds need to be broken to allow a chain to move. In physical terms this means that about every 5 charged repeat units on a polyelectrolyte chain make up one Kuhn monomer. These Kuhn monomers have a rigid structure which can only move if all the charge units that it’s carrying break. Fitting these $\tau$ values with the Spruijt et al. model (Equation 3.4), results in time having a very weak salt dependence. This is due to the missing $N$ term in their equation, which shows that the dissociation of only one bond is not enough to allow a chain to move. Finally, to find the molecular weight dependence of $\tau$, $\tau_0$ was plotted against degree of polymerization ($n$).
Figure 3.16. \( \tau_0 \) dependence on IBMA-Na degree of polymerization.

Figure 3.16 shows that the \( \tau_0 \) dependence has a stronger slope with increasing degree of polymerization, which might be due to the fact that there is a larger amount of entanglement. However, this change in slope will be ignored and all data points will be treated as one identity to provide the final part of our model giving the following equation:

\[
\tau[c_s, n] = 2 \times 10^{-20} \cdot n^{1.9} \cdot \text{Exp}(5.5 \cdot l_B \cdot \text{Exp}(-\sqrt{8\pi \cdot l_B \cdot c_s \cdot N_A}))
\] (3.8)

This is the final equation of our model, which gives the approximate time (\( \tau \)) when \( G' \) and \( G'' \) are equal, as a function of molecular weight and salt concentration. A 1.9 power degree of polymerization dependence was calculated, which suggest that
these coacervates have Rouse behavior.

3.3.3.1 Vertical Shift Factors

In order to obtain master curves for coacervates containing IBMA-Na 320K, we had to include vertical shift factors for each salt concentration to obtain good overlapping. It was observed that the vertical shift factors show the same salt dependence as swelling values (Figure 3.3), suggesting that $a$ represents the same physical significance as $Q \cdot F$.

![Figure 3.17](image)

**Figure 3.17.** Comparison of $Q \cdot F$ and vertical shift factor $a$ as a function of salt concentration for PDADMAC + IBMA-Na 320K coacervates.

Figure 3.17 shows that $a$ values are overall similar to $Q \cdot F$ values, excluding some data points which are larger than expected (especially 0.3 M and 0.7 M NaCl). This overshoot in $a$ values is due to experimental error, where the coacervate did
not stick to the plate very well, giving lower than expected modulus. Irrespective of the scattered data, the vertical shifts follow the trend of the swelling, which suggests that the crosslink density in the gel decreases as the salt concentration increases.[48] Thus, some ionic crosslinks in the network get permanently screened and do not form new ionic linkages.

To further test vertical shift factor idea, $QF \cdot G$ master curves were constructed for the remaining IBMA-Na molecular weights. The results of these superpositions are shown in Figures (3.18, 3.19, 3.20)

![Figure 3.18](image-url)

