

# Temperature-Induced Vesicle Aggregation in Catanionic Surfactant Systems: The Effects of the Headgroup and Counterion

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The peculiar nature of temperature-induced vesicle aggregation (TIVA) in some catanionic surfactant systems is systematically investigated. On the basis of a general analysis of the intervesicular interactions, the main driving force for this phenomenon is considered to be the intervesicular hydrophobic interaction among the exposed hydrophobic part of the surfactant headgroups. The addition of an oppositely charged hydrophobic salt to the catanionic vesicle systems is also found to promote the occurrence of TIVA. In fact, TIVA can be induced in ordinary catanionic vesicle systems by the addition of an oppositely charged hydrophobic counterion.

## Introduction

Vesicles, which have a bilayer membranous structure with an inner aqueous phase, are involved in many biological processes. Usually, vesicles are constituted by double-chained amphiphiles, such as phospholipids. However, a great deal of work has demonstrated the possibility of vesicle formation from single-chained surfactants under specific conditions. This is the case for mixtures of anionic and cationic surfactants (referred as “catanionic surfactant”), which can mimic the structure of phospholipids through the electrostatic association of their polar headgroups. Different from the liposomes, catanionic vesicles can form spontaneously and exhibit high stability. Over the past few decades, a great deal of work has been done to investigate the unique properties of catanionic vesicles.<sup>1–8</sup>

Membrane fusion is an essential molecular event involved in many cellular processes, such as exocytosis, endocytosis, intracellular vesicle transport, fertilization, viral infection, etc.<sup>9–13</sup> It is generally agreed that vesicle aggregation or adhesion is the initial step for the fusion of the vesicles or membranes. Therefore, the elucidation of the molecular mechanism of vesicle aggregation could greatly contribute to a better understanding of these biological phenomena and may also advance applications of vesicles in other fields.

Normally, vesicle aggregation can be induced by external additives. Salt- and polymer-induced vesicle aggregations have been well-studied in numerous papers.<sup>14–18</sup> Recently, a peculiar temperature-induced vesicle aggregation (TIVA) was reported in a catanionic surfactant system of *n*-dodecyltributylammonium bromide/sodium *n*-dodecylsulfate (DTBAB/SDS) by our group.<sup>19</sup> It was found that vesicle aggregation can be triggered just by increasing the temperature above a critical value ( $T_c$ ) without any additives. This provides a novel and simple way for controlling vesicle aggregation. In this work, further investigation on this interesting phenomenon was made with the aim to explore its nature and mechanism. In combination with the experimental results and discussion on various intervesicular interactions, it is proposed that the intervesicular hydrophobic interaction among the exposed hydrophobic groups is the main reason for the occurrence of this phenomenon. Besides, it has been proven by other groups<sup>31–35</sup> that hydrophobic counterions can effectively bind to the vesicle surface and increase the hydrophobic interaction between adjacent vesicles. On the basis of the above viewpoints, the effects of two hydrophobic salts, i.e., tetrabutylammonium bromide (Bu<sub>4</sub>NBr) and sodium 2-naphthalenesulfonic acid (SNS), were also studied, respectively. It is interesting to find that the addition of an oppositely charged hydrophobic salt can induce the occurrence of TIVG in conventional catanionic surfactant systems, which cannot have such TIVA phenomenon before adding hydrophobic salt.

## Experimental Section

**Materials.** Quaternary ammonium bromides were prepared by the reaction of 1-bromododecane and the corresponding trialkylamine as described in our previous paper.<sup>19</sup> Abbreviations of the quaternary ammonium bromides are listed as follows: DTAB, *n*-dodecyltrimethylammonium bromide; DTEAB, *n*-dodecyltriethylammonium bromide; DTPAB, *n*-dodecyltripropylammonium bromide; DTBAB, *n*-dodecyltributylammonium bromide; and DDMBAB, *n*-dodecyltrimethylbutylammonium bromide. *n*-Dodecylpyridinium chloride

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(DPCI) was synthesized from 1-bromododecane and pyridine. Sodium laurate (SL) was prepared by neutralizing lauric acid with NaOH in ethanol; then, the solvent was removed, and SL were dried. Lauric acid was the product recrystallized 5 times from 95% ethanol. SDS and sodium *n*-dodecylsulphonate (SDSO<sub>3</sub>) were bought from Acros Organics Co. and used as received. The purity of the surfactants was examined, and no surface tension minimum was found in the surface tension curves. Deionized water was treated with KMnO<sub>4</sub> and distilled before use. Sodium bromide was calcined at 500 °C over 6 h. The other reagents were products of A. R. Grade.

