

Clouding: Origin of Phase Separation in Oppositely Charged Polyelectrolyte/Surfactant Mixed Solutions

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The phase behavior in the system of cationic modified poly(vinyl alcohol) (CPVA)–sodium dodecylsulfate (SDS)–water has been investigated. Samples were found phase separated near electroneutral mixing at CPVA concentrations $\leq 6\%$, while in a medium CPVA concentration of 7–12%, the phase separation disappeared and the system transformed into bluish homogeneous solution. At $\geq 13\%$ CPVA concentrations, the mixed systems became colorless homogeneous. Preclouding phenomenon was observed in 5–8% CPVA–SDS mixed systems at an electroneutral mixing ratio. The addition of inorganic salts, such as Na_2SO_4 , NaCl, NaBr, and NaSCN, could exclude the bluish and phase separation phenomenon that was found to be caused by the increase of clouding point in these systems. The clouding phenomenon was proven to be the origin of the phase separation in the CPVA–SDS mixed system. The ability for the inorganic salts to increase the clouding point follows the order of the Hofmeister series.

Introduction

Clouding is a phenomenon generally observed in nonionic surfactant and water-soluble polymer solutions when the solution is heated to a threshold temperature,^{1,2} which is known as clouding point (CP). Occurrence of the clouding phenomenon is rare with the ionic polymer or surfactants, presumably because the large electrostatic repulsion between the aggregates prevents phase separation in most cases.^{3–6} However, a few cationic surfactant solutions also show cloud-point behavior.^{7–11} Appell and Porte found clouding points at high concentrations of sodium chlorate salt in aqueous solutions of either CTAB or cetyl pyridinium bromide (CPyBr).⁷ In a later study, Warr and co-workers showed that quarternary ammonium surfactants with tributyl headgroups exhibit cloud points in binary aqueous solution.⁸ Adding salt to these surfactant solutions lowers the cloud-point temperature.⁹ Recently, Kumar et al. have reported that adding salts with large hydrophobic cations to anionic surfactants can lead to clouding when such behavior is absent in the pure surfactants.^{12–15} Moreover, it was well established that the addition of ionic surfactants increases the cloud points of their nonionic counterparts,^{16,17} and the increase depends on composition of the mixed micelles. Bales and Zana found that the cloud point of aqueous solutions of tetrabutylammonium dodecyl sulfate is a function of the concentration of counterions in the aqueous phase.¹⁸ Valaulikar and Manohar have demonstrated that the increase in cloud point can be described in terms of the surface charge per micelle, which is responsible for electrostatic repulsion between the micelles.¹⁹

In comparison to the phenomenon in the binary surfactant or polymer systems, less attention has been paid to the clouding phenomenon in surfactant/polymer mixed systems,²⁰ especially in oppositely charged polymer–surfactant mixed ternary systems. During the last several decades, large efforts were made on the understanding of the interaction and phase behavior in these systems.^{21–25} It has been well documented that the mixing

of an aqueous solution of an ionic polymer with an oppositely charged surfactant generally results in an associative phase separation due to the favorable electrostatic interaction between the two species.^{26–28} In this process a concentrated phase is formed that is enriched in both the charged polymer and the surfactant. However, the phase separation could be eliminated by addition of proper amounts of salts.^{29,30} In a series of reports of Thalberg et al.,^{23–25,30–32} they found that addition of low concentrations of NaBr leads to a reduction of the two-phase region of the phase diagram. The changes in phase behavior on addition of salt have been reproduced by a simple theoretical model based on the Flory–Huggins theory,³⁰ which gives an insight into the physical origin of the phase behavior. In a following report of Hansson, it was found that NaCl has a much weaker effect than NaBr on reduction of the two-phase region.²⁹ They ascribed that a force other than electrostatic interaction was functioning in that case, but no further study was carried out on this topic.

In this research, we focused on the mixed system of cationic modified poly(vinyl alcohol) (CPVA) and oppositely charged surfactant–sodium dodecyl sulfate (SDS). It is surprising to find that the essential origin for the phase separation is clouding in this mixed system. The clouding point for the mixed system is so low that at room temperature the system already separates into two phases—which has been taken as a normal phase behavior in the oppositely charged surfactant/polyelectrolyte mixed systems. Besides, we also investigated the unusual clouding increase phenomenon in anionic surfactant SDS–CPVA mixed solutions with the addition of Na_2SO_4 , NaCl, NaBr, and NaSCN. It reveals that all these salts increase the CP of the mixed solution, which is totally different from the well-known rules of the salt's effect on the CP.

