Mesophase Separation in Polyelectrolyte-Mixed Micelle Coacervates

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Mesophase separation has been identified in a polycation/anionic−nonionic mixed micelle system formed by the coacervation of poly(diallyldimethylammoniumchloride)/sodium dodecylsulfate-Triton X-100 in 0.40 M NaCl. The resultant dense, optically clear fluid was studied by turbidity, dynamic light scattering (DLS), and rheology. The presence of two diffusion modes in DLS points to microscopic heterogeneity: coexistence of micelle-rich (dense) domains with micelle-poor (dilute) domains. With an increase in temperature above 20 °C, the turbidity rises rapidly along with the intensity of the slow mode. The concomitant decrease in the diffusivity of the slow mode signals an increase in the effective viscosity of the dense domain. With further increase in temperature, dramatic shear thinning is observed, and finally, macroscopic phase separation can be identified by centrifugation. At a temperature near that for quiescent phase separation, we observe shear-induced phase separation. We propose a mechanism to explain the connection between temperature- and shear-induced mesophase separation.

Introduction

Complex coacervation is a spontaneous liquid/liquid phase separation that frequently accompanies the mixing of two oppositely charged polyelectrolytes (PEs). The more dense phase is concentrated in macroions, and this coacervate is in equilibrium with the relatively dilute macroions in the continuous phase or supernatant.[1] Similar phase separation can occur between polyelectrolytes and oppositely charged colloids, such as micelles,[2,3] proteins,[4] and even dendrimers.[5] Polyelectrolyte−polyelectrolyte and polyelectrolyte−colloid coacervation have found applications in cosmetic formulations[6] and in pharmaceutical microencapsulation.[7,8] These applications and some fascinating biological implications[9] have recently motivated studies of the mechanism of coacervation and the factors that influence it, although attention to this phenomenon is only gradually attaining the level of interest displayed by researchers 50 years ago[9−14] with the result that many coacervating systems have not been explored with modern methods.

While the early studies considered in detail the range of conditions under which coacervates form, there are few reports on the internal structure of coacervates, partly because of the typically enormous polydispersity of the macromolecular components of the coacervates, leading to heterogeneity on many length scales. Reduction of the polydispersity by using polyelectrolytes of low M_w/M_n and purified globular protein leads to optically clear, viscous fluids amenable to many techniques. Bohidar et al.[15] explored the nature of coacervates of the protein bovine serum albumin (BSA) and the polycation poly(diallyldimethylammonium chloride) (PDADMAC) using dynamic light scattering (DLS) and rheology. Two models were put forward: (I) macroion-rich domains dispersed in a continuum of macroion-poor domains near the percolation limit, and (II) a semidilute solution of PDADMAC chains with interchain friction modulated by transient BSA−PDADMAC association. Such results may suggest that no single model based on a single type of frozen domain or heterogeneity can encompass the full set of properties. They also indicate that the viscosity of coacervates, and presumably their microstructures, are highly responsive to the strength of the protein−PE interaction, which for protein−polycation systems decreases with added salt or increases with increasing pH. In the protein−polyanion system of whey protein and gum Arabic,[16] a maximum viscosity was found at pH 4.0, at which point the protein mixture is positive and the complex polyanion weakly negative. Strong electrostatic interaction in that system also produces high coacervate viscosity and strong shear thinning above a critical shear rate.

Studies of colloid−PE coacervate structure and properties have been virtually confined to protein−PE systems. But replacement of protein by mixed micelles yields a much simpler coacervating system in that the colloidal particle has a unidirectional, pH-independent, and isotropic surface charge that can be quantitatively assessed.[17] Piculell et al.[18] found that aqueous systems containing sodium polyacrylate (NaPA) and the surfactant cetyltrimethylammonium bromide (CTABr) can separate into a concentrated phase and a dilute phase and described this as an ion-exchange process, wherein polyacrylate ions displace micellar

