

# Characterization of the Ultralow Interfacial Tension in Liquid–Liquid Phase Separated Polyelectrolyte Complex Coacervates by the **Deformed Drop Retraction Method**

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# **Supporting Information**

ABSTRACT: Dilute droplets form upon changing the temperature of a phase separated polyelectrolyte complex coacervate. This provides an in situ approach to measure the interfacial tension between supernatant (dilute droplet) and dense coacervate by the deformed drop retraction (DDR) method. The aqueous coacervate, formed via a model 1:1 by charge stoichiometric polyelectrolyte blend, exhibits ultralow interfacial tension with the coexisting phase. DDR finds the interfacial tension scales as  $\gamma = \gamma_0 (1 - C_s/C_{s,c})^{\mu}$ , with  $\mu = 1.5 \pm 0.1$ ,  $\gamma_0 = 204 \pm 36 \ \mu\text{N/m}$ , and  $C_{s,c} = 1.977 \ \text{mol/L}$ . The value of  $\mu$  independently validates the classical exponent of 3/



2. The scaling holds between  $C_s/C_{s,c}$  of 0.75 to 0.94, the closest measurements to date near the critical salt concentration ( $C_{s,c}$ ). The temperature dependence of the interfacial tension is consistent with observed lower critical solution phase behavior and classical scaling. A detailed account of the DDR method and validation of assumptions are demonstrated.

# ■ INTRODUCTION

The interfacial width and interfacial tension between equilibrium phases of immiscible or partially miscible neutral polymer blends are governed by the statistical segment length and Flory–Huggins interaction parameter  $(\chi)$ .<sup>1</sup> The case, however, with charged polymers (polyelectrolytes) remains unsettled due to additional contributions from long-range electrostatic interactions, the multicomponent nature (polymer, salt, and water), and lack of quantitative phase diagrams.<sup>2,3</sup> Associative phase separation of mixtures of oppositely charged polyelectrolytes provides a model system with dense liquid phase (coacervate) coexisting with a polymer-poor liquid phase.4

Qin et al. derived an expression for the interfacial tension for polyelectrolyte coacervates near the critical salt concentration  $(C_{s,c})$  at fixed temperature (T).<sup>5</sup> They show the interfacial tension scales near the critical point as

$$\gamma \cong \left(\frac{k_{\rm B} T a}{\nu}\right) \frac{\left(1 - C_{\rm s}/C_{\rm s,c}\right)^{3/2}}{N^{1/4}} \tag{1}$$

where v is the reference volume (typically water), a is the statistical segment length under theta conditions, N is the degree of polymerization, and  $k_{\rm B}$  is Boltzmann's constant. The interfacial tension vanishes with  $(1 - C_s/C_{s,c})$  to the 3/2 power and compares favorably with experimental data.<sup>6,7</sup> Lytle and co-workers applied self-consistent field theory and Monte Carlo simulations and observed the same 3/2 scaling with the supernatant salt concentration difference.<sup>8,9</sup> Riggleman and coworkers used field-theoretic simulations and also observed the 3/2 scaling as well as consider the role of excluded volume (solvent quality) with fixed electrostatic strength.<sup>8</sup> These predictions are qualitatively consistent with the earlier interpretation by Spruijt et.al., who first experimentally observed the 3/2 scaling but derived by an effective Flory-Huggins interaction parameter  $(\chi_{\rm eff})$ .<sup>6</sup> They expanded  $\chi_{\rm eff}$  near the critical salt concentration to recover  $\gamma \propto (C_{\rm s,c} - C_{\rm s})^{3/2}$ . It is assumed that the bare  $\chi$  between polymer and solvent cancels out if it does not depend on salt concentration. These predictions imply that the role of polymer-solvent van der Waals interactions appears relatively unimportant when considering the effect of salt. Therefore, the balance between the entropy of mixing and charge correlations control the vanishing interfacial tension near the critical salt concentration, as opposed to the polymer-solvent interactions. An independent study of how polymer-solvent interactions are incorporated into the interfacial tension in coacervates remains to be addressed. This is typically studied through the temperature dependence of the Flory-Huggins interaction parameter.

