Adsorption of Oligomer Type Surfactants on Iron Oxide

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Synopsis. Adsorption of oligomer type surfactants synthesized from acrylic acid, acrylonitrile, and 1-dodecanethiol on α-Fe_2O_3 was examined by measuring adsorption isotherms and zeta potentials. It was found that the adsorption behavior of oligomer type surfactants on α-Fe_2O_3 was influenced by the pH of suspensions and further by the differences of composition of oligomer type surfactants.

Recently, from the standpoints of environment pollution and of conservation of resources, water-base paints[1)] have been preferred instead of organic-base ones. The preparation of stable pigment dispersions requires the addition of dispersants. Many kind of surfactants[2—5)] have been utilized for this purpose. Of these surfactants, oligomer type surfactants[6—10)] have been developed and employed for dispersion of pigments due to suitable properties, such as improvement of film formation and resistance for water vapor.

In this work, to understand the interactions of oligomer type surfactant and pigment surface in aqueous solution, the adsorption of oligomer type surfactants synthesized from acrylic acid, acrylonitrile, and 1-dodecanethiol on α-Fe_2O_3 is examined by measuring adsorption isotherms and zeta potentials.

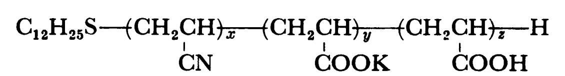
Experimental

Materials. The oligomer type surfactant used in this study was synthesized[10)] by co-oligomerization of acrylic acid, acrylonitrile, and 1-dodecanethiol, followed by neutralization with potassium hydroxide. The chemical structure and analytical properties of the oligomers are given in Table 1. All the chemicals were of reagent grade. The water used was purified by passing through Milli-Q Reagent Grade Water Systems until its specific conductivity fell below 10^{-7} Ω^{-1} cm^{-1}.

As a pigment, α-Fe_2O_3 was supplied by Titan Chemicals; it was washed with water sufficiently to remove impurities and then dried. The specific surface area of this pigment was determined to be 6.35 m^2/g by nitrogen adsorption at its liquid temperature.

Measurements. A 20 ml portion of oligomer aqueous solution was placed in an L-shaped test tube and α-Fe_2O_3 (0.3 g) was added in; then the test tube was shaken at 25 °C. After at least 2 h, having reached adsorption equilibrium, the sample was separated by using a Milli-pore filter. The concentration of supernatant solution was determined with UV spectrophotometer by measuring the absorbancy at 215 nm.

Table 1. Chemical structure and analytical properties of oligomer type surfactants



$$C_{12}H_{25}S-\!\!\!\underset{\substack{|\\ CN}}{(CH_2CH)}_x\!-\!\underset{\substack{|\\ COOK}}{(CH_2CH)}_y\!-\!\underset{\substack{|\\ COOH}}{(CH_2CH)}_z\!-H$$

	$\overline{M}_w$[a)]	x	y	z	$\dfrac{y+z}{x+y+z}$
Oligomer(I)	1320	3.6	7.0	2.2	0.72
Oligomer(II)	1530	0.0	9.5	3.8	1.00

a) Mean molecular weight calculated from elemental analysis.

The zeta potential of α-Fe_2O_3 after the adsorption was measured using a Pen Kem Laser 500.

The surface tensions of oligomer type surfactant aqueous solutions were determined by a modified Wilhelmy type surface tension meter (Shimadzu ST-1) at 25 °C.

Results and Discussion

Before a study of adsorption of oligomer type surfactant on pigments, it is important to characterize the surface properties of the oligomer type surfactant aqueous solution. The surface tension of oligomer type surfactant(I) as a function of the concentration in the absence and in the presence of HCl was measured.[10)] In the absence of HCl, the surface tension curve of oligomer type surfactant(I) was similar to that of an ordinary surfactant like sodium dodecyl sulfate, while the surface tension value over a relative low concentration became lower in the presence of HCl, indicating that some -COO^-K^+ groups in oligomer(I) molecule are converted to -COOH groups by addition of HCl, resulting in enhancement of surface activity due to decrease of repulsion forces between -COO^-K^+ groups and of the hydrophilicity of oligomer(I) molecule. Thus, oligomer type surfactant exhibits an appreciable surface activity.

Figure 1 gives the adsorption isotherms of oligomer(I) on α-Fe_2O_3 in the absence and in the presence of HCl. All three isotherms were Langmuir type; furthermore, the amount adsorbed of oligomer(I) on α-Fe_2O_3 increased with an increase of the concentration of HCl added. Also, to elucidate the interaction of oligomