Temperature-induced vesicle to micelle transition in cationic/cationic mixed surfactant systems

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Abstract

Temperature-induced vesicle to micelle transition (VMT), which has rarely been reported in cationic/cationic mixed surfactant systems, was systemically studied in a didodecyldimethylammonium bromide (DDAB)/dodecyltrimethylammonium chloride (DTAC) aqueous solution. We investigated the effect of temperature on DDAB/DTAC aqueous solutions by means of turbidity, conductivity, cryo-TEM, UV-vis spectrophotometer, and steady-state fluorescence spectrometer. It was found that increasing temperature could induce the transformation from vesicle to micelle in this cationic/cationic mixed surfactant system. The degree of the transformation can be easily controlled by the operation temperature. Additionally, by adjusting the proportion of the mixed cationic/cationic systems and employing cationic surfactants with different chain-lengths, we are able to conclude that the hydrophobic tail length of the surfactant affects the aggregation behavior in cationic/cationic mixed surfactant systems as a function of temperature. It is universal to induce the transformation from vesicle to micelle by temperature in cationic/cationic mixed surfactant systems. A

possible mechanism for the temperature-induced VMT was proposed based on the experimental results.

1. Introduction

The study of mixed surfactant systems is an important topic because the surfactants in the solutions often produce a synergetic effect, new functions, and new organized molecular assemblies.[1] Since the example of a spontaneous formation of vesicle from mixed cationic and anionic single chain surfactants was reported in 1989, this filed has attracted considerable attention and interest in recent years.[2] Various mixed surfactant systems, including cationic/cationic, nonionic/nonionic, anionic/nonionic, and zwitterionic/anionic surfactant systems, have been found to form vesicles in dilute aqueous solutions at the appropriate proportion and concentration.[3] Micelles and vesicles, as two important types of organized assemblies, have essential impacts on the basic research and practical application by regulating their mutual transitions. The conversion between micelles and vesicles has attracted considerable attention because these equilibrium aggregates can serve as biological model membranes,[4,5] containers for encapsulation and eventual release of drugs, flavors, and fragrances,[6] and microreactors for the formation of a range of inorganic nanoparticles.[7] It is important for us to understand micelle to vesicle transition under external conditions and the reverse process in their technological applications. The transformation between micelle and vesicle can be realized by the variation of external conditions.[8] Among them, the physical-chemical factors have great impact on the molecular inter-atomic forces of the surfactants, and controlling these factors can afford an easier way to realize the regulating process. These factors mainly include the composition, ratio, temperature, additives (organic, polymer, metal nanoparticles, and proteins) and force fields of the surfactant in aqueous solution.[9] Temperature is the most easily controlled factor from the list above, which attracts a great deal of attention. Meanwhile, the temperature-sensitive systems are convenient for investigating the stage of individual surfactants in the aggregate's transition process because the transition can be cycled or stopped at any required step during the measurements. Significant research about the transition between micelles and vesicles controlled by temperature in different mixed surfactant system, including anionic/cationic, bolaamphiphiles/anionic, zwitterionic/anionic and anionic/nonionic surfactants systems, has been fully developed in recent years.[10] Compared with the others mixed surfactant system, only a few studies on the cationic/cationic mixed surfactant systems has been reported to show a spontaneous formation of vesicles in solution.[3e,3h,11] It is generally acknowledged that there was a strong repulsion between the same kinds of ionic charge. The self-assembly transformation was due to the interaction between the aggregation molecules. So far no work has been presented to show that the aggregation behavior of cationic/cationic mixed surfactant systems can be regulated by extrinsic triggers such as temperature.

In this work, we investigated the effect of temperature in didodecyldimethylammonium bromide (DDAB)/dodecyltrimethylammonium chloride (DTAC) (x_{DDAB}=0.3, c_{total}=0.030 M) aqueous solution by means of turbidity, conductivity, TEM, UV-vis spectrophotometer, and steady-state fluorescence spectrometer. It was found that temperature could induce the transformation from vesicle to micelle in DDAB/DTAC aqueous solutions And that the degree of the transformation can be easily controlled by the operation temperature. Additionally, by adjusting different proportions and employing cationic surfactants with different chain-lengths, we are able to show that the hydrophobic tail length of the surfactant affects the aggregation behavior in cationic/cationic mixed surfactant systems as a function of temperature. It is universal to induce the transformation from vesicle to micelle by temperature in cationic/cationic mixed surfactant systems. A possible mechanism for the temperature-induced vesicle to micelle transition (VMT) in cationic/cationic mixed surfactant systems was proposed based on the experimental results.

2. Experiment

2.1 Materials

DDAB (99%) and DTAC (99%) were purchased from Aladdin Industrial Inc. Trimethyltetradecylammonium chloride (TTAC, 99%) and hexadecyltrimethylammonium chloride (HTAC, 99%) were purchased from Xiya Reagent Co., Ltd. Pyrene, dimethyl yellow and Methyl orange (A.R.) were purchased from Sinopharm Chemical Reagent Co., Ltd. They were used without further purification. All solutions were prepared with deionized water.