**Fluorescence Anisotropy Studies.** Steady-state fluorescence anisotropy (*r*) was measured on a F4500 Hitachi spectrofluorometer equipped with a thermostated cell holder and filter polarizers that used the L-format configuration.<sup>20</sup> 1,6-Diphenyl-1,3,5-hexatriene (DPH) was used as the fluorescence probe. The concentration of DPH was adjusted to 1.0 μmol by adding an appropriate amount of 1.0 mmol ethanol stock solution, and then the solution was stirred vigorously for 48 h. The excitation wavelength was 350 nm, and the emission was monitored at 430 nm. The *r* value was calculated by employing the equation

$$r = (I_{VV} - GI_{VH}) / (I_{VV} + 2GI_{VH}) \quad (1)$$

where *I*<sub>VV</sub> and *I*<sub>VH</sub> are the fluorescence intensities polarized parallel and perpendicular to the excitation light and *G* is the instrumental correction factor ( $G = I_{VV}/I_{VH}$ ). The fluorescence lifetime of DPH ( $\tau_f$ ) in the vesicle membrane was measured by an Edinburgh FLS920 time-resolved fluorescence spectrophotometer.

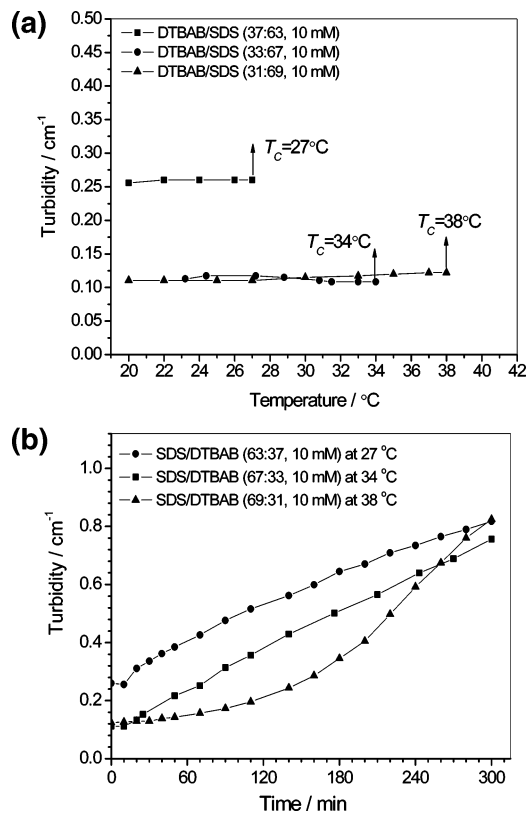
**Turbidity Measurement.** Turbidity measurements were carried out with a temperature-controlled 752C UV–vis spectrophotometer (Shanghai Analysis Instruments Co.) at 500 nm. The turbidity was measured after the solution was thermostated for 1 h. The *T*<sub>c</sub> was defined as the temperature at which the turbidity begins to increase with time.

**Transmission Electron Microscopy (TEM).** Samples for TEM were prepared by the negative-staining technique with a uranyl acetate water solution. First, the sample was thermostated at a given temperature for 1 h. Then, a carbon Formvar-coated copper grid (230 mesh) was put into the solution for 5 min. The filter paper was employed to suck away the excess solution on the copper grid. After that, the copper grid was transferred into the uranyl acetate solution, which was thermostated at the same temperature. After 1 min, the grid was taken out and excess liquid was also sucked away by a filter paper. A JEM-100CX electron microscope was employed in the microscopic observation. In addition, for each solution, at least three TEM samples were prepared and observed independently to exclude the artifacts as possibilities.

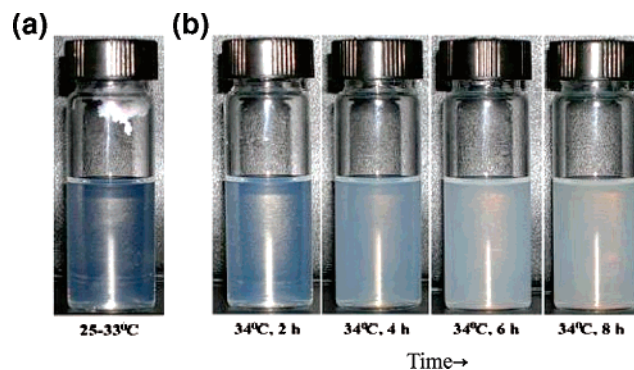
**ζ Potential.** ζ potentials were measured using a temperature-controlled ZetaSizer 2000 (Malvern Instruments Ltd.) ζ potential analyzer.