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bromide counterions with a gain in entropy that drives the reaction. We examined the phase behavior of a polycation−anionic/nonionic mixed micelle system, poly(diallyldimethylammonium chloride)/sodium dodecylsulfate-Triton X-100, over a wide range of surfactant compositions, ionic strengths, and polycation molecular weights using turbidimetry, DLS, and electrophoresis.[2,3] The interrelationship among the ionic strength, surfactant/polyelectrolyte (PE) stoichiometry, PE molecular weight, and micellar ionic surfactant mole fraction at critical conditions for coacervation were expressed as phase boundaries, with an accompanying molecular model. More recently,[19] these studies were expanded to include complex effects of temperature since these systems generally become biphasic upon heating through either liquid−liquid or liquid−solid separation. We followed the temperature-induced phase transition for the PDADMAC−SDS/TX-100 system by turbidimetry. While this transition appeared rather broad, spanning 5−10 °C, it decreased to 1−2 °C when TX-100 was replaced by $C_{12}E_8$ and then to less than 0.3 °C when the commercial $C_{12}E_8$ was replaced by a monodisperse form of the same surfactant. This shows the first-order nature of this phase transition, which would be infinitely sharp if polydispersity could be eliminated. Most significantly, preliminary observations of the concentrated liquid phase isolated by centrifugation (i.e., the coacervate) disclosed a number of interesting optical and rheological properties. Since control of phase state could be important in many applications, we now further explore the behavior of the coacervate phase using turbidity, DLS, and rheology. The results of DLS of the coacervate point to microscopic heterogeneity, highly sensitive to temperature. Temperature-dependent rheological measurements suggest that transitions similar to those induced by temperature might also be induced by shear and thus connects this work to the extensive body of literature on shear-induced phase separation (SIP) of wormlike micelles[20−26] and polymers.[27−29] This work, however, is the first report of SIP for a polymer−micelle complex.

Experimental Section

Materials. Poly(diallyldimethylammonium chloride) (PDADMAC) was prepared by free-radical aqueous polymerization of diallylmethylammonium chloride.[30] The weight-average molecular weight (M_w) of the purified lyophilized polymer was determined by light scattering as 2.19×10^5, but the sample will be referred to according to number average (from membrane osmometry): $M_n = 1.41 \times 10^5$. Triton X-100 (TX100), sodium dodecyl sulfate (SDS, purity > 99%), and NaCl were purchased from Fisher. All were used without further purification. Milli-Q water was used in all experiments.

Coacervate Preparation. SDS (60 mM) and PDADMAC−TX100 mixed solution (PDADMAC, $C_p = 3$ g/L; TX100, 20 mM) were prepared separately in 0.4 M NaCl. Then, SDS was added to the mixed PDADMAC−TX100 solution gradually to attain a mole fraction of SDS (Y = [SDS]/{[SDS] + [TX100]}) = 0.38. The resultant suspensions were stirred for 15 min. The strongly turbid samples were centrifuged for at least 2 h at 3500 rpm at 22 °C, to yield an upper dilute phase and lower dense phase ("coacervate") (both optically clear). (The difference between this finding and the turbidity observed on subsequent heating of the coacervates might be attributable to a hysteresis behavior previously observed[19]). The dense phase, with a characteristic volume yield of 8% was separated for further examination.

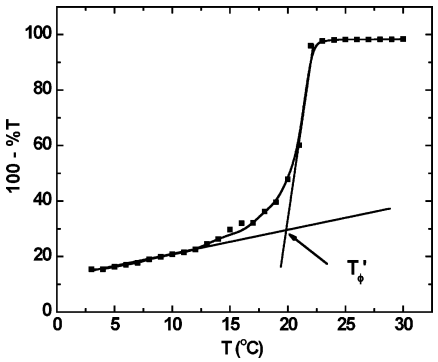

Figure 1. Turbidity as a function of temperature for PDADMAC/TX100−SDS coacervate, showing operational definition of T_Φ'.

Turbidimetric Measurement. Turbidity, reported as 100 − %T (±0.2%T), was measured using a Brinkmann PC 800 colorimeter ($\lambda = 420$ nm) equipped with a 2.0 cm path length fiber-optics probe. Turbidity values were recorded when the meter response was constant for 2 min. Duplicate measurement gave reproducible results.

Dynamic Light Scattering (DLS). DLS measurements were carried out on the coacervate at scattering angle 90° at temperatures from 15 to 30 °C (±0.5 °C) with an ALV instrument equipped with a model 5000 Multi-tau digital correlator, and employing a 300 mW Ar-Ion laser source operating at 514 nm. The correlation functions of the scattering data were analyzed via the method of regularization (CONTIN)[31] and then used to determine the distribution of the diffusion coefficients (D_{app}).

