

# Study of Interaction between Cetyltrimethylammonium Bromide and Poly(acrylic acid) by Rheological Measurements

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Interaction between the cationic surfactant cetyltrimethylammonium bromide (CTAB) and the anionic polyelectrolyte poly(acrylic acid) (PAA), having molecular weight by viscosity of 750 kDa, is investigated by rheological measurements. Upon addition of 1 or 0.5 wt % CTAB to the semidilute PAA solutions with concentration ranging from 0.04 to 0.1 wt %, the insoluble complex salts (the surfactant ion + the polyion) precipitate. In contrast, with addition of 2 or 3 wt % CTAB to the aforementioned PAA solutions, evidence of transition from shear-thinning to nearly Newtonian behavior is observed. The origin of this observation appears to lie in the fact of formation of more compact PAA/CTAB aggregates, because the radii of gyration,  $R_g$ , of PAA coils have been reduced by about 60% with addition of 2 wt % CTAB by static light-scattering measurements. Furthermore, pH measurements also reveal the possible formation of “ion pairs” between PAA and CTAB as the pH values of the PAA solutions decrease with addition of CTAB. That is, the pH values of the solutions containing PAA and CTAB together are less than those of neat PAA or CTAB solutions. This implies that addition of CTAB leads to more acids dissociated from the acrylic acid monomers on the poly(acrylic acid) macromolecules.

## 1. Introduction

The interaction between surfactants and polymers in aqueous colloidal systems has been the focus of intense fundamental and applied research.<sup>1–4</sup> Attention to this topic mainly arises from their wide-ranging applications. For example, the surfactant–polymer systems can often be found conjointly in personal-care products and detergents.<sup>1,5</sup> Addition of polymers could effectively reduce the critical micelle concentration (cmc) of surfactants and, thus, increase the detergency.

In contrast, surfactants and polymers are used in many applications mainly for their individual function rather than for those arising out of their mutual interactions.<sup>1</sup> For instance, surfactants are used for emulsifying and solubilizing the immiscible substances, while polymers are usually employed to control the rheology of solutions and suspensions. When present together, polymers and surfactants can interact with each other and lead to unwanted and undesirable properties, such as the formation of precipitates of surfactant–polymer complexes<sup>1,6–8</sup> and alteration of the rheological properties to different extents. Addition of surfactants with concentrations near their cmc could significantly increase the viscosity of the surfactant–polymer systems.<sup>1,9–12</sup> In contrast, reduction of viscosity and transition from non-Newtonian to Newtonian behavior, induced by addition of polymers to the surfactant solutions, was reported as well.<sup>6,13–15</sup>

Surfactant molecules interact with polymers at a critical aggregation concentration (cac) forming micelle-like clusters along the polymer chain.<sup>5</sup> The interactions between polymers and surfactants, in general but not necessarily all, arise from the electrostatic forces, hydrophobic interactions among the hydrophobic moieties on surfactants and polymers, and hydrogen bonding between surfactant headgroups and polymers.

Moreover, the interactions among the ionic surfactants and oppositely charged polyelectrolytes exhibit quite differently.<sup>16–20</sup> The mixtures of the surfactant and polyelectrolytes with opposite charges often show very strong tendency to phase separate<sup>18,19</sup> and lead to insoluble complex salts, in which monomeric units of polyelectrolyte form salt bonds with the surfactant headgroups and the hydrophobic segments of surfactants provide additional stabilization.<sup>5</sup> Leung and co-workers<sup>16,17</sup> found that addition of a small amount of the anionic surfactant sodium dodecyl sulfate (SDS) to the cationic polyelectrolytic solution formed insoluble complexes that could be redissolved again in excess SDS solutions because of micellar solubilization. Similar redissolution of the insoluble polymer–surfactant complexes has been reported elsewhere for the system containing CTAB and an anionic polyelectrolyte, sodium hyaluronate,<sup>21</sup> as well.