Experimental Section

Sodium dodecyl sulfate (SDS) is from Serva Feinbiochemica GmbH&Co. The cationic modified poly(vinyl alcohol) (CPVA) is from Wacker Company and was used as received. The

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TABLE 1: Components and Hydrolysis Degree of CPVA

	CPVA
hydrolysis degree	94.0%
poly(vinyl acetate)	5.7
poly(vinyl alcohol)	89.8
DADMAC	4.4

components in the CPVA are listed in Table 1. Sodium chloride, sodium bromide, sodium thiocyanate, and sodium sulfate are all analytical grade product. All the water used in this article is double distilled.

Stock polymer solutions were prepared by weighing water into a container containing a certain amount of CPVA. The mixture was magnetically stirred for 1 h at room temperature to obtain homogeneous clear solution. Then the proper amount of SDS was weighed into a bottle and dissolved with the stock polymer solution to prepare the required SDS/CPVA mixed systems. In this article, the mixing ratio refers to SDS:CPVA in weight percent.

Turbidity measurement was done on a Shimizu 250 UV spectrometer with a 1 cm quartz cell in the thermostat (± 0.5 °C). Absorbance was recorded at 633 nm, which was not absorbed by the polymer and surfactant.

For clouding point determination, the inorganic salts containing SDS/CPVA mixed solutions were prepared by weighing certain grams of salts into the mixed solutions. The clouding points were obtained by placing glass tubes (containing the sample solution with or without salts) into a temperature-controlled bath, the temperature of which was ramped at the rate of 0.2 °C/min near the clouding point, and onset clouding was noted by visual inspection.

Small-angle X-ray scattering (SAXS) experiments were performed by using a lab modified Kratky camera, which covers the scattering vector q range from 0.05 to 4 nm⁻¹. The camera and the data treatment have been described elsewhere.³³

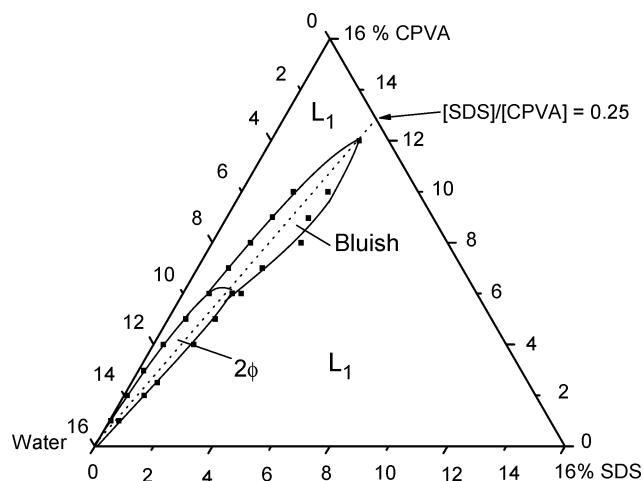
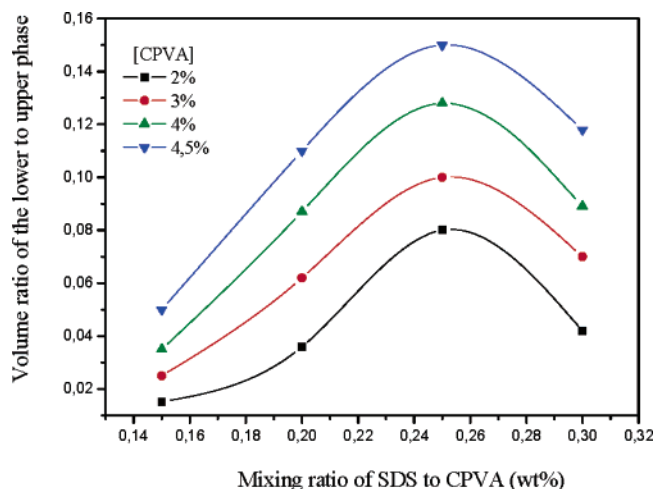
Conductivity measurements were performed with an Automatic Precision Bridge (Wayne Kerr B905) and a glass electrode (WTW LTA/S). The cell constant was calibrated on every measurement by KCl aqueous solution (7.47458 g/Kg of water, $\kappa = 1.2852$ S/m).