Rheology. Rheological measurements were performed on a stress-controlled rheometer (TA instrument, AR2000) fitted with Couette geometry. Samples were slowly loaded into the double concentric cylinders, and 30 min was allowed for thermal equilibration. From stress sweep tests, the linear viscoelastic region was determined to extend at least up to a strain of 0.8%. Frequency sweep experiments were performed at a low amplitude of strain (0.1%), covering the range 0.1−628.3 rad/s. At lower frequencies, the time required for measurements was long and difficulties arose due to evaporation or condensation. Steady sweep experiments were measured at increasing shear rate from 1 to 200 s^{-1}. Characterization of sample was completed at different temperatures (in the range 8−30 °C).

Results

Temperature-Induced Phase Separation of Coacervate−Turbidity. Monitoring the turbidity during phase separation is a convenient technique to study phase separation. The dependence of turbidity on temperature for PDADMAC/TX100−SDS coacervate is shown in Figure 1. The curve closely resembles ones used to describe the initial formation of coacervates from dilute solution,[19] for which we have used a similar operational definition of the phase-separation temperature, T_Φ. Here, for the coacervate itself, $T_\Phi' = 20.0 \pm 0.5$ °C is assumed to correspond to the onset of the formation of aggregates of sufficient size to scatter visible light. The flattening of the curve at $T > 22$ °C only signifies that transmittance is too low to provide a detector response: morphological changes clearly continue to take place. Obviously, heterogeneities on a micrometer scale are formed by increasing temperature. Phase separation at $T > T_\Phi'$ is demon-

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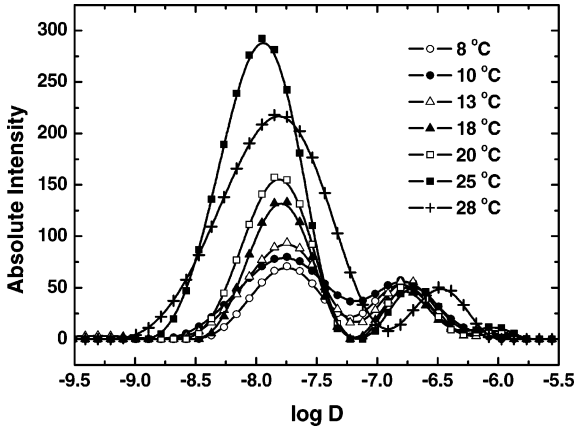

Figure 2. Absolute intensity vs log D for PDADMAC/TX100−SDS coacervate as a function of temperature. Result at 30 °C not shown for clarity, see text.

strated by the formation of two phases upon centrifugation. It should be pointed out that the appearance of a critical temperature for coacervate itself (T_Φ') does not arise directly from transitions of the surfactant. The cloud point of the surfactant system at $Y = 0.38$ is above 65 °C, which is much higher than the value of T_Φ'. Regarding the Krafft point, the polyelectrolyte-free system freezes at −3 °C, while the coacervate freezes at −7 °C. Finally, coacervates at all temperatures are far more viscous than polyelectrolyte-free solutions of identical surfactant concentration, indicating that the structure of the coacervate is uniquely different from that of the micellar solution.