To characterize the polymer–surfactant interactions, there are more than 20 different techniques reported in the literature.<sup>2–4,22–23</sup> Rodenhiser and Kwak<sup>23</sup> provided very good general accounts on these techniques. Despite a great variety of work having been carried out on polymer–surfactant systems, the detailed mechanisms of the polymer–surfactant interactions are not well understood yet.<sup>24</sup>

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**TABLE 1: Phenomenological Observation on the Systems Containing Poly(acrylic acid), PAA, and the Cationic Surfactant CTAB at 25 °C**

	0.5 wt % CTAB	1 wt % CTAB	2 wt % CTAB	3 wt % CTAB
0.04 wt % PAA	large lumps of crystal formed	small lumps of crystals formed	cloudy solution, no precipitate	clear
0.06 wt % PAA	large lumps of crystal formed	small lumps of crystals formed	cloudy solution, no precipitate	clear
0.08 wt % PAA	large lumps of crystal formed	small lumps of crystals formed	cloudy solution, no precipitate	clear
0.10 wt % PAA	large lumps of crystal formed	small lumps of crystals formed	cloudy solution, no precipitate	slightly cloudy

For the studies of interactions in the surfactant–polymer systems with opposite charges, sodium dodecyl sulfate (SDS) and alkyltrimethylammonium halide, such as cetyltrimethylammonium bromide (CTAB), are among the most prevalent surfactants, so poly(acrylic acid) (PAA), as well as sodium polyacrylate (NaPA), are among the most popular polymers. In this work, the anionic polyelectrolyte PAA and the cationic surfactant CTAB are selected as the model system because their individual properties are known and could be found elsewhere in the literature.<sup>25–29</sup>

When present conjointly, poly(acrylic acid) and the cationic surfactants alkyltrimethylammonium bromide or chloride have been in the subjects of many research reports in the past decades.<sup>6,18–20,30–37</sup> With fluorescence probe studies, Choi and Kim<sup>36</sup> found that the critical aggregation concentrations (cac) of polymer-bound surfactants are functions of the polymer concentrations and could be as small as less than 1% of the critical micelle concentrations. Furthermore, Fundin et al.<sup>30</sup> applied the time-resolved fluorescence quenching method to estimate the aggregation numbers of the micelles, which can be expressed as a function of the concentration ratio of CTAB to PAA monomers, and to study the effect of chain lengths of cationic surfactants on the bindings of the anionic polyelectrolytes. Indeed, the interaction of surfactant with polyelectrolyte and formation of aggregates often start at surfactant concentration far below cmc.<sup>35</sup> Kiefer et al.<sup>33</sup> reported that the onset of binding by tetradecyltrimethylammonium bromide (TTAB) to PAA or poly(methacrylic acid) (PMA) is significantly influenced by changes in the polymer conformation and hydrophobicity. Ilekci et al.<sup>18,19</sup> proposed, from their experimental observations on the system containing CTAB and NaPA, that the association results from an ion-exchange process, in which the polyacrylate ions displace some bromide counterions of the surfactant aggregates. Yoshida et al.<sup>31,32</sup> reported the effect of pH on electrostatic interaction and hydrogen bonding between PAA and CATC/C<sub>12</sub>E<sub>8</sub> mixed micelles. They discovered that hydrogen bonding dominates the interactions at low pH and discovered the possible formation of “ion pairs” between PAA and surfactants. Likewise, Cavaiano et al.<sup>24</sup> found that hydrogen bonding and hydrophobic force play very important roles in the interactions between PAA and the zwitterionic surfactant tetradecyldimethylaminooxide (C<sub>14</sub>DMAO), which precipitate even at very low pH.

For the aforementioned studies of polymer–surfactant systems with opposite charges, rheological measurement is seldom employed. This is mainly attributed to the difficulty owing to the formation of the insoluble surfactant–polymer complex salts (the surfactant ion + the polyion) in conjoint presence of the soluble simple salt made of the two oppositely charged simple ions dissociated from surfactants and polymers, respectively. Indeed, the shear behaviors of the 1 wt % SDS solutions with addition of two different cationic polyelectrolytes were reported as “highly irreproducible” by Leung et al.,<sup>16</sup> who, instead, proposed that the oscillatory-type rheometer was necessary for further studies on the shear behaviors in such systems.<sup>16</sup>

It is, thus, the purpose of this work to attempt to provide more understanding in the shear behavior of the surfactant–

polymer systems with opposite charges. As aforementioned, PAA and CTAB are chosen for this work. The effect of the aggregate size on the rheological behavior is assessed as well by using the static light scattering technique. In this report, we will give the details from our observations on the surfactant-induced transition of non-Newtonian to nearly Newtonian behavior in the PAA solutions with addition of 2 or 3 wt % CTAB. Discussions are attempted to shed light in more theoretical understandings.

