Soft Matter

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/softmatter

Dual stimuli-responsive self-assembly transition in zwitterionic/anionic surfactant systems

*Wei Li, * Yanjuan Yang, Lifei Liu, Xiuniang Tan, Tian Luo, and Junya Shen*

Department of Chemistry, Capital Normal University, Beijing, 100048, China

Corresponding author, Tel: +86-10-68903086, e-mail addresses: wli@cnu.edu.cn

Abstract: Temperature and pH responsiveness is important to biological applications in protein reconstitution, gene delivery and controlled drug release. The temperature and pH dual responsive self-assembly transition, vesicle-to-micelle transitions(VMTs) and micelle-to-vesicle transitions(MVTs), in dodecyl sulfonatebetaine (DSB)/sodium bis(2-ethylhexyl) sulfosuccinate (AOT) aqueous solution are investigated. Various experimental techniques including cryogenic transmission electronic microscopy, UV-vis spectrum, fluorescence spectrum, conductivity, and zeta potential were employed to verify the transformation process. Encapsulation of calcein was further applied in the study. The results showed that the self-assembly transition in DSB/AOT aqueous solution is reversible and can be controlled by temperature and pH. It is anticipated that utilizing simple stimuli methods to realize unique self-assembly behaviour in dilute aqueous solution may offer new possibilities in the cancer diagnosis and therapy.

1. Introduction

Surfactants in aqueous solution can self-assemble to form different ordered structures, such as micelle, vesicle, liquid crystal and so on. Micelle and vesicle, as two important types of organized assemblies, have been fully studied fundamentally and practically, especially in their mutual transition. The conversion between them has attracted considerable attention because of its extensive uses in many fields such as demulsification system for petroleum, templating media in materials synthesis, drug delivery and release system in pharmaceutics, and gene transport in biological science.[1] Micelle-to-vesicle transitions (MVTs) in surfactant self-assembly systems have been widely studied with simple methods, such as light, temperature, pH, magnet, electronic, CO_2, electrolytes and hydrophobic additives,[2] for stimulus-responsive materials.[3] Temperature is of the most easily controlled factor in all above, resulting in its great interest. pH has attracted most attention for cancer therapy because the cancerous tissue regions and intracellular compartments are more acidic than normal tissues.[1b] In particular, combination of the temperature and pH has obvious relevance to biological applications in protein reconstitution, gene delivery and controlled drug release, since sick tissues and organs often display abnormal temperature and pH.[2] Moreover, it is important especially for cancer diagnosis and therapy because cancer cells exhibit notable characteristics such as acidic pH due to glycolytic cycle and higher temperature due to their higher proliferation rate.[4] However, conventional surfactants with multiple stimuli sensitivity are still rare.[5] A development of dual pH- and temperature-responsive surfactants system for drug

delivery applications still remains challenges. Because it is very difficult to design and synthesize the diverse supramolecular compounds and surfactants which possess the various groups respond to the exterior different stimuli. Thereby, development of a dual responsive and easy accessible system is necessary and urgent.

It is well-known that many biological or synthetic self-assemblies and interfaces are composed of surfactant mixtures. Since self-assemblies composed of mixed surfactants occur in biological fluids, mixed surfactants are very often preferred in industrial preparations and pharmaceutical and medicinal formulations for the purpose of solubilization, suspension, dispersion etc. [6] Thus, for most practical applications mixed surfactants are used rather than single surfactants. In recent years, mixed surfactant systems containing anionic and cationic surfactants have attracted tremendous attention because they exhibit spontaneous formation of stable unilamellar vesicles in dilute solutions.[7] Kaler et al. were the first to report this in a study on three different cationic/anionic surfactant systems.[7a] Since then, numerous other cationic/anionic systems have been investigated.[7] There are many reports in the literature on the studies of different combinations of mixed surfactant system viz. cationic/cationic, nonionic/nonionic, anionic/nonionic, etc.[8] Solubilization behavior of different compounds in the mixed micellar solution has been observed to be better than individual surfactant micelles. Although a lot of effort has been devoted to understanding the behaviour of cationic/anionic systems, only a few studies on the zwitterionic/anionic systems have been reported.[9] They have revealed that zwitterionic surfactants often have strong interaction with anionic surfactants.

Recently, we reported that compressed CO_2 can induce MVTs in dodecyl sulfonatebetaine (DSB)/sodium bis(2-ethylhexyl) sulfosuccinate (AOT) surfactant system.[10] The CO_2-induced MVTs in the zwitterionic/anionic surfactant system is reversible and the degree of MVTs can be easily controlled by adjusting the pressure. In this work, the temperature and pH dual responsive self-assembly transitions in DSB/AOT aqueous solution have been investigated. Various experimental techniques including cryogenic transmission electronic microscopy (cryo-TEM), UV-vis spectrum, fluorescence spectrum, and Zeta potential were employed to verify the transformation process. In addition, it is interesting to note that the above transition in DSB/AOT system can be reversible at different temperatures and pH, i.e., the system can be switchable from vesicles to micelles or from micelles to vesicles upon temperature and pH value. We hope that the present work will shed new light on the "switch" self assemblies and provide researchers with a well-controlled formulation for future studies.

2. Experiments

2.1. Materials

DSB (>99% purity) was provided by Tokyo Chemical Industry CO. Ltd. AOT (99% purity) was purchased from Sigma. Calcein (A. R. Grade) and cobalt chloride (A.R. Grade) were purchased from Sinopharm Chemical Reagent CO. Ltd. and Xilong Chemical CO. Ltd., respectively. Dimethyl yellow (A. R. Grade) and methyl orange (A. R. Grade) were purchased from Sinopharm Chemical Reagent CO. Ltd. Hydrochloric acid (36-38%, A.R. Grade) was purchased from Beijing chemical works.