Dynamic Light Scattering (DLS). Because the phase separation of coacervate is temperature-induced, changes in the coacervate with temperature could be reflected in alterations of diffusive modes. Measurements carried out at multiple angles for coacervates of the same polyelectrolyte with protein instead of micelle support the interpretation of DLS modes in this range of Γ as colloidal particle diffusivities.[15] Figure 2 shows the distribution of DLS apparent diffusion coefficients (D_{app}) at temperatures up to and beyond T_Φ'. Since the scattering intensity of the polymer is so much weaker than that of the micelle, the presence of consistently well-resolved diffusion modes points to different spatial and temporal variations in micelle concentration, consistent with microscopic heterogeneity of the coacervates even well below T_Φ'. Since the apparent diffusion coefficient for the fast mode ($1.5-4.5 \times 10^{-7}$ cm^2•s^{-1}) is very close to that for the mixed micelles alone in PE-free 0.4 M NaCl ($D = 2.5 \times 10^{-7}$ cm^2•s^{-1}), we attribute the fast mode to micelles in the coacervate whose motions are almost unconstrained in a fluid continuum. Similarly, the slow mode should correspond to micelles whose diffusion is strongly restrained by polyelectrolyte. It is entirely reasonable to correlate these fast and slow modes with the dilute and dense domains previous observed by Cryo-TEM[32] for an identical coacervate, shown in Figure 3. Like DLS, Cryo-TEM primarily reports on micelle domains, but electroneutrality considerations would indicate that micelle-rich regions are stabilized by high polyelectrolyte segment density. While the exact peak widths and shapes for each component in a multimodal distribution are subject to assumptions built into the fitting algorithms, the mean positions and relative intensities of resolved modes can be reasonably robust, as demonstrated for protein−polyelectrolyte coacervates.[15] These results are shown in Figure 4. The apparent diffusion coefficient of the fast mode shifts to larger diffusivities at $T > T_\Phi'$, indicating that micelle diffusion in the dilute domains becomes less constrained at higher temperature. However, at 25 °C, the slow mode diffusion coefficient goes through a minimum (to be discussed below) while its intensity (both absolute and as % of total scattering) goes through a maximum, in contrast to the intensity of the fast diffusion coefficient which does not depend on temperature. Results at 30 °C (not shown in Figure 2 for clarity of presentation) indicate continuation of the trend at high temperature: further decrease in slow mode intensity, no change in fast mode intensity but increase in D_{fast}. The appearance of large variations in the D_{app}, together with the change in the absolute scattering intensities of slow mode, suggests dramatic changes in aggregation state induced by temperature.

Rheology. The apparent coexistence of dense domains and dilute domains leads to the question of their arrangement, in that either of those two could be the continuous phase in which the other is embedded. Although the sample preparation temperature was not precisely determined in ref 32, it is certain that the continuous dense domain seen in Figure 3 refers to a coacervate only a few degrees above T_Φ', leaving in question the interconnectedness of coacervate at $T > 25$ °C. Rheology provides the best insight into this question, since viscoelastic properties reflect the connectivity or percolation of domains in heterogeneous materials. To characterize the mechanical properties of coacervates, the dynamic moduli G' (elastic) and G'' (viscous) were measured with frequency sweep experiments with temperature varying from 8 to 30 °C at a constant strain of 0.1%, which was determined to be in the linear regime. In frequency sweep experiments, the values of the viscous modulus G'' were always higher than the values of the elastic modulus G', indicating the highly viscous character of the coacervate. Figure 5 shows the effect of temperature on the frequency-dependent viscous modulus. This viscous character may indicate that a suspending fluid dominates the mechanical properties. The value of G'' shows a gradual decrease between 8 and 25 °C and a marked decrease at higher temperature.

Coacervate viscosity (η) was determined by carrying out steady-state experiments. The dependence of viscosity on shear rate over the temperature range used for DLS is plotted in Figure 6. When $T < T_\Phi'$, the flow curves are characterized by a slightly shear thinning behavior. The influence of temperature on the zero shear viscosity (η_o) follows the turbidity plot of Figure 1: insensitive to temperature at $T < 14$ °C; changing more strongly in the range 15 °C $< T <$ 20 °C; and then dropping dramatically at higher temperature (where the turbidity rises strongly, signaling entry into the two-phase region), at which point the shear thinning becomes remarkable.

Discussion

One may assume that the coacervate studied here formed at 22 °C from soluble (mulitpolymer) aggregates close to electoneutrality.[2,3] Such soluble aggregates have been observed both by Cryo-TEM[32] and DLS[2] as 45−100 nm diameter objects, too large to contain only a single PE macroion. At incipient coacervation, the coalescence of these aggregates can be promoted by polarizability, in which transient polycation-segment-rich regions in one interpolymer complex interact with micelle-sulfate-rich domains of another, the end result being more efficient ion-pairing of polycation residues and micelles, as the peripheries of intrapolymer soluble complexes are eliminated. A consequence of this is the release of small ions, providing an entropic driving force for higher-order aggregation and coacervation.[19] Elemental analyses of such coacervates suggest they might contain excess N^+ (relative to SO_3^-) neutralized by Cl^-.[33] The counterions