## 2. Experimental Section

The cationic surfactant hexadecyltrimethylammonium bromide, also known as cetyltrimethylammonium bromide (CTAB), with molecular weight equal to 363.9 g/mol was purchased from Sigma. The phase diagram of the CTAB–water system is made available by Hertel and Hoffman.<sup>25</sup> Its critical micelle concentration (cmc) is ca.  $9.3 \times 10^{-4}$  M or 0.034 wt %, <sup>25,26</sup> and spherical micelles exist from the cmc up to about 0.2–0.3 M or approximately 8 wt %.<sup>26</sup> That is, the isotropic phase and spherical micelles dominate in the 2 and 3 wt % CTAB solutions employed in the present study.

Anionic polyelectrolyte poly(acrylic acid) (PAA), having molecular weight by viscosity ( $M_v$ ) equal to 750 kDa reported by the manufacturer, were acquired from Aldrich. Deionized water from a Milli-Q purification system (Millipore) having resistivity greater than 18.2 M $\Omega$ ·cm was used in sample preparation. All chemicals were of reagent grade and used as received.

Stock solutions containing 0.2 wt % PAA in water were prepared. The stock solutions were agitated for 10 min and placed on a shaker at 160 rpm for 24 h to achieve complete dissolution and equilibrium. Likewise, the 4 wt % stock solutions of the cationic surfactant CTAB were prepared at about 35 °C. The CTAB–PAA mixtures were similarly stirred for 10 min and shaken at 160 rpm for 24 h. The concentration of CTAB in the polymer–surfactant system was preferably set at 2 or 3 wt %. The reason will be described in more detail in Results and Discussion.

A Haake RS 75 Rheostress rheometer equipped with the circulating waterbath to control the variation of temperature within 0.1 °C was employed for the rheological measurements. The double-gap cylinder sensor DG 41 was used according to the viscosity of the measured samples. The DG 41 sensor is able to provide very good measurement of viscosity near that of water. However, owing to the design limit of the rheometer, the minimal shear rate had to be set at about 50 s<sup>−1</sup> to ensure the reliability of our experimental results. The Brookhaven Light Scattering system equipped with the BI-200SM goniometer and Static Light Scattering Software version 2.09 was utilized to measure the radii of gyration,  $R_g$ , of the surfactant–polymer aggregates and the polymer itself. All of the measurements were carried out at 25 °C.

## 3. Results and Discussion

Table 1 describes the phenomenological observation of the CTAB/PAA solutions at 25 °C. Crystals formed in the PAA