Steady-state rheological measurements were carried out on a Haake RS300 rheometer in a viscosity vs shear rate sweep mode. The measuring device consists of a cylinder-double gap setup. A water-saturated chamber was employed to avoid water evaporation during the measurements.

Results

1. Phase Behavior. Figure 1 shows the pseudoternary phase diagram of the SDS–CPVA–water mixed system at room temperature (22 °C). It is clear, at a fixed [CPVA] $\leq 6\%$, the systems demix into two isotropic liquid phases at proper SDS concentration. Lower or higher SDS concentration leads to isotropic, one-phase solutions. The dotted line in Figure 1 is the electroneutral mixing of SDS and CPVA. It is clear that the two-phase region is near this line. In the two-phase regime, the lower phase is colorless viscous, whereas the upper phase is water-like.

The volume of the lower phase is only less than 15% and varies significantly with the mixing ratio of SDS and CPVA at fixed CPVA concentration. The maximum volume of the lower phase, however, appears at almost the same mixing ratio of [SDS]/[CPVA] = 0.25 (Figure 2), which is the electroneutral mixing of CPVA and SDS (Figure 2), in solutions with different CPVA concentrations.

**Figure 1.** Phase diagram in SDS/CPVA mixed systems (22 °C).**Figure 2.** Volume of the lower phases changes with the mixing ratio of SDS/CPVA.

At the electroneutral mixing ratio, the volume of the lower phase increases first with the enhancement of the total concentration to a maximum then decreases, until 0 volume of the lower phase is reached, i.e., one homogeneous phase appears at the CPVA concentration higher than 7% (Figure 3 a). In fact, at higher than this concentration, the mixed system is homogeneous no matter how the content of SDS is changed. However, the system is bluish in the CPVA concentration of 7–12% in a certain SDS concentration range. Out of this SDS regime or at higher CPVA content, only colorless homogeneous one-phase solutions can be obtained. Quite similar to the case of the biggest lower phase volume, the darkest bluish color also appears at the electroneutral mixing ratio of SDS to CPVA, as illustrated in Figure 3 for the turbidity at 633 nm for the 8% CPVA–2% SDS mixed system (Figure 3b).

The formation of two liquid phases is often observed in oppositely charged surfactant/polymer mixed systems, due to the strong electrostatic interaction. The inclusion of a whole phase transition behavior from two phases via one bluish phase finally to one colorless phase is, however, similar to (pre)-clouding in some polymer or nonionic surfactant systems.^{34,35} Therefore, we will focus our study on the solutions in the two-phase and bluish regions in the phase diagram.

2. Observation of Clouding Point (CP). Mixed solutions with different mixing ratios at fixed CPVA concentration were examined at 0–100 °C. For solutions with [CPVA] $\leq 4\%$, the two phases existed in the whole temperature range; while those