2.2. Phase behaviour study

Phase behaviour of the DDAB/DTAC mixed surfactant solution was measured by direct observation. DDAB/DTAC (x_{DDAB}=0.3, c_{total}=0.030 M, x_{DDAB}= $c_{\mathrm{DDAB}}/c_{\mathrm{total}}$) mixed aqueous solutions were prepared and placed in a water bath at a desired temperature, the phase behavior was observed and photographed at different temperatures. The temperature of the water bath was controlled by HAAKE D8 temperature controller with an accuracy of ±0.1°C.

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 in the mixed surfactant system. UV absorbance was recorded after DDAB/DTAC (x_{DDAB}=0.3, c_{total}=0.030 M) aqueous solutions were kept in the thermostatic bath at the desired temperature for at least 30 minutes.

The micropolarity of the solution was studied using methyl orange and dimethyl yellow as the probes in the study. The procedure was similar to the turbidity measurement process discussed above. The main difference was that two surfactant solutions with a 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, the time needed for the temperature changes was less than 2 minutes.

2.4. Conductivity measurement

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 aqueous KCl solutions at 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 adjusted by using a HAAKE D8 temperature controller with an accuracy of ±0.1°C. After thermal equilibrium had been reached, the conductivity of the solution was recorded.

2.5. Cryogenic Transmission Electron Microscopy

Samples for Cryogenic TEM were prepared in a vitrification robot system (Vitrobot). A drop of the solution was put on a holey carbon-coated copper grid, the excess of solution was spread to create a thin liquid film over the grid and was then immediately plunged into liquid ethane at its freezing point. Following the vitrification step, samples were transferred to a liquid nitrogen environment by the use of a cold stage unit (Gatan model 626) in 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.

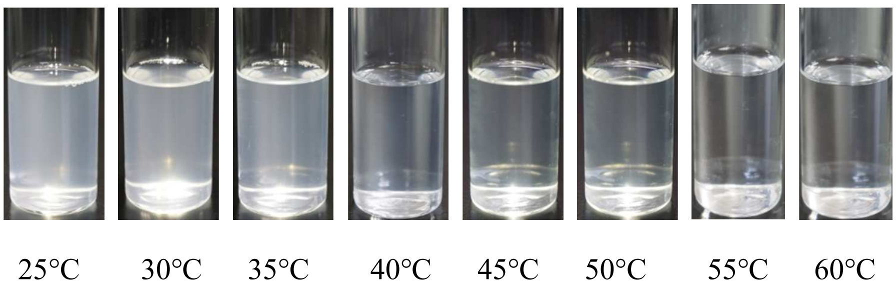
3. Results and discussion

3.1. Phase behavior with increasing temperature

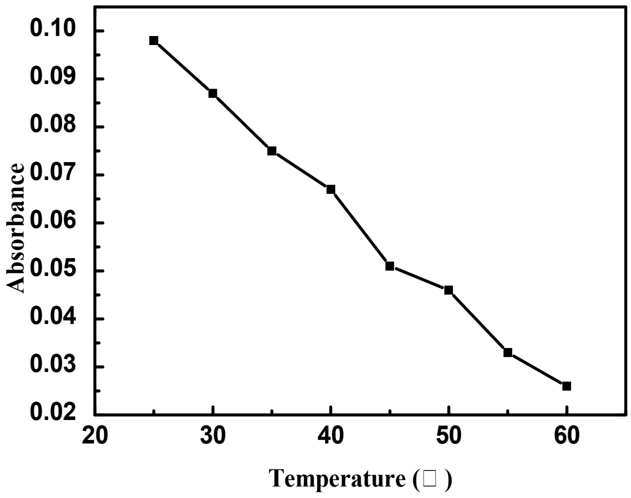
DDAB/DTAC (x_{DDAB}=0.3, c_{total}=0.030 M) aqueous solutions are slightly bluish at

25°C (Figure 1a), which is typical of the presence of vesicles. [3e] When the solution is gradually heated to 60°C, a transition from slightly bluish to transparent and colorless is observed, indicating that the state of aggregation has been changed into another state in the solution.[12]

UV-Vis spectroscopic analysis is often used to measure the turbidity of solutions.[12,13] In this study, the turbidity of the surfactant solutions with increasing temperature is observed with this method. As is shown in Figure 1b, the UV absorbance of the solution varies at different temperature. The UV absorbance of the solution is nearly to 0.10 at 25°C. The turbidity decreases gradually as the solution is heated to 60°C, and the UV absorbance is also decreased to 0.03. The variation of turbidity with temperature is consistent with the direct observation.



(a)



(b)

Figure 1. (a) Photographs and (b) UV absorbance of the variation in DDAB/DTAC (x_{DDAB}=0.3, c_{total}=0.030 M) aqueous solutions at different temperatures.