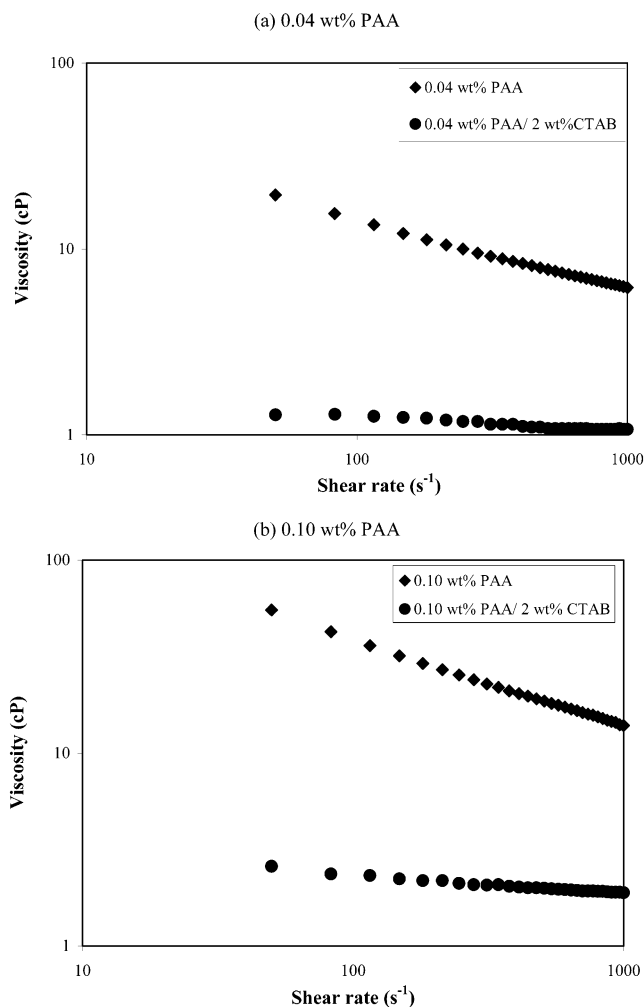
solution with addition of 0.5 or 1 wt % CTAB. This is similar to those observed by Li et al.<sup>6</sup> in the system containing 25 mM CTAB, that is, about 0.9 wt %, and 15 mM sodium salicylate (NaSal) with addition of PAA, having viscosity-averaged molecular weight of 600 kDa, at a concentration of 1, 2, and 5 g/L, that is, 0.1, 0.2, and 0.5 wt %. They claimed that addition of PAA at these concentrations to the CTAB/NaSal solution simply caused heavy precipitation.

The crystals found in the systems listed in Table 1 are believed to be the insoluble CTAB–PAA complexes. There is a great tendency for nucleation of CTAB–PAA crystals to occur, a phenomenon frequently described as phase separation.<sup>18,19</sup> The use of alkaline with pH in the range of 10–12 ( $>pK_b$  of CTAB) and PAA having a lower molecular weight, for example, at 450 kDa, failed to arrest phase separation. As the charge ratio between surfactant and polymer approaches unity, it is known that the polymer–surfactant complex loses water solubility and precipitates from solution.<sup>38</sup>

The insoluble crystals can then be redissolved again in excess CTAB micellar solutions having overall concentrations of 2 and 3 wt %. The solution became slightly cloudy, but no precipitates were ever observed over a long period up to a week. Indeed, no phase separation and precipitates in these “cloudy” PAA–CTAB solutions were observed at temperature from 25 to 85 °C with an increment of 5 °C. The redissolution of the insoluble surfactant–polymer complex salts has also been reported by Robb and Stevenson<sup>34</sup> in the system containing PAA and Synperonic NP13, an ethoxylated nonyl phenol ether from ICI, below pH 3. They discovered that the amount of the surfactant required to redissolve the insoluble complex is linearly dependent on the polymer concentration. In contrast to the nonionic surfactant used in Robb and Stevenson’s study,<sup>34</sup> the cationic surfactant CTAB is employed in this study and the resultant CTAB/PAA solution gives the pH value at about 3. One would expect similar redissolution behavior taking place in the presence of excess surfactant. It is, thus, the concentration of the CTAB in this study is preferentially set at 2 and 3 wt %.

As mentioned previously, the solutions containing the polymer PAA at less than 0.10 wt % and the cationic surfactant CTAB of 2 wt % usually exhibit a slightly milky appearance at 25 °C. Increasing the polymer concentration to more than 0.1 wt % in the polymer–surfactant solutions makes it more difficult for sample preparation and for the measurements of the radii of gyration, because the solutions become more viscous and cloudy. More cloudy solutions indicate severe multiple scattering, which is always unwanted on the light scattering measurements.<sup>39</sup> Thus, it is imperative to limit the concentration of the polymer to be less than 0.1 wt % during the whole experiments.