They were used without further purification. Double-distilled water was used throughout the experiments.

2.2. Phase behaviour

Phase behaviour of the DSB/AOT aqueous solution was measured by direct observational method. DSB/AOT (4:6, c_{total}=0.020M) aqueous solution was prepared and placed in water bath at a desired temperature. The phase behavior was observed, and photos were taken at different temperature in the process of rising and lowing temperature separately. The temperature of the water bath was controlled by HAAKE D8 temperature controller with an accuracy of ±0.1℃.

2.3. UV-vis absorption spectrometry

Turbidity and micropolarity of mixed solution at different temperatures were carried out with a UV-vis absorption spectrometer, which was produced by Beijing General Instrument Company (Model TU-1810) with a resolution of 0.1 nm. To determine the turbidity, the absorbance was monitored at the wavelength of 514.5 nm where no absorbance was observed for the mixed surfactant system. UV absorbance was recorded after DSB/AOT (4:6, c_{total}=0.020M) aqueous solution was kept in the thermostatic bath at the desired temperature for more than 30 minutes.

The micropolarity of the solution was studied using methyl orange and dimethyl yellow as the probes. The procedures were similar to those of study the turbidity discussed above. The main difference was that two surfactant solutions with the probe methyl orange or dimethyl yellow were loaded into the sample cell. The concentrations of methyl orange and dimethyl yellow in the solution were 2.5 and 0.2

μM respectively. The temperature was controlled by an external thermostatic bath in the measurement of turbidity and micropolarity, and the time needed for the temperature changes was less than 2 min in the study.

2.4. Cryogenic Transmission Electron Microscopy

The samples were prepared in a vitrification robot system (Vitrobot). A drop of the solution was put on holey carbon-coated copper grid, the excess of solution was spread to create a thin liquid film over the grid and then it was rapidly plunged into liquid ethane at its freezing point. Following the vitrification step, samples were transferred in a liquid nitrogen environment by the use of a cold stage unit (Gatan model 626) into the electron microscope, FEI Tecnai 12 G2 TWIN TEM, operating at 120 kV. The working temperature was kept below −175°C, and the images were recorded with a Gatan 794 CCD camera and analyzed by Digital Micrograph 3.6 software.

2.5. Conductivity

A conductivity meter with a precision of ±0.5%, which was produced by the Shanghai Precision Scientific Instrument Co. (Model DDS-307), was used to determine the conductivity. Both the working and counter electrodes were made of Pt foil (thick: 0.3 mm). The cell constant was calibrated with KCl aqueous solution of different concentrations. In a typical experiment, a suitable amount of surfactant solution was placed in a constant-temperature water bath. The temperature of the water bath was controlled by using a HAAKE D8 temperature controller with an accuracy of ±0.1°C. After thermal equilibrium had been reached, which was known

from the fact that conductivity was independent of time, the conductivity of the solution was recorded.

2.6. Zeta potential

The zeta potential values of the aggregates were determined by means of electrophoretic mobilities, using a Malvern Zetasizer-Nano-ZS90 commercial instrument operating with a 4mW He-Ne laser (633 nm wavelength). The measurements were performed by checking the electrophoretic mobilities of the aggregates as determined by laser Doppler velocimetry. Zeta potentials were measured using a temperature-controlled ZetaPlus (Brook Heaven Co.)

2.7. Encapsulation of calcein

The apparatus and procedures to study the encapsulation of calcein of the surfactant systems were same as those used previously.[10] The encapsulation of the formed vesicles and the bilayer permeability were characterized by using calcein (a model compound) as the fluorescent marker and cobalt chloride as the quenching agent. Steady-state fluorescence intensity was measured by a fluorescence spectrophotometer Hitachi F-4500. The concentration of calcein in the bulk solution was kept at 1 mM. Calcein was added into the solution before vesicles were formed to maintain their concentration identical on the inner and outer sides of the bilayer after vesicle formation, followed by 100 mL cobalt chloride (0.1 mM) to quench any external calcein in bulk solution. The fluorescence intensity of calcein was monitored using an excitation wavelength of 495 nm and an emission wavelength of 515 nm. The excitation and emission slits were set at 5 nm. The temperature of fluorescence

measurements was controlled by an external thermostatic bath, and the time needed for the temperature changes was less than 2 min in the study.

3. Result and discussion

3.1. Phase behaviour

The temperature-responsive behaviour of the DSB/AOT aqueous solution can be observed directly from the appearance in turbidity. The visible change of the appearance in turbidity is given in Figure 1. The DSB/AOT (4:6, c_{total}=0.020M) aqueous solution was slightly bluish at 25°C, as shown in Figure 1, which has been proved to be the vesicle.[11] The turbidity decreased with the increased temperature. The increased temperature transformed the turbid blue solution into colorless, which indicated the reduction of vesicles. The solution became almost clear and transparent at 60°C, indicating that the state of aggregation had been changed into other state in the solution. When the temperature dropped to 30°C, the solution returned to slightly bluish, which indicated that the aggregation had been changed again.

Figure 1. Photographs of DSB/AOT (4:6, c_{total}=0.020 M) aqueous solution at different temperatures.

3.2. Turbidity

Turbidity change of DSB/AOT aqueous solution can be measured by UV-visible absorption spectrum. It was shown in Figure 2. We can see from the figure that UV absorbance value of the solution was high at 25°C, and it decreased gradually with the increase of temperature. The decreasing absorbance values showed the decreasing turbidity of the solution, which was coinciding with the appearance in turbidity directly observed. The turbidity further illustrated that temperature could be an influencing factor in transforming the aggregation state of DSB/AOT aqueous solution. While when the temperature dropped to 25°C, the UV absorbance of the solution returned to the original value gradually. These two lines didn't coincide with each other. It may be due to the different transition rate in these two transformation process.

