Enhanced Concentration Fluctuations in Model Polyelectrolyte Coacervate Mixtures along a Salt Isopleth Phase Diagram

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ABSTRACT: A temperature ($T$)-versus-polymer concentration ($c_p$) representation leads to nonoverlapping coexistence curves prepared from different initial polymer concentrations along a salt isopleth of aqueous mixtures of charge-stoichiometric, oppositely charged polydisperse polyelectrolytes. This effect was explained by an unequal salt concentration ($c_s$) between equilibrating phases that improves the relationship between the common point, an increase in concentration polymerization ($\nu_{eff}$) and, in some, cases re-entrant and upper critical solution temperature (UCST) behavior. A crossover from mean field to Ising behavior of aqueous semidilute sodium poly(styrene sulfonate) with BaCl$_2$ salt was observed by small-angle neutron scattering in a UCST system. Of present interest are the multicomponent aqueous mixtures or blends of oppositely charged polyelectrolytes. Such mixtures with or without salt exhibit properties with practical significance as adhesives, structured membranes, and coatings as well as vaccine adjuvants and therapeutic delivery of proteins and mRNA. These mixtures undergo associative liquid–liquid phase separation into a polyelectrolyte-poor supernatant and polyelectrolyte-rich phase (coacervate) with an upper critical salt concentration when studied as $c_s$ and $c_p$ phase diagrams at fixed temperature. These multicomponent mixtures were first explained by the Voorn–Overbeek (VO) mean-field theory that extends the entropy of mixing from the FH theory to include the Debye–Hückel theory of electrolytes. The VO theory predicts phase separation under the simplifying assumptions of no account of intermolecular associations between oppositely charged polyelectrolytes, ion correlations are treated as dissolved.
salt and decomposed polyelectrolyte, and no polymer—solvent enthalpic interactions (heat of mixing is zero). 57–33 Since the original VO theory, theoretical and computer simulation advances address many of these basic assumptions including evidence for the importance of counterion entropy 36–38 as recently reviewed. 34–36 In particular, when the ion correlations from the connectivity of the polyelectrolyte are included, the propensity of coacervation increases in terms of the critical charge density of the polyelectrolyte or critical salt concentration compared to the VO theory. 39 When the polymer—solvent interactions are included through $\chi$, there is better agreement with binodal measurements. 26

The van der Waals interaction energy, parameterized by $\chi$, and the ion correlations are becoming increasingly important to explain recent measurements on coacervation. For example, $c_s-c_p$ phase diagrams with homologous polyelectrolytes were fit by an extended VO theory that includes $\chi$ between the polyanion—polycation bound segment and solvent- and ion-binding equilibria for different $N$s and polymer polarities. 30 A decrease in the critical salt concentration with lower charge density, controlled by hydrophilic ethylene oxide comonomer content, was observed with a different homologous polyelectrolyte system and compared to Gibbs ensemble computer simulations. 32 Lastly, mixtures of oppositely charged hydrophilic and hydrophobic polyelectrolytes, via aliphatic polymers or polypeptides, shift the $c_s-c_p$ binodals and are explained by the solvent quality for the backbones via a combination of FH theory with an effective $\chi$ and ion correlations that include connectivity using the random phase approximation. 31

Neutral polymer blends and oppositely charged polyelectrolyte mixtures straddle the more general problem of solvophobic phase separation and Coulombic phase separation, which on theoretical grounds expects classical exponents. 31 The scaling of the interfacial tension with reduced salt concentration were first observed by Spruit et al. 42 and Priftis et al. 43 They measure the interfacial tension scaling exponent ($\mu$) in polyelectrolyte coacervates and expected by classical theory that $\mu = 3/2$. 44 Measurements closer to the critical salt concentration, also from within the two-phase region, did not observe deviations from the predicted classical scaling. 45,46 If the state of miscibility includes solvophobic contributions from $\chi$, then oppositely charged polyelectrolyte mixtures should also exhibit phase separation driven by the temperature dependence of the polymer—solvent interactions. Recent measurements on potassium poly(styrene sulfonate) (KPSS) and poly(diallyldimethylammonium) bromide (PDADMAB) indeed show phase separation upon heating or lower critical solution temperature (LCST) behavior. 47 These results complement the known $c_s-c_p$ phase diagrams 16,44 and expands the behavior to the $T-c_p-c_s$ phase space. UCST was also observed under different conditions and interpreted as a solid—liquid phase transition, while the hydration state of the polyeion binding plays a crucial role in the LCST. 48–49 Even though an LCST is not a natural result from the original FH theory with a single $\chi$ parameter, such behavior occurs theoretically by considering solution, 48 hydrogen bonding, 51,52 and mutual and self-associations within the lattice cluster theory. 51 The temperature dependence of the static dielectric constant ($\varepsilon$) of the solvent appears in the strength of the ion correlations via the Bjerrum length ($l_B$) that equates thermal energy to the Coulombic potential energy between separated charges and the Debye screening length ($\kappa^{-1}$). Due to the temperature dependence of $\varepsilon$ of water, 48,53 $l_B$ slightly increases with increasing $T$ and may contribute to the state of miscibility in addition to $\chi$. The liquid state theory by Zhang et al. predicts an increase in $l_B$ raises the $c_s-c_p$ phase envelope, which is consistent with LCST behavior. 50,51 Adhikari et al. showed that the ion correlations and dipolar attractions of strength $\sim l_B^4$ strongly couples to the temperature dependence of $\chi$ leading to LCST, UCST, and mixed behavior depending on the choice of parameters. 52 These phase behaviors represent the complex interplay of solvophobic and electrostatic-driven phase separation in multicomponent mixtures (two polyelectrolytes, salt ions, and solvent) where the entropy of mixing of components, including contributions mediated by the counterion release upon ion binding, are all expected to play an active role in phase stability. 50 Such entropic origins of complexity due to small molecule counterion release, enthalpic attraction, 50 and dipolar short-range interactions 52 provide unique characteristics when compared to neutral polymer blends and solutions. Additionally, since chain association or soluble complexes 54–56 form in the one-phase region, there is a need to understand how this couples to macrophase separation. 54

A salt isopleth on the $T-c_p$ plane allows for a convenient study of liquid—liquid phase separation and critical behavior starting from the one-phase region in mixtures of polyelectrolytes. This study addresses the pseudobinary coexistence curves, phase diagrams, and scattering properties in the one-phase region of the model system KPSS—PDADMAB complexes as charge-symmetric (1:1) mixtures upon approach to phase separation. The initial $c_p$ and $T$ were systematically varied with constant $c_s$ (salt isopleth). Proton nuclear magnetic resonance ($^1$H NMR) and ultraviolet—visible (UV—Vis) spectroscopy measure an asymmetric distribution of the polycations and the polyanions in each phase to determine the points of total polymer concentration on the binodal, while static light scattering (SLS) and turbidity measurements were used to determine the spinodal and cloud point temperatures, respectively. The concentration fluctuations measured by SLS upon approach to the phase boundary were interpreted with the Ornstein—Zernike equation. We describe the mean field and crossover to fluctuation regime in the associative multicomponent mixtures of polyelectrolytes that complements neutral polymer solutions 65 and blends 66–68 and are consistent with Fisher renormalization near the critical point. The present studies propose concepts and phase diagram data to understand how the chain association of oppositely charged polyelectrolytes couples to fluctuations near the phase boundary that are projections along a three-dimensional $T-c_s-c_p$ phase envelope with a line of critical points.

**EXPERIMENTAL SECTION**

**Materials.** Sodium poly(styrene sulfonate) (NaPSS) and poly(diallyldimethylammonium chloride) (PDADMAC) were both purchased from Sigma-Aldrich. Characterization led to both polymers have charge fractions of 100%. The NaPSS and PDADMAC solutions were first ion-exchanged to give KPPS and PDADMAB, respectively. The procedures were as follows: 250 mL of 3 mol/L KBr solution was added to 20 mL of NaPSS (or PDADMAC) then pressed through an Ultracel ultrafiltration disc membrane (molecular mass cutoff = 3 kg/mol) by nitrogen pressure under mixing in an Amicon stirred cell equipped with a selector valve and a reservoir. This step was repeated four times so that the Na$^+$ (or Cl$^-$) was quantitatively replaced by K$^+$ (or Br$^-$). Dialfiltration was then conducted to remove the excess KBr until the conductivity of the filtrate was negligible. The purified KPPS- and PDADMAB solution were filtered through 0.22 μm cellulose
acetate membranes and then freeze-dried to yield dry polymer powder that was further heated to 120 °C under vacuum to remove residual water and then stored in a desiccator to avoid absorbing water from air. X-ray photoelectron spectroscopy (XPS) validated the quantitative exchange of Na⁺ and Cl⁻ counterions to K⁺ and Br⁻ (Figure S2). Aqueous size-exclusion chromatography led to substantially different molar mass characterization than from the manufacturer. Their relative mass-average molecular mass (Mₐ) and polydispersity (D) were characterized by size exclusion chromatography (SEC; Figure S1 of Supporting Information) with KPS having an Mₐ = 196 kg/mol with D = 2.8 and PDADMA Mₐ = 60 kg/mol with D = 2.76 relative to polystyrene pyridine standards. These polymers were polydisperse and provide a working system to probe the phase behavior.

**Preparation of Polyelectrolyte Complex Solutions.** The purified, dry KPS and PDADMA were dissolved separately in ultrapure water to prepare 1.00 mol/L stock solutions. These stock solutions were added to predetermined volumes of aqueous KBr stock solution (4.00 mol/L) and vortex-mixed to give clear KPS–KBr and PDADMA–KBr solutions with known final salt concentration (cₛ) and polymer concentration (cₚ). The two solutions were then transferred to a separate 1.5 mL Eppendorf tube and mixed under vigorous agitation. The resulting polyelectrolyte complex solution was stored at 5 °C (below LCST) overnight prior to use.

**Cloud Point Determination.** The cloud point temperatures of the KPS–PDADMA complex solutions were determined by 532 nm wavelength laser light transmission, as defined by the inflection points of the transmission curves (Figure S3), upon heating at a rate of 0.2 °C/min.

**Phase Separation and Extraction.** The Eppendorf tube containing the polyelectrolyte complex solution was equilibrated in a water bath with temperature control with precision of ±0.1 °C (Isotemp, Fisher Scientific) for at least 2 h. When T ≥ 40 °C, a DuraSeal film was placed between the tube and the lid to minimize the air gap, thus minimizing water evaporation during the equilibration. After the solution had phase-separated into two transparent phases with no visual droplets or cloudiness separated by a meniscus, the entire volume (700 to 2000 μL) of the supernatant was extracted by pipette into a separate vial. Following the prompt removal of the residual supernatant, 50 to 200 μL of the coacervate was extracted and diluted in 2.00 mol/L KBr solution in a separate vial.

**UV–Visible Spectroscopy.** The concentration of PSS was determined by UV–Vis spectroscopy with a PerkinElmer UV–Vis/NIR Lambda 900 Spectrometer. The supernatant and coacervate extracts were independently diluted to cₛ = (2 × 10⁻⁴ to 1 × 10⁻³) mol/L in a 1 cm path length quartz cuvette and measured for absorbance between 250 to 800 nm. PDADMA has negligible UV–Vis absorbance over the entire wavelength range, while the PSS exhibits a known characteristic absorbance between 250 nm to 270 nm (Figure S4a). The PSS concentration (cₚₚₚ) was determined using the absorbance at 262 nm and the Beer–Lambert law with a calibration curve valid up to cₚₚₚ = 1 × 10⁻² mol/L (Figure S4b).