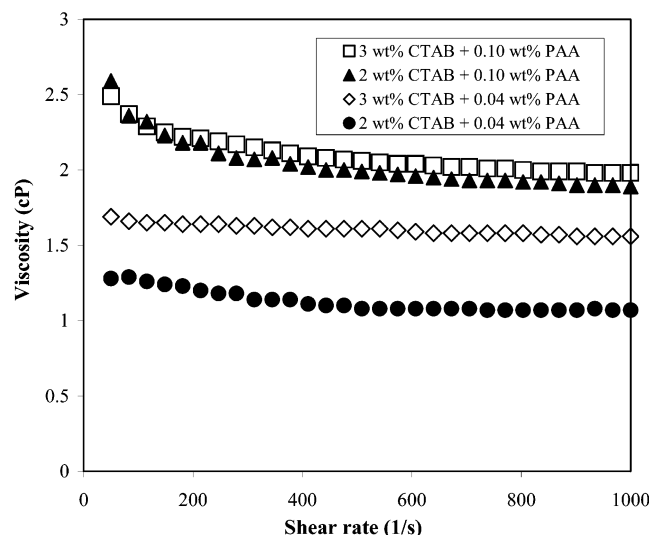
It is of note to mention that the Krafft point of CTAB in the presence of PAA is near the ambient temperature (ca. 22 °C). It is evident from the fact that clear crystals formed when the surfactant–polymer solution was left over at the ambient temperature for a few hours. The solution then turned clear again when heated in the water bath for a few degrees in Kelvin. With slight deviations from the phase diagram of CTAB/water system by Hertel and Hoffmann,<sup>25</sup> Laughlin<sup>40</sup> reported that, instead, the upper critical temperature of the Krafft boundary is 30 °C and the corresponding concentration of CTAB at eutectoid is 24 wt %, while the Krafft temperature of CTAB in water is found at 26 °C by Rico and Lattes.<sup>41</sup> These values are slightly higher, about 3 to 4 °C, than those reported by Hertel and Hoffmann.<sup>25</sup>



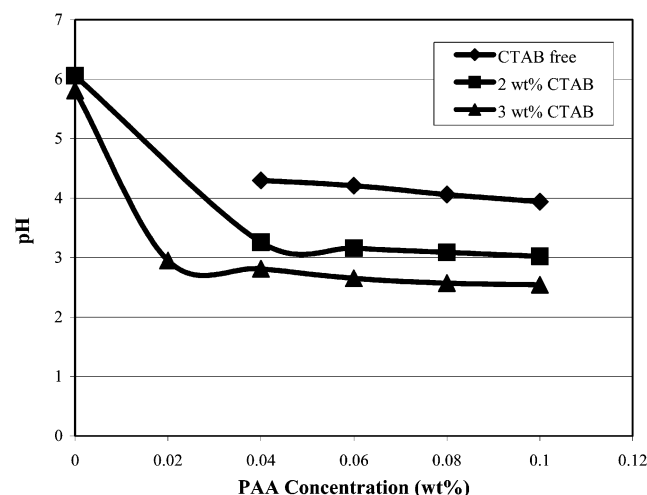
**Figure 1.** Viscosity curves of 0.04 and 0.10 wt % poly(acrylic acid) with and without addition of 2 wt % CTAB as a function of shear rate: (a) 0.04 wt % PAA; (b) 0.10 wt % PAA.

In addition to the critical micelle concentration (cmc), another critical surfactant concentration known as critical aggregation concentration (cac) corresponds to the onset of formation of PAA/CTAB aggregates. The cac is usually lower than the cmc of the surfactant alone. Studies have shown that below cac the interaction primarily takes place between polymer and surfactant monomers and that the polymer–micelle aggregates dominate above the cac.<sup>42</sup> The use of 2 or 3 wt % CTAB solutions in this study ensures that micelles instead of monomers are the predominant species.

Figure 1 shows the viscosity of the polymer solution at 0.04 and 0.10 wt % with or without addition of 2 wt % CTAB. It clearly demonstrates that the shear-thinning behavior is indeed observed in the pure polymer solutions. In contrast, addition of 2 wt % CTAB to the 0.04 wt % PAA solution significantly reduced the viscosity of the solution to ca. 1.3 cP, nearly independent of shear rates in the range of this study. Likewise, the 0.10 wt % PAA solution with addition of 2 wt % CTAB shows nearly Newtonian behavior in contrast to the shear-thinning behavior in the pure 0.1 wt % PAA solution (Figure 1b). The viscosity of the PAA–CTAB solution ranges from 2.6 to 1.9 cP. It is clear that the addition of cationic surfactant CTAB to the anionic polymer PAA solution effectively transforms the solution from a non-Newtonian fluid to the nearly Newtonian one. Likewise, addition of 3 wt % CTAB to the aforementioned 0.04 and 0.10 wt % PAA solutions also