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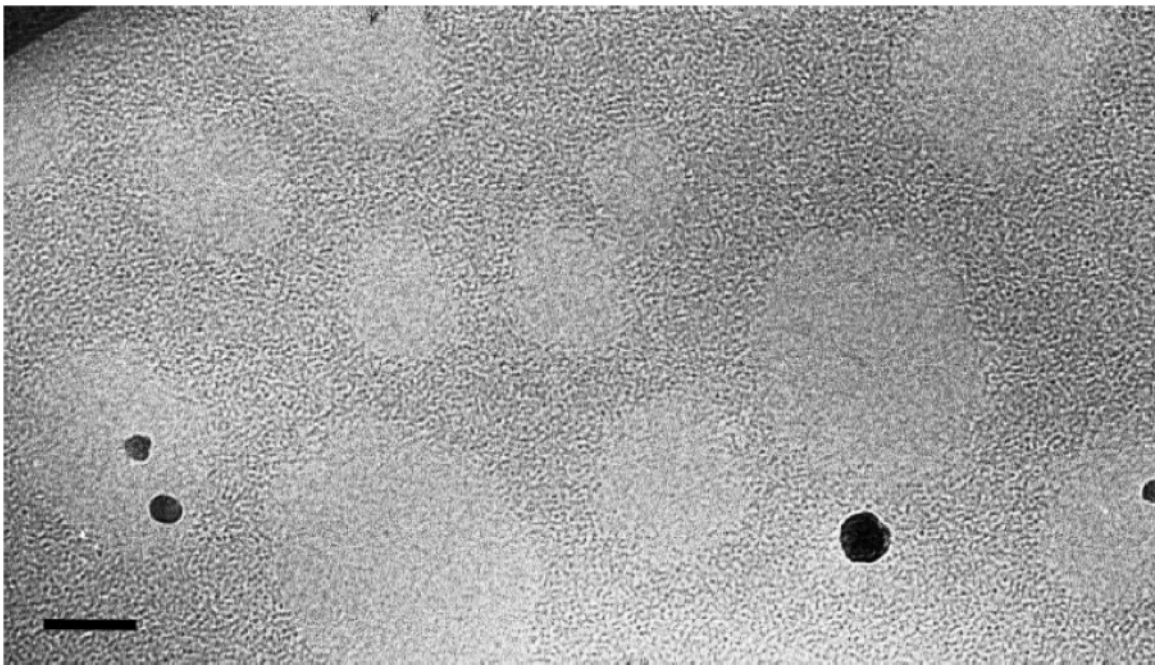

Figure 3. Cryo-TEM image of PDADMAC/TX100-SDS coacervate. ($Y = 0.37$, $C_p = 2$ g/L) (from ref 32). Bar = 100 nm. Sample preparation temperature 25 ± 2 °C.

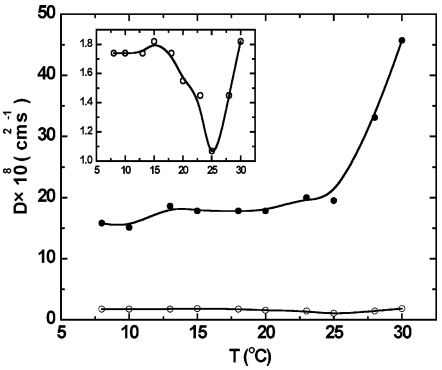

Figure 4. Dependence of diffusion coefficients on temperature. (●) fast mode; (○) slow mode. Inset: expansion of D_{app} for the slow mode.

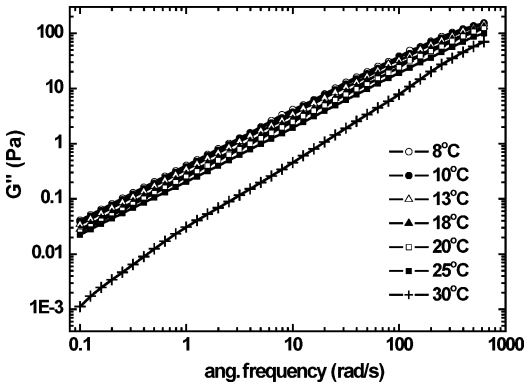

Figure 5. Frequency-dependent viscous moduli (G'') of PDADMAC/TX100−SDS coacervate constant strain of 0.1%, as a function of temperature.

expelled in this process form micelle-depleted pools within the coacervates, their significant volume fraction, φ_1, accounting in part for the high water content (95%) of the coacervates, and for the fast diffusion mode observed in DLS, almost equal to those of polymer-free micelles in dilute salt. The proposal that counterion expulsion is the entropic driving force for coacervation is also consistent with the apparent absence of an enthalpy for coacervate formation[34] and more recent differential scanning calorimetry (not shown) in which the change in enthalpy with temperature is almost zero.