**1H Nuclear Magnetic Resonance.** 1H NMR was conducted on a Bruker 600 UltraShield spectrometer with an autosampler. Prior to the experiments, the supernatant and the diluted coacervate extracts were dried under vacuum to completely remove water and then redissolved in predetermined amounts of D₂O containing 1.50 mol/L KBr and 5.51 × 10⁻³ mol/L 3-(trimethylsilyl) propionic-2,2,3,3-d₄ acid sodium salt (TMSP-d₄). The KBr in D₂O, together with the KBr in the dried extracts, added up to above 2 mol/L total salt concentration and therefore suppressed any phase separation in the 1H NMR sample. The TMSP-d₄ served as the internal reference with which the integration area of the PSS⁻ and the PDADMA⁺ peaks were compared so both concentrations can be determined. After this step, the samples were transferred into heavy-walled NMR tubes (Wilmad, 5 mm outer diameter, 2.2 mm inner diameter) and 1H NMR spectra were collected. Even with the high salt concentration, the quality of the spectra was sufficient (Figure S5) to allow for integrations with an error of ≤10%. Because a proportion of protons were missing in the spectra regardless of the relaxation time Tₙ, resulting in the apparent decrease in the PSS⁻ and PDADMA⁺ peak integration area relative to the theoretical values, a semiquantitative analysis was used. First, a series of 1H NMR standards with known cₚₚₚ and cₚₛₛₛ were prepared so their Sₛ/Sₚ and Sₚ/Sₛ can be determined (Sₛ, Sₚ, and Sₛₛₛ stand for the peak integration area of the polyanion, polycation, and reference, respectively). As in the standards, the molar ratios between the polyanions, the polycations, and the reference are known; therefore, the theoretical peak integration area of the polyanions and the polycations, Sₛₛₛ and Sₛₛₛ, can be calculated. The activity factors, α and β, are defined as α = Sₛ/Sₛₛₛ and β = Sₛₛₛ/Sₛₛ, which indicate the percentage of H NMR-active protons in the two polyelectrolytes. They depend on cₛ and cₚ (Figure S6). It was observed that α and β are almost constant at cₛ ≈ 0.050 mol/L and cₚ = (2.1 to 2.7) mol/L; therefore, all the dried samples were diluted to approximately this molar density, and α and β were applied to convert the 1H NMR-active polymer concentrations to the actual concentrations in the samples.

**Small-Angle Neutron Scattering.** SANS measurements were conducted on the NG830 beam line at National Institute of Standards and Technology (NIST) Center for Neutron Research, Gaithersburg, Maryland. The configurations used an average neutron wavelength (λ) of 6.0 Å with wavelength spread (∆λ/λ) of 0.14. The scattering vector (q) range covered 0.003 to 0.5 Å⁻¹. Polyelectrolyte complex solutions in 1 mm quartz path-length baffle cells were thermostatically controlled within a nine-position temperature-controlled sample environment with ±0.1 °C precision. The temperature range of 16.2 to 19.8 °C were studied with an equilibration of 20 min prior to data collection. The two-dimensional scattering patterns collected by the image detector were reduced to absolute intensities and then azimuthally averaged and converted to 1D profiles as per standard protocols.

**Static Light Scattering.** SLS measurements were performed with a modified Brookhaven BI-200SM using a wavelength of 532 nm laser light from a Coherent VERDI diode-pumped solid-state laser operating in TEM₀₀ mode. The laser power was finely adjusted by neutral density filters. Glan-laser polarizer and analyzer (Thorlabs) were used under the vertical polarizer and vertical analyzer condition for all experiments. Samples contained within cylindrical glass cuvettes were placed in a decalin index-matching vat with temperature controlled by a recirculating bath to a precision of ±0.1 °C and sample temperature determined by a platinum resistance thermometer placed within the vat. The scattered intensity (Iₛ) was collected between scattering angles of 20 to 140° in 10° increments enabled by the precision goniometer and detector arm. Iₛ was normalized by the angle-dependent scattering volume, and reduced to Rayleigh ratios using the SANS correction factor (Rₛₛₛ) using the expression Iₛ/Rₛₛₛ = 2.13 × 10⁻³ cm⁻¹ at 532 nm at 25 °C. Dust-free samples were essential for SLS measurements, so all homogeneous, one-phase samples were filtered through 0.45 μm PVDF disc filters at 5 °C into clean, dust-free cylindrical light-scattering cells. For samples subject to higher temperature (>40 °C), a thick layer of silicone oil (5 cSt, Sigma-Aldrich) was added to the air/supernatant interface to suppress water evaporation. The temperature was elevated toward the cloud points, determined by separate laser transmission experiments with 20 min equilibration time for each temperature increment. Independent measurements of the differential refractive index increment (dn/dc) reveal small differences between the polyelectrolyte in salt solutions, with values of 0.169 cm³/g for KPS and 0.155 cm³/g for PDADMA in 0.1 mol/L KBr at λ = 535 nm at 25 °C.

**Estimating Critical Concentration.** The sample preparation was conducted in a manner as described but within NMR tubes. Minimizing water evaporation was essential for reproducible results; therefore, as with SLS studies, a layer of silicone oil was used to minimize water evaporation. The NMR tube was immersed in a temperature-controlled water bath with precision of 0.1 °C and heated at 1 °C/h until the solution turned translucent. The sample was then held at this temperature to allow for phase separation into clear phases separated by a meniscus. Photographs were taken as soon as the meniscus was observed.
RESULTS AND DISCUSSION

Mixtures of oppositely charged polyelectrolytes may lead to liquid–liquid phase separation with an apparent upper critical salt concentration, LCST, and UCST. The following results examines in more depth the initial polymer concentration dependence and interrelationships of the common upper critical salt concentration with LCST behavior.

Polyelectrolyte Partitions Asymmetrically upon Liquid–Liquid Phase Separation. The effect of initial total polymer concentration ($c_{p,0}$) on the $T-c_p$ phase diagram was studied along a KBr salt isopleth. Figure 1a–c shows $c_{p,0}$ of 0.10, 0.20, and 0.30 mol/L, respectively, in moles of monomer repeat unit for KPSS and PDADMAB initially mixed at 1:1 stoichiometry by charge such that $c_{PSS,0} = c_{PDADMA,0} = (1/2)c_{p,0}$. The initial salt concentration ($c_{s,0}$), defined as the total concentration of the added salt and the polyelectrolyte counterions, was fixed at 1.80 mol/L. Under these conditions, the cloud point temperatures ($T_{cp}$) are near room temperature (Figure S3) and measured upon heating from $c_{p,0}$ and shown as solid green triangles.