The comparison to theory was enabled by development of suitable measurement methods. The capillary rise approach first applied by De Ruiter and Bungenberg-de Jong described several measurement challenges including low optical contrast

Received: July 18, 2019 Revised: September 21, 2019 Published: September 27, 2019 and sensitivity of the meniscus profile to wall-surface chemistry. Lim et al.<sup>10</sup> and Spruijt et al.<sup>6</sup> applied colloidal probe atomic force microscope while Priftis et al.<sup>7</sup> used the surface force apparatus. These techniques determine the interfacial tension from the force-distance curve with sensitivity on the order of nN to pN. These methods are challenging due to the sample loading, creating suitable coacervate/dilute phase interface, gravity-induced flow during measurements and surface contamination. Further, the compression and separation speed of the probe surfaces between the capillary bridge must be considered when evaluating the interfacial tension.7 These pioneering efforts improved the fundamental understanding of the low interfacial tension exhibited by associative polyelectrolyte phase separation. However, measurements closer to the apparent critical salt concentration require an improved sensitivity as the interfacial tension vanishes. One such technique to overcome these challenges is the deformed drop retraction (DDR) method developed by Luciani and co-workers.<sup>11</sup>

The DDR method introduces a spherical drop of liquid and immiscible fluid matrix. After an applied shear deforms the drop into an ellipsoidal shape, the zero-applied shear shaperetraction kinetics are quantified by a characteristic shape retraction time governed by the force balance of interfacial tension and viscous drag. The interfacial tension may be determined by additional independent measurements of the coacervate to dilute phase viscosity ratio. The DDR method has broad applicability to immiscible polymer blends,<sup>12–16</sup> biopolymers,<sup>17</sup> effects of nanoparticles additives to polymer blends,<sup>18</sup> and isotropic to nematic transition in liquid crystalline polymers.<sup>19</sup> A microfluidics method is also available for applicable systems.<sup>20</sup> A recent review by Minale discusses fluid mechanic models of droplet deformation.<sup>21</sup>

We apply the DDR method on a model polyelectrolyte complex coacervate system. The phase diagram for liquid–liquid phase separation was used to form spherical drops of dilute phase within the dense coacervate matrix. This in situ droplet formation is a direct consequence of the lower critical solution temperature (LCST) phase behavior in this system.<sup>22</sup> DDR measures the interfacial tension between coexisting equilibrium phases. The model system, instrumentation, measurements of rheological properties, in situ droplet formation, and results of effect of salt concentration and temperature are discussed in the context of available theoretical predictions.

# EXPERIMENTAL METHODS

**Materials and Sample Preparation.** Sodium poly-(styrenesulfonate) (NaPSS) with mass-average relative molar mass ( $M_w$ ) of 200 kg/mol and poly(diallyl dimethylammonium chloride) (PDADMAC) with  $M_w$  of 150 kg/mol were purchased from Sigma-Aldrich, Inc. as 30% and 20% by mass solution in water, respectively. The counterions of these polymers were ion-exchanged to obtain potassium poly(styrenesulfonate) (KPSS) and poly(diallyl dimethylammonium bromide) (PDADMAB).<sup>23</sup>

Polyelectrolyte coacervates were prepared by mixing aqueous solutions of anionic and cationic polymers at 1:1 charge stochiometric ratio at 10 °C. An initial concentration of 0.15 mol/L of monomer unit was used for all of the polyelectrolyte solutions. A predetermined amount of salt was added to each stock polymer solution before mixing. The two solutions of oppositely charged polyelectrolytes are combined and mixed by the aid of a vortex for 30 s. The phase separated solution is left undisturbed for 2 h before centrifugation at *g* = 10 000 m/s<sup>2</sup> for 15 min at 10 °C. This results in a clear polymer

poor supernatant and dense clear polymer-rich complex coacervate separated by a meniscus. Subsequently, samples are stored at 10  $^{\circ}$ C for 1 day, followed by 6 days at 5  $^{\circ}$ C before measurements. The sample cuvettes were sealed by vacuum grease and parafilm to prevent evaporation.

Viscosity and Dynamic Shear Modulus Measurements. Viscosity and viscoelastic moduli of the coacervate phase was measured by an Ares G2 rheometer in a cone-plate geometry with a cone diameter of 25 mm and a cone angle of 1°. The coacervate phase and supernatant were separated and transferred to the rheometer cell at 25 °C for independent measurements. The shear viscosities of the coacervate at different salt concentrations and temperatures are measured by applying shear rates in the range 0.01 to 1 s<sup>-1</sup>. The torque response for a shear rate below 0.03 s<sup>-1</sup> from the samples with  $C_s > 1.55$  mol/L was below the instrument resolution. Data at shear rates below 0.01 s<sup>-1</sup> were limited by noise and neglected. The coacervate was equilibrated for at least 1 h after each temperature change before beginning the shear rate sweeps. The zeroshear viscosities were estimated from the intercept of the viscosity plateau of the flow curve at low shear rates. After heating these extracted phases visual inspection does not see bulk phase separation, however, a thin cloudy layer can be observed at the air/coacervate interface. We expect this to have a negligible effect on the measured stress as the major contribution comes from the coacervate domain.