**Figure 3.18.** Master curve of PDADMAC+IBMA-Na 6K coacervates using time-salt superposition with horizontal and vertical shift factors. Vertical shift factors ($QF$) are given in Table 3.2. □ Symbol indicates the storage modulus $G'$, and ◦ is the loss modulus $G''$. 
Figure 3.19. Master curve of PDADMAC+IBMA-Na 65K coacervates using time-salt superposition with horizontal and vertical shift factors. Vertical shift factors (QF) are given in Table 3.2. □ Symbol indicates the storage modulus $G'$, and ◦ is the loss modulus $G''$. 
Figure 3.20. Master curve of PDADMAC+IBMA-Na 165K coacervates using time-salt superposition with horizontal and vertical shift factors. Vertical shift factors (QF) are given in Table 3.2. □ Symbol indicates the storage modulus $G'$, and ◦ is the loss modulus $G''$. 
The good overlap that can be achieved in these figures reaffirms that coacervate’s crosslink density decreases with increasing salt concentrations.
In this thesis we studied soluble and insoluble polyelectrolyte complexes at different polyanion molecular weights and salt concentrations. Soluble complexes aided in determine the charge fraction at the isoelectric point. The isoelectric point of coacervates, obtained through zeta-potential and viscosity measurements, revealed no direct dependence to the molecular weight of polyanions. Eliminating the varying degree of sodium counterion content on IBMA-Na chains, by dividing by $\alpha_{IBMA-Na}$, showed that higher molecular weight polyanion form coacervate that are further away from stoichiometry. Larger polyelectrolytes have larger topological constraints and have a higher tendency to form tadpoles, where uncomplexed parts of the chain remain in solution. In addition to that, viscosity measurements revealed that the continuous addition of polyelectrolyte into a net-neutral sediment (coacervate) causes chains to resolubilize, returning to being non-stoichiometric soluble complexes. Swelling measurements on stoichiometrically balanced polyelectrolyte complexes also allowed us to qualitatively study the overall charge of the system. At the low salt concentration limit, as molarity goes to 0, coacervates that swell up have polyelectrolyte characteristics due to the counterions that induce osmotic pressure. Coacervate the keep constant mass at low salt concentration are net-neutral. Increasing salt concentration causes the system to initially shrink and then eventually swell up again. The shrinking arises due to ions’ high Debye lengths which screen long range repulsions. As the Debye length decreases with increasing salt concentration, the system transitions from screening repulsions to screening short range electrostatic attraction between the oppositely charged poly-
electrolytes. The screening of attractions are polyampholyte characteristics which was observed for all molecular weight coacervate approximately equally. The extent of swelling observed at low salt concentration is due to the number of uncomplexed sites, and the swelling at high concentration is due to the number of complexed sites. We also developed a simple model to explain G’ and G” intercepting point at different polyanion molecular weights and salt concentrations. Increasing molecular weight of IBMA-Na revealed an increase in moduli, caused by the higher degree of bridging. Hence, increasing molecular weight required more time for the system to relax. Salt concentration dependence on the other hand, influenced the association time between oppositely charged polyelectrolytes. As the Debye length is decreased, more ionic crosslinks are screened which shortens the association time. Thus, salt screening sets the time scale for the viscoelastic transition from elastic character at high frequencies (low salt) to viscous character at low frequencies (high salt). In addition to the model, the viscoelasticity observed in this system obeys time-salt superposition,[32] which allows us to access time-scales otherwise inaccessible.

Future work includes studying polyanions with a higher hydrophobic copolymer, allowing us to potentially observe changes in coacervates water content to study property differences. In addition, studying the morphology of these polyelectrolyte complexes using SAXS, to observe how the hydrophobic and hydrophilic regions phase separate.
Appendix A

Model Derivation

Coulomb Law:

\[ E = \int_{\infty}^{r} F = \int_{\infty}^{r} \frac{e^2}{4\pi \cdot \epsilon \cdot \epsilon_0 \cdot r^2} = \frac{-e^2}{4\pi \cdot \epsilon \cdot \epsilon_0 \cdot r} \]  (A.1)

Debye Length:

\[ E \approx \frac{e^2(n_+ - n_-)^2}{\epsilon \cdot \epsilon_0 \cdot r} \approx \frac{c^2(r^3 \cdot C_s)}{\epsilon \cdot \epsilon_0 \cdot r} \approx \frac{e^2 \cdot r^2 \cdot C_s}{\epsilon \cdot \epsilon_0} \]
\[ kT \approx \frac{e^2 \cdot r_D^2 \cdot C_s}{\epsilon \cdot \epsilon_0} \]
\[ r_D^2 \approx \frac{kT \cdot \epsilon \cdot \epsilon_0}{e^2 \cdot C_s} \approx \frac{1}{l_B \cdot C_s} \]
\[ r_D = \sqrt{\frac{1}{8\pi \cdot l_B \cdot C_s \cdot N_{avo}}} \]  (A.2)

Bjerrum Length:

\[ kT = \frac{e^2}{4\pi \cdot \epsilon \cdot \epsilon_0 \cdot l_B} \]
\[ l_B = \frac{e^2}{4\pi \cdot \epsilon \cdot \epsilon_0 \cdot kT} \]  (A.3)

Yukawa Potential:

\[ E_a = \text{Energy to break electrostatic attractions at distance by also taking into} \]
account Debye screening affect (Yukawa Potential).

\[ E_a = E_{\text{Coul}} \cdot \exp\left(\frac{-\sigma}{r_D}\right) \]