Phase separation into polyelectrolyte-poor supernatant (left branch) and polyelectrolyte-rich dense coacervates (right branch) show an asymmetric polymer partitioning. UV–Vis measurements of the $c_{PSS}$ illustrate the LCST behavior. However, the NMR measurements show that the supernatant has a concentration of PDADMA slightly higher than PSS, while in the coacervate, PSS is in excess. This information was absent in UV–Vis alone. While the partitioning of polymers appears unequal by charge, a conservation of mass from the initial concentration was verified such that

$$\frac{c_{PSS,1} \cdot \phi_1 + c_{PSS,2} \cdot \phi_2}{c_{PSS,0}} \approx \frac{c_{PDADMA,1} \cdot \phi_1 + c_{PDADMA,2} \cdot \phi_2}{c_{PDADMA,0}} = 1.0 \pm 0.1$$

(Figure S7 and Table S1), with the subscripts 1 and 2 indicating the supernatant and the coacervate, respectively, and $\phi_i$ representing the volume fraction of each phase such that $\phi_1 + \phi_2 = 1$.

Figure 1 shows phase separation into nonstoichiometric polyion phases that differs from a common assumption of phase separation into equimolar associates. Nonstoichiometric polyelectrolyte complexes were observed in polyelectrolyte multilayers (PEMUs) and solid polyelectrolyte complexes. Porcel and Schlenoff analyzed the composition of a solid complex formed by 1:1 stoichiometry of NaPSS:PDADMAC and observed a molar ratio of 1.17:1 PSS:PDADMA after thorough rinsing with water to remove the supernatant and the excess counterions. This is remarkably similar to our observations, considering the different sample preparation methods, molecular mass distribution of the polymers, counterions, and salt concentrations. They attributed the nonstoichiometric effect to the topological constraints in the polymer matrix that prevent complete complexation (intrinsic charge compensation) between polycations and polyanions, as well as the presence of mesoscale pores that may sequester free chains. A separate study observed that annealing the solid complex in 2.5 mol/L NaCl, the complex expelled extrinsic charges (counterions bound to the polyelectrolyte) from the pores and resulted in a 1:1 PSS:PDADMA composition.

However, PEMUs and solid polyelectrolyte complexes are representative of kinetically frozen systems with high viscosity and low water content. In contrast, the supernatant and coacervates in this study are highly hydrated and liquid-like, so the effect of topological constraints and porosity should not factor into the present study. This quantification of nonstoichiometry in the polyelectrolyte coacervates, starting from an initial 1:1 stoichiometry by charge, was unexpected. This behavior may be partially explained by preferential solvation of...
the polymers supported by the fact that KPSS precipitated in the presence of 4.0 mol/L KBr, while the PDADMAC did not (Figure S8). This solvent quality trend is consistent with the observations that NaPSS partially precipitated in 4.5 mol/L NaCl, while PDADMAC was soluble.56 These solubility and solvation differences suggest a need for two different FH interaction parameters, \( \chi \), whereas most analytical theories treat the polycations and polyanions as a pair represented by one effective interaction parameter (\( \chi_{eff} \)) with the solvent. In the case of homologous polyelectrolytes that share the same backbone and differ only by the pendant charged group, a single \( \chi_{eff} \) could quantify the \( c_{p,0} \) binodal measurements.30 A modification of analytical theories with a separate \( \chi \) between the polyanion and polycation with solvent may be sufficient to show unequal partitioning but also increases the complexity.31,81,83,84 In such a case, under the same \( c_i \) and \( T \), the effective interaction parameters of the polymer and solvent would be unequal such that \( \chi_{PDADMA-water} < \chi_{PSS-water} \), which conceptually implies that PDADMA has preferential partitioning in the water-rich phase, leading to an excess of PSS in the coacervate. Such pair-wise interactions are directly incorporated into liquid-state theory with solvent as a continuum.56

While no phase diagrams were reported, UCST behavior49 was observed in addition to LCST in the PSS/PDADMA complex with added KBr. The 1:1 stoichiometric mixtures by charge used a reported higher molecular mass of PSS than PDADMA, but no polydispersity or counterion exchange was reported. Such behavior was not observed by us across a wider range of polymer concentrations49 and likely reflects additional complicating aspects of asymmetry of the chain length, polydispersity in molecular mass, and maintenance of one salt pair. The role of polydispersity cannot be ruled out, considering the dependence of molecular mass on binding.82

**Pseudobinary Coexistence Curves in the \( T-c_{p,0} \) Plane.**

The three pseudobinary coexistence curves in Figure 1 are replotted in Figure 2 with the total polymer concentration \( c_p = c_{PSS} + c_{PDADMA} \). Unexpectedly, these binodal curves do not overlap onto one curve. This shows that the pseudobinary representation is \( c_{p,0} \)-dependent near the cloud point on the \( T-c_{p,0} \) phase diagram.

Figure 2. \( T-c_{p,0} \) phase diagram of KPSS–PDADMAB complexes in \( \text{H}_2\text{O} \) based on the NMR data from Figure 1. The square and triangle symbols represent the binodal points and the cloud points, respectively. Error bars represent one standard deviation estimated from the uncertainty in the sampling micropipette volumes and NMR peak integrations averaged from five samples.

Figure 3 shows a pronounced shift in the supernatant branches, more so than the coacervate branches. Additionally, under fixed \( c_p \) higher \( c_{p,0} \) is correlated with a lower propensity of phase separation, or smaller miscibility gap, as shown by the narrowing of the two-phase region. This new observation of an apparent \( c_{p,0} \) dependence can be explained by considering negative tie lines in the \( c_i - c_p \) phase diagram (Figure 3a).

Figure 3. Schematics of two types of polyelectrolyte complex phase diagrams: (a) The \( c_i-c_p \) phase diagram showing negatively sloped tie lines (dashed lines) and resulting equilibrium phase concentrations (open symbols), starting from three different \( c_{p,0} \) within the two-phase region (filled symbols). (b) The \( T-c_p \) phase diagram with dashed horizontal tie line connecting the supernatant and the coacervate branches (open symbols) from one \( c_{p,0} \) (filled symbol). (c) \( T-c_{p,0} \) phase space in which the phase separation (solid symbols and dashed lines) takes place at fixed \( T \) and within the shaded \( c_i-c_{p,0} \) plane and projected upon the \( T-c_p \) plane. This leads to apparent \( c_{p,0} \)-dependent phase boundaries (open symbols and the dotted lines) along the \( c_p \) axis. (d) Envisioned 3D surface that shows how a line of critical points (yellow solid line) appears at the surface at different temperatures. Example initial concentrations are shown to meet the surface upon heating.