## Results and Discussion

**Peculiar TIVA in the DTBAB/SDS System.** Figure 1 shows the heating turbidity curves of three DTBAB/SDS vesicular solutions with the total surfactant concentration of 10 mM and different mixing molar ratios of 37:63, 33:67, and 31:69, respectively. It can be noted that, when the temperature is below *T*<sub>c</sub>, the turbidity of these systems remains almost constant (Figure 1a). However, when the temperature reaches *T*<sub>c</sub>, the turbidity begins to increase with time (Figure 1b). The critical temperature of these three solutions was found to be 27, 34, and 38 °C, respectively. Such a transition is also clearly shown from the change of the macroscopic appearance in Figure 2. When the TEM and light-scattering methods were employed as described in ref 19, the increase of turbidity is proven to be the consequence



**Figure 1.** (a) Turbidity heating curves before the critical temperature for the systems of DTBAB/SDS (10 mM) with different mixing ratios of 37:63, 33:67, and 31:69, respectively (the arrow indicates the location of the critical temperature). (b) Variation of turbidity with time at the critical temperature for the above systems.



**Figure 2.** (a) Macroscopic appearance of the DTBAB/SDS (33:67, 10 mM) system from 25 to 33 °C. (b) Variation of the macroscopic appearance with time at 34 °C for the DTBAB/SDS (33:67, 10 mM) system.

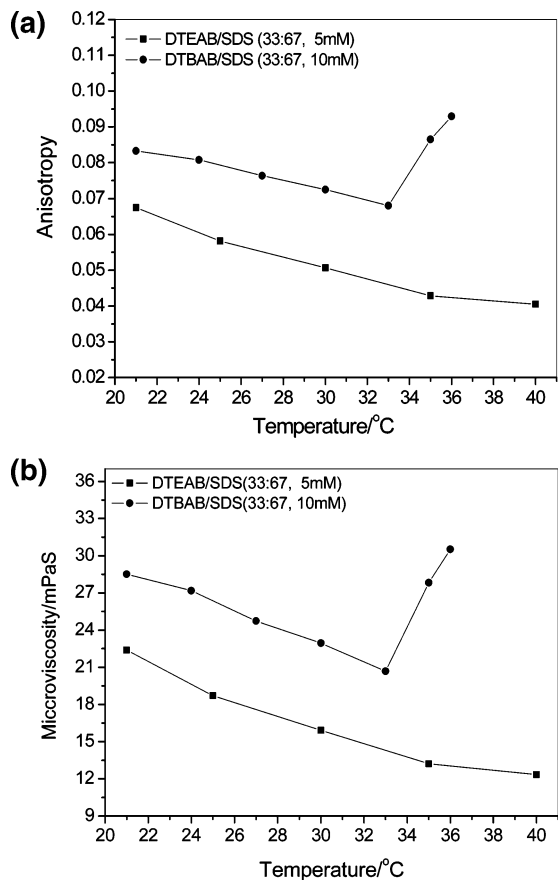
of a TIVA similar to our previous paper<sup>19</sup> and *T*<sub>c</sub> can also be considered as the critical temperature for the occurrence of vesicle aggregation.

To obtain a further understanding of TIVA in the DTBAB/SDS system, membrane microviscosity was tracked during the process of vesicle aggregation through fluorescence anisotropy measurements. The microviscosity ( $\eta_m$ ) of the vesicle membrane can be calculated from the steady-state fluorescence anisotropy (*r*) of the probe by the Perrin–Stokes–Debye equation:<sup>21</sup>