The viscosity of the dilute phase was measured on a cone-plate geometry of diameter 50 mm and a cone angle  $1^{\circ}$  on a stress-controlled Thermo Scientific HAAKE MARS III rheometer. Shear viscosities of the dilute phase at varying salt concentrations and temperatures were measured by applying shear rates in the range of 1 to 100 s<sup>-1</sup>. The supernatant sample was equilibrated for 15 min at each temperature before performing measurements.

**Drop Retraction Measurement Setup.** The drop retraction measurements are performed by combining a shear cell (Linkam optical shear system CSS450) with a wide field upright microscope (Olympus BX51) and halogen light source as shown in Figure 1. The



**Figure 1.** Schematic of the setup for the deformed drop retraction measurement. An example of coacervate in equilibrium with the dilute phase is shown on the left.

shear cell uses two parallel quartz plates with upper plate diameter of 30 mm and lower plate diameter of 40 mm that are in thermal contact with a simultaneously controlled top and bottom metal heating plates. The bottom plate operates in oscillatory, steady rotation or step-shear modes enabled by a stepper motor with velocity resolution 0.001 rad/s. The gap between the two plates can be adjusted in the range 5 to 2500  $\mu$ m by translating the top plate by a stepper motor. A combination of heating coil and regulated flow of liquid nitrogen around the sample cell using a Linkam LNP pump allows a precise control over the sample temperature. The CS450 and Linkam LNP are controlled by the Linksys 32 software.

Approximately 250 to 400  $\mu$ L of coacervate was placed at the center of the lower quartz plate of cell followed by the remaining

volume (1150 to 1000  $\mu$ L) of dilute phase to fill the annular space. The top quartz plate was positioned to ensure the coacervate spreads between the plates and fills the optical window (diameter = 2.5 mm) that is offset by 8 mm from the plate center. The exposed edge was sealed by silicone oil (~500  $\mu$ L) to prevent evaporation. The fixed gap between the plates varied from 500 to 800  $\mu$ m for different measurements. The sample was left undisturbed for 1 h to equilibrate after loading and assembly. Spherical drops of dilute phase are generated in the narrow sample gap within the observation window by utilizing the LCST phase behavior as described earlier.

The widefield upright microscope with 20× LMPlan objective observed the in situ formed droplets. A Pylon viewer software recorded images at 5 frames per second to 50 frames per second using a Basler acA2040–90um CCD camera with pixel size 2.2  $\mu$ m × 2.2  $\mu$ m.

ImageJ was used to identify the liquid–liquid interfaces on the image and determine the semimajor axis (l) and minor axis (b) of the ellipsoidal drops. The interfaces were identified through the EDM Binary operations of BioVoxxel macro [https://imagej.net/BioVoxxel\_Toolbox]. The macro values for the *erode*, *dilation*, *open*, and *close* operations under EDM were manually determined. Subsequently, an ImageJ routine was used for batch processing of the time sequence of images.

The temperature dependence of the interfacial tension was determined by successive stepwise increments from an initial equilibrium temperature. For each temperature step, the sample was equilibrated as described previously with waiting times,  $t_w$ , that decreased with increasing temperature, but within the range of 1 to 3 h.

**Theoretical Background for Shape Retraction of a Deformed Drop.** The interfacial tension between the continuous media (coacervate) and droplet (coexisting dilute phase) was measured from the kinetics of shape evolution of a deformed drop under a zero-shear condition. In this method, a spherical drop of dilute phase was initially deformed to an ellipsoid by a steady shear rate in a parallel plate geometry. Upon cessation of the applied shear rate, the shape retraction of the deformed drop is subsequently described by the time evolution of a symmetric, positive-definite, second rank tensor **S**, the eigenvalues of which represent square semi axes of the ellipsoid. This interface contraction during shape retraction, characterized by the time evolution of **S**, depends on the interfacial tension and hydrodynamic drag. Assuming that the drop volume is preserved, Mo et al. derived the expression for the temporal evolution of eigenvalues of **S** as follows<sup>24</sup>

$$\frac{d\lambda_{i}}{dt} = -\frac{\gamma}{\eta_{c}R_{0}} \frac{40(p+1)}{(2p+3)(19p+16)} \left(\lambda_{i} - \frac{3}{\sum_{i}^{3}\frac{1}{\lambda_{i}}}\right)$$
(2)