Figure 3a,c illustrates how to rationalize these pseudobinary observations. In Figure 3a, following the negatively sloped tie lines, any initial composition within the \( c_i-c_p \) phase envelope will phase separate into a polymer-rich, salt-poor phase and a polymer-poor, salt-rich phase. In this study, we fixed the initial salt concentration, \( c_{i,0} \) and systematically increased \( c_{p,0} \). This is equivalent to traversing horizontally through the \( c_i-c_{p,0} \) phase diagram parallel to the \( c_i \) axis. This is represented by the three colored solid symbols (black, red, and blue) in the order of increasing \( c_{p,0} \). Assuming identical tie-line slopes,29 these three \( c_{p,0} \) will phase-separate into three pairs of different binodal points (open black, red, and blue circles), with the lowest \( c_{p,0} \) having the largest polymer concentration difference in the two daughter phases. In Figure 3c, we consider the phase space with an additional vertical \( T \) axis of the same polyelectrolyte complex system. Under this scenario, the phase separation in the \( c_i-c_{p,0} \) plane is projected onto the \( T-c_p \) plane that align these binodal points along the isotherm with nonoverlapping features. For simplicity, Figure 3c only demonstrates the case of one temperature, but by inference, the \( c_{p,0} \)-dependence is a general feature for all \( T \)s. Therefore, the connection of all binodals with identical \( c_{i,0} \) will lead to multiple nonoverlapping...
pseudobinary curves on the $T_{cp}$ plane, one shown for example, which is consistent with our observations. This explanation provides a proof of concept in constructing a 3D phase diagram of polyelectrolyte complexes in Figure 3d that accounts for the pseudobinary observations. Figure 3d will be discussed in more depth in the sections on concentration fluctuations and the location of the critical polymer concentration along a salt isopleth. The overall miscibility gap would describe the LCST, such that at low temperature and high salt, only 1 $\Phi$ is present. Ylitalo et al.\textsuperscript{85} independently predicted the nonoverlapping trends of the pseudobinary phase diagram (Figure 2) based upon a liquid-state theory for coacervation, which includes the essential physics, in particular, of the chain connectivity contributions to the electrostatic correlation term in the free energy and the temperature dependence of the solution dielectric constant. Their theory recovers a negative tie line on the $c_i$-$c_p$ plane that is essential to predict the nonoverlapping pseudobinary diagrams with an LCST where higher polymer concentration led to an apparent narrowing and vertical shift. The opposite result would be observed with the Voorn–Overbeek theory because it predicts positive sloped tie lines, even though it may recover an LCST when considering the details of the dielectric constant. We expect alternate theoretical approaches to recover predictions similar to Figure 2 if plotted in the manner suggested.

Previous studies of two different $c_i$,$p$\textsuperscript{8} ($c_{PSS,0}$ of 0.15 and 0.30 mol/L) at a higher fixed $c_i$ = 2.0 mol/L KBr\textsuperscript{47} show that increasing $c_{p}$ shifted the polymer-rich coacervate branch slightly to a higher concentration of PSS as measured by UV–Vis. The present study shows with more systematic data that higher $c_{p}$ leads to an upward shift of the binodal temperatures and narrowing of the miscibility gap. The differences between the two studies is most likely caused by a change in slope of the tie line on the $c_i$-$c_p$ plane closer to the critical salt concentration at room temperature that can lead to a different projected (Figure 3c) shift on the pseudobinary representation. Secondary effects are improved purification methods and, especially, the counterion purity that was validated by XPS. The increase in the cloud point temperatures with increasing $c_{p,0}$ at fixed $c_i$ remains the key conclusion by both studies but now with improved NMR methods to measure the concentrations.

**Scattering Properties in the One-Phase Region Approaching the Cloud Point.** The measurements of the pseudobinary phase diagrams are complemented by SANS and SLS within the one-phase region. SANS on the dense polyelectrolyte complexes have characterized the structure of the coacervate phase as well as chain conformation via a method of contrast variation or contrast-matching strategy.\textsuperscript{78,86,87} The SANS study uses a full contrast approach where there are no deuterium-labeled chains; the contrast is provided by the hydrogen-rich polymers in salt-containing D$_2$O solvent, while SLS probes the refractive index fluctuations arising from solvent, polymer, and salt.

Figure 4 shows SANS and SLS data for $c_i$ = 1.80 mol/L and $c_{p,0}$ = 0.30 mol/L with $T_{cp}$ = 20.1 °C for a sample prepared in D$_2$O that illustrates the resolution limits. The SLS data are vertically scaled to the absolute-intensity SANS measurements by the scale factor $b$. Interestingly, SANS shows only a small increase in scattering at the lowest $q$ (ranges indicated by arrows) as the sample is heated from 16.2 up to 0.3 °C below $T_{cp}$. The characteristic size (correlation length) cannot be reliably determined by SANS. However, the structure on the chain dimension and segmental length scales are weakly dependent on temperature, and the mid-$q$ region can be fit by a power law with $I(q)\sim q^{-3}$ with fractal dimension ($D_f$) of 1.83 ± 0.05. The scattering spectrum is completed by SLS (low-$q$ range) data. SLS provides a sensitive measurement of temperature-dependent concentration fluctuations at length scales defined by $1/q$. SLS was used to characterize these correlations within the one-phase region upon approaching $T_{cp}$ in aqueous solutions.

The light-scattered intensities, $R_\text{LS}(q)$, systematically increase with $T$ within the $c_{p,0}$ range from 0.10 to 0.60 mol/L. Figure 5 shows an example of the SLS profiles of $c_{p,0}$ = 0.20 mol/L from 17.8 to 21.7 °C. The intensity plateau at low-$q$ ensures the largest scale fluctuations are measured as the two-phase region is approached. Additional $R_\text{LS}(q)\sim q$ plots (Figure S9) are in the Supporting Information.