As the temperature is increased beyond 22 °C, the turbidity rises rapidly (Figure 1) along with an increase in the intensity of the DLS slow mode and a decrease in its diffusivity (Figure 2). These results suggest an increase in the effective viscosity of the dense domain (slow mode region) corresponding to its desolvation, and thus to an increase in contrast of the two domains (see Figure 2, for 25 °C). At the same time, neither the amplitude nor the diffusivity of the fast mode shows any change, signifying a retention of dilute domain structure. Further increase in temperature, e.g., from 25 to 30 °C, gives a clear indication of phase separation through the large visual turbidity (arising from greater contrast as the dense mode becomes more dense) and most directly from the fact that centrifugation of the coacervate at 28 °C gives a new coacervate and supernatant.[19] The large increase in fast mode diffusivity at these temperatures suggests expansion of the volume available to "free micelles" φ_1 in dilute domains. Phase separation is not infinitely sharp but progresses continuously above 25 °C. At some temperature in this region, it seems likely that desolvation of the dense domains makes it no longer possible for the dense domains to be the continuous phase as in Figure 3. This may offer an explanation for the minimum in the slow mode at 25 °C seen in Figure 4. Desolvation of dense domains with an increase in effective viscosities may be the primary result of an increase in temperature in the range 16−25 °C. However, upon further dense domain contraction, those regions become small and discontinuous, with concomitant increase in the boundaries between dilute and dense domains. The contribution to the slow mode signal of rapid exchange of micelles at these interfaces might lead to the increase in D_{slow} above 25 °C. An increase in domain interfaces with refractive indices intermediate between those of dense and dilute domains

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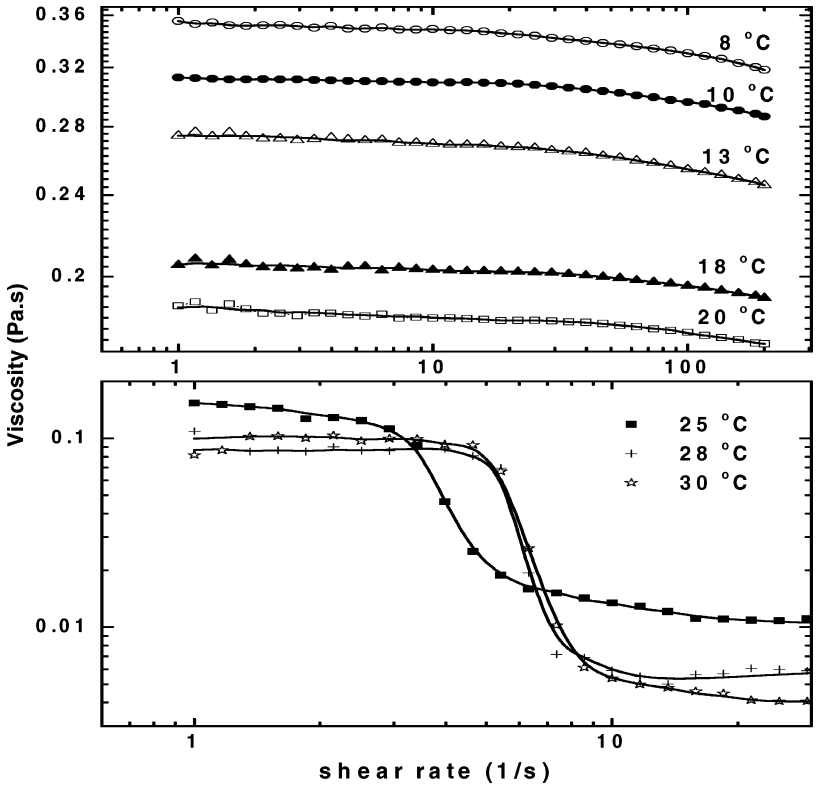

Figure 6. Viscosity of PDADMAC/TX100−SDS coacervate as a function of shear rate at different temperatures.

could also account for the maximum in the intensity of D_{slow} at 25 °C. Such speculations about changes in micromorphology clearly need to be supported by additional imaging as a function of temperature.