3.2. Cryogenic TEM characterization

To further investigate the 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 2 (a) suggests that aggregations in the solution are almost vesicles. The diameter of most of them is more than 100nm. When the temperature is increased to 40°C, the size of the vesicle decreased to less than 100nm, the overall number of vesicles decreases whilst the presence of micelles is observed (Figure 2b). When heated to 55°C, almost all the vesicles transform to micelles (Figure 2c), and the diameter of the micelles is about 10 nm.

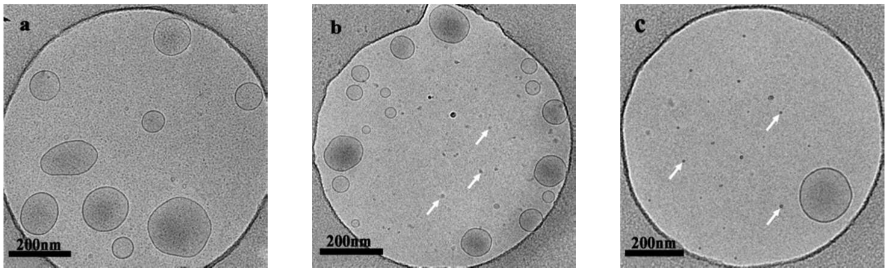


Figure 2. Cryo-TEM images of DDAB/DTAC (x_{DDAB}=0.3, c_{total}=0.030 M) aqueous solutions at (a) 25°C, (b) 40°C, and (c) 55°C.

3.3. Conductivity study

Conductivity determination is one of the most useful techniques to study aggregation in surfactant solutions,[13,14] and the results can provide information on the transition from micelles to vesicles.[13,15] The conductivity is controlled by the free ion concentration in the solution.[12,13a] and increases with the contribution of the free ion in solution. Figure 3 shows the change of conductivity in DDAB/DTAC aqueous solutions at different temperatures. The conductivity increases quickly with the increase of temperature, which means the concentration of free ions increases in the solution. At lower temperature ranges, DDAB/DTAC aqueous solution mainly aggregates as vesicles, and the free ions are mostly concentrated in the bilayer of the vesicles, resulting in a lower conductivity value. As the temperature is increased, most vesicles transformed to micelles, and a part of vesicle bilayer in the solution disappears. This releases free ions into the bilayer, leading to an increase of the conductivity. The turning point appears at 45°C may be regarded as transition from multilayer to monolayer vesicles in the solution.[15a] This result is in accordance with the VMT process of the former research.[12,13a]

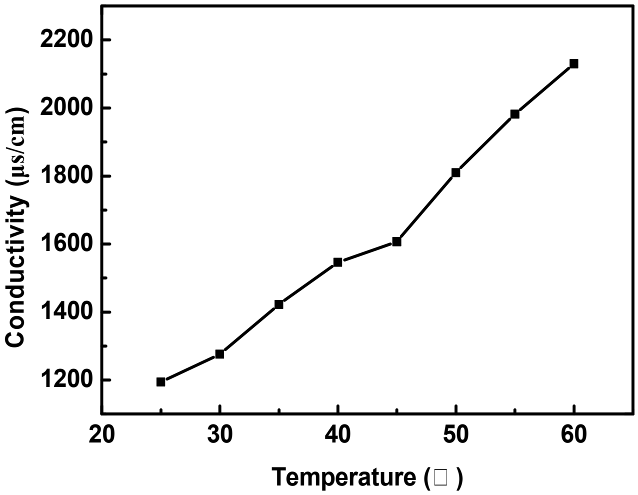


Figure 3. Variation of conductivity with temperature in DDAB/DTAC (x_{DDAB}=0.3, c_{total}=0.030 M) aqueous solutions.

3.4. Fluorescence-probe study

To further investigate the transformation from vesicles to micelles with temperature, pyrene has been encapsulated in the vesicles as fluorescence probe. The intensity ratio of the first and the third vibronic peak in the fluorescence spectra of pyrene (I_1/I_3) is very sensitive to solvent polarity and therefore this property has been widely used to measure the micropolarity of bilayer.[16] Pyrene, which is soluble in the interiors of the micelles, was used as the indicator for the micropolarity change when vesicles endured a structural transition. Figure 4 shows the change of I_1/I_3 in the solution at varying temperature and the higher value of I_1/I_3 indicates a more polar environment. A decrease of the I_1/I_3 ratio is observed when the solution is heated to a higher temperature. The results imply that pyrene initially solubilized in vesicles layers is released and then enters the more ordered layers of the mixed micelles. On the other hand, large vesicles turning into small micelles providea less polar membrane area.