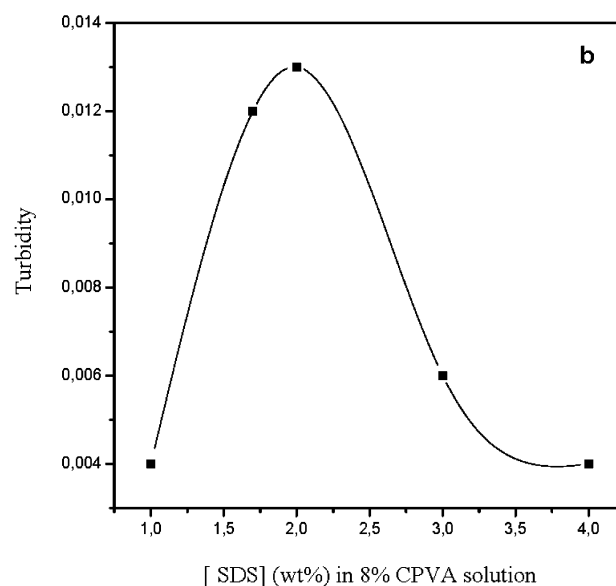
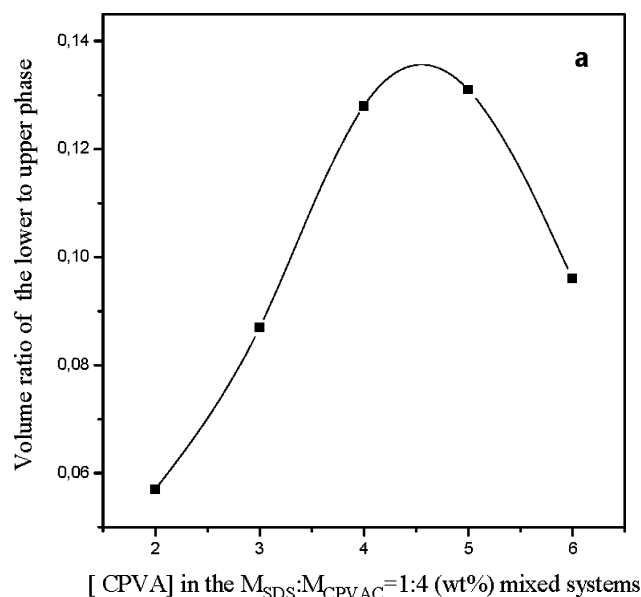


Figure 3. (a) Volume ratio of the lower to upper phase changes with total concentration and (b) turbidity changes with [SDS] in 8% CPVA solutions.

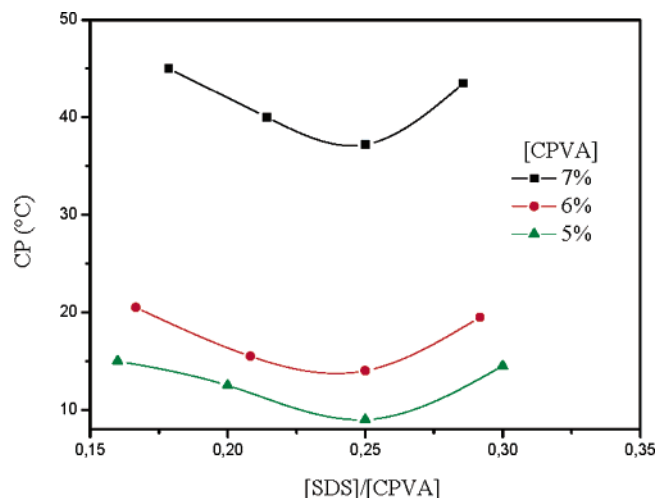


Figure 4. The CP changes with the mixing ratio of [SDS]/[CPVA].

with [CPVA] \geq 8% are always staying in one homogeneous phase at 0–100 °C. However, the clouding phenomenon is found in 5–7% CPVA solutions. It should be noticeable that before a dramatic phase separation is observed, the mixed solutions become bluish, which is the so-called preclouding phenomenon.^{34,35} The clouding point obtained in Figure 4 is the dramatic phase separation temperature.

It is clear that, at fixed [SDS]:[CPVA], the CP increases with CPVA concentration. However, the increase is not linear. It seems that the CP difference between the 6% and 7% CPVA system is about 20 °C, while it is 5 °C for the 5% and 6% CPVA systems. At a given CPVA concentration, the CP changes with the mixing ratio, and shows a minimum at electroneutral mixing, i.e., [SDS]/[CPVA] = 0.25. This result is reasonable due to electrostatic interaction between SDS and CPVA in the mixed solutions. With the mixing ratio of CPVA and SDS slightly deviating from the electroneutral ratio, the excess charge in the mixed systems will result in an energy barrier between the complexes, which finally leads to the higher CP temperature. Further deviation from the electroneutral mixing will, however, introduce too many charges on the complex so that no clouding can be attained within 100 °C.

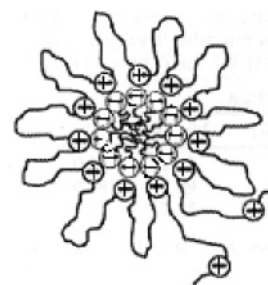


Figure 5. Schematic illustration of the interaction of a SDS micelle with CPVA. The counterions of the surfactant and of the polyelectrolyte section associated with the micelle are free in solution (not shown).