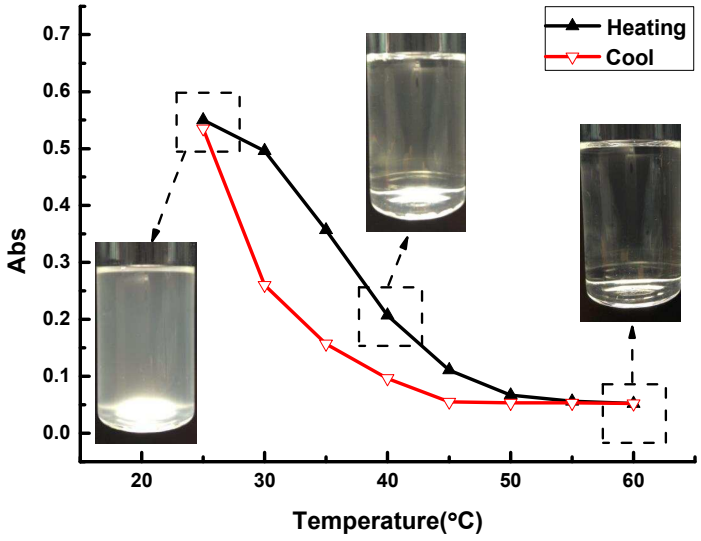
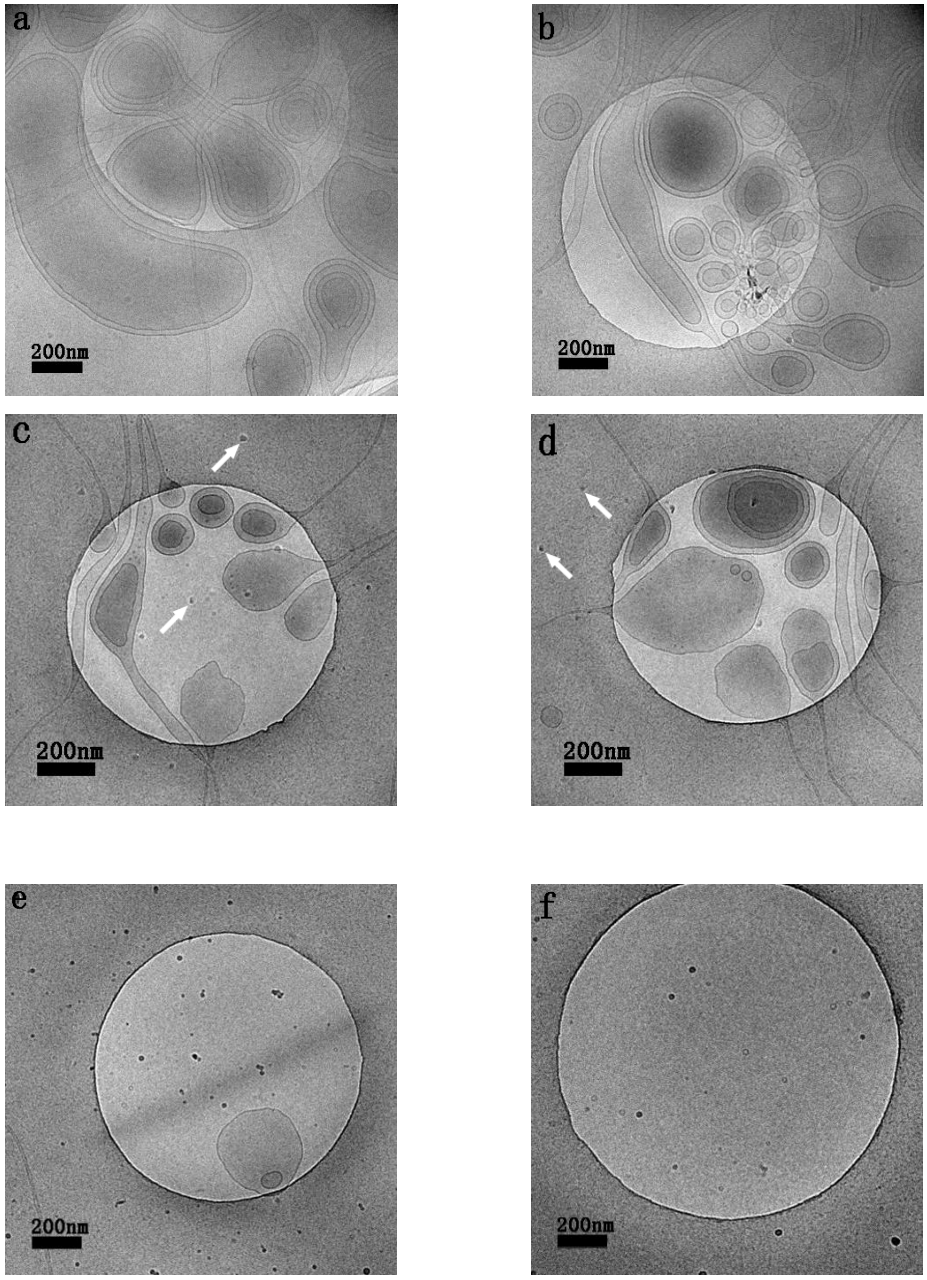


Figure 2. Turbidity changes of DSB/AOT (4:6, c_{total}=0.020 M) aqueous solution at different temperatures.