Here,  $\lambda_i$  (i = 1, 2, and 3) represents three eigenvalues of S and are given by  $\lambda_1 = l^2$ ,  $\lambda_2 = b^2$ , and  $\lambda_3 = w^2$ ;  $\eta_c$  is the coacervate viscosity; and p is the viscosity ratio =  $\eta_d/\eta_c$ , where  $\eta_d$  is the viscosity of the dilute phase. Using simultaneous equations of  $\frac{d\lambda_1}{dt}$  and  $\frac{d\lambda_2}{dt}$ , we can find

$$S(t) = \lambda_1 - \lambda_2 = S_0 \exp\left(-\frac{t}{\tau}\right)$$
(3)

Here, S(t) measures the shape deformation as a function of time after cessation of shear and  $S_0$  is the initial deformation.  $\tau$  is the characteristic time of shape retraction as defined by

$$\tau = \frac{\eta_c R_0}{\gamma} \frac{(2p+3)(19p+16)}{40(p+1)} \tag{4}$$

These predictions are applicable to the experimental case where the third semiaxis (*w*) perpendicular to the field of view is not known. This model does not consider the effect of viscoelasticity on the retraction time. However, it may be applicable for viscoelastic liquids with stress relaxation time  $\tau_s \ll \tau$ . The model was previously verified by simulation studies<sup>25</sup> and used to measure the interfacial tension of coexisting polymer melts.<sup>16,26</sup>

# RESULTS

**Viscoelasticity and Zero-Shear Viscosity.** At a zerostress condition, the shape-retraction kinetics of a deformed drop depends on the interfacial tension and the viscous drag in the absence of other relaxation mechanisms. As indicated by eq 4, independent measurements of the zero-shear viscosities of the coexisting coacervate ( $\eta_c$ ) and dilute phases ( $\eta_d$ ) are needed. The dependence of the zero-shear viscosity of the KPSS/PDADMAB coacervate on the KBr salt concentration and temperature are shown in Figure 2a,b, respectively. The viscosity ratio  $p = \eta_d/\eta_c$  is of the order of  $10^{-3}$  which suggests the viscous drag of the coacervate is the controlling factor for shape-retraction.



**Figure 2.** Variation of zero-shear viscosity ( $\eta_c$ ) and viscosity ratio  $p = \eta_d/\eta_c$  (Insets on the right) with (a) salt concentration at fixed T = 25 °C and (b) temperature for  $C_s$  in KPSS/PDADMAB. Inset II shows the dependence of G'/G'' measured at frequency  $\omega = 10$  rad/s on  $C_s$  at T = 25 °C. Dashed lines are guide to the eye. While error bars are shown, they may be smaller than the symbols used.

Polyelectrolyte complex coacervates may exhibit viscoelastic liquid or viscoelastic solid behavior. Therefore, the model requirement that the viscous modulus exceeds the elastic modulus, G'' > G' must be evaluated. Further, the applicability of the shape-retraction model requires that the stress relaxation upon cessation of the applied stress can be decoupled from the drop shape-retraction time scale. We approximate this condition by comparing the stress relaxation time ( $\tau_s$ ) as less than the droplet shape relaxation time ( $\tau$ ).

Figure 2a inset II shows that KPSS/PDAMAB coacervates exhibit  $\frac{G'}{G''} < 0.1$  at an applied frequency  $\omega = 10 \text{ rad/s}$  for  $C_s > 1.5 \text{ mol/L}$ . In fact, frequency sweep measurements<sup>23</sup> observe that G'' > G' up to  $\omega = 400 \text{ rad/s}$  for  $C_s$  in the range 1.8 mol/L to 1.5 mol/L, and T in the range 10 to 50 °C. These data show the necessary conditions for the DDR model presented here. Further, the stress relaxation of the coacervate occurs immediately after the deforming stress is withdrawn as



**Figure 3.** Stress relaxation at 5% applied strain which lies in the linear viscoelastic regime in coacervate with salt concentrations  $C_s$  in the range 1.4 to 1.8 mol/L at 20 °C.

 $\tau_{\rm s}$  remains within 1 s for  $C_{\rm s} \geq 1.5$  mol/L and decreases rapidly to 0.07 s at  $C_{\rm s} = 1.8$  mol/L. At  $t > \tau_{\rm s}$ , stress response fluctuates around a plateau value as the torque response from the coacervate reaches instrument resolution. Two conditions are necessary to apply eq 4; the stress relaxation time must be smaller than the droplet retraction time ( $\tau_{\rm s} < \tau$ ) and the elastic modulus must be less than the viscous modulus (G' < G''). These conditions are experimentally observed for  $C_{\rm s} \geq 1.5$  mol/L. Therefore, we restrict application of DDR within the ranges of validity.