The decrease in turbidity when the sample is cooled below the temperature of coacervate preparation (from 22 to 14 °C) is more gradual, as is the decrease in slow mode scattering intensity. This could arise from either a diminution in the contrast between the two domains related to structural changes or a reduction in the number of micelles in dense domains. Since the diffusivity of both modes is essentially constant in this temperature range, it seems more reasonable to suggest that the change in intensity is due to a migration of micelles into the dilute domains upon decrease in temperature in this range with a reduction in dense domain volume fraction, φ_2.

Below 14 °C the decrease in turbidity is essentially linear, and the only change in DLS is the decrease in the intensity of the slow mode. In a manner opposite to the processes described above for heating, counterions are regained by dense domains, which then become more solvated and less dense. As the their volume fraction, φ_2, grows, they become more interconnected and bulk viscosities increase slightly, reflecting the compensating effects of more interconnected but less viscous dense domains. Only small changes in total scattering intensity and turbidity are observed in this region because changes in overlap among soluble aggregates in the coacervate are modest. For a similar reason, the change in D_{slow} is also small.

The effect of temperature on G'' and viscosity is difficult to reconcile with a model that accounts for the scattering and turbidity results. In particular, the phase separation that must be taking place on different length scales at temperature above 22 °C does not appear to produce any dramatic effects and the zero-shear viscosity (Figure 6) decreases almost linearly with temperature. A desolvation of the dense continuous domains seen in Figure 3 with increasing temperature should increase viscosity, but at the same time contraction of those domains (decrease in φ_2) decreases their connectivity, so that the dilute domain begins to dominate rheological properties. The decrease in viscosity with increasing temperature suggests the importance of the second effect which could be augmented by a reduction in the viscosity of the dilute domain if the concentration of micelles therein drops as φ_1 increases. The most prominent effect of temperature is on shear thinning which emerges dramatically at $T > 25$ °C (Figure 6). It is possible that the viscosity of the continuous phase is so low at $T < 25$ °C that the system deforms readily under shear, perhaps with elongation of the dilute phase droplets.[35] Only when the dense phase simultaneously contracts and disconnects do we see a significant shear effect.

The sensitivity of coacervate to simple gravitational shear flow is manifested in the direct visualization of shear gradients as coexisting regions of turbidity whose presence also attests to the viscosity of the system (Figure 7). The coacervate flows very slowly at first, but as it enters the narrow tip of the pipet, exhibits a dramatic increase in flow rate, like the shear thinning behavior observed by rheology at $T > 20$ °C. Turbid zones are then seen along the shear gradients. This behavior is only seen in proximity to the temperature T_Φ', as obtained in Figure 1.

A fundamental question is the relationship among the transitions observed by the three techniques of turbidity, DLS, and rheology, closely related to the question of the relationship between temperature- and shear-induced phase separation. Turbidity, a blunt instrument, indicates small and gradual change below 15 °C, and much more rapid change above 20 °C, with a transitional intermediate region. With regard to DLS, a transition appears to occur in the vicinity of 25 °C, where the diffusivity of the fast mode begins to rise rapidly, while the diffusivity of the slow mode attains a minimum. In concert with the Cryo-TEM image, this can be best explained by the expulsion of solvent from dense domains into dilute domains, i.e., progressive phase separation. The fact that the amplitude of the fast mode does not

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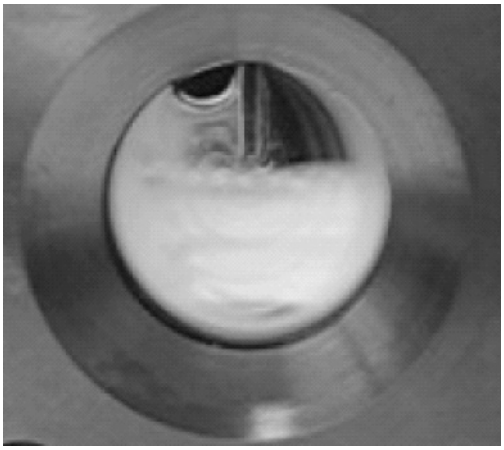