**Figure 2.** Effect of added CTAB on the viscosity of poly(acrylic acid) solutions.

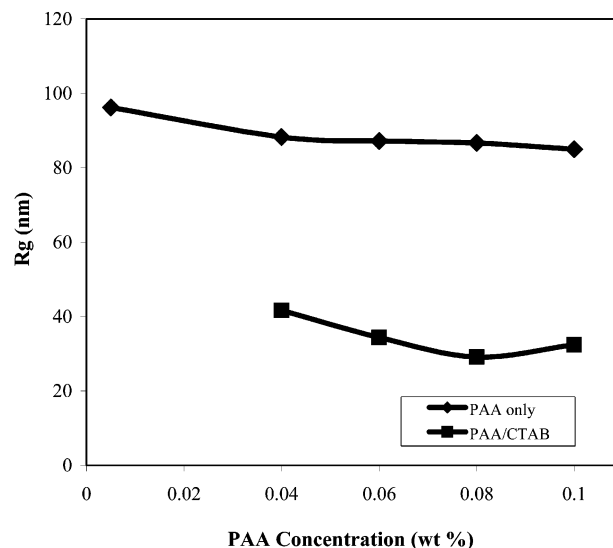


**Figure 3.** Effect of added CTAB on the pH values of poly(acrylic acid) solutions.

decreased the viscosity of PAA solutions to about 1.6 cP and to that ranging from 2.5 to 2 cP, respectively (Figure 2).

The interaction between the cationic surfactant and the anionic polymer is obvious from the pH measurements (Figure 3). The pH values of the CTAB–PAA solutions are somewhat lower than those of the solutions having neat PAA or CTAB only. For example, the pH values of the 2 and 3 wt % CTAB solutions are near 6.1 and 5.8, respectively, while they range from 4.3 to 3.9 for polymer solutions containing PAA from 0.04 to 0.10 wt %. Nonetheless, the pH values of the PAA–CTAB solutions containing polymer from 0.04 to 0.10 wt % and 2 or 3 wt % CTAB vary from 3.3 to 3.0 and from 3.0 to 2.5, respectively, which are significantly lower than those of PAA and CTAB only.

PAA is often classified as an anionic polymer (polyelectrolyte). It is a soft Lewis acid consisting of  $-\text{COOH}$  groups along the polymer coil that ionizes partially in aqueous medium depending on the pH value of the system. For an aqueous solution of the weak acid, HX, the degree of dissociation,  $\alpha$ , is commonly defined as the molar ratio of  $\text{X}^-$  to HX.<sup>43</sup> Hence,  $\alpha$  in the surfactant-free PAA solutions of 0.10 and 0.04 wt % are almost the same near 0.009. In contrast, addition of 2 wt % CTAB into the PAA solutions of 0.10 and 0.04 wt % increases  $\alpha$  to 0.072 and 0.11, respectively, accounting for an 8-fold and



**Figure 4.** Radii of gyration,  $R_g$ , of poly(acrylic acid) with and without addition of 2 wt % CTAB as a function of the polymer concentration.

a 12-fold increase in the degrees of dissociation, correspondingly. Increasing the CTAB concentration to 3 wt % raises the degree of dissociation in PAA solutions of 0.10 and 0.04 wt % roughly to 0.21 and 0.28, denoting almost a 25-fold and a 31-fold significant increase.