A full analysis of the stress relaxation in polyelectrolytes and polyelectrolyte complex coacervates is beyond the scope and deserves a full study. We empirically observe that stress relaxation was separated from the droplet retraction in the late stages for the salt concentration and temperature ranges investigated here. This cannot be a general effect, since lower salt concentration limited the study due to stress relaxation times that far exceeds the time scale of droplet retraction. In order to include this additional effect an appropriate methodology would be needed to interpret the nonexponential retraction time after cessation of shear. Since DDR with a shear cell does not measure stress, data taken from a rheometer with ability to view DDR would be best to directly address the important effects of stress relaxation.

In Situ Drop Formation in the Coacervate Domain. This coacervate system exhibits lower critical solution phase behavior.<sup>22</sup> Micron-sized spherical drops form within the coacervate upon increasing temperature. At the sample preparation temperature  $(T_i)$  associative phase separation leads to dense polymer-rich coacervates and polymer-poor supernatant. After increasing the temperature from  $T_i$  to  $T_{\psi}$  new equilibrium conditions  $(C_p, C_s)$  are established as governed by tie-lines as illustrated by Figure 4. While the kinetics of phase separation was not studied, a nucleation and growth mechanism appear responsible as viewed by the dilute spherical droplets that form within the coacervate domain. These micron-scale droplets remain kinetically trapped in the coacervate matrix for a time that depends on the viscoelasticity and concentration of the coacervate.

The insets to Figure 4 show how the droplets are formed in the coacervate phase for DDR analysis. After increasing the temperature from  $T_i = 15$  °C (Figure 4a) to  $T_f = 25$  °C, polydisperse drops form within the coacervate domain (Figure 4b) for  $C_p = 0.3$  mol/L and  $C_s = 1.8$  mol/L and after



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Figure 4. Schematic of the phase diagram showing the shaded 2-phase region with sample at  $T_i$  phase separates into equilibrium dilute and concentrated coacervate phases. An increase in temperature to  $T_f$  leads to a change in equilibrium concentrations. Inset (a) shows the initially uniform KPSS/PDADMAB coacervate at  $C_s = 1.8$  M at 15 °C. After increasing the temperature to 25 °C, many spherical dilute drops form. The drop density and size changes with time with shearing at different waiting time  $t_w$  at 25 °C. The 100  $\mu$ m scale bar are shown.

equilibration for 10 min. Next, a shear rate of 0.001 s<sup>-1</sup> was applied for a waiting time  $(t_w)$  that causes coalescence of domains (Figure 4c) after  $t_w = 2$  h. Well-separated spherical drops of initial radius  $(R_0)$  in the range 10 to 50  $\mu$ m are obtained after  $t_w = 3$  h (Figure 4d). For DDR the test drop was separated from other drops by at least  $2R_0$  and from plate surface by at least  $4R_0$ . This minimizes effects of interactions with the wall and the interference of other drops. Drops are left unperturbed for a minimum of 30 min before DDR measurements.

Drop Retraction Time Scales with Equilibrium **Radius.** After preparing the required spherical drop, a step strain was applied such that  $2l/R_0 > 3$ . Upon cessation of the applied shear at t = 0, the drop achieves an axisymmetric ellipsoidal shape as time progresses.<sup>27</sup> A time-sequence of images showing the shape retraction of a drop with  $R_0 = 16.7$  $\mu$ m in KPSS/PDADMAB coacervate with  $C_p$  = 0.3 mol/L and  $C_{\rm s}$  = 1.65 mol/L at 25 °C is shown in the insets of Figure 5. Initially, S exhibits nonexponential decay with time. At  $t > t_e =$ 4 s, S follows exponential evolution at low deformation limit as shown in Figure 5. In the inset (e) of Figure 5, the shape parameter S is replotted as a function of rescaled time  $t_r$ , where  $t_r = t - t_e$  with  $t_e$  set to 4 s in a such way that the time evolution of S follows simple exponential decay at  $t > t_e$ . In general,  $t_e$ depends on  $R_0$ , initial deformation and  $\tau_s$  in the absence of any other interaction. Application of a large deformation allows the deformed drop to gain axisymmetric shape and minimizes the effect of stress relaxation in continuous coacervate domain at t $< t_{\rm e}$ . Then at longer times the shape relaxation would be dominated by the interfacial tension and viscous drag at small deformation that leads to an exponential evolution of the drop shape by eq 2.

Since our approach cannot reproduce a specific drop size, it remains challenging to develop a quantitative correlation of  $t_e$ with salt concentration or temperature. However, a qualitative observation was  $t_e$  rapidly decreased from 23 to 2 s between salt concentration of 1.55 to 1.85 mol/L from an approximate initial deformation, (l - b)/(l + b), ~0.4 ± 0.1 and  $R_0 \approx 23 \pm$ 3  $\mu$ m, consistent with the trends of stress relaxation in Figure 3. We tabulated selected data of  $t_e$  in the Supporting Information when the initial droplet size and deformation are similar.