3.3. Cryo-TEM

To further investigate the behaviours of aggregation and transformation in the solution, cryo-TEM was employed to confirm the self-assembled structures in the study. At ambient temperature (25°C), Figure 3 (a, b) suggested that aggregations in the solution was vesicle colloidal mixture, including unilamellar and multilamellar vesicles. The diameter of most of them was more than 200nm. When the temperature was increased to 40°C, large dimensional vesicles almost disappeared and the size of the aggregation decreased, accompanied with a decrease in the amount of vesicle and an increase in the amount of rod-like and spherical micelles (Figure 3c, d). This showed that the vesicles turned to the rod-like and spherical micelles with increase of the temperature. When heated to 55°C, almost all the vesicles and rod-like micelles transformed to spherical micelles (Figure 4e, f), and the diameter of the spherical micelles was not more than 10 nm. It showed that the vesicles finally transformed into spherical micelles in the mixed surfactant solution. Experiments were further conducted by decreasing the temperature to 40°C, the cryo-TEM images suggested the existence of vesicles along with some rod-like and spherical micelles (Figure 4g, h). This implied that some spherical micelles transformed to rod-like micelles and vesicle with decreased temperature. When cooled to 25°C, the aggregations in the solution were almost multilamellar vesicles (Figure 4i, j). Meanwhile, the size of these aggregates increased to more than 200nm. The results implied that the self-assembly transition in the solution underwent changes from the vesicle to the rod-like micelle and to the spherical micelle with increased temperature. It further showed that the VMTs were reversible and can be controlled by the temperature in

DSB/AOT aqueous solution.



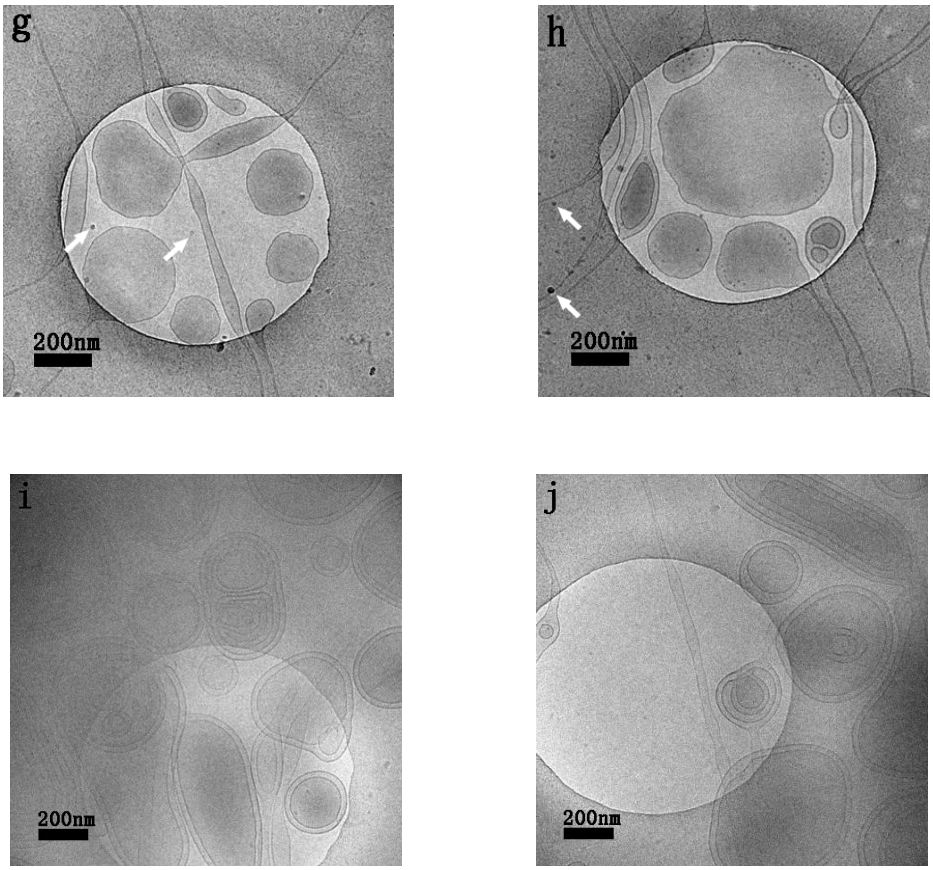


Figure 3. Cryo-TEM images of DSB/AOT (4:6, c_{total}=0.020M) aqueous solution at 25°C (a, b), 40°C (c, d), 55°C (e, f), 40°C (g, h), and 25°C (i, j).

3.4. Conductivity

The conductivity is controlled by the free ion concentration in the solution.[2f] The conductivity increases with the contribution of the free ion in the solution. Figure 4 showed the change of conductivity in DSB/AOT aqueous solution at different temperatures. The conductivity increased quickly with increased temperature, which meant the concentration of free ions increased in the solution. At lower temperature range, DSB/AOT aqueous solution mainly aggregated as vesicles, and the free ions were mostly concentrated in the bilayer of vesicles, resulting in a lower conductivity value. As temperature rose, most vesicles transformed to micelles, and a part of

vesicle bilayer in the solution disappeared, releasing free ions in the bilayer, leading to the increase of conductivity. As temperature decreased, the surfactant molecules in the vesicle bilayer did not contribute to the conductivity any further after the bilayer segments closed up to form vesicles, which resulted in the decrease in conductivity.[12] These two lines also didn't coincide with each other, which was attributed to the different transition rate between the two transformation processes.