Figure 7. Appearance of shear-induced phases separating along shear lines under gravitational flow. $T = 21 \pm 1$ °C.

change suggests that micelles are not being expelled into the dilute domains upon heating. There is no direct information on the likelihood of PE expulsion into dilute domains, but recent SANS studies of a PE−protein system indicated expulsion of PE and PE counterions upon phase separation of a PE−protein complex.[36]

The effect of the temperature on the shear-dependent viscosity in Figure 6 follows the turbidity in Figure 1 in the sense that both tend to change somewhat linearly with temperature below 15 °C, display a dramatic change between 20 and 25 °C, and essentially exhibit no change above 25 °C. This suggests that the phenomena being observed by turbidity and by viscosity are closely related, the most likely explanation being that susceptibility to shear-induced phase separation is maximal at temperatures close to the temperature of quiescent thermally induced phase separation. Thus, the similarity in the temperature course of the three techniques indicates that they are probing closely related phenomena and encourage us to consider the molecular basis for this relationship.

Both temperature- and shear-induced phase separation arise because both an increase in temperature and an increase in shear enhance micelle−PE binding. The effect of temperature is through the entropy of small ion release concomitant with the ion-pairing of micelle sulfates and PE cationic residues. The effect of shear is to align PE chains and ellipsoidal micelles, as indicated schematically in Figure 8. Under shear, the chains of polyelectrolyte may elongate with respect to each other, replacing intrapolyelectrolyte-micelle interactions with interpolyelectrolyte−micelle interactions, i.e., the association of micelles with more than one PE chain. This ordering can maximize micelle−polyelectrolyte contacts, facilitating the expulsion of small ions. In both cases, ion-expulsion leads to desolvation due to osmotic effects. Consequently, the dense domain becomes more compact, and dilute domains more dilute. When φ_2/φ_1 falls below a critical value, dense domains can no longer be continuous and the viscosity drops. This shear-induced phase separation is strongly reminiscent of shear-banding in systems of wormlike micelles,[37,38]

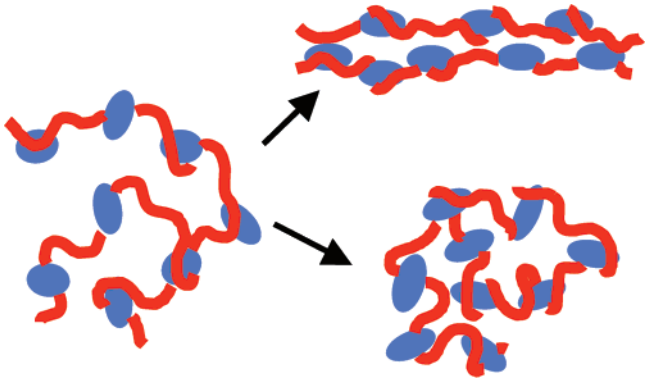

Figure 8. Schematic representation of shear- and temperature-induced phase separation for PDADMAC/TX100−SDS coacervate. Both processes involve loss of counterions arising from increased polyelectrolyte−micelle interactions, but by an intercomplex vs intracomplex mechanism for the former.

also caused by shear-induced structure.[39−44] Ionic micelles form wormlike dimensions as the repulsive forces among the head group are relieved by binding small ions, a role that may be played by the polyelectrolyte in the present case. Optical measurements as a function of both shear and temperature are currently underway to explore this potentially novel version shear-banding and to allow us to place this phenomenon in the broader context of shear-banding theory.[45]

Conclusions

Turbidimetry, DLS, and rheology have been used to elucidate the phase behavior of a polycation/mixed micelle coacervate. DLS indicates mesophase separation within the coacervates into dense and dilute domains, with remarkably high micelle diffusivity within the latter. Increasing the temperature increases the contrast of the two domains, eventually leading to phase separation. A temperature-induced transition from dense-domain-continuous mesophase structure to dilute-domain-continuous structure en route to phase separation appears likely. Similar transitions appear to be accomplished by shear at fixed temperature.

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