Both results contribute to the decrease of I_1/I_3.[17] In Figure 4, the ratio decreased from 1.27 to 1.18 with the increasing temperature. Therefore, the decrease in the I_1/I_3 ratio supported the argument that the vesicles transformed into micelles gradually in solution with the increasing temperature. The result is also in accordance with the VMT process of the former research.[12,17]

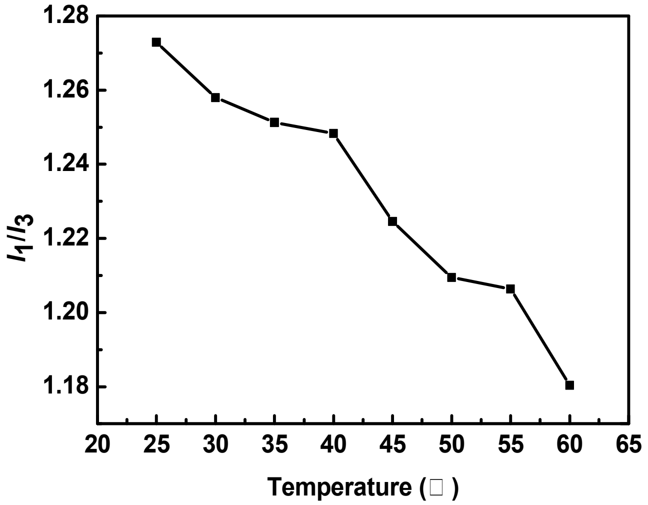


Figure 4. Dependence of I_1/I_3 band ratio in the fluorescence spectra of pyrene on temperature in DDAB/DTAC (x_{DDAB}=0.3, c_{total}=0.030 M) aqueous solutions.

3.5. Micropolarity characterization

The variation of micropolarity has been used to study the mechanism of vesicle-to-micelle transitions at the molecular level. Hydrophilic methyl orange (MO) and hydrophobic dimethyl yellow are used as probes. The maximum absorption wavelength (λ_{max}) of MO is sensitive to the polarity of the environment, and shifts to longer wavelengths as the polarity increases.[13c,18] Figure 5 shows the UV spectra of MO in DDAB/DTAC aqueous solutions at different temperatures. Evidently, the UV absorbance decreases monotonically with the increase of temperature, corresponding to the absorption of the solution turbidity. Meanwhile, the $\lambda_{\max}$ increases from 412nm to 416nm with the increasing temperature. We know that the MO probes solubilize in the aqueous solutions when surfactant molecules exist in the forms of micelle, $\lambda_{\max}$ shifts to longer wavelengths with the increasing polarity of the medium. And in the vesicle, the MO probes reside in the interfacial region of the vesicle, $\lambda_{\max}$ is also red-shifted with the increasing polarity.[13c,18] At the low temperature, the surfactants exist mainly in the forms of vesicles. The MO probes are located in the bilayer/water interface region. While at the high temperature, some surfactant molecules are transformed from vesicle to micelle. More and more MO probes solubilize in the water, where the environment of the dye becomes more polar. Therefore, $\lambda_{\max}$ increased and some MO molecules enter in the aqueous phase, which is consistent with the previous research.[12,13c]

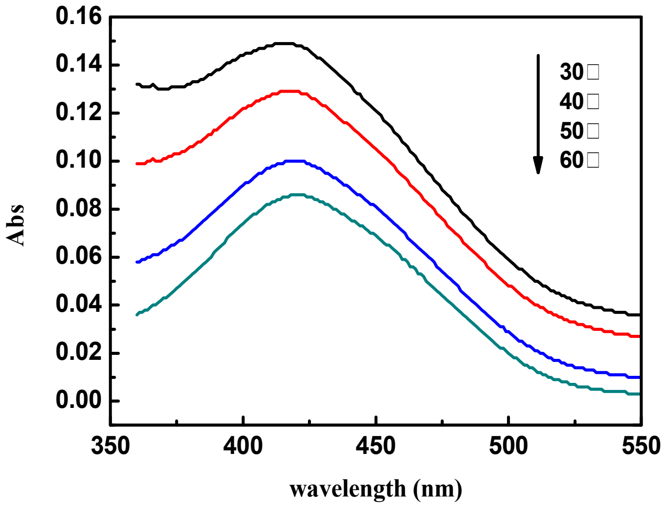
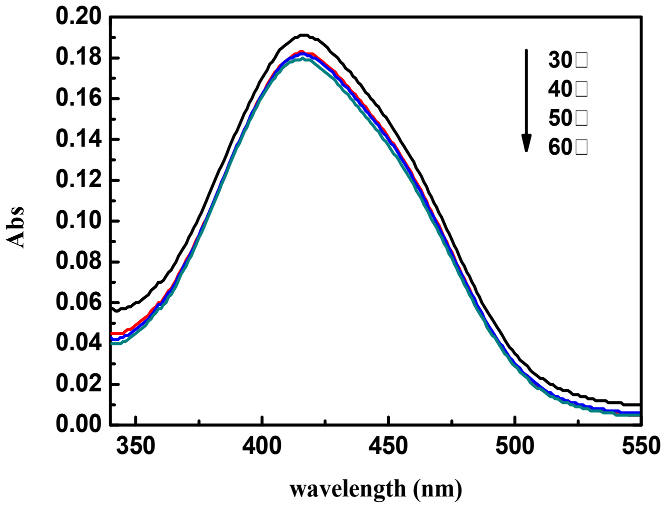
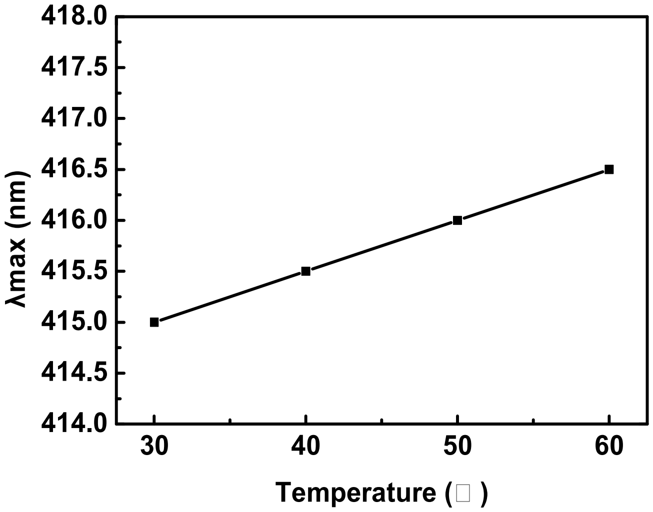