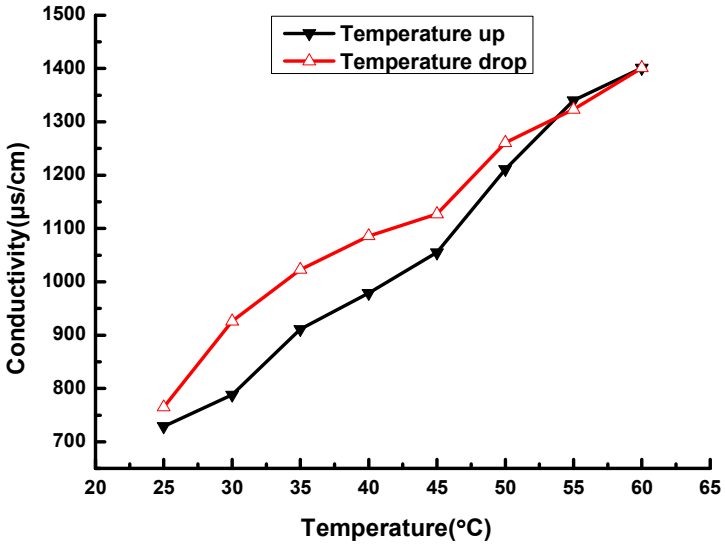


Figure 4. Dependence of electrical conductivity on temperature in DSB/AOT (4:6, c_{total}=0.020M) aqueous solution.

3.5. Zeta potential

Zeta potential indicates the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed micellar aggregates. The variation in zeta potential of DSB/AOT aqueous solution at different temperature is shown in Figure 5. Initially, when temperature rose from 25°C to 55°C, the zeta potential value increased from −119.0mv to −32.5mv, which showed that large

vesicles transformed to small spherical micelles in this region.[14] When temperature dropped to ambient temperature, zeta potential value decreased from −32.5mv to −109.5mv. This result is in accordance with the MVTs process in the literature.[14]

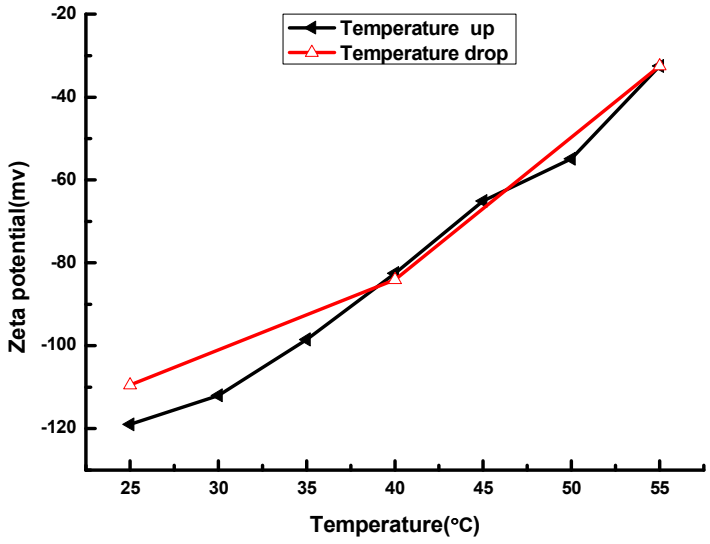


Figure 5. Dependence of zeta potential on temperature in DSB/AOT (4:6, c_{total}=0.020M) aqueous solution.

3.6. Micropolarity characterization

The variation of micropolarity is usually used to study the mechanism of VMTs at the molecular level. Hydrophilic methyl orange (MO) and hydrophobic dimethyl yellow were used as probes. The maximum absorption wavelength (λ_{max}) of MO is sensitive to the polarity of the environment, and the λ_{max} shifts to longer wavelength as the polarity increases.[15] Figure S1 shows the UV spectra of MO in DSB/AOT aqueous solution at different temperatures. Evidently, the UV absorbance decreased monotonically with increasing of the temperature, corresponding to the absorption of the solution turbidity. Meanwhile, the λ_{max} increased from 438nm to 458nm with

increasing of the temperature. This can be explained by the fact that more surfactant exists in the form of vesicles at lower temperature, and polarity of the bilayer/water interface where MO located is weaker. With increase of the temperature, the VMTs occurred and more micelles existed in the solution, more water entered the region where MO existed. Therefore, λ_{max} increased and some MO molecules existed in the aqueous phase. On the other hand, dimethyl yellow, the hydrophobic probe, can also demonstrate the transition in the solution, since it has less effect on the electrostatic interaction in the mixed surfactant systems.[16] Figure S2 illustrates the UV spectra of dimethyl yellow in DSB/AOT aqueous solution at different temperatures. Similarly, the UV absorbance of dimethyl yellow decreased monotonically with increasing of the temperature. The λ_{max} of dimethyl yellow shifted from 407.5nm to 409.5nm when the temperature rose from 25°C to 55°C. The red shift of λ_{max} indicated that the polarity of the environment of the dye became stronger with increase of the temperature. A reasonable explanation was that more surfactant existed in the form of vesicles at 25°C, and the probe existed in the bilayer of the vesicles. When the temperature was increased to 55°C, there were more micelles in the solution. Therefore, the hydrophobic probe distributed in the hydrophobic core of micelles where the polarity became stronger than before. When the temperature was dropped, VMTs occurred in the mixed system and the λ_{max} had a blue shift.