3. Interaction between SDS and CPVA. There are many models illustrating the interaction between polymer and surfactants. The most extensive one is the pearl-necklace model for the nonionic polymer and ionic surfactant mixed system, which shows that surfactant micelles are bound to the hydrophobic part of polymer chains like a necklace.³⁶ This structure seems to be valid also in systems of a polyelectrolyte and an oppositely charged surfactant, as indicated from fluorescence results,^{37–39} and is in agreement with the marked cooperativity in surfactant binding to polyelectrolytes.^{40–42}

In our systems, the concentration of SDS is much higher than its cmc, 8×10^{-3} M, which corresponds to about 0.23% in weight percent. Therefore, it is reasonable that the micelles exist in all the studied systems. This conclusion can be proved by the small-angle X-ray scattering (SAXS) results.

Figure 6 shows the result of SAXS experiments. The scattering intensity of the mixed system $I(\text{CPVA}+\text{SDS})$ differs significantly from the simple addition of the scattering intensities of the single components $I(\text{CPVA}) + I(\text{SDS})$ at low q region. This indicates that strong interaction between SDS and CPVA occurred. A broad peak centered at $q = 1.8 \text{ nm}^{-1}$ for both curves is observed, which can be attributed to the scattering peak of the sulfate groups of SDS in the micelle. This result suggests that complexes with SDS micelles wrapped by CPVA monomers as illustrated in Figure 5 are formed in the mixed systems. However, the CPVA–SDS micelles cannot be totally electro-neutral even at electroneutral mixing due to the binding of

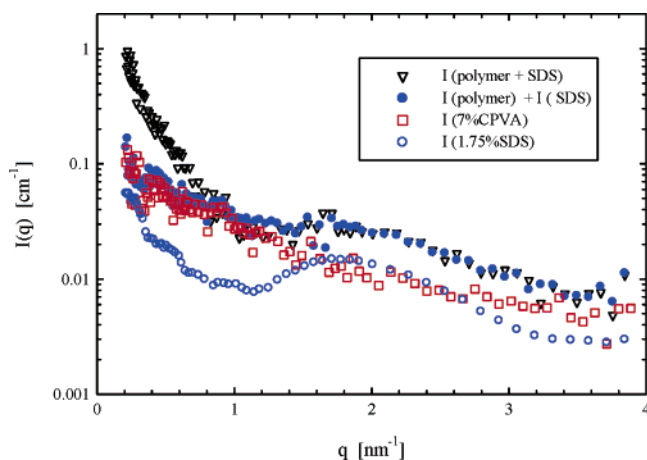


Figure 6. Comparison of the scattering intensity of the mixed system of 1.75% SDS–7% CPVA (triangles: $I(\text{CPVA}+\text{SDS})$) and the simple summation of the scattering intensities of two single components (filled circles: $I(\text{CPVA}) + I(\text{SDS})$). The scattering intensities of the single systems 1.75% SDS (open circles: $I(\text{SDS})$) and 7% CPVA (squares: $I(\text{CPVA})$) are also shown for reference.

TABLE 2: The Comparison of Conductivity between the Simple Summation of the Respective Conductivity Values of Single SDS (a) and CPVA (b) Solution Systems ($\kappa_a + \kappa_b$) and Their Mixed System ($\kappa_{(a+b)}$)

	solutions (wt %)	κ , ms/cm, at 25 °C	solutions (wt %)	κ , ms/cm, at 25 °C
a	1.75% SDS (0.061 M)	3.41	2% SDS (0.069 M)	4.05
b	7% CPVA	5.41	8% CPVA	6.10
$\kappa_a + \kappa_b$		8.82		10.15
$\kappa_{(a+b)}$	0.061 M NaCl	9.27	0.069 M NaCl	10.51
		11.47		13.29

counterions. Since the activity of the counterions at the lower concentration range is greater than that at the higher concentration, the greater concentration of free counterions in bulk solution is in parallel with less binding of counterions onto micelles. In other words, the degree of counterion binding to micelles is lower at lower concentration than that at higher concentration. This leads to an increase in concentration of CPVA^+DS^- complexes which are electrically neutralized. Eventually the micellar complexes can be separated from the bulk solution. In contrast, as the activity of the small counterions decreases at concentrated solution, more ions could bind to the complex, which build up energy barriers for the phase separation. The conductivity data in Table 2 give powerful proof for the binding of counterions on the complexes of the CPVA–SDS micelle.

