# Miscibility and Distribution of Counterions in Mixed Adsorbed Films of Surfactants Studied by Surface Tension and Total-Reflection XAFS Methods

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"Specific ion effect" has been one of the important issues of colloid and interface sciences. Many phenomena in the colloid, polymer and interface systems containing electrolytes or counterions show pronounced ion specificity.

As a first step to investigate the counterion specificity in the miscibility and structure of the adsorbed films, we employed dodecyltrimethylammonium bromide (DTAB) - dodecyltrimethylammonium tetrafluoroborate ($DTABF_4$) aqueous solutions, measured their surface tensions, and then analyzed these data by a thermodynamic treatment. The surface tensiometry showed that $BF_4^-$ was more effective than $Br^-$ in lowering the surface tension. The phase diagram of adsorption (PDA) demonstrated that the surface was richer in $BF_4^-$, but the fraction of $Br^-$ ions at the surface was slightly enhanced compared to the ideal mixing. These were explained in terms of the size and dehydration energy of counterions.

Then the total reflection X-ray absorption fine structure (TR-XAFS) measurement was applied to the adsorbed film at the surface of aqueous solutions of surfactant mixtures composed of DTAB) and $DTABF_4$. The obtained XAFS spectra were decomposed as linear combination of two specific spectra corresponding to the fully hydrated bromide ion (free-Br) and the partially dehydrated bromide ion adsorbed to the hydrophilic group of surfactant ion (bound-Br) at the surface. The ratio of free- and bound-Br ions was determined as a function of surface tension and surface composition of the surfactants. Taking also the composition evaluated in our previous studies on DTAB-dodecyltrimethylammonium chloride (DTAC) and hexylmethylimidazolium bromide (HMIMBr) – hexylmethylimidazolium tetrafluoroborate ($HMIMBF_4$) systems into consideration, the relation between counterion distribution at the solution surface and synergism between surfactants was deduced for the case that two surfactant have common surfactant ion but different counterions.