$$\eta_m = k_B T \tau_f / [v_m (r_0/r - 1)] \quad (2)$$

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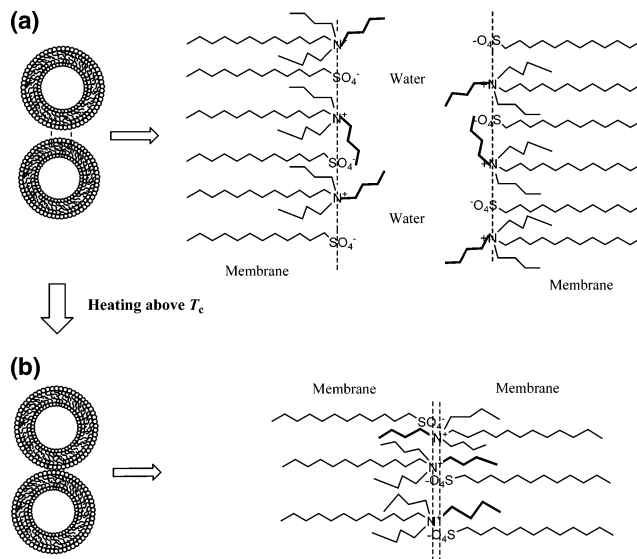
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**Figure 3.** Variations of (a) measured fluorescence anisotropy  $r$  and (b) calculated microviscosity  $\eta_m$  with temperature for the DTBAB/SDS (33:67, 10 mM) and DTEAB/SDS (33:67, 5 mM) systems, respectively (Above 34 °C, the  $r$  for the DTBAB/SDS system was measured after the solution was thermostated for 1 h).

where  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature,  $\tau_f$  is the fluorescence lifetime of DPH, and  $v_m$  is the effective molecular volume of the DPH probe and was estimated to 313 Å.<sup>3,22</sup>  $r_0 = 0.362$  is the fluorescence anisotropy of DPH in a medium of infinite viscosity.<sup>23</sup> The variation of  $r$  and calculated  $\eta_m$  as a function of the temperature for the DTBAB/SDS (33:67, 10 mM) system was plotted in parts a and b of Figure 3. For a comparison, the DTEAB/SDS (33:67, 5 mM) system was also studied, in which no TIVA phenomenon was observed within the temperature range studied. For the DTEAB/SDS (33:67, 5 mM) system, the value of  $\eta_m$  decreases gradually as the temperature increases from 20 to 40 °C. For the DTBAB/SDS (33:67, 10 mM) system, the decrease of  $\eta_m$  can also be seen as the temperature increases from 20 to 33 °C, indicating that the hydrocarbon chains in the vesicle membrane pack more loosely upon heating.<sup>24–26</sup> However, when the temperature increases above 34 °C ( $T_c$  of the system), an abrupt increase of microviscosity is observed, which indicates that the hydrocarbon chains in the vesicle membranes have a closer packing conformation. As will be discussed below, the abrupt increase of microviscosity can be attributed to the occurrence of TIVA.

**Role of Hydrophobic Groups on the Surfactant Headgroup in TIVA.** The classical Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory provides a successful explanation of the stability



**Figure 4.** Schematic illustrations of the DTBAB/SDS vesicle membrane in aqueous solution (a) before and (b) after  $T_c$ , respectively.

of colloid systems in terms of van der Waals attraction and electrostatic double-layer repulsion.<sup>27,28</sup> Usually, the variation of the van der Waals attraction upon heating is insignificant over a limited temperature range.<sup>29</sup> On the other hand, our result showed that the  $\zeta$  potential of the DTBAB/SDS (33:67, 10 mM) system remains constant around  $T_c$ ,<sup>19</sup> which indicates that the electrostatic double-layer repulsion is almost unvaried. Hence, the origin of TIVA cannot be simply explained by the DLVO theory. Therefore, it is probable that another kind of interaction should be responsible for the occurrence of TIVA.

A further study on TIVA in other cationic surfactant systems reveals the relationship between this interesting phenomenon and the surfactant headgroup. It is found that the TIVA phenomenon was also observed in the systems of DTBAB/SDSO<sub>3</sub> and DTBAB/SL. However, no TIVA phenomenon can be observed in the systems of DTAB/SDS, DTEAB/SDS, DTPAB/SDS, and DPCI/SDS within the temperature range studied. Considering the fact that DTBAB has the longest alkyl chains on the headgroup among the studied cationic surfactants, it can be assumed that the butyl group on the DTBAB headgroup plays an important role in the process of TIVA. Figure 4a shows the schematic illustration of DTBAB/SDS vesicle membranes below  $T_c$ . It can be noted that because of the steric restriction it is infeasible for all of the three butyl chains on the DTBAB headgroup to bend into the inner hydrophobic region of the membrane. Therefore, one or two butyl chains will stretch out to locate at the outer hydrophilic layer and be exposed to water. As a result, the attractive hydrophobic interaction may take place between adjacent vesicles.<sup>30,31</sup> On the other hand, the hydrophobic interaction is considered to increase with temperature.<sup>32–37</sup> Thus, it can be expected that, for the DTBAB/SDS system, when