It is clear that at electroneutral mixing, the conductivities in both the 7% and 8% CPVA–SDS mixed systems [$\kappa_{(a+b)}$] are higher than the simple summation of single solutions ($\kappa_a + \kappa_b$), suggesting the binding of CPVA to SDS micelle is stronger than the binding of counterions to CPVA or SDS micelles. On the other hand, the conductivities in the mixed systems are apparently lower than that of the comparable single NaCl solutions, indicating a large number of counterions are bound to the CPVA–SDS complexes. The binding degree calculated from the conductivity data for the 7% and 8% CPVA–SDS mixed systems are 0.19 and 0.21, respectively, which is in agreement with the prediction of the ion activity result. If we exclude the concentration effect by dividing the binding degree with total concentration (wt %), reduced binding degrees of 2.17% and 2.10% for the two solutions are derived, respectively.

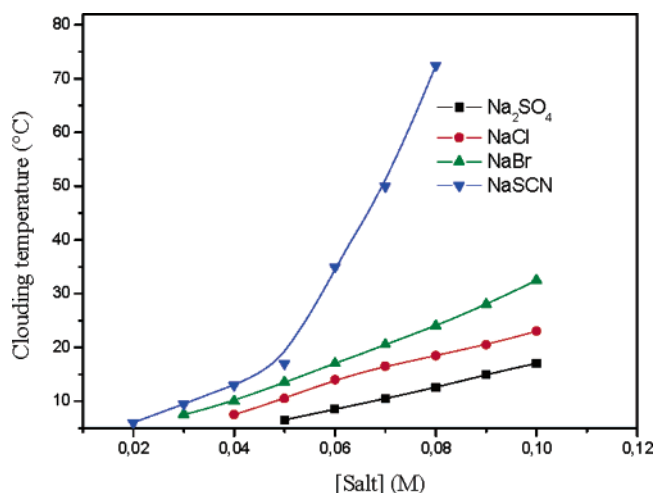


Figure 7. The CP changes with inorganic salts in 0.5% SDS–2% CPVA mixed systems.

These values can be taken as effective charge densities to restrain phase separation in the CPVA–SDS mixed systems.

4. CP Elevation in SDS–CPVA Solution with Addition of Inorganic Salts. Figure 7 shows the effect of different inorganic salts, Na_2SO_4 , NaCl, NaBr, and NaSCN, on the CPs in 0.5% SDS–2% CPVA mixed system. We have known from the pretext that before addition of any inorganic salts, this system is already separated into two phases. However, with addition of Na_2SO_4 , NaCl, NaBr, or NaSCN, the clouding phenomenon was observed. It is interesting to note that in all the salt-contained systems, the CP increases with increasing salt concentration. It is well-known that simple inorganic salts on the left-hand side of the Hofmeister series, such as PO_4^{3-} , CO_3^{2-} , HPO_4^{2-} , SO_4^{2-} , OH^- , F^- , and Cl^- , tend to lower the CP of nonionic surfactants;^{43,44} and in most cases, the CP in the mixed systems of ionic surfactant and nonionic polymers also decreases with increasing salt concentration. For example, Marszall observed in his experiments that when NaCl is added to the SDS–Triton X-100 surfactant solution where SDS is present in small amounts, the CP is lowered.⁴⁵ They speculated that the original charge distribution is swamped and the corresponding repulsions are screened, resulting in a dramatic cloud point lowering. As far as we know, no reports about the effect of salts on the clouding point of the oppositely charged surfactant/polyelectrolyte mixed systems have appeared. The most general knowledge on oppositely charged surfactant/polyelectrolyte mixed systems is the phase separation near electroneutral mixing. This kind of phase separation can be deleted by addition of the proper amount of inorganic salts.^{31,32,37} Surprisingly, it seems that the essential origin of the phase separation in our system is clouding—room temperature is already well above its clouding point, therefore phase separation is observed. With addition of inorganic salts to this system, the cloud point could be enhanced to above the room temperature—so that phase separation is eliminated.

