

## Behavior of Endocrine Disruptors in Cationic Surfactant Solution Containing $\beta$ -Cyclodextrin

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Recent studies have clarified the definition of endocrine disrupting chemicals (EDCs), identified research needs. Nonylphenol (NP) is known to be an endocrine disruptor. NP has a carbon chain and a phenolic group in molecule structure. NP is used as a material of non-ionic surfactant, nonyl phenoletoxylate. Also, the degradation process of its surfactant sewage can release the suspicious NP into the environment. On the other hand,  $\beta$ -estradiol ( $\beta$ -E2) is a major estrogen and has the highest activity on our human body. It is used in obstetric treatments. NP and  $\beta$ -E2 are being observed in soil and water. Therefore, it is very interesting to investigate the interaction between ionic surfactants and those endocrine disruptors. NP and  $\beta$ -E2 have such low solubilities in water. We used hydrophilic modified (2-hydroxypropyl)- $\beta$ -cyclodextrin (hp- $\beta$ -CD) to enhance the solubility of NP. Hp- $\beta$ -CD is constituted of seven glucose units and forms a ring which has a hydrophilic outer surface and a hydrophobic inner cavity and well known to incorporate guest molecules in the hydrophobic cavity predominantly. In addition, we have carried out voltammetric measurements of  $I_2/I^-$  to investigate the behaviour of NP and  $\beta$ -E2 in the hexadecyltrimethylammonium (HTA<sup>+</sup>) monolayer formed at a platinum electrode surface.

Hp- $\beta$ -CD increased the solubility of NP in water but did not change the maximum surface excess of NP. It indicates that the hp- $\beta$ -CD containing NP does not adsorb onto the air-solution interface. Both NP and  $\beta$ -E2 decreased the critical micelle concentration (*cmc*) of HTA<sup>+</sup>. It is caused by the micelle stabilization which is possibly due to (1) the attractive force between the hydroxyl groups and the  $\pi$  electrons of aromatic rings in NP/ $\beta$ -E2 and the positive charged ammonium portion of HTA<sup>+</sup> and (2) the hydrophobic interaction between NP/ $\beta$ -E2 and HTAB. Also, the EDC molecules occupy the hp- $\beta$ -CD cavity so that the HTA<sup>+</sup> molecule in that cavity is removed to increase the concentration of HTA<sup>+</sup> free monomer. However, NP decreased the *cmc* values more significantly than those of  $\beta$ -E2. NP has a long carbon chain in itself and is similar to HTA<sup>+</sup> ion in molecular structure. It possibly causes a higher affinity between HTA<sup>+</sup> and NP in micelle. From fluorescence anisotropy measurement, the addition of EDCs made the micellar surface pack more rigidly. From dynamic light scattering measurement, the addition of EDCs made the hydrodynamic radius ( $R_H$ ) of micelle larger. In our pyrene fluorescence  $I_1/I_3$  measurement, the polarity in micelle did not change with the addition of EDCs. Therefore, this increase in  $R_H$  is not due to the invasion of water in micelle but due to the invasion of EDC molecules. From cyclic voltammetry, we observed a reductive adsorption peak at 5 mM of HTA<sup>+</sup> (see the figure). This peak is caused by the reduction of  $I_2$  molecules adsorbed onto the HTA<sup>+</sup> monolayer formed at the electrode surface. In the presence of NP, the reduction peak disappeared but did not in the presence of  $\beta$ -E2 although the reduction peak became smaller. This result indicates that the NP adsorbs onto the HTA<sup>+</sup> monolayer at the electrode surface very strongly to make the  $I_2$  molecules on the layer free.