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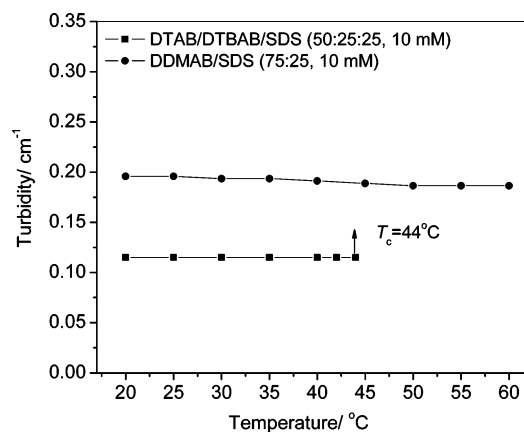
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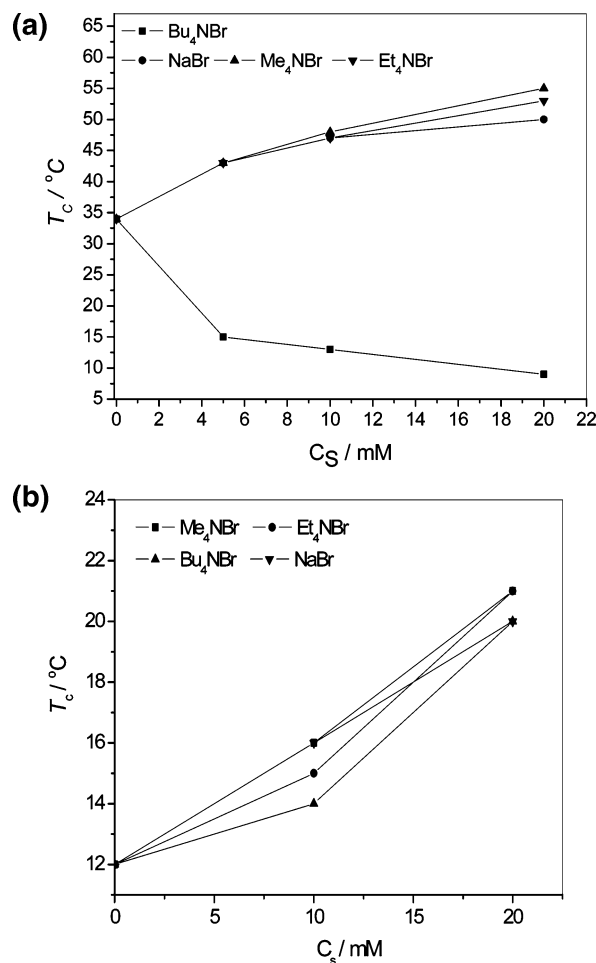


**Figure 5.** Turbidity heating curves for the systems of DDMAB/SDS (75:25, 10 mM) and DTAB/DTBAB/SDS (50:25:25, 10 mM).

the temperature is below  $T_c$ , the electrostatic double-layer repulsion is dominant, which prevents vesicles from aggregating. With temperature increasing, the hydrophobic interaction among the butyl chains is gradually enhanced. Finally, when the temperature reaches  $T_c$ , the repulsion between the vesicles is overcome by the hydrophobic interaction and vesicle aggregation takes place. Thus, it is reasonable to believe that the intervesicular hydrophobic interaction is probably the main driving force for the occurrence of TIVA. Figure 4b shows the possible schematic illustration of the DTBAB/SDS vesicle membrane above  $T_c$ . When the vesicle aggregation occurs, the exposed butyl chains will penetrate into the hydrophobic interior of another vesicle to minimize the total free energy.<sup>38,39</sup> Consequently, the hydrocarbon chains in the membrane will pack more tightly, and membrane microviscosity will increase as mentioned above.