**Figure 5.** Shape-parameter S(t) as a function of retraction time t for a drop of equilibrium radius 16.7  $\mu$ m in KPSS/PDAMAB coacervate at  $C_s = 1.65 \text{ mol/L}$  and  $T = 25 \,^{\circ}\text{C}$ . The solid line is a fit to eq 3 for  $t > t_o$ , which sets a boundary (vertical dashed line) between exponential and nonexponential decay. Insets a-d show the time-evolution of the drop shape, with semi axes l and b, that retracts to the equilibrium radius  $R_0$ . Inset (e) shows evolution of  $S(t_c)$  as a function of  $t_r = t - t_e$ . The solid line is a fit to eq 3. The scale bar represents a length of 40  $\mu$ m.

Figure 6a shows different  $C_{sr}$ , T, and  $R_0$  with an exponential relaxation obtained via shift in the rescaled time  $t_r = t - t_e$ . For each sample, the values of  $t_e$  is defined at the point where S(t) shows transition from nonexponential to exponential decay with time. The characteristic time  $\tau$  for the shape retraction is



**Figure 6.** (a) Time evolution of the normalized shape-parameter *S* as a function of rescaled time  $t_r$  for drops of varying sizes, temperatures, and salt concentrations of coacervate. The solid lines are exponential fits as given by the eq 3. (b) Superposition of the normalized  $S/S_0$  as a function of the rescaled time  $(t_r/\tau)$ . Inset shows linearity of  $\tau$  with  $R_0$  for  $C_s = 1.8 \text{ mol/L}$  at 25 °C.

determined by fitting  $S(t_r)$  to eq 3. After normalization of the ordinate by  $S(t_r = 0)$  and abscissa by  $\tau$  all the shape relaxation curves superimpose in Figure 6b.

eq 4 suggests that  $\tau$  is linearly dependent upon  $R_0$  if the material parameters ( $\eta_c$ ,  $\gamma$ , and p) are not a function of size. These predictions were validated under different  $C_s$  and T conditions (Supporting Information). One example is given by the inset to Figure 6b. A straight line, through the origin of  $\tau$  versus  $R_0$  fit each data set. The variability in  $\tau$  for different  $R_0$  may represent uncontrolled contributions of shear relaxation, presence of nearby drops, and boundary effects.

# DISCUSSION

The range of  $C_s$  and T studied minimize the effects of viscoelastic relaxations of the medium, maintain G'/G'' < 0.1 and  $p \ll 1$ . Additionally, the analysis of shape retraction time is performed after an empirical waiting time beyond which the retraction process showed a single exponential form in the small deformation limit. Therefore, the interfacial tension was determined by eq 4 from the slope of  $\tau$  versus  $R_0$  and independent measurements of  $\eta_c$  and p.

The dilute drops are stable for times longer than the experimental time scale. Lowering the salt concentration leads to a longer stability time and reduced average size. We speculate that this is due to the coupled quench-depth within the two-phase region and the increased viscosity difference with lower salt concentration. This combination during the late stages of phase separation can slow the kinetics of droplet coalescence.

Increasing the Salt Concentration Lowers the Interfacial Tension. Figure 7 shows  $\gamma$  as a function of



**Figure 7.** Interfacial tension as a function of  $C_s$  for KPSS/PDADMAC at 25 °C and  $C_s/C_{s,c}$  in the inset. The regression result to the power law model leads to  $\gamma = (204 \pm 36)(1 - C_s/C_{s,c})^{1.5\pm0.1} \mu$ N/m with fixed  $C_{s,c} = 1.977$  mol/L. Square symbol shows  $C_{s,c}$  measured by turbidimetry. The uncertainties (error bars) are estimated by one standard deviation from the mean of at least 5 independent measurements for each  $C_{s}$ .

added KBr  $C_s$  at 25 °C. The magnitude of  $\gamma$  is on the order of tens of  $\mu$ N/m and illustrates the sensitivity of the DDR method. Increasing  $C_s$  lowers the interfacial tension and is consistent with previous studies. The lower interfacial tension at higher salt concentration is related to the phase diagram on the  $C_s - C_p$  plane. High salt concentration leads to the one-phase region. The interfacial tension should vanish<sup>28</sup> near the transition from two-phase to one-phase solution at the critical KBr salt concentration ( $C_{s,c}$ ). Cross-comparison between different systems will lead to different magnitudes in  $\gamma$ , but

