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Novel Counter Anion Effects of Added $[Co(NH_3)_6]X_3$ ($X^- = Cl^-, Br^-, I^-$, or ClO_4^-) on Surface Tension Reduction in Aqueous Solutions of Anionic Surfactants

Sieng Sovanna,[1] Takayoshi Suzuki,[1] Masaaki Kojima,[1] Satoshi Tachiyashiki,[2] and Masakazu Kita*[3]
[1]*Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushima-naka, Okayama 700-8530*
[2]*Kagawa Nutrition University, 3-9-21 Chiyoda, Sakado 350-0288*
[3]*Graduate School of Education, Okayama University, 3-1-1 Tsushima-naka, Okayama 700-8530*

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Surface tension of anionic surfactant solutions, sodium dodecyl sulfate (SDS) or sodium dodecylbenzenesulfonate (SBS) decreases remarkably in the presence of $[Co(NH_3)_6]X_3$ (2.50 mM) ($X^- = Cl^-, Br^-, I^-$, or ClO_4^-) at 298 K, depending on the kind of counter anion X^-. The magnitude of reduction is in the order $ClO_4^- \geq I^- > Br^- > Cl^-$ for SDS solutions and $ClO_4^- > Cl^- > Br^- > I^-$ for SBS solutions at 0.03 mM surfactant concentrations.

The effect of added NaCl on the surface tension of aqueous solutions of sodium dodecyl sulfate (SDS) has been reported that the presence of the salt reduces the surface tension and critical micelle concentration (CMC) of SDS solutions relative to that of the salt-free system.[1,2] The higher the salt concentration, the lower the surface tensions and CMC. The effect is due mainly to the electric double layer (the existence of electrostatic contribution to the surface pressure). In our previous study,[3] we investigated the surface tension of aqueous solutions of anionic surfactants, SDS and SBS (sodium dodecylbenzenesulfonate), with hydrophilic cobalt(III) complexes, $[Co(NH_3)_6](ClO_4)_3$ and $[Co(en)_3](ClO_4)_3$ (en = ethylenediamine), and hydrophobic cobalt(III) complexes, $[Co(bpy)_3](ClO_4)_3$ (bpy = 2,2′-bipyridyl) and $[Co(phen)_3](ClO_4)_3$ (phen = 1,10-phenanthroline). Addition of the Co(III) complex into SDS or SBS solutions caused a significant surface tension reduction (STR) in aqueous solutions of these surfactants, suggesting formation and adsorption of 1:1 and 1:2 association complexes, $\{[complex](S)\}^{2+}$ and $\{[complex](S)_2\}^{+}$ ($S^- = DS^-$ or BS^-).

In this study, we have investigated the surface tensions of aqueous solutions of anionic surfactants (SDS and SBS) with $[Co(NH_3)_6]X_3$ ($X^- = Cl^-, Br^-, I^-$, and ClO_4^-) to disclose the effects of anions, and we have found two new types of counter anion effects (CAEs) of the cobalt(III) complex on the STR.

Figures 1 and 2 show STR phenomena in aqueous SDS and SBS solutions with $[Co(NH_3)_6]X_3$ (2.50 mM) ($X^- = Cl^-, Br^-, I^-$, or ClO_4^-) at 298 and 303 ± 0.1 K, respectively. The results at 293 K were similar to those at 298 K, and the results at 308 K were similar to those at 303 K.

The relatively large STR means that the electrostatic repulsion among the anionic surfactants is reduced by the presence of $[Co(NH_3)_6]^{3+}$, probably by forming an association complex with the complex cation at the water surface. The plateau values (γ^*) of SDS with a Co(III) complex are larger than those of SBS. This indicates that the association between $[Co(NH_3)_6]^{3+}$ and BS^- is more extensive on the surface than that between $[Co(NH_3)_6]^{3+}$ and DS^-, because the greater hydrophobicity of BS^- relative to DS^- allows the association complex of BS^- to be partitioned from the bulk solution to the surface to a greater extent than that of DS^-. The γ^* values of SDS with $[Co(NH_3)_6]X_3$ at 298 K in Figures 1 and 3 become larger in the order $Cl^- < Br^- < ClO_4^- \cong I^-$. The differences in γ^* values of SDS solutions with different X^- decreased at 303 and 308 K, as shown in Figure 3.