**Increase in Concentration Fluctuations near Phase Separation.** The data, such as in Figure 5 and in the
Supporting Information, are quantified by the Ornstein–Zernike (OZ) equation with \( R_{\text{vv}}(q) \) described by

\[
R_{\text{vv}}(q) = R_{\text{vv}}(0)/(1 + q^2 \xi^2)
\]

(1)

where \( \xi \) is the correlation length of the concentration fluctuations and the zero-angle scattered intensity \( R_{\text{vv}}(0) \). A typical OZ plot of Figure 6a shows fits to eq 1 over the entire \( q \)-range for each temperature between \( c_{p,0} = 0.10 \) to 0.40 mol/L (Figure S10). Interestingly, at higher \( c_{p,0} \), \( R_{\text{vv}}(q) \) deviates from the OZ equation at the low-\( q \) and becomes time-dependent (Figures S10 and S11). The deviation and a time-dependent scattering occurs even after thermal equilibration, just below the cloud point temperature for \( c_{p,0} = 0.50 \) mol/L (Figure 6b) and 0.60 mol/L (Figure S10d). Nonlinearity at low \( q \) in the OZ plots may arise from entering the metastable region where nucleation and growth takes place, leading to scattering by larger structures outside the instrument resolution or complications due to multiple scattering.

When this deviation occurred, as can be seen at 43.8 and 44.1 °C in Figure 6b, we take note of this temperature and exclude the data above this temperature from further OZ analysis and interpretation in order to present the most reliable estimates of \( \xi \) and \( R_{\text{vv}}(0) \).

The temperature dependence of \( \xi \) and \( R_{\text{vv}}(0) \) at different \( c_{p,0} \) are shown in Figure 7. A divergence in \( \xi \) and \( R_{\text{vv}}(0) \) as the temperature increases is observed at concentrations higher than 0.10 mol/L and is consistent with the approach to the LCST. The critical temperature \( (T_c) \) and spinodal temperatures \( (T_s) \) are estimated by extrapolation procedures from scattering data in binary polymer mixtures that can be quite complex with a crossover from mean field behavior to fluctuations. When this deviation occurred, as can be seen at 43.8 and 44.1 °C in Figure 6b, we take note of this temperature and exclude the data above this temperature from further OZ analysis and interpretation in order to present the most reliable estimates of \( \xi \) and \( R_{\text{vv}}(0) \).

Characterization of the Spinodal Temperature. Near the critical and spinodal temperature, \( \xi \) and \( R_{\text{vv}}(0) \) will diverge with characteristic scaling. The value of \( R_{\text{vv}}(0)^{-1} \) is formally related to the susceptibility or isothermal osmotic compressibility by taking into consideration the prefactors for the scattering contrast. In such a case, a free energy of mixing model for coacervation may be tested against systematic data, which is beyond the scope of the present study. We consider the main result that \( R_{\text{vv}}(0) \) is a measure of the structure factor, such that \( R_{\text{vv}}(0) \sim (\chi_s - \chi_{\text{eff}})^{-1} \) where \( \chi_s \) is the value of the Flory–Huggins interaction parameter at the spinodal line that may be predicted based upon a Gibbs free energy of mixing and \( \chi_{\text{eff}} \) would have a characteristic temperature dependence. \( \chi_{\text{eff}} \) may also include dependencies on the salt concentration via Debye screening length due to the screened electrostatic repulsion between charged segments as considered in
polyelectrolyte solutions and between complexed polyelectrolyte segments and the solvent in coacervate phase diagrams. The temperature and composition dependence of χ are often evaluated by SANS. The following are the expected dependencies for polymer mixtures if characterized by a single Flory–Huggins interaction parameter (χ) with an inverse temperature dependence and the spinodal χ_s ∼ 1/T_s:

\[ \xi \sim \left| \frac{1}{T} - \frac{1}{T_s} \right|^{-\nu} \]  
\[ R_{vv}(0) \sim \left| \frac{1}{T} - \frac{1}{T_s} \right|^{-\gamma} \]  

In binary mixtures, mean-field theory predicts \( \nu = 1/2 \) and \( \gamma = 1 \), such that if \( \xi^{-2} \) and \( R_{vv}(0)^{-1} \) are plotted versus \( 1/T \), a linear dependence would be expected far from the critical region as the phase transition is approached from the one-phase region. The exponents for binary mixtures with critical fluctuations are expected to follow Ising criticality with \( \nu = 0.63 \) and \( \gamma = 1.26 \).

Figure 8 displays \( R_{vv}(0)^{-1} \) and \( \xi^{-2} \) versus inverse temperature for \( c_{p,0} = 0.40 \text{ mol/L} \). The linear dependence far from the phase boundary was expected by mean-field theory but with noticeable deviation. The linear dependence can define a mean-field spinodal temperature \( (T_{s,ml}) \), which are quite close between the two extrapolations that lead to an average of \( (310 \pm 4) \) K. When considering the curvature, the estimate of \( T_s \) depends upon the method of extrapolation. We chose to simultaneously fit \( R_{vv}(0)^{-1} \) and \( \xi^{-2} \) as a function of the reduced temperature \( (\epsilon = |1/T - T_s|/T) \) close to the phase boundary by excluding the linear region with eqs 4 and 5.

\[ R_{vv}^{-1}(0) = R_{vv,0}^{-1} |\epsilon|^{\nu_{s,0}} \]  
\[ \xi^{-2} = \xi_{0}^{-2} |\epsilon|^{2\gamma_{s,0}} \]  

By this method, a common \( T_s \) is estimated, which uses both datasets with two prefactor amplitudes \( \xi_{s,0} \) with dimension of length and \( R_{vv,0}^{-1} \) with dimension of inverse scattered intensity, and two exponents \( \nu_{s,0} \) and \( \gamma_{s,0} \) as fit parameters. A nonlinear regression with uncertainty weighting was used for a systematic study across the five highest concentrations with 0.40 mol/L shown in Figure 8. The lowest concentration (0.10 mol/L) did not show any curvature, and the mean-field expression was sufficient. The purpose of this analysis was to estimate \( T_s \) in a systematic way, while the effective indices and amplitudes provide added insight into the fluctuations and molecular scale details, respectively.