# Macromolecules

the values of  $\gamma$ , will be sensitive to the proximity to the phase boundary.<sup>29</sup>

The phase diagram data of Wang and Schlenoff,<sup>30</sup> reanalyzed by Salehi and Larson,<sup>31</sup> guides the critical polymer concentration in the current system. While the tie lines were not determined in that work, a critical polymer concentration, near the maxima, falls between 0.033 and 0.067 volume fraction ( $\phi_{p,c}$ ). The present data have an initial polymer volume fraction based upon 0.15 mol/L for each polymer that leads to PDADMAB ( $\phi^+ = 0.02$ ) and KPSS ( $\phi^- = 0.017$ ) or total  $\phi_p \approx 0.037$  and comparable to  $\phi_{p,c}$ . Therefore, we discuss the present measurements within this context as  $C_{s,c}$  is approached from below the transition. An interpretation for universal behavior of the interfacial tension should be considered along with the shape of the coexistence curve, temperature dependence of the isothermal osmotic compressibility and correlation length.<sup>32</sup>

In order to compare the present measurements to the available mean field predictions,  $C_{s,c}$  at 25 °C was estimated by turbidity measurements as  $C_{s,c} = 1.977 \text{ mol/L}$  (Supporting Information). Figure 7 inset shows that  $\gamma = \gamma_0(1 - C_s/C_{s,c})^{\mu}$  with  $\mu = 1.5 \pm 0.1$  and  $\gamma_0 = 204 \pm 36 \,\mu\text{N/m}$ . This result agrees with predictions by Qin et al.<sup>5</sup> and Lytle et al.<sup>9</sup> and systematic CP-AFM measurements by Spruijt et al.<sup>6</sup> The present data, however, are closer to the critical polymer concentration and the scale of  $C_s/C_{s,c}$  between 0.75 to 0.94, whereas the interpretation by Qin shows the scaling to hold across available data between  $C_s/C_{s,c}$  0.1 to 0.8. These measurements illustrate the mean field scaling extends closer to the apparent critical concentration.

The calculation of the interfacial tension considers the Voorn-Overbeek model that includes the entropy of mixing of polymer, salt, and water and Debye–Hückel electrostatic correlation free energy. A contribution from short-range van der Waals interactions phenomenologically encompassed by the enthalpy of mixing via the Flory–Huggins parameter was not considered. The success of the Qin et al. theory suggests that charge correlations out-weigh such Flory–Huggins terms. This may not be surprising, but as guided by neutral polymer binary blends, the phase stability and interfacial widths are intimately determined by the interaction parameter. Therefore, it is natural to study the effect of temperature at fixed  $C_s$ .

Increasing Temperature Increases the Interfacial Tension. The equilibrium properties of polyelectrolyte and polyelectrolyte complex coacervate systems are far less understood than neutral polymer solutions and blends. In symmetric immiscible neutral polymer blends, the interfacial tension, may be described by the Helfand-Tagami self-consistent field theory,  $\gamma = \sqrt{\chi/6}\rho_0 bk_B T$ , far from the critical point, where  $\rho_0$  is the number-average monomer density and the remaining variables as defined previously.

Figure 8 shows  $\gamma$  as a function of temperature at  $C_{\rm s} = 1.6$  and 1.8 mol/L. The increase in  $\gamma$  with T shows that higher temperature leads to an increased cohesive energy between the supernatant and coacervate phases. An increasing quench depth into the two-phase region increases the interfacial tension. This was observed by immiscible neutral polymer blends by Anastasiadis et al. and Vinckier et al.<sup>33</sup> for systems that exhibits upper critical and lower critical solution temperatures, respectively.

The effect of temperature on the phase diagram and interfacial tension typically provides a manner to evaluate the



**Figure 8.** Interfacial tension versus *T* for KPSS/PDADMAB at  $C_s$ = 1.6 mol/L ( $\blacktriangle$ ) and 1.8 mol/L ( $\blacksquare$ ). The uncertainties (error bar) shown are estimated by one standard deviation from the mean of at least 5 measurements for each *T*. Linear fit to mean field prediction shown as the solid line.