Figure 5. Dependence of UV-vis spectra for MO with temperature in DDAB/DTAC (x_{DDAB}=0.3, c_{total}=0.030 M) aqueous solutions.

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.[19] Figure 6a illustrates the UV spectra of dimethyl yellow in DDAB/DTAC aqueous solutions at different temperatures. As with MO, the UV absorbance of dimethyl yellow decreases monotonically with the increasing temperature. The λ_{max} of dimethyl yellow shifts from 415.0nm to 416.5nm when the temperature rises from 30°C to 60°C (Figure 6b). The red shift of λ_{max} indicates that the environment of the dye becomes more polar with increasing temperature. A reasonable explanation is that more surfactants exist in the form of vesicles at ambient temperature, and the probe exists in the bilayer of the vesicles. When the temperature is increased, there are more micelles in the solution. Therefore, the hydrophobic probe becomes distributed in the hydrophobic layer of micelles where the environment of the dye becomes more polar than before. The result is also in line with that of the former study.[12,13c]



(a)

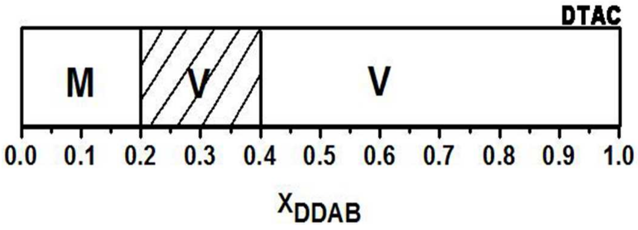


(b)

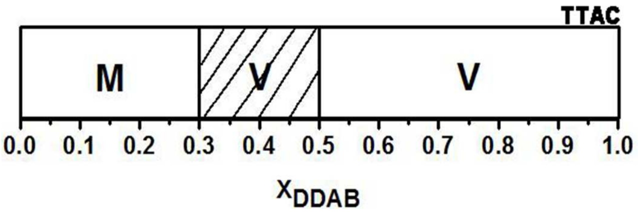
Figure 6. Dependence of (a) UV-vis spectra and (b) λ_{max} of dimethyl yellow on temperature in DDAB/DTAC (x_{DDAB}=0.3, c_{total}=0.030 M) aqueous solutions.

3.6. The effective region of VMT in DDAB/DTAC system and other DDAB/cationic surfactant systems

To further investigate the applicability of VMT induced by temperature in cationic/cationic mixed surfactant systems, different concentrations of x_{DDAB} in DDAB/DTAC system and other DDAB/cationic surfactant systems have been stuided. Figure 7(a) shows the phase diagram of DDAB/DTAC system at c_{total}=0.030 M with the variation of x_{DDAB}. The effective region of VMT which can be induced by temperature is near the micelle region ($0.2<x_{DDAB}<0.4$) in DDAB/DTAC system. Further work demonstrates that the temperature-induced VMT can also be found in other DDAB/cationic surfactant systems, such as DDAB/TTAC and DDAB/HTAC (the UV absorbance variation with temperature are shown in Figure S1 and Figure S2). Figure 7(b) and (c) show the phase diagram of DDAB/TTAC and DDAB/HTAC system at c_{total}=0.030 M with the variation of x_{DDAB}. From Figure 7(b), we can see that the vesicle formation in DDAB/TTAC starts when x_{DDAB}=0.3, and the effective region of VMT induced by temperature is between 0.3 to 0.5 of x_{DDAB}. Similarly, the effective region of the DDAB/HTAC system is $0.45<x_{DDAB}<0.55$, which is near the micelle region in Figure 7(c). It is implied that the VMT induced by temperature can be easily realized at the region near the micelle in the DDAB/cationic surfactant system. Because the double-chained molecules (DDAB) prefer to aggregate in the form of vesicles, the DDAB/cationic mixtures can form vesicles at low x_{DDAB} but require enough c_{total}.[11a] With the increase of the chain length of the single-chain cationic surfactant, the vesicle formation in the DDAB/cationic mixtures becomes difficult at the same c_{total}. Meanwhile, the effective regions of VMT induced by temperature become rightward and narrow in the phase diagrams.