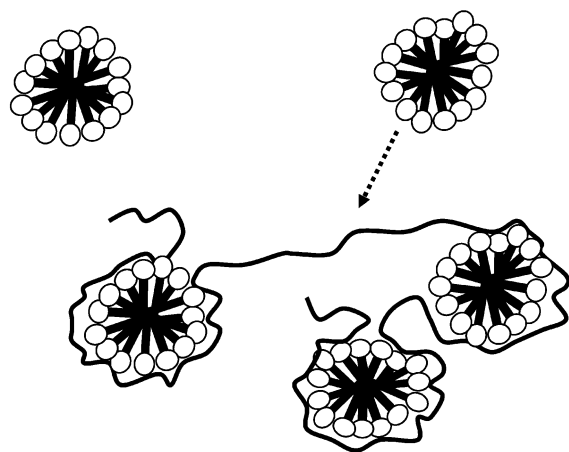
This clearly indicates that “strong” ion pairs are formed in the PAA–CTAB solutions.<sup>43</sup> PAA is considered as a weak Lewis acid, while CTAB is acting as a weak Lewis base. The formation of the ion pairs can liberate more acids from acrylic acid monomers of the PAA macromolecules to the bulk solutions and, thus, decreases the pH values. With addition of 2 wt % CTAB, it implies more CTAB molecules available to be bound on each PAA macromolecule in the 0.04 wt % PAA solution than that in the 0.10 wt % PAA solution. Likewise, addition of 3 wt % CTAB to the 0.10 wt % PAA solution indicates more CTAB molecules available to be attached on each PAA coil than that with addition of 2 wt % CTAB. That is, more acids can be dissociated from the former systems and this leads to the lower pH value in the PAA–CTAB solution. This is consistent with the observation of the increase in the degree of dissociation,  $\alpha$ , in the PAA solutions with decreasing polymer concentration at a fixed concentration of CTAB, and the increasing  $\alpha$  in the PAA solutions of the same concentration with increasing concentration of CTAB.

It is noteworthy to mention that the pH dependence on the concentration of CTAB, in contrast to the dependence on the PAA concentration in our study, was also reported by Fundin et al.,<sup>30</sup> who studied the interaction of CTAB and PAA ( $M_w = 90$  kDa) by using different techniques.

Another indirect evidence of forced dissociation of acids from PAA molecules was also observed in the  $\zeta$  potential measurements. The  $\zeta$  potentials of 0.1 wt % PAA solution and 2 wt % CTAB solutions were found around  $-25$  and  $3$  mV, respectively. However, the  $\zeta$  potential of the solution having 2 wt % CTAB and 0.1 wt % PAA together could not be experimentally obtained because of the too high ionic strength, found in the aforementioned solution where both CTAB and PAA are present conjointly, beyond the applicable range of the  $\zeta$  potentiometer.

Figure 4 clearly shows the radii of gyration of polymer coils and the CTAB–PAA aggregates as a function of PAA concentration. The overlap concentration<sup>44</sup>  $c^*$  of PAA is estimated to be about 0.34 g/L, or 0.034 wt %, using the measured radius of gyration at about 96 nm in 0.001 wt % PAA





**Figure 5.** Schematic diagram of PAA/CTAB complex in equilibrium with free micelles.<sup>45</sup>

solution with the assumption that PAA at such concentration is in dilute region. The estimation indicates that the PAA concentration in our study is slightly higher than  $c^*$ . The radii of gyration of the PAA aggregates in polymers solutions from 0.04 to 0.10 wt % are slightly reduced to the value near 85 nm. On the contrary, the radii of gyration of surfactant–polymer aggregates are found in the range between 30 and 40 nm. Clearly, addition of the CTAB to the polymer solutions leads to more compact but less entangled aggregates. More entangled macromolecules tend to demonstrate non-Newtonian behavior. The shear-thinning behavior occurs consequently as the transformation of the structures from more to less entanglement takes place under the applied stress.

Coincidentally, Li et al.<sup>6</sup> reported their observation on the striking polymer-induced transition of non-Newtonian to Newtonian fluids in the CTAB/NaSal solutions containing 25 mM CTAB and 15 mM sodium salicylate (NaSal), in which the long entangled wormlike micelles were observed. Consequently, the polymer-induced *wormlike-to-spherical-micelle* transition was noticed with addition of poly(propylene oxide) having molecular weights of 1000 and 4000 Da, or poly(vinyl methyl ether) of 27 kDa.<sup>6</sup>