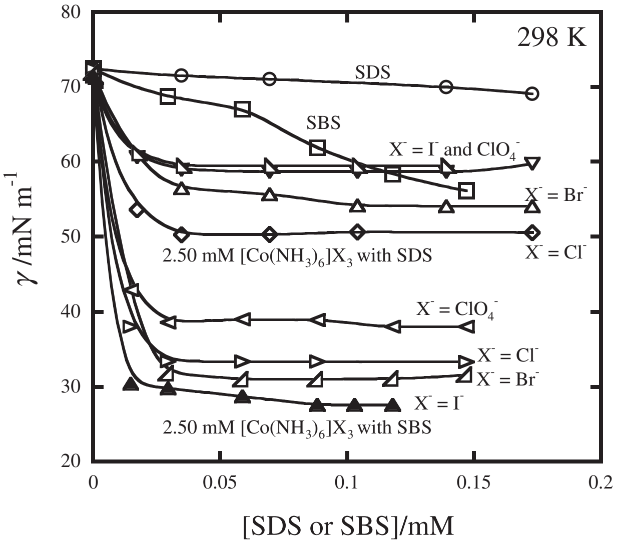

Figure 1. Surface tensions of SDS and SBS aqueous solutions with $[Co(NH_3)_6]X_3$ (2.50 mM) ($X^- = Cl^-, Br^-, I^-$, or ClO_4^-) at 298 ± 0.1 K: (◇) SDS with $[Co(NH_3)_6]Cl_3$, (△) SDS with $[Co(NH_3)_6]Br_3$, (▽) SDS with $[Co(NH_3)_6](ClO_4)_3$, (◺) SDS with $[Co(NH_3)_6]I_3$, (▷) SBS with $[Co(NH_3)_6]Cl_3$, (◿) SBS with $[Co(NH_3)_6]Br_3$, (▲) SBS with $[Co(NH_3)_6]I_3$, (◁) SBS with $[Co(NH_3)_6](ClO_4)_3$.

In SBS with $[Co(NH_3)_6]X_3$, the order of the γ^* values at 298 K was $I^- < Br^- < Cl^- < ClO_4^-$, as shown in Figure 2. On the other hand, at 303 and 308 K, similar γ^* values were obtained for all X^- anions, as shown in Figures 2 and 3.

The CAEs of SDS and SBS solutions with the complex salts at 298 K were in the range 9–11 mN m^{-1}. Figures 1 and 3 reveal that the strong CAE was present only below 298 K where a counter anion controls the interaction between surfactant anions and complex cations.

Figure 3 shows comparisons of γ^* values for three systems, (A) $[Co(NH_3)_6]X_3$, (B) SDS with $[Co(NH_3)_6]X_3$, and (C) SBS with $[Co(NH_3)_6]X_3$, at different temperatures. The γ^* values of systems (A) and (B) decreased with increasing temperature. This phenomenon is normally observed because the attractions among water molecules on the surface are weakened by thermal motions. On the other hand, the γ^* values of (C) for $X^- = Br^-$ and I^- increased with increasing temperature, resulting in the same order of γ^* values for $X^- = Cl^-, Br^-, I^-$, and ClO_4^- as for

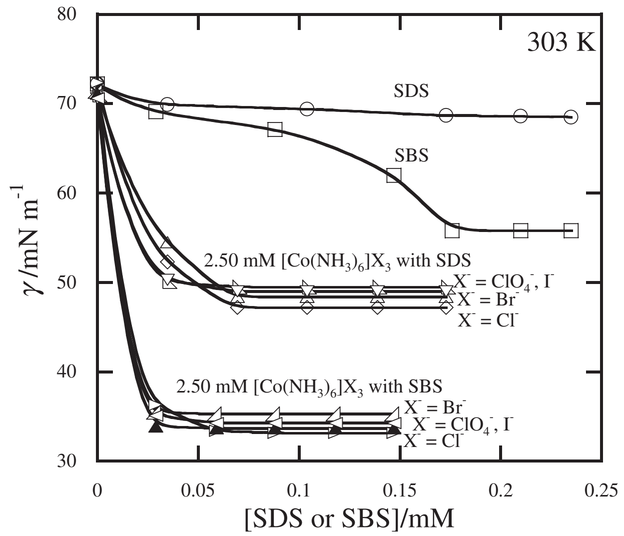

Figure 2. Surface tensions of aqueous SDS and SBS solutions with $[Co(NH_3)_6]X_3$ (2.50 mM) ($X^- = Cl^-$, Br^-, I^-, or ClO_4^-) at 303 ± 0.1 K: (○) SDS, (□) SBS, (◇) SDS with $[Co(NH_3)_6]Cl_3$, (△) SDS with $[Co(NH_3)_6]Br_3$, (◺) SDS with $[Co(NH_3)_6]I_3$, (▽) SDS with $[Co(NH_3)_6](ClO_4)_3$, (▷) SBS with $[Co(NH_3)_6]Cl_3$, (◿) SBS with $[Co(NH_3)_6]Br_3$, (▲) SBS with $[Co(NH_3)_6]I_3$, (◁) SBS with $[Co(NH_3)_6](ClO_4)_3$.

(B), although the orders below 298 K were quite different from those of (B).