To further examine the effect of the hydrophobic group, another cationic surfactant with asymmetric alkyl chains on the headgroup, namely, *n*-dodecyltrimethylbutylammonium bromide (DDMBAB), was synthesized and two catanionic vesicle systems were studied. One is the DDMBAB/SDS (75:25, 10 mM) system, and the other is the DTAB/DTBAB/SDS (50:25:25, 10 mM) system. It is obvious that the concentration of butyl chains on the surfactant headgroup is the same for these two mixed systems. However, the situation is completely different for these two systems with the temperature increasing. From Figure 5, it can be noted that vesicle aggregation occurs in the DTAB/DTBAB/SDS (50:25:25, 10 mM) system when the temperature reaches 44 °C, while no TIVA was observed in the mixed DDMAB/SDS (75:25, 10 mM) system over the studied temperature range. Considering the fact that there is only one butyl chain on the DDMBAB headgroup, the butyl chain is able to bend into the hydrophobic region of the vesicle bilayer to avoid contact with water. Hence, the concentration of hydrophobic groups exposed on the vesicle surface is relatively low, and intervesicular hydrophobic interaction is too weak to induce TIVA. This result reveals that not all of the hydrophobic parts on the headgroup but only those exposed on the vesicle surface will contribute to the occurrence of TIVA and determine the  $T_c$  value.

**Effects of Hydrophobic Salts.** The above result and discussion proposed that the hydrophobic group exposed on the vesicle surface is responsible for the occurrence of TIVA. On the basis of this viewpoint, it is reasonable that the addition of hydrophobic salt can effectively influence the TIVA in catanionic vesicle systems because hydrophobic salt can strongly bind to the surface of aggregates through both electrostatic and hydrophobic

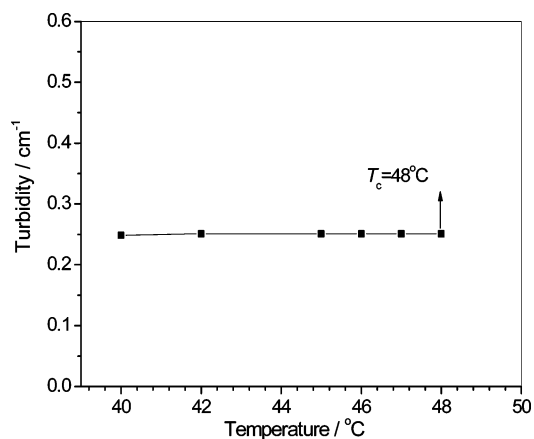


**Figure 6.** Effects of  $\text{Bu}_4\text{NBr}$ ,  $\text{Et}_4\text{NBr}$ ,  $\text{Me}_4\text{NBr}$ , and  $\text{NaBr}$  on  $T_c$  of the (a) DTBAB/SDS (33:67, 10 mM) and (b) DTBAB/SDS (75:25, 20 mM) systems.

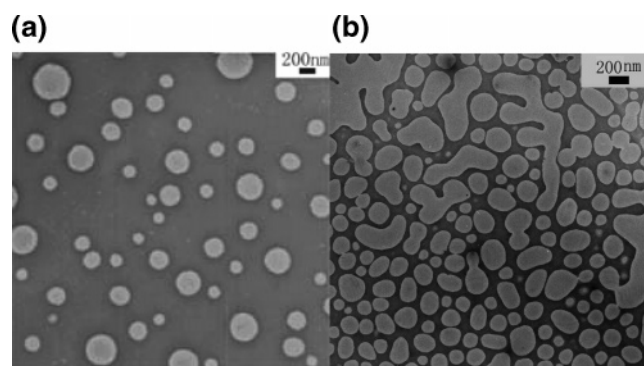
interactions and increase the concentration of the exposed hydrophobic groups.