(a)



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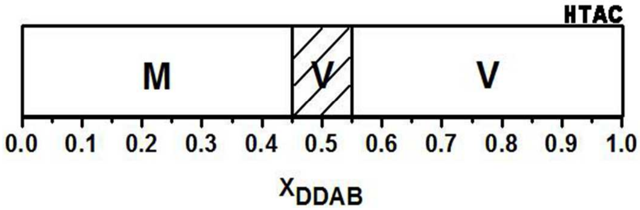


(c)

Figure 7. Phase diagrams for (a) DDAB/DTAC, (b) DDAB/TTAC and (c) DDAB/HTAC aqueous solutions with c_{total}=0.030 M. The shadowed area is the effective region of VMT induced by temperature. M = micelles, V = vesicles.

3.7. Mechanism for VMT in cationic/cationic surfactant systems induced by temperature

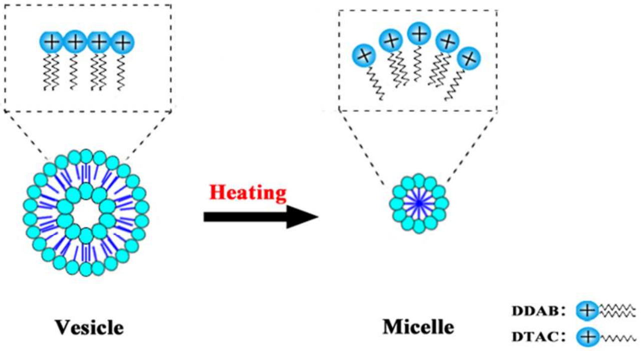
According to the molecular characteristics (shape, size and nature), surfactant molecules are expected to form optimum aggregates with a minimum free Gibbs energy.[20] The formation of spherical or rodlike micelles, vesicles, or plane bilayers and so on is governed by the packing parameter p, proposed by Israelachvili.[20] $p < 1/2$ for micelles and $1/2 < p < 1$ for vesicles or lamellar structures where p is defined as $\frac{v}{al}$, v is the surfactant tail volume, l is the tail length, and a is the average headgroup area. In general, the transformation of self-assembled aggregates depends on the variation of weak interactions.[21,22] In particular, for surfactant systems, the average surfactant headgroup area a is usually thought to be sensitive to the variation of weak interactions when the molecular structure of the surfactant does not change.[20]

According to the above results, we attempt to understand and reveal the mechanism on how temperature drives the morphological transitions of the aggregates in cationic/cationic mixed surfactant systems, which is schematically presented in

Scheme 1. In the process of vesicle formation, hydrophobic interactions are essential (i.e., the hydrocarbon moiety of double-chained surfactant prefers the hydrophobic environment of single-chained surfactant in aggregates). For vesicles formed by the mixed DDAB and DTAC surfactant, it has been shown that the DTAC molecules are incorporated into outer monolayers to some extent but excluded from inner monolayers and their vicinities in the inner water pools.[3h] An increase in temperature corresponds to faster motion of the molecules. With the increase of temperature, the surface charge density decreases, this means the dissociation degree also decreases, due to a greater electrostatic repulsion between the similar cationic polar heads. The electrostatic attraction between molecules gradually decreases with the increasing temperature, which increases the distance of catanionic surfactant head groups. Thus, the average head group area is increased, which means a is enlarged. As a result, p reduces below 0.5, promoting the formation of micelle, and the transformation from vesicles to micelles.

The mixture of a single-chained surfactant, which tends to aggregate in micelles, and a double-chained surfactant, for which the vesicle aggregation is favored, is well known to form spontaneous and thermodynamically stable mixed vesicles[23] and/or mixed micelles depending on the surfactant concentration range and/or surfactant relative ratio. It is very difficult for two kinds of single-chained surfactant mixtures to form the vesicles. For a given double-chained surfactant (DDAB), the increase on the length of the single-chained surfactant slightly increases the diameter of vesicle formed by the mixtures, which can be seen from Figure S1 and S2. As the single-chained surfactant formed the outer monolayer of the bilayer, the width of the bilayer will be enlarged with the increasing chain length of the single-chained surfactant. The UV absorbance of the solution, which implied the diameter of vesicle in the solution, is 0.10 for the DDAB/DTAC system at 25°C (Figure 1), 0.30 for the DDAB/TTAC system at 25°C (Figure S1) and 0.46 for the DDAB/HTAC system at 25°C (Figure S2). The experimental evidence is consistent with the above explanation.

It is anticipated that utilizing this simple stimuli method to realize unique self-assembly behavior in dilute aqueous solution may offer new possibilities in cancer diagnosis and therapy. As temperature is crucial for living organisms, the system also provides inspiration for biomimicry by using mixed surfactant system.