Coulomb attraction dominate when \( \sigma \ll r_D \), and screening dominates at \( \sigma \gg r_D \).

\[ E_a = \frac{kT \cdot l_B}{r} \cdot \exp\left(-\sigma \sqrt{8\pi \cdot l_B \cdot C_s \cdot N_{\text{avo}}} \right) \quad (A.4) \]

**Arrhenius Equation:**

\[ \tau = \tau_0 \cdot \exp(N \cdot \frac{E_a}{kT}) \]

\[ \tau = \tau_0 \cdot \exp(N \cdot \frac{l_B}{r} \cdot \exp(-\sigma \sqrt{8\pi \cdot l_B \cdot C_s \cdot N_{\text{avo}}} \)) \quad (A.5) \]
Appendix B

Raw Rheology Data

IBMA-Na 320 kg/mol
Deionized Water

Figure B.1. Frequency sweep on IBMA-Na 320K + PDADMAC coacervate at 23 °C. Coacervate was equilibrated in deionized water before running this experiment.
Supernatant

**Figure B.2.** Frequency sweep on IBMA-Na 320K + PDADMAC coacervate at 23 °C. Coacervate was left in its supernatant.

0.2 M NaCl

**Figure B.3.** Frequency sweep on IBMA-Na 320K + PDADMAC coacervate at 23 °C. Coacervate was equilibrated in 0.2 M NaCl before running this experiment.
0.3 M NaCl

Figure B.4. Frequency sweep on IBMA-Na 320K + PDADMAC coacervate at 23 °C. Coacervate was equilibrated in 0.3 M NaCl before running this experiment.

0.5 M NaCl

Figure B.5. Frequency sweep on IBMA-Na 320K + PDADMAC coacervate at 23 °C. Coacervate was equilibrated in 0.5 M NaCl before running this experiment.
0.7 M NaCl

Figure B.6. Frequency sweep on IBMA-Na 320K + PDADMAC coacervate at 23 °C. Coacervate was equilibrated in 0.7 M NaCl before running this experiment.

0.9 M NaCl

Figure B.7. Frequency sweep on IBMA-Na 320K + PDADMAC coacervate at 23 °C. Coacervate was equilibrated in 0.9 M NaCl before running this experiment.
1.1 M NaCl

Figure B.8. Frequency sweep on IBMA-Na 320K + PDADMAC coacervate at 23 °C. Coacervate was equilibrated in 1.1 M NaCl before running this experiment.

1.3 M NaCl

Figure B.9. Frequency sweep on IBMA-Na 320K + PDADMAC coacervate at 23 °C. Coacervate was equilibrated in 1.3 M NaCl before running this experiment.
Figure B.10. Frequency sweep on IBMA-Na 165K + PDADMAC coacervate at 23 °C. Coacervate was equilibrated in deionized water before running this experiment.
Supernatant

Figure B.11. Frequency sweep on IBMA-Na 165K + PDADMAC coacervate at 23 °C. Coacervate was left in its supernatant.

0.2 M NaCl

Figure B.12. Frequency sweep on IBMA-Na 165K + PDADMAC coacervate at 23 °C. Coacervate was equilibrated in 0.2 M NaCl before running this experiment.
0.3 M NaCl

Figure B.13. Frequency sweep on IBMA-Na 165K + PDADMAC coacervate at 23 °C. Coacervate was equilibrated in 0.3 M NaCl before running this experiment.

0.5 M NaCl

Figure B.14. Frequency sweep on IBMA-Na 165K + PDADMAC coacervate at 23 °C. Coacervate was equilibrated in 0.5 M NaCl before running this experiment.
0.7 M NaCl

![Graph](image1)

**Figure B.15.** Frequency sweep on IBMA-Na 165K + PDADMAC coacervate at 23 °C. Coacervate was equilibrated in 0.7 M NaCl before running this experiment.

0.9 M NaCl

![Graph](image2)

**Figure B.16.** Frequency sweep on IBMA-Na 165K + PDADMAC coacervate at 23 °C. Coacervate was equilibrated in 0.9 M NaCl before running this experiment.
IBMA-Na 65 kg/mol

Deionized Water

Figure B.17. Frequency sweep on IBMA-Na 65K + PDADMAC coacervate at 23 °C. Coacervate was equilibrated in deionized water before running this experiment.
Supernatant

Figure B.18. Frequency sweep on IBMA-Na 65K + PDADMAC coacervate at 23 °C. Coacervate was left in its supernatant.