As a kind of hydrophobic salt,  $\text{Bu}_4\text{NBr}$  was investigated for the effect of TIVA in the DTBAB/SDS (33:67, 10 mM) system. As expected, an obvious decrease of  $T_c$  with  $\text{Bu}_4\text{NBr}$  addition was observed (Figure 6a). This may be attributed to the binding of the cationic  $\text{Bu}_4\text{N}^+$  on the vesicle surface through both electrostatic and hydrophobic interactions.<sup>31–35</sup> Thus, the concentration of the hydrophobic groups that are exposed on the vesicle surface increases, and the intervesicular hydrophobic interaction was greatly enhanced. Therefore, the addition of  $\text{Bu}_4\text{NBr}$  can also facilitate TIVA for the DTBAB/SDS (33:67, 10 mM) system, and a lower temperature is required to induce vesicle aggregation. The above result also demonstrates that the hydrophobic groups that are exposed on the vesicle surface, are the key factor for the occurrence of TIVA, and the addition of hydrophobic salt is a simple and effective way to increase the intervesicular hydrophobic interaction and will be helpful toward the occurrence of the TIVA. However, further investigation shows that the hydrocarbon chain length on the polar groups of the hydrophobic salt is also very important for the TIVA. For a comparison, the effects of another two tetra-alkylammonium bromides with a shorter alkyl chain, i.e., tetramethylammonium ( $\text{Me}_4\text{NBr}$ ), tetraethylammonium ( $\text{Et}_4\text{NBr}$ ), as well as  $\text{NaBr}$ , were studied. In contrast to the effect of  $\text{Bu}_4\text{NBr}$ , an obvious increase of  $T_c$  with the addition of  $\text{Me}_4\text{NBr}$  and  $\text{Et}_4\text{NBr}$  was observed in Figure 6a, showing a similar effect as  $\text{NaBr}$ . This may be attributed to the fact that both  $\text{Me}_4\text{NBr}$  and  $\text{Et}_4\text{NBr}$  have relatively short

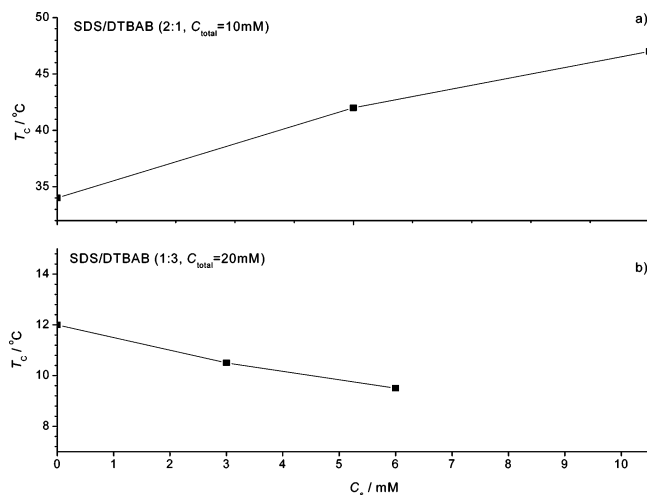
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**Figure 7.** Turbidity heating curve of the DTPAB/SDS (33:67, 5 mM) system upon the addition of 10 mM  $\text{Bu}_4\text{NBr}$  before  $T_c$  (the arrow indicates the location of the critical temperature).



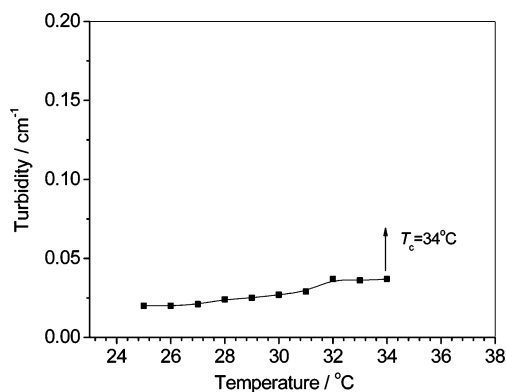
**Figure 8.** Micrographs for the DTPAB/SDS (33:67, 5 mM) system upon the addition of 10 mM  $\text{Bu}_4\text{NBr}$  when it was (a) at 47 °C and (b) heated to 49 °C for 1 h, respectively.



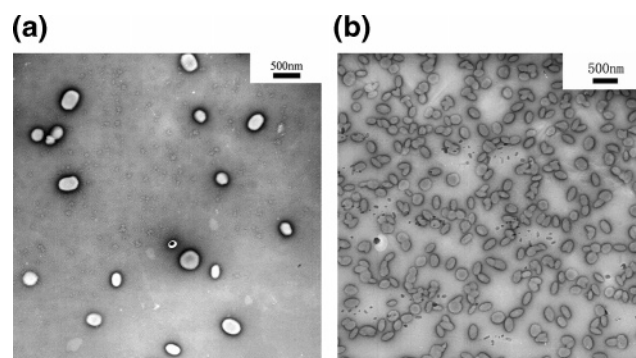
**Figure 9.** Effect of SNS on  $T_c$  of the (a) DTBAB/SDS (33:67, 10 mM) and (b) DTBAB/SDS (75:25, 20 mM) systems.

alkyl chains on the N atom and cannot obviously increase the intervesicular hydrophobic interaction. Thus, these two salts worked just like a conventional electrolyte, such as NaBr.