3.7. Encapsulation of calcein in vesicles

VMTs can be further applied in encapsulating the fluorescent guest. It is characterized by using calcein (a model compound) as the fluorescent guest and

cobalt chloride as the quenching agent.[10] The two compounds are commercially available and there is no separation of vesicles from bulk media. The entrapment quantity of calcein in vesicles was deduced according to the difference of fluorescence intensity before and after quenching. Calcein was added into the solution before the formation of vesicles to maintain the concentration identical on both sides (inside and outside) of the vesicle bilayer after the formation of vesicles, followed by adding 100 μL cobalt chloride (0.1 mM) to quench the external calcein in bulk solution. [10, 17] First of all, the fluorescence intensity of calcein at different ratios of DSB/AOT from 0.1 to 0.9 in the solution was measured and the results were shown in Figure 6. It was clear that the fluorescence intensity was very high (more than 7000) when the ratio was below 0.5, while the fluorescence intensity was less than 500 when the ratio was above 0.5. This implied that only when the ratio of DSB/AOT was below 0.5 can the vesicles come into formation. The vesicles kept calcein from being quenched by Co^{2+} in DSB/AOT aqueous solution. The fluorescence intensity was proportional to the fluorescence concentration of calcein in the solution. As the quenching agent, cobalt chloride was added into the vesicle solution. Calcein which was outside of the vesicle (in the external solvent to be exactly) was quenched. The other calcein entrapped inside the vesicle escaped from being quenching. So the fluorescence intensity was proportional to volume of aqueous core in vesicles. It was illustrated in the Scheme S1. Moreover, the fluorescence intensity of calcein decreased gradually when the ratio of DSB/AOT changed from 0.1 to 0.4. It further implied that the volume of aqueous core in vesicle decreased with the increasing of

the DSB/AOT ratio in the solution. The fluorescence intensities of calcein quenched by Co^{2+} in DSB/AOT aqueous solution at different temperature and ratio of DSB/AOT are shown in Figure S3. At ambient temperature, the original fluorescence intensity in vesicle solution was high, but decreased after being quenched in the buffer solutions, suggesting that a certain amount of calcein was entrapped in the vesicles. The fluorescence intensities decreased with increasing of the temperature, which was due to the occurrence of VMTs in the solution. Thus, the calcein entrapped by vesicles was released and quenched by Co^{2+} in the solution (Scheme S1). It was consistent with the above result.

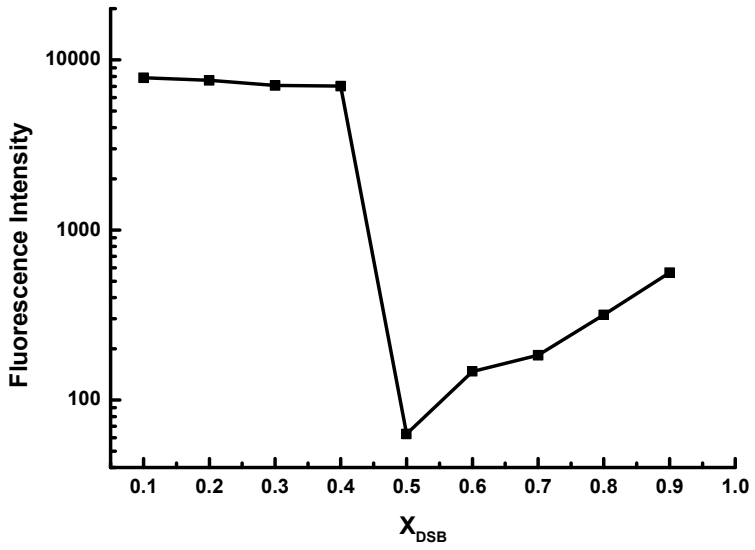


Figure 6. Dependence of fluorescence intensity on ratio in DSB/AOT aqueous solution.

3.8. pH-responsive behaviour of DSB/AOT aqueous solution

The pH-responsive behaviour of DSB/AOT aqueous solution can be investigated by visual observation and fluorescence technology. The photographs of DSB/AOT

aqueous solution with different pH were shown in Figure S4. DSB/AOT aqueous solution was slightly bluish at neutral solution, as shown in Figure S4a. Precipitate was formed immediately when pH of the solution was decreased to 5.25 as shown in the photograph in Figure S4b. However, when the solution returned to neutral with the addition of ammonia, the precipitate dispersed, and the aqueous solution was slightly bluish again (Figure S4c). To investigate the transition of aggregates in DSB/AOT aqueous solution with pH, hydrophobic dimethyl yellow was used as the probe to character the variation of micropolarity as the above method. The result verified that the occurrence of VMTs with adjusting pH of the solution (Figure S5).

To further investigate the pH-switch aggregate transitions in DSB/AOT aqueous solution, the encapsulation of fluorescent guest was also employed in the study. The fluorescence intensities of calcein quenched by Co^{2+} in DSB/AOT aqueous solution at different pH are shown in Figure 7. From the curve of X_{DSB}=0.4, we can see that the original fluorescence intensity of calcein was high, suggesting that a certain amount of calcein was entrapped in vesicles. With the decrease of the pH value, the fluorescence intensities decreased sharply. When pH value decreased to 4.33, the fluorescence intensities of calcein were almost quenched completely. While the pH of the solution turned to neutral with the addition of acid, the fluorescence intensities increased to the original value. For the solution of X_{DSB}=0.1, the fluorescence intensities at neutral solution were higher than that of X_{DSB}=0.4. While the pH of the solution decreased to 4.33, fluorescence intensities almost disappeared, which was same with that of X_{DSB}=0.4.