Salt Isopleth Phase Diagram with Critical Polymer Concentration. Figure 9 shows the cloud point (solid black squares) and spinodal (solid red circles) temperatures for all \( c_{p,0} \). When \( c_{p,0} \leq 0.40 \text{ mol/L} \), all \( T_s \)s are well above \( T_{cp} \), such that the spinodal curve is within the cloud point phase envelope as expected. However, when \( c_{p,0} \geq 0.50 \text{ mol/L} \), an unexpected crossover between the cloud point and spinodal point occurs. In this concentration range, deviations from the OZ equation near \( T_{cp} \) were observed at low \( q \). Even though the samples are in thermal equilibrium, there is a kinetic effect at these higher concentrations readily observable by SLS but not obvious by turbidity. We assume that the probability of nucleation remains low along with slow growth kinetics within the metastable region. The boundaries between the metastable and unstable regions are presently unknown in such polyelectrolyte complexes, but in light of this discrepancy, we add the temperature where the time-dependent scattering and deviation from OZ equation occurred to signify likely nucleation and growth with open black squares. The \( T_{cp} \) defined by the inflection point from a first derivative of the laser transmission curve cannot simply be slowed down from the programmed temperature heating rate (0.2 °C/min), since prolonged heating causes water evaporation. Evaporation and subsequent condensation near the sample cuvette cap increases the concentration and increases the \( T_{cp} \). Evaporation was minimized by use of a mineral oil solvent trap.

![Figure 8](image1.png)

**Figure 8.** The \( c_{p,0} = 0.40 \text{ mol/L} \) data for left axis, \( R_{vv}(0)^{-1} \) (solid red squares), and right axis, \( \xi^{-2} \) (solid blue squares), as a function of \( 1/T \). The solid lines are independent fits that extrapolate to the mean-field spinodal temperature with fixed \( \nu = 1/2 \) and \( \gamma = 1.0 \), while the dashed lines are results from simultaneous fits to eqs 4 and 5 with a common \( T_s \), with nonlinear least squares regression with uncertainty weights. The inset provides an expanded view of the fits to the fluctuation model. The uncertainties (error bars) are estimated by one standard deviation to the fit and may be smaller than the symbols.

![Figure 9](image2.png)

**Figure 9.** Salt isopleth phase diagram with \( T_{cp} \) and \( T_{sp} \) of KPSS–PDADMAC complexes with \( c_{p,0} \leq 0.10 \) to 0.60 mol/L at \( c_s = 1.80 \text{ mol/L} \) of KBr. Predicted metastable region between the cloud point and spinodal point is shaded. Estimate critical polymer concentration and critical temperature are shown as solid blue triangles for near-symmetric tie lines. While error bars are shown, they may be smaller than the symbols used.
These results expand upon prior efforts with higher polymer concentrations and, for the first time, the spinodal temperatures. Figure 9 represents a pseudobinary phase diagram formed by an initial salt isopleth. Each cloud point would represent one point on the $T_\text{c} - c_\text{p}$ phase surface upon heating as shown in Figure 3d from an initial polymer concentration. The region between the cloud point (or kinetic point) and the spinodal point suggests a narrow metastable region (hatched emphasis). Interestingly, a deep temperature quench should observe an unstable region with spinodal decomposition but passing through the metastable region, with exception to the critical point. Along these lines, notice that the cloud point and spinodal temperatures appear to converge from low polymer concentration and meet between $c_{\text{p,0}} = 0.4$ to 0.5 mol/L in Figure 9. While this appears at an arbitrary polymer concentration, it can be rationalized to be a critical point by Figure 3d. In the $T_\text{c} - c_\text{p}$ phase diagram, the minima would meet at a critical point on the plot of $c_\text{c} - c_\text{p}$ at fixed temperature. This will appear as a line of critical points (yellow line in Figure 3d) on the $T_\text{c} - c_\text{c}$ surface. The critical polymer concentration for a given salt isopleth will appear as a single point along a series of cloud points across multiple initial polymer concentrations of a salt isopleth as shown by the dashed line in Figure 3d and cloud points in Figure 9. Conceptually, the critical polymer concentration would occur at the point where the spinodal and binodal meet.

Measurements of the critical concentration and critical temperature is a challenging problem for complex fluids. Near the critical point, the properties exhibit universal features, but impurities, multiple components, and polydisperse polymers introduce additional complications to compare with predictions. We sought to independently estimate the critical total polymer concentration ($c_{\text{p,c}}$) by examining the crossing of volume fractions via tie lines from different initial polymer concentrations. We estimate the KPSS–PDADMAB $c_{\text{p,c}}$ solution that phase-separates into equal volumes (tie lines equal) 50/50 (volume fraction) supernatant/coacervate as close to $T_\text{op}$ as possible.65

Figure 10 shows $c_{\text{p,0}} = 0.40$ and 0.46 mol/L exhibited coacervate volume fractions of 0.40 and 0.62, respectively, which guided a concentration in between with a coacervate volume fraction of 0.53 for $c_{\text{p,0}} = 0.43$ mol/L closest to 50/50 (volume fraction) supernatant/coacervate, which is a signature of close to the critical condition in two-phase mixtures. From this concentration, the critical polymer volume fraction ($\phi_{\text{p,c}}$) at the critical temperature $T_\text{c} = 44.0 ^\circ\text{C}$ and fixed salt concentration of 1.80 mol/L was estimated as $\phi_{\text{p,c}} = 0.059$ using $\rho_{\text{KBr}} = 2.75$ g/cm$^3$ and $\rho_{\text{pol}} = 1.13$ g/cm$^3$, where $\rho_{\text{KBr}}$ and $\rho_{\text{pol}}$ are the mass densities of KBr and average of the polyelectrolytes. This critical temperature and $c_{\text{p,c}}$ are shown as solid blue triangles in Figure 9.