On the basis of the results that the addition of  $\text{Bu}_4\text{NBr}$  can greatly facilitate TIVA of the DTBAB/SDS (33:67, 10 mM) system, further experiments were performed to investigate the effect of hydrophobic salt addition in the ordinary catanionic vesicle system, where no TIVA can be detected over the studied temperature range. The catanionic vesicle system DTPAB/SDS (33:67, 10 mM), with a  $\zeta$  potential of  $-80$  mV, was selected with the consideration that  $\text{Bu}_4\text{N}^+$  will bind strongly to the vesicle



**Figure 10.** Turbidity heating curve of the DTEAB/SDS (75:25, 10 mM) system upon the addition of 10 mM SNS before  $T_c$  (the arrow indicates the location of the critical temperature).



**Figure 11.** Micrographs for the DTEAB/SDS (75:25, 10 mM) system upon the addition of 10 mM SNS when it was (a) at 33 °C and (b) heated to 35 °C for 1 h, respectively.

surface because of the electrostatic interaction. Interestingly, after the addition of 10 mM  $\text{Bu}_4\text{NBr}$ , vesicle aggregation occurs at the critical temperature of 48 °C, which is clearly demonstrated by turbidity (Figure 7) and TEM characterizations (Figure 8). In comparison to the variation of the surfactant molecular structure, i.e., changing the polar headgroup from the triethyl to tributyl group, it is a more convenient way for the addition of the hydrophobic salts to induce TIVA.

However, the addition of  $\text{Bu}_4\text{NBr}$  is not always effective to promote TIVA in catanionic vesicle systems. In fact, for a positively charged DTBAB/SDS (75:25, 20 mM) vesicle system, the addition of  $\text{Bu}_4\text{NBr}$  increases the critical temperature for TIVA just as NaBr,  $\text{Me}_4\text{NBr}$ , and  $\text{Et}_4\text{NBr}$  (Figure 6b). This can be attributed to the fact that the DTBAB/SDS (75:25, 20 mM) vesicle is positively charged and  $\text{Bu}_4\text{N}^+$  cannot effectively bind onto the vesicle surface.

For positively charged vesicle systems, the effect of another hydrophobic salt, namely, SNS, was examined. Unlike  $\text{Bu}_4\text{NBr}$ , SNS has a negatively charged hydrophobic counterion  $\text{NS}^-$ . According to the above discussion, it is suggested that  $\text{NS}^-$  can bind strongly to the positively charged DTBAB/SDS (75:25, 20 mM) vesicles rather than DTBAB/SDS (33:67, 10 mM) vesicles. Hence, the addition of SNS is expected to lead to a decrease of  $T_c$  for the DTBAB/SDS (75:25, 20 mM) system but an increase of  $T_c$  for the DTBAB/SDS (33:67, 10 mM) system, which is co-incident with the results shown in Figure 9. Similarly, an ordinary positively charged vesicle system can be induced to have the ability of TIVA with the addition of SNS. The DTEAB/SDS (75:25, 10 mM) is such a vesicle system, with a  $\zeta$  potential of 34 mV at 25 °C. As shown in Figures 10 and 11, the addition of 10 mM SNS to the DTEAB/SDS (75:25, 10 mM) system can cause the occurrence of TIVA with a critical temperature of

34 °C. Thus, it is demonstrated that the addition of a hydrophobic counterion can effectively facilitate the occurrence of TIVA for oppositely charged catanionic vesicle systems. This provided a simple and convenient way to investigate and control the vesicle aggregation in the mixed catanionic surfactant systems.

### Conclusion

The TIVA in catanionic surfactant systems is mainly attributed to the intervesicular hydrophobic interaction originating from the hydrophobic groups that are exposed on the vesicle surface. The addition of an oppositely charged hydrophobic counterion to the vesicle system can significantly increase the intervesicular hydrophobic interaction and even induce an ordinary catanionic vesicle system with the ability of TIVA. Our previous work<sup>40</sup> has demonstrated that temperature variation is an effective method

of tuning intra-aggregate interaction and inducing a micelle–vesicle transition in some catanionic systems. In this work, we have further pointed out that under proper conditions temperature variation can control the reassembling of aggregates through a change of interaggregate interactions. We hope that this work may advance the understanding on temperature-controlled transitions of organized assemblies in solutions and promote applications in related fields.

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