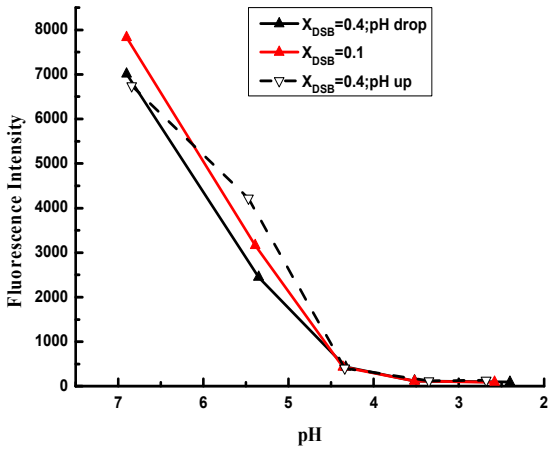
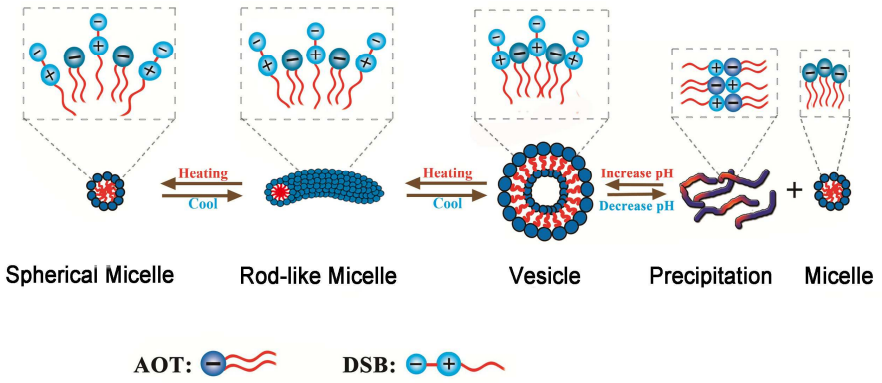


Figure 7. Dependence of fluorescence intensity on pH value and proportion in DSB/AOT aqueous solution.

According to the results above, we attempt to understand and reveal the mechanism of how temperature and pH drive the morphological transitions of the aggregates in aqueous solution, which is schematically presented at the top of Scheme 1. For the transition regulated by temperature, the geometry rule has been widely used to explain the transformations of organized assemblies, where p is a packing parameter: $p < 1/2$ for micelles and $1/2 < p < 1$ for vesicles or lamellar structures.[18] p is defined as V/al, where V is the surfactant tail volume, l is the tail length, and a is the average headgroup area. The electrostatic attraction between cation of DSB and anion of AOT decreases gradually with increased temperature in surfactant solution, and the distance of catanionic surfactant headgroups increases.[19] Thus the average headgroup area is increased, which means a is enlarged. As a result, p reduces to fewer than 0.5, promoting the formation of micelle. The rod-like micelle appeared first for the value of p was higher than that of the spherical micelle. With increased the temperature, the

value of *a* continued to increase, while that of *p* reduced to the critical point and the spherical micelle formed. Thus, this process can be concluded that the transformation from vesicles to rod-like micelle and to spherical micelle is heating-induced. On the contrary, the electrostatic attraction increases with decreased temperature, accordingly the average headgroup area *a* decreases. Thus the value of *p* increases to over 0.5, and the aggregates transformed into vesicles. The transformation process from spherical micelle return to rod-like micelle and vesicles realized.

For the transition with pH, the possible reason may be due to the attraction between cation and anion.[20] During the transition process, the precipitation was formed because of the intense attraction between cation of DSB in the acid solution and anion of AOT, and the surplus anion of AOT self-assemble to form the micelles (Scheme 1). When the pH of the solution was below 4.33, the fluorescence intensities almost died out, i.e. most vesicles in the solution were transformed into precipitation and AOT micelles. When the solution returned to neutral, the precipitation and micelles were transformed into vesicles with the showing of the fluorescence intensities. It implied that the interaction force, strengthened by the acidity, was strong enough to overcome the attraction force between cation and anion.



Scheme 1. Mechanism of the vesicle-to-micelle transition in DSB/AOT (4:6, c_{total}=0.020M) aqueous solution.

Conclusion:

In the present study, temperature and pH responsiveness are systematically studied in zwitterionic/anionic (DSB/AOT) mixed surfactant systems. It is demonstrated that the self-assembly transition controlled with temperature undergoes changes from the vesicle to the rod-like micelle and to the spherical micelle, which is observed by the cryo-TEM. With increase of the DSB/AOT ratio in the solution, the volume of aqueous core in vesicle decreased. Meanwhile, the self-assembly transition from vesicle to micelle also can be regulated with pH in this zwitterionic/anionic mixed surfactant systems. With decreasing of the pH value, the vesicles in the solution were decreased sharply. When the pH decreased to 4.33, the vesicles almost disappeared and transformed into micelle. It was reversible for this self-assembly transition regulated with temperature and pH in DSB/AOT aqueous solution. The geometry rule can be used to explain the transformations of organized assemblies with temperature

for the changes of average headgroup area. For the transition with pH, the possible reason may be due to the attraction between cation and anion. It is anticipated that utilizing this simple stimuli methods to realize unique self-assembly behaviour in dilute aqueous solution may offer new possibilities in the cancer diagnosis and therapy. As both temperature and pH are crucial for living organisms, the system also provides inspiration for biomimicry by using mixed surfactant system.

Acknowledgement

This work was supported by Beijing Natural Science Foundation（2142011）and General Program of Science and Technology Development Project of Beijing Municipal Education Commission (No. KM201310028007).

References

1 (a)P. M, Pileni, Nat Mater, 2003, 2, 145-150; (b)I. W. Hamley, Angew. Chem. Int. Ed., 2003, 115, 1730-1752; (c)Y. Li, D. Wang, Z. Hao, J. Hao and C. C. Han, Chem. Eur. J., 2007, 13, 4782-4785.