**Apparent Critical Region and Crossover of Characteristic Length Scales Due to Chain Association.** $\xi$ increases from $\sim 90$ Å at $T < T_\text{c}$ to larger than 700 Å as $T \to T_\text{c}$ as shown in Figure 11 for $c_{\text{p,0}} = 0.40$ mol/L. In order to put such results on an intuitive scale, consider that in dilute solution (0.02 mol/L) at the same 1.80 mol/L salt concentration, the hydrodynamic radius ($R_h$) of the KPSS and PDADMAB polymers are 75 and 63 Å, respectively (Figure S12). These $R_h$ are an upper bound in chain dimensions, since polyelectrolyte size decreases with increasing polymer concentration from the dilute to semidilute regimes due to the screening of electrostatic and excluded volume interaction. In neutral polymer solutions, such as polystyrene in cyclohexane with well-defined phase diagrams, Melnichenko et al. showed by SANS that in the $\theta$-region, $\xi < R_h$ while in the vicinity of the critical temperature, $\xi > R_h$. The crossover length scale in the susceptibility (proportional to the scattered intensity) is the polymer size ($R_h \approx 11$ nm, in their case), such that Ising behavior occurs when $\xi > R_h$. Interestingly, Schwahn and Pipich do not observe such a crossover criteria with aqueous solutions of associating poly(ethylene oxide). The main result from the polyelectrolytes is that the dominant structural length scale becomes $\xi$ and exceeds the expected chain dimensions even far from the phase boundary. The fluctuations and departure from mean-field behavior arises from the additional associative behavior of oppositely charged polyelectrolytes in the one-phase region, which is a distinguishing characteristic from neutral polymer solutions, such as polystyrene in cyclohexane. This associative behavior with $D_t$ of $1.83 \pm 0.05$ must span multiple chains well below the phase transition.
boundary as shown by the relative values of $\xi$ and $R_g,\text{PSS}$ in Figure 11. This result is different from LCST neutral polymers and gels that show $D_1$ to vary from $5/3$ to 2 with increasing temperature consistent with a change in solvent quality from good solvent to $\Theta$ conditions.97 While these electrostatic-driven associations may appear through polycation–polyanion binding or dipolar attraction of ion pairs, the form was captured by the Landau–Ginzburg classical theory of fluctuations that gives rise to the observed OZ scattering. These fluctuations appear enhanced when far from conditions of macrophase separation through mesoscale soluble complexes (or inter-polyelectrolyte complexes) with sizes of $>100$ nm as observed in dilute solutions as studied for host–guest interactions,62,100 simplexes,63 stoichiometry of mixing,64,98,99 and molecular mass.101

For $c_p,0 = 0.40$ mol/L, the reduced temperature varies between 0.0536 $< \epsilon < 0.0076$ with effective indices $\nu_{\text{eff}} = 0.79 \pm 0.06$ and $\gamma_{\text{eff}} = 1.16 \pm 0.08$, that deviate from mean-field theory and demonstrate the importance of fluctuations. The effective indices and amplitudes from simultaneous fits to eqs 4 and 5 are provided in Table 1. The critical amplitudes depend on the molecular details of the system101 and show that $\xi_{\text{eq}}$ are smaller than the chain dimensions yet larger than expected by molecular liquids. Typically, $\gamma = 2\nu$, which was used for the lowest concentration; otherwise, we observe $\gamma_{\text{eff}} < 2\nu_{\text{eff}}$. This coincides with the theoretical relation of $\gamma = (2 - \eta)\nu$, where $\eta$ is the correlation function exponent,04 that characterizes the shape of the structure factor at $q \xi > 1$, while binary mixtures may be characterized by one order parameter within a theory for fluctuations. The present water, salt, and two distinct polymers are multicomponent mixtures that complicate such interpretation with additional order parameters in concentration as well as those related to charge regulation.24,105 Notably, diluted critical polymer blend mixtures are better described by Fisher’s renormalized critical exponents, where $\gamma' = 1.39$ and $\nu' = 0.71$.7,8 Due to the high salt concentration and measurements near the critical concentration, these mixtures may represent highly diluted polymer blends when considering the observed exponents. However, this does not explain the broader phase diagram relationships and projection of pseudobinary mixtures. Further study of the critical exponents closer to the critical temperature at the critical concentrations may reveal if the current measurements have reached the asymptotic values.

### CONCLUSIONS

The one-phase region in mixtures of oppositely charged polyelectrolytes exhibit concentration fluctuations that often appear as a low-$q$ upturn in SANS measurements but are within SLS resolution. The one-phase region is not homogeneous due to the structure from the associative nature of polyelectrolytes mixtures that is enhanced near the LCST liquid–liquid phase-separation boundary. Within the phase envelope, an asymmetric partitioning of PSS and PDADMA was observed and speculated to be due to the difference in the solubility parameters for the separate polyelectrolytes in the presence of high KBr salt. In this respect, the enthalpic interactions, typically considered by a FH interaction parameter, may need interaction parameters between each polyelectrolyte and solvent rather than one parameter. However, considering this complexity, when the phase diagrams are replotted in terms of temperature versus total polyelectrolyte concentration, the nonoverlapping coexistence curves are observed for different initial 1:1 stoichiometric mixtures of polymer concentrations. This logical result was due to the negative tie lines observed on the $c_1 - c_0$ phase diagrams and illustrate that the $T - c_0$ phase diagrams would provide a miscibility gap surface with a line of critical salt and critical polymer concentrations at each temperature. Only one salt isopleth was studied in this respect and characterized by pseudobinary phase diagrams.

The spinodal temperatures within the $T - c_p$ phase diagrams were characterized by Ornstein–Zernike scattering that follows the Landau–Ginzburg theory of fluctuations. The spinodal temperatures were estimated on a mean-field plot with effective critical indices and amplitudes. A crossover from mean-field to fluctuation regime was shown. This apparent critical behavior shows the correlation length far exceeds the expected critical indices and shift in the mean-field critical temperature. A crossover behavior was observed close to the measured critical polymer and salt concentration as discovered through equal volume observation. The effective critical indices with reduced temperature are not in quantitative agreement with the accepted 3D Ising values for binary mixtures but are consistent with deviations due to Fisher renormalization of diluted critical mixtures, such that the coacervate mixtures may theoretically behave as a highly diluted polymer blend. This may be a reasonable description if charged interactions are largely screened, yet these are multicomponent systems, not binary mixtures, so one does not expect 3D Ising criticality. The compelling evidence of large-scale fluctuations within the one-phase region, often observed as soluble complexes, show that chain association is enhanced near the phase boundary. A true test of Ising fluctuations would require attention to these phase diagrams with new proposed identification of the critical concentration.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://doi.org/10.1021/acs.macromol.1c02001.
Additional $R_p(q)$—$q$ and Ornstein–Zernike plots; X-ray photoelectron spectroscopy determination of counterion exchange; laser transmission curves to determine cloud point temperatures; example of UV–Visible spectra and calibration curve; SLS plots showing onset of kinetics of phase separation after thermal equilibration; polyelectrolyte hydrodynamic radius estimates; isotope effect on cloud point temperature (PDF)

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**Notes**

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**ADDITIONAL NOTE**

“Certain equipment, instruments or materials are identified in this paper in order to adequately specify the experimental details. Such identification does not imply recommendation by the National Institute of Standards and Technology, nor does it imply the materials are necessarily the best available for the purpose.

**REFERENCES**


Complex Coacervates.