In an attempt to explain the effect of added CTAB at 2 and 3 wt % on the rheological properties of the PAA solutions, a schematic diagram of CTAB/PAA complex in equilibrium with free micelles is accordingly presented as Figure 5. Each polymer chain may gather together with several micelles to form complexes stabilized by hydrophobic and electrostatic interactions.<sup>30</sup> The most probable mechanism between negatively charged PAA coil and positively charged CTAB micelles is the electrostatic attraction, as illustrated in the Figure 5. The headgroups of the positively charged micelles tightly bind with the negatively charged acidic sites on the polyelectrolyte. In addition, there may be van der Waals forces, and the electrostatic correlation forces arise from the attractions between the polyelectrolyte segments bound to the micelles and the charges of the temporarily uncovered patches on the neighboring micelles.<sup>4,7,20</sup>

The outcome of the surfactant bindings by electrostatic attraction is normally a reduction in the viscosity of the system and a loss of polymer solubility to the point of charge reversal.<sup>45</sup> Macroscopically, the above events may lead to dramatic changes in the viscosity of the system due to, first, collapse of the polymer coils, followed by a rapid expansion after charge reversal has taken place.

Our experimental findings convincingly show that CTAB addition lowers the viscosity and radii of gyration of PAA,

indicating a collapse in the polymer conformation. This could be attributed to the overwhelming surfactant-to-polymer ratio (e.g., 2 wt % CTAB to 0.1 wt % PAA or equivalently 4 mol of CTAB to 1 mol of acrylic acid monomer in PAA). With surfactant-to-polymer ratio larger than unity, the surfactant–polymer complexes will be saturated with surfactant and free micelles coexist with the complexes.<sup>30</sup> Under these circumstances, significant screening effect caused by the free micelles on the hydrodynamic virial coefficient is found and the effective repulsion between the complexes increases, accordingly.<sup>30</sup> This constitutes the so-called “self-salt” effect exhibited by CTAB and its counterion,  $\text{Br}^-$ , and the effect of saturating PAA with CTAB.<sup>46</sup> Free counterions and unassociated CTAB micelles contribute to ionic strength of the solution that shields the increasingly charged PAA/CTAB aggregates and counteracts any increase in  $R_g$ . After saturation of the PAA, the excess CTAB charges PAA no further but does continue to increase the ionic strength and shielding.<sup>30</sup> Ultimately, the overall effect is a collapsed and compact structure induced by electrostatic screening, thus leading to the reduction of viscosity.

Alternatively, similar to but different from that schematically shown as Figure 5, other conjecture on the transition of the non-Newtonian fluid to the nearly Newtonian one is proposed according to the redissolution phenomenon of the CTAB–PAA in excess surfactant micelles. The redissolution can be considered with the micellar-solubilization phenomenon,<sup>16,17</sup> in which the surfactant–polymer complexes become hydrophobic, as their hydrophilic sites, that is, the  $\text{COO}^-$  on PAA and  $\text{N}^+$  on CTAB, are associated and occupied by forming insoluble salt bonds. Such hydrophobic complex salts can be dissolved in the excess CTAB micelles that act as steric solubilization agents for the surfactant–polymer complexes. These complex-contained micelles are still isotropic and compact. The shapes of the resulting polymer–surfactant complex-contained micelles will not be far away from the spherical shapes of CTAB at these concentrations. Consequently, they will show Newtonian behavior, accordingly.<sup>26</sup>

#### 4. Conclusion

Interaction of the cationic surfactant CTAB and the anionic polyelectrolyte PAA is studied by rheological measurements. Addition of CTAB with concentration less than 1.0 wt % to the semidilute PAA solution having concentration less than 0.10 wt % simply causes heavy precipitation. Such insoluble CTAB–PAA complexes can be redissolved with further addition of CTAB to 2 or 3 wt %. The resulting PAA/CTAB solutions exhibit nearly Newtonian behavior, in contrast to the shear-thinning behavior in solutions containing PAA only. The transition is believed to arise from the formation of the more compact PAA/CTAB complexes, as the radii of gyration  $R_g$  of PAA coils have been significantly reduced by about 60% with addition of 2 wt % CTAB. The pH values of the PAA/CTAB solutions are less than those of neat CTAB or PAA solutions, which indicate the possible formation of “ion pairs” and thus increase of the degree of dissociation of PAA.

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