Scheme1. Temperature-responsive aggregation behavior of DDAB/DTAC (x_{DDAB}=0.3, c_{total}=0.030M) aqueous solutions from 25°C to 60 °C.

Conclusion:

In the present study, temperature responsiveness is systematically studied in anionic/anionic (DDAB/DTAC) mixed surfactant systems. It is demonstrated that the self-assembly transition controlled with temperature undergoes changes from the vesicle to micelle, which is observed by the cryo-TEM. The geometry rule can be used to explain the transformations of organized assemblies with temperature for the changes of average head group area. It is anticipated that utilizing this simple stimuli method to realize unique self-assembly behavior in dilute aqueous solutions may offer new possibilities in cancer diagnosis and therapy. As temperature is crucial for living organisms, the system also provides inspiration for biomimicry by using mixed surfactant system.

Acknowledgements

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References

1. Y. Jiang, H. Chen, S. Z. Mao, P. Y. Luo, Y. R. Du and M. L. Liu, *J. Phys. Chem. B.*, 2011, 115, 1986–1990.
2. E. W. Kaler, A. K. Murthy, B. E. Rodriguez and J. A. Zasadzinski, *Science*, 1989, 245, 1371–1374.
3. (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; (e) M. I. Viseu, K. Edwards, C. S. Campos and S. M. B. Costa, *Langmuir*, 2000, 16, 2105–2114; (f) G. Montalvo and A. Khan, *Langmuir*, 2002, 18, 8330–8339; (g) S. Ghosh, D. Khatua and J. Dey, *Langmuir*, 2011, 27, 5184–5192; (h) M. Aratono, N. Onimaru, Y. Yoshikai, M. Shigehisa, I. Koga, K. Wongwailikhit, A. Ohta, T. Takiue, B. Lhoussaine, R. Strey, Y. Takata, M. Villeneuve and H. Matsubara, *J. Phys. Chem. B.*, 2007, 111, 107–115.

4. *Surfactant Science Series 62*; Vesicles, ed. M. Rosoff, Marcel Dekker Inc., New York, 1996.
5. *Handbook of biological physics*, ed. R. Lipowsky and R. Sackmann, Elsevier, Amsterdam, 1995.
6. D. D. Lasic, *Angew. Chem., Int. Ed. Engl.*, 1994, 33, 1685–1698.
7. I. Yaacob, A. C. Nunes and A. Bose, *J. Colloid Interface Sci.*, 1995, 171, 73–84.
8. (a) M. Antonietti and S. Forster, *Adv. Mater.*, 2003, 15, 1323–1333; (b) A. J. Ryan, S. P. Armes and A. Blanazs, *Macromol. Rapid Commun.*, 2009, 30, 267–277.
9. (a) Y. Li, B. S. Lokitz and C. L. McCormick, *Angew. Chem., Int. Ed.*, 2006, 45, 5792–5795; (b) D. S. H. Qin, Y. Geng, E. Discher and S. Yang, *Adv. Mater.*, 2006, 18, 2905–2909; (c)K. S. Soppimath, C. W. Tan and Y. Y. Yang, *Adv. Mater.*, 2005, 17, 318–323;(d) J. Rodriguez-Hernandez and S. Lecommandoux, *J. Am. Chem. Soc.*, 2005, 127, 2026–2027; (e) S. Liu and S. P. Armes, *Angew. Chem., Int. Ed.*, 2002, 41, 1413–1416; (f) H. Yin, Z. Zhou, J. Huang, R. Zheng and Y. Zhang, *Angew. Chem., Int. Ed.*, 2003, 42, 2188–2191;(g) S. Dai, P. Ravi and K. C. Tam, *Soft Matter*, 2008, 4, 435–449; (h) J. Z. Du and R. K. O'Reilly, *Soft Matter*, 2009, 5, 3544–3561; (i) J. Babin, M. Pelletier, M. Lepage, J. F. Allard, D. Morris and Y. Zhao, *Angew. Chem., Int. Ed.*, 2009, 48, 3329–3332; (j)V. Yesilyurt, R. Ramireddy and S. Thayumanavan, *Angew. Chem., Int. Ed.*, 2011, 50, 3038–3042; (k) C. Kordel, C. S. Popeney and R. Haag, *Chem. Commun.*, 2011, 47, 6584–6586; (l) J. Jiang, X. Tong and Y. Zhao, *J. Am. Chem. Soc.*, 2005, 127, 8290–8291; (m) Q. Jin, G. Y. Liu, X. S. Liu and J. Ji, *Soft Matter*, 2010, 6, 5589–5595; (n) A. P. Goodwin, J. L. Mynar, Y. Ma, G. R. Fleming and J. M. Frechet, *J. Am. Chem. Soc.*, 2005, 127, 9952–9953; (o) Q. Yan, Y. Xin, R. Zhou, Y. W. Yin and J. Y. Yuan, *Chem. Commun.*, 2011, 47, 9594–9596; (p) H. Yin, S. Lei, S. Zhu, J. Huang and J. Ye, *Chem. Eur. J.*, 2006, 12, 2825–2835.
10. (a) Y. L. Sun, S. S. Wang, X. Han and Z. X. Chen, *J. Phys. Chem. B*, 2012, 116, 12372−12380; (b) H. Yin, J. Huang, Y. Lin, Y. Zhang, S. Qiu and J. Ye, *J. Phys. Chem. B*, 2005, 109, 4104–4110; (c) J. Hao, H. Hoffmann and K. Horbaschek, *J. Phys. Chem. B*, 2000, 104, 10144–10153; (d) E. Opatowski, D. Lichtenberg and M.