It is clear in Figure 7 that for Na_2SO_4 , NaCl, and NaBr systems, the CPs increase linearly with salt concentrations lower than 0.1 M; in the higher than 0.1 M salt range, no clouding is detected. For the NaSCN system, the CP–[NaSCN] curve showed a break at [NaSCN] = 0.05 M. At [NaSCN] lower than 0.05 M, the CPs increase slowly, but 3 times faster after 0.05 M is reached. It is also clear that the minimum salt concentration required for the appearance of CP depends on the type of salt. We can see from Figure 7 that the minimum [salt] necessary for the same SDS–CPVA mixed solutions for the appearance

of CP is 0.05, 0.04, 0.03, and 0.02 M corresponding to Na_2SO_4 , NaCl, NaBr, and NaSCN, respectively (e.g., the starting point of each curve from the bottom shows the minimum [salt]). At the same [salt], NaSCN yields the highest CP and Na_2SO_4 the lowest CP. These results indicate that the ability to increase the CPs in the SDS/CPVA mixed systems is in the following order: $\text{Na}_2\text{SO}_4 < \text{NaCl} < \text{NaBr} < \text{NaSCN}$.

Hansson et al. have reported that NaBr showed stronger ability than NaCl in eliminating the phase separation.²⁹ They mentioned that other forces than electrostatic interaction should be responsible for this phenomenon. In fact, the effect of inorganic salt on clouding of nonionic surfactants has been extensively reported. The focus has been on two main categories of ions. Those in one category, which is believed to be the anions on the left-hand side of the Hofmeister series, such as PO_4^{3-} , CO_3^{2-} , HPO_4^{2-} , SO_4^{2-} , OH^- , F^- , and Cl^- , usually decrease the clouding point, while those in the right-hand side, such as Br^- , I^- , and SCN^- , increase it.^{26,27,43,44} In these cases, the corresponding cations of the small inorganic salts show no obvious effect on the clouding. Two mechanisms have been proposed to explain the Hofmeister series behavior.^{27,28} In one mechanism, inorganic salts affect the solvent property of water. It holds that the interactions between water and the salt molecules on the left-hand side of the Hofmeister series are considered weaker than those between water molecules, so that water molecules prefer to form networks through hydrogen bonds. Therefore, these anions are called structure makers which decrease solute solubility (salting-out). On the contrary, the anions on the right-hand side of the Hofmeister series interact more strongly with water, leading to the damage of water structures, and are called structure breakers, increasing solute solubility (salting-in). In an alternative mechanism, the salting-in and salting-out phenomena are directly related to adsorption and desorption of ions to the hydrophilic parts of the amphiphiles. The controversy between the two mechanisms has not been solved yet. However, it seems that the anions on both the left- and right-hand sides of the Hofmeister series increase the CP in our SDS/CPVA mixed systems, and the order of the counterion effect shown in Figure 7 correlates with the position of the ions in the Hofmeister series. Therefore, we infer that the binding of anions to the SDS–CPVA mixed micelles plays an important role in this system. The polarization ability of anions increases in the order of the Hofmeister series, which naturally leads to stronger binding in the same order. It can be expected that, due to the binding of anions to the CPVA molecules, the CPVA shells that wrapped on the surface of SDS micelles will exfoliate, which will reduce the interaction between CPVA and SDS. The more salt, the stronger the binding; the stronger the binding, the less salt is required to increase the same CP. This can be proven from the SAXS results. Figure 8 shows the salt's effect in 7% CPVA–1.75% SDS mixed systems. Three phenomenon should be noted in this figure: (1) the scattering intensity decreases with increase of [NaCl] in low q range, indicating the interaction between the CPVA and SDS being reduced by addition of NaCl; (2) the interaction reduced by 0.08 M NaSCN is similar to that by 0.12 M NaCl, which is in agreement with the CP observation result; and (3) the micelles of SDS did not change obviously with addition of salt, which is a hint that the anions prefer to bind to the CPVA molecules, vice versa, this kind of binding of anions weakened the interaction between CPVA and SDS micelles.