interaction parameter in neutral polymer blends. However, such a transparent theory is not yet available for polyelectrolyte coacervates. In the context of analytical and continuum models, this is partly due to several temperature-dependent variables including effective Flory-Huggins interaction parameter, Bjerrum length, Debye-Screening length, and binding equilibrium constants between ions and polyions. However, mean field theory expects the interfacial tension between the two phases to scale as  $\gamma = \gamma_0 |1 - T/T_c|^{\mu}$ , with the classical exponent  $\mu = 3/2$  and 1.26 for the Ising universality class.<sup>32</sup> Since the data in Figure 8a are far from the critical temperature, we apply a mean field plot of  $\gamma^{2/3}$  versus T to estimate the mean field critical temperature,  $T_{c,mf} = 254 \pm 8$  K, and amplitude,  $\gamma_{\rm o}$  = 260 ± 80  $\mu$ N/m, for the C<sub>s</sub> = 1.6 mol/L data in Figure 8b. The sample with  $C_s = 1.8 \text{ mol/L}$  have too few data points for this analysis. The transition from two-phase to one-phase was not observed down to ~273 K. An independent measurement of the transition to the one-phase region with vanishing interfacial tension was preceded by sample freezing. Typical coacervate solutions and aqueous salt solutions froze at -19 °C. This limited the test of the extrapolated mean field critical temperature that was possible for the salt concentration dependent study.

#### CONCLUSIONS

Dispersed droplets of dilute phase are generated within the coacervate by temperature changes within the two-phase region of the LCST phase diagram. This droplet formation occurs due to the equilibration to new tie lines by changing temperature. Droplets with appropriate size and stability persist for hours and enable DDR analysis. The DDR approach has a simple sample loading, direct contact between equilibrating coacervate and supernatant phases, no gravityinduced flow during measurements and less sensitivity to surface contamination. While the physical origin of the droplet stability and size deserves further study, the DDR approach provides sensitivity from mN/m to  $\mu$ N/m scale after independent viscosity measurements of the dilute and coacervate phases. The measurements at the critical polymer concentration find  $\gamma \approx (1 - C_s/C_{s,c})^{\mu}$ , with  $\mu = 1.5 \pm 0.1$  and  $C_{\rm s,c}$  = 1.977 mol/L. The scaling index  $\mu$  agrees with the theoretical prediction of 3/2 and implies that charge correlation effects outweighs the contributions by the Flory-Huggins interaction parameter. The interfacial tension increases with increasing temperature consistent with LCST behavior with scaling associated with classical exponents.

However, data closer to the critical temperature are desirable to properly evaluate the scaling index.

## ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.9b01491.

Stability of unperturbed droplets, estimate of critical salt concentration, shear viscosity flow profiles, shape relaxation time dependence on initial droplet radius, tables of interfacial tension and  $t_{\rm e}$  data (PDF)

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# Notes

The authors declare no competing financial interest.

# ACKNOWLEDGMENTS

This work was supported by the National Institute of Standards and Technology (NIST) Materials Genome Initiative. We are grateful to Dr. Kalman Migler (NIST) for access to the shear cell and microscope facilities used in this study and discussions with Dr. Debra Audus (NIST). Official contribution of the National Institute of Standards and Technology; not subject to copyright in the United States. Certain commercial equipment and materials are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation by the National Institute of Standards and Technology nor does it imply that the material or equipment identified is necessarily the best available for this purpose.

# SYMBOLS

 $\gamma$ , interfacial tension

 $C_{s}$ , added salt concentration

 $C_{s,\sigma}$  critical salt concentration for coacervate to uniform solution transition

- $C_{\rm p}$ , polymer concentration
- $\nu$ , reference volume parameter
- $k_{\rm B}$ , Boltzmann's constant
- $\tilde{N}$ , degree of polymerization
- *a*, statistical segment length of polymer under theta condition
- $T_{c}$ , critical temperature
- $\chi$ , Flory–Huggins interaction parameter
- *l*, length of semimajor axis of an ellipsoid
- b, length of semiminor axis of an ellipsoid
- $t_{wl}$  equilibration time to achieve well-separated droplets
- S, second rank tensor describing shape of a deformed ellipsoid
- $\lambda_{i}$ , eigenvalues of S
- $\eta_c$ , zero-shear viscosity of coacervate
- $\eta_{d}$ , zero-shear viscosity of coexisting dilute phase
- p, viscosity ratio  $\eta_{\rm d}/\eta_{\rm c}$
- $R_0$ , equilibrium radius of a drop
- $\tau$ , characteristic time for drop shape retraction

 $\tau_{\rm s}\!\!\!,$  stress relaxation time in coacervate

G', elastic modulus

G'', viscous modulus

 $\omega$ , angular frequency of applied oscillatory strain

 $T_{i}$ , initial equilibration temperature

 $T_{\rm fr}$  final equilibration temperature

 $t_{e}$  time at which **S** starts exhibiting simple exponential decay  $t_{r}$  rescaled time duration for **S** exhibiting simple exponential decay

 $\phi_{\rm p}$ , polymer volume fraction

 $\phi_{\rm p,c}$  polymer volume fraction at critical point

 $\rho_0$ , number-average monomer density

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