0.2 M NaCl

Figure B.19. Frequency sweep on IBMA-Na 65K + PDADMAC coacervate at 23 °C. Coacervate was equilibrated in 0.2 M NaCl before running this experiment.
0.3 M NaCl

![Graph](image)

**Figure B.20.** Frequency sweep on IBMA-Na 65K + PDADMAC coacervate at 23 °C. Coacervate was equilibrated in 0.3 M NaCl before running this experiment.

0.5 M NaCl

![Graph](image)

**Figure B.21.** Frequency sweep on IBMA-Na 65K + PDADMAC coacervate at 23 °C. Coacervate was equilibrated in 0.5 M NaCl before running this experiment.
0.7 M NaCl

Figure B.22. Frequency sweep on IBMA-Na 65K + PDADMAC coacervate at 23 °C. Coacervate was equilibrated in 0.7 M NaCl before running this experiment.

0.9 M NaCl

Figure B.23. Frequency sweep on IBMA-Na 65K + PDADMAC coacervate at 23 °C. Coacervate was equilibrated in 0.9 M NaCl before running this experiment.
Figure B.24. Frequency sweep on IBMA-Na 6K + PDADMAC coacervate at 23 °C. Coacervate was equilibrated in deionized water before running this experiment.
Supernatant

Figure B.25. Frequency sweep on IBMA-Na 6K + PDADMAC coacervate at 23 °C. Coacervate was left in its supernatant.

0.2 M NaCl

Figure B.26. Frequency sweep on IBMA-Na 6K + PDADMAC coacervate at 23 °C. Coacervate was equilibrated in 0.2 M NaCl before running this experiment.
**0.3 M NaCl**

![Graph](image1)

**Figure B.27.** Frequency sweep on IBMA-Na 6K + PDADMAC coacervate at 23 °C. Coacervate was equilibrated in 0.3 M NaCl before running this experiment.

**0.5 M NaCl**

![Graph](image2)

**Figure B.28.** Frequency sweep on IBMA-Na 6K + PDADMAC coacervate at 23 °C. Coacervate was equilibrated in 0.5 M NaCl before running this experiment.
Zeta-Potential Fitting

IBMA-Na 320 kg/mol

IBMA-Na Titrant

Figure C.1. Zeta-potential measurements on non-stoichiometric soluble PE-complex as a function of 1-X. Sample was made using IBMA-Na 320K + PDADMAC with IBMA-Na as titrant at 23 °C.

\[
ZP = 41.01 - 29.11 \cdot x + \frac{38.67 \cdot \text{atan}(1.5 \times 10^{24} \cdot x^{100.1})}{x^{0.037}} \\
(C.1)
\]
Figure C.2. Zeta-potential measurements on non-stoichiometric soluble PE-complex as a function of \( X \). Sample was made using IBMA-Na 320K + PDADMAC with PDADMAC as titrant at 23 °C.

\[
ZP = -59.34 + 79.43 \cdot x + \frac{15.09 \cdot atan(7.34 \times 10^9 \cdot x^{21})}{x}
\]  

(C.2)
Figure C.3. Zeta-potential measurements on non-stoichiometric soluble PE-complex as a function of 1-X. Sample was made using IBMA-Na 165K + PDADMAC with IBMA-Na as titrant at 23 °C.

\[
ZP = 40.94 - 31.42 \cdot x + \frac{33.7 \cdot \text{atan}(7.05 \times 10^{24} \cdot x^{93.4})}{x^{0.0974}}
\]  
(C.3)
Figure C.4. Zeta-potential measurements on non-stoichiometric soluble PE-complex as a function of $X$. Sample was made using IBMA-Na 165K + PDADMAC with PDADMAC as titrant at 23 °C.

\[ ZP = -56.58 + 74.59 \cdot x + \frac{15.51 \cdot \text{atan}(1.16 \times 10^{10} \cdot x^{29.91})}{x} \]  