M. Kozlov, *Biophys. J.*, 1997, 73, 1458-1467.

11. (a) M. Z. Tian, Y. X. Fan, G. Ji and Y. L. Wang, *Langmuir* , 2012, 28, 12005−12014; (b) M. I. Viseu, K. Edwards, C. S. Campos and S. M. B. Costa, *Langmuir*, 2000, 16, 2105-2114.
12. W. Li, Y. J. Yang, L. F. Liu, X. N. Tan, T. Luo and J.Y. Shen, *Soft Matter*, 2015, 11, 4283–4289.
13. (a) W. Li, J. Zhang, Y. Zhao, M. Hou, B. Han, C. Yu and J. Ye, *Chem. Eur. J.*, 2010, 16, 1296–1305; (b) W. Li, Y. Yang, T. Luo, J. Zhang and B. Han, *Phys. Chem. Chem. Phys.*, 2014, 16, 3640–3647; (c) W. Li, J. Zhang, S. Cheng, B. Han, C. Zhang, X. Feng and Y. Zhao, *Langmuir*, 2009, 25, 196–202.
14. (a) A. Pizzino, M. P. Rodriguez, C. Xuereb, M. Catt, E. V. Hecke, J. M. Aubry and J. L. Salager, *Langmuir*, 2007, 23, 5286–5291; (b) J. Allouche, E. Tyrode, V. Sadtler, L. Choplin, J. L. Salager, *Langmuir*, 2004, 20, 2134–2138.
15. (a) L. M. Zhai, J. Y. Zhang, Q. X. Shi, W. J. Chen and M. Zhao, *J. Colloid Interface Sci.*, 2005, 284, 698–703; (b) A. Mohanty, T. Patra and J. Dey, *J. Phys. Chem. B.*, 2007, 111, 7155–7159.
16. K. Kalyanasundaram, J. K. Thomas, *J. Am. Chem. Soc.*, 1977, 99, 2039–2041.
17. T. Kodama, A. Ohta, K. Toda, T. Katada, T. Asakawa and S. Miyagishi, *Colloids Surf. A.*, 2006, 277, 20–26.
18.(a) D. M. Zhu, Z. A. Schelly, *Langmuir*, 1992, 8, 48–50; (b) M. J. Clarke, K. L. Harrison, K. P. Johnson and S. M. Howdle, *J. Am. Chem. Soc.*, 1997, 119, 6399–6406.
19. Y. Yan, J. B. Huang, Z. C. Li, F. Han, J. M. Ma, *Langmuir*, 2003, 19, 972–974.
20. J. N. Israelachvili, D. J. Mitchell and B. W. Ninham, *J. Chem. Soc., Faraday Trans.* 2, 1976, 72, 1525–1568.
21. (a) D. Philp, J. F. Stoddart, *Angew. Chem., Int. Ed.*, 1996, 35, 1154–; (b) S. Paul, G. N. Patey, *J. Phys. Chem. B.*, 2007, 111, 7932–7933;(c) K.Wang, H. Q. Yin, W. Sha, J. B. Huang and H. L. Fu, *J. Phys. Chem. B*, 2007, 111, 12997–13005; (d) H. Q. Yin, Y. Y. Lin, J. B. Huang and J. P. Ye, *Langmuir*, 2007, 23, 4225–4230; (e)Y. Y. Lin, X. Han, X. H. Cheng, J. B. Huang, D. H. Liang and C. L. Yu, *Langmuir*, 2008,

24, 13918–13924.

22. J. N. Israelachvili, *Intermolecular and Surface Forces*, Academic Press: London, 1992.

23. (a) M. Rosoff, *Vesicles*, Marcel Dekker Inc., New York, 1996; (b) P. C. A. Barreleiro, G. Olofsson, W. Brown, K. Edwards, N. M. Bonassi and E. Feitosa, *Langmuir*, 2002, 18, 1024–1029; (c) M. I. Viseu, K. Edwards, C. S. Campos, S. M. B. Costa, *Langmuir*, 2000, 16, 2105–2114; (d) E. Junquera, R. Arranz and E. Aicart, *Langmuir*, 2004, 20, 6619–6625; (e) E. Junquera, P. del Burgo, R. Arranz, O. Llorca, E. Aicart, *Langmuir*, 2005, 21, 1795–1801.

Temperature-induced vesicle to micelle transition in cationic/cationic mixed surfactant systems

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Realization of the vesicle to micelle transitions in cationic/cationic mixed surfactant systems by temperature stimuli.