2 (a)J. Eastoe and A. Vesperinas, Soft Matter, 2005, 1, 338; (b)H. Yin, Z. Zhou, J. Huang, R. Zheng and Y. Zhang, Angew. Chem. Int. Ed., 2003, 42, 2188-2191; (c)Y. Yi, D. Jinfeng, C. Bo, J. Zan, C. Li and L. Xuefeng, Soft Matter, 2013, 9, 1458-1467; (d)P. Brown, A. Bushmelev, C. P. Butts, J. Cheng, J. Eastoe, I. Grillo, R. K. Heenan and A. M. Schmidt, Angew. Chem. Int. Ed., 2012, 51, 2414-2416; (e)T. Koji, O. Yoichi, K. Yukishige, Y. Norio, Ohkubo, S. Hideki and A. Masahiko, Journal of the American Chemical Society, 2004, 126, 12282-12283; (f)W. Li, J. Zhang, Y. Zhao, M. Hou, B. Han, C. Yu and J. Ye, Chem. Eur. J., 2010, 16, 1296-1305; (g)J. Wang, A. Song, X. Jia, J. Hao, W. Liu and H. Hoffmann, J. Phys. Chem. B., 2005, 109, 11126-11134; (h)H. Yin, S. Lei, S. Zhu, J. Huang and J. Ye, Chem. Eur. J., 2006, 12, 2825-2835.

3 Z. Chu, C. A. Dreiss and Y. Feng, Chemical Society reviews, 2013, 42, 7174-7203.

4 K. Zhou, Y. Wang, X. Huang, K. Luby-Phelps, B. D. Sumer and J. Gao, Angew. Chem. Int. Ed., 2011, 50, 6109-6114.

5 (a)J. Bigot, B. Charleux, G. Cooke, F. Delattre, D. Fournier, J. Lyskawa, L. Sambe, F. Stoffelbach and P. Woisel, Journal of the American Chemical Society, 2010, 132, 10796-10801; (b)H. Wu, J. Dong, C. Li, Y. Liu, N. Feng, L. Xu, X. Zhan, H. Yang and G. Wang, Chem Commun 2013, 49, 3516-3518.

6 (a)R. Bury, C. Treiner, J. Chevalet, A. A. Makayssi and C. Acta, 1991, 251, 69-77; (b)M. A, B. R and T. C, Langmuir, 1994, 10, 1359-1365.

7 (a)E. W. Kaler, A. K. Murthy, B. E. Rodriguez and J. A. Zasadzinski, Science, 1989, 245, 1371-1374; (b)A. Shioi and T. A. Hatton, Langmuir, 2002, 18, 7341-7348.

8 (a)E. H. Md, R. D. Akhil, K. R. Animesh and P. M. Satya, Langmuir, 1996, 12, 4084-4089; (b)S. B. Sulthana, P. V. C. Rao, S. G. T. Bhat, T. Y. Nakano, G. Sugihara and A. K. Rakshit, Langmuir, 2000, 16, 980-987; (c)C. M, C. L, O. O, P. L and V. V, Langmuir, 1998, 14, 5994-5998; (d)S. B. Sulthana, P. V. C. Rao, S. G. T. Bhat and A. K. Rakshit, J. Phys. Chem. B., 1998, 102, 9653-9660.

9 (a)C. C. N, D. D. N, A. K. P, P. A. K and L. A, Langmuir, 2004, 20, 565-571; (b)J. R. Milton, Langmuir, 1991, 7, 885-888; (c)O. D. D. L, I. García-Mateos, a. Vel and M. M, Colloids Surf. A, 2005, 270 271, 153-162.

10 W. Li, Y. Yang, T. Luo, J. Zhang and B. Han, Physical chemistry chemical physics : PCCP, 2014, 16, 3640-3647.

11 L. M. Zhai, G. Z. Li, Z. W. Sun., Colloids and Surfaces A, 190 (2001) 275–283.

12 A. Pizzino, M. P. Rodriguez, C. Xuereb, M. Catte, E. Van Hecke, J. M. Aubry and J. L. Salager, Langmuir, 2007, 23, 5286-5288.

13 A. Mohanty, T. Patra and J. Dey, J. Phys. Chem. B., 2007, 111, 7155-7159.

14 Y. L. Sun, S. S. Wang, X. Han and Z. X. Chen, J. Phys. Chem. B.,2012, 116, 12372-12380.

15 W. Li, J. Zhang, S. Cheng, B. Han, C. Zhang, X. Feng and Y. Zhao, Langmuir, 2009, 25, 196-202.

16 Y. Yan, J. Huang, Z. Li, F. Han and J. Ma, Langmuir, 2003, 19, 972-974.

17 (a) L. M. Zhai, J. P. Zhao, M. Zhao, Y. J. Chen and L. J. Zhang, J. Dispersion Sci. Technol., 2007, 28, 455; (b) K. Tomoko, T. Akira, M. Kiminori and I. Fumiyoshi, Colloids Surf., B, 2002, 27, 323.

18 J. N. Israelachvili, D. J. Mitchell and B. W. Ninham, J. Chem. Soc., Faraday Trans.2, 1976, 72, 1525-1568.

19 (a) K. Wang, H. Q. Yin, W. Sha, J. B. Huang and H. L. Fu, J. Phys. Chem. B 2007, 111, 12997-13005. (b) H. Q. Yin, Y. Y. Lin, J. B. Huang and J. P. Ye, Langmuir 2007, 23, 4225-4230.

20 Y. Y. Lin, X. Han, X. H. Cheng, J. B. Huang, D. H. Liang and C. L. Yu, Langmuir 2008, 24, 13918-13924.