(C.4)
IBMA-Na 65 kg/mol

IBMA-Na Titrant

Figure C.5. Zeta-potential measurements on non-stoichiometric soluble PE-complex as a function of 1-X. Sample was made using IBMA-Na 65K + PDADMAC with IBMA-Na as titrant at 23 °C.

\[ ZP = -26.79 - 19.24 \cdot x + \frac{39.19 \cdot \text{atan}(2.51 \times 10^{-11} \cdot x^{-29.23})}{x^{0.012}} \]  
(C.5)
Figure C.6. Zeta-potential measurements on non-stoichiometric soluble PE-complex as a function of $X$. Sample was made using IBMA-Na 65K + PDADMAC with PDADMAC as titrant at 23 °C.

$$ZP = -64.64 + 79.19 \cdot x + \frac{16.91 \cdot atan(1.91 \times 10^9 \cdot x^{33.85})}{x}$$  \hspace{1cm} (C.6)
**IBMA-Na 6 kg/mol**

**IBMA-Na Titrant**

![Graph showing zeta-potential measurements](image)

**Figure C.7.** Zeta-potential measurements on non-stoichiometric soluble PE-complex as a function of 1-X. Sample was made using IBMA-Na 6K + PDADMAC with IBMA-Na as titrant at 23 °C.

\[ ZP = -22.78 - 9.5 \cdot x + \frac{33.82 \cdot \text{atan}(1.61 \times 10^{-9} \cdot x^{-29.6})}{x^{0.0124}} \]  

(C.7)
Figure C.8. Zeta-potential measurements on non-stoichiometric soluble PE-complex as a function of $X$. Sample was made using IBMA-Na 6K + PDADMAC with PDADMAC as titrant at 23 °C.

\[
ZP = -43.816 + 63.22 \cdot x + \frac{11.44 \cdot \text{atan}(1.16 \times 10^{10} \cdot x^{32.07})}{x}
\]  
(C.8)
Dielectric Relaxation Spectroscopy

Figure D.1. $\epsilon'$ data of PDADMAC+IBMA-Na polyelectrolyte complexes for all four molecular weights. Coacervates were equilibrated in deionized water to remove any excess ions from the system. Measurements were ran at 25 °C.
Figure D.2. $\epsilon''$ data of PDADMAC+IBMA-Na polyelectrolyte complexes for all four molecular weights. Coacervates were equilibrated in deionized water to remove any excess ions from the system. Measurements were ran at 25 °C.

Figure D.3. $\tan(\delta)$ data of PDADMAC+IBMA-Na polyelectrolyte complexes for all four molecular weights. Coacervates were equilibrated in deionized water to remove any excess ions from the system. Measurements were ran at 25 °C.
Appendix E

pH Titrations

IBMA-Na 6K

Figure E.1. pH values of supernatant at different $X$ fractions using both PDADMAC and IBMA-Na 6K as titrants. Measurements were collected at 25 °C.
Figure E.2. pH values of supernatant at different $X$ fractions using both PDADMAC and IBMA-Na 65K as titrants. Measurements were collected at 25 °C.
Figure E.3. pH values of supernatant at different $X$ fractions using both PDADMAC and IBMA-Na 165K as titrants. Measurements were collected at 25 °C.
Figure E.4. pH values of supernatant at different $X$ fractions using both PDADMAC and IBMA-Na 320K as titrants. Measurements were collected at 25 °C.
Table E.1. Fraction of positively charged units ($X$) in the coacervate at the isoelectric point for different IBMA-Na molecular weights using pH measurements of the supernatant.

<table>
<thead>
<tr>
<th>IBMA-Na Molecular Weight (kg/mol)</th>
<th>X</th>
<th>PDADMAC Titrant</th>
<th>IBMA-Na Titrant</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.45</td>
<td>0.55</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>0.45</td>
<td>0.51</td>
<td>0.85</td>
<td></td>
</tr>
<tr>
<td>165</td>
<td>0.42</td>
<td>0.51</td>
<td>0.83</td>
<td></td>
</tr>
<tr>
<td>320</td>
<td>0.42</td>
<td>0.48</td>
<td>0.77</td>
<td></td>
</tr>
</tbody>
</table>


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Deutsche Schule:
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