In solutions of anionic surfactant (S^-) with $[Co(NH_3)_6]X_3$, changes in γ^* values can be considered by assuming the following equilibria (eqs 1–3),

$$X^- \text{ (bulk)} \rightleftharpoons X^- \text{ (surface)} \qquad (1)$$

$$[Co(NH_3)_6]^{3+} \text{ (b)} + X^- \text{ (b)} \rightleftharpoons \{[Co(NH_3)_6]X\}^{2+} \text{ (b)} \qquad (2)$$

$$[Co(NH_3)_6]^{3+} \text{ (b)} + S^- \text{ (s)} \rightleftharpoons \{[Co(NH_3)_6](S)\}^{2+} \text{ (s)} \qquad (3)$$

If we consider eqs 1–3, competition between eqs 1 and 3 will lead to the results observed for the SDS system; eq 1 is less dependent on ion association of X^- with the complex cation (eq 2) and mainly dependent on the hydrophobicity (or, hydration energy) of X^- ($Cl^- = -369\,kJ\,mol^{-1}$, $Br^- = -336\,kJ\,mol^{-1}$, $I^- = -298\,kJ\,mol^{-1}$, and $ClO_4^- = -244\,kJ\,mol^{-1}$);[4] ClO_4^- with the smallest hydration energy is most readily adsorbed at the water surface among counter anions. Because the surface area is partly occupied by adsorbed X^-, competitive adsorption between X^- and the association complex at the water surface (eqs 1 and 3) is probably responsible for the order of γ^* with respect to X^-: γ^* must be the largest for ClO_4^- that is adsorbed most readily at the surface, with least adsorption of the association complex $\{[Co(NH_3)_6](DS)\}^{2+}$. For the SBS system, on the other hand, because of the higher hydrophobicity or greater adsorbing ability of BS^- relative to DS^-, $\{[Co(NH_3)_6](BS)\}^{2+}$ in eq 3 must be dominant at the water surface, and the contribution of X^- (surface) in eq 1 must be negligible for the adsorption equilibrium. For this system, eq 3 depends directly on the extent of ion association (eq 2): Cl^- ion with the largest ion association constant[5] most inhibits formation of the association complex $\{[Co(NH_3)_6](BS)\}^{2+}$ at the surface by competing with the formation of $\{[Co(NH_3)_6]X\}^{2+}$ ($X^- = Cl^-$) in bulk solution (eq 2), and thus, γ^* value of the Cl^- system becomes the largest among the counter anions. Thus, the trends in γ^* values below 298 K can be interpreted by consideration of the equilibrium (eq 3). On the other hand, at the higher temperature of 308 K, the orders of γ^* values are similar to each other. We suppose that the equilibrium in eq 3 may shift to the right and that the same species $\{[Co(NH_3)_6](S)\}^{2+}$ may dominate the water–surfactant interactions. These interpretations of novel CAE in anionic surfactant with $[Co(NH_3)_6]X_3$ are among the presumptions that should be examined in detail using another approach in the future.

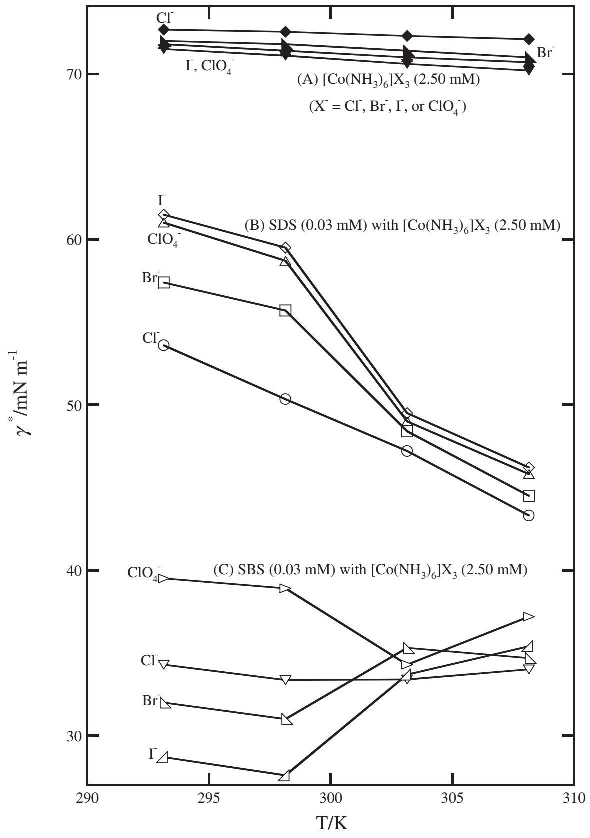

Figure 3. Surface tension values (γ) of (A) $[Co(NH_3)_6]X_3$ (2.50 mM) and plateaued values of surface tensions (γ^*) for (B) SDS, or (C) SBS, aqueous solutions with $[Co(NH_3)_6]X_3$ (2.50 mM) ($X^- = Cl^-$, Br^-, I^-, or ClO_4^-) as a function of temperature (K): (◆) $[Co(NH_3)_6]Cl_3$, (◣) $[Co(NH_3)_6]Br_3$, (▲) $[Co(NH_3)_6]I_3$, (▼) $[Co(NH_3)_6](ClO_4)_3$, (○) SDS with $[Co(NH_3)_6]Cl_3$, (□) SDS with $[Co(NH_3)_6]Br_3$, (◇) SDS with $[Co(NH_3)_6]I_3$, (△) SDS with $[Co(NH_3)_6](ClO_4)_3$, (▽) SBS with $[Co(NH_3)_6]Cl_3$, (◺) SBS with $[Co(NH_3)_6]Br_3$, (◿) SBS with $[Co(NH_3)_6]I_3$, (▷) SBS with $[Co(NH_3)_6](ClO_4)_3$.

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