With the above analysis, the decrease of viscosity for the mixed systems will be expected with the increase of added salt. Figure 9 gives the viscosity variation with the addition of NaCl

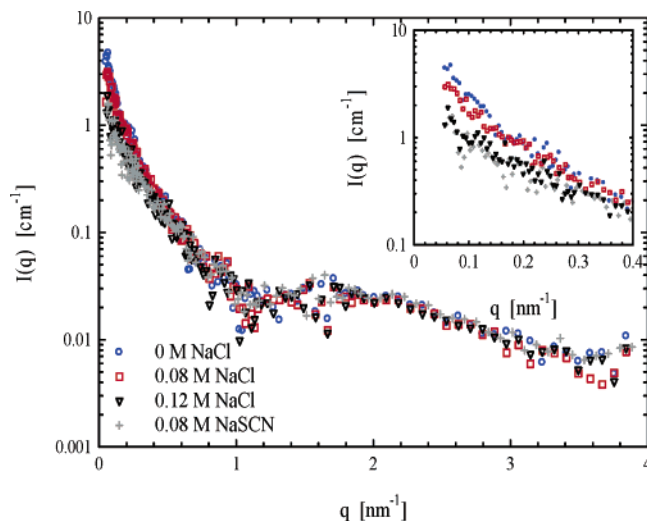


Figure 8. Scattering intensities of the SDS/CPVA mixed system at different salt concentrations, as indicated in the key. For the sake of clarity, the inset shows the graph in the low q region again.

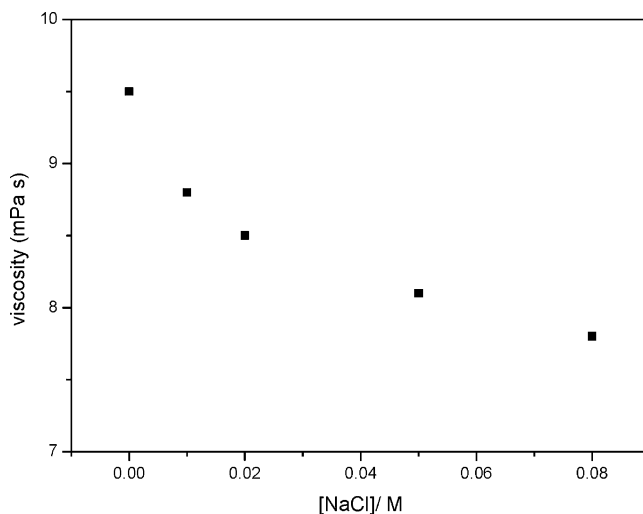


Figure 9. The viscosity change with [NaCl] in the 1.75% SDS–7% CPVA mixed system.

in 1.75% SDS–7% CPVA mixed system at 25 °C. It is noticeable that in all cases, the systems are Newtonian fluids, which agree with the wrapped-global micelle model proposed in the pretext. Up to our expectation, a decrease of zero-shear viscosity from 9.5 to 7.8 mPa s as the [NaCl] changes from 0 to 0.1 M was observed.

Conclusions

Phase separation in SDS–cationic modified PVA (CPVA) mixed systems was found to be a clouding phenomenon. At CPVA concentration lower than 4%, the clouding point was so low that only separated phases were observed in the range of 0–100 °C. On the contrary, the clouding point in solutions with CPVA concentration higher than 8% was so high that only bluish homogeneous solution can be observed. Clouding points for 5%, 6%, and 7% CPVA–SDS mixed systems were found to increase with total concentration and show a minimum at the electroneutral mixing. SDS micelles wrapped by CPVA monomers due to electrostatic interaction existed in all the systems. Small counterions could bind to the shell-like CPVA–SDS micelles, which leads to the surface charge excess for the complex. A certain unit binding degree of counterions is required to elevate the clouding point in the mixed solutions. Addition

of inorganic salt could increase the clouding point in the SDS–CPVA mixed solutions, and their ability follows the order of the Hofmeister series. This was explained by the binding of anions to the CPVA–SDS mixed micelles. The anions on the right-hand side have a stronger ability to bind to the CPVA, which weakened the interaction between CPVA and SDS micelles and increased the surface charge densities of the micelle. As a result, the clouding point was increased and the viscosity of the mixture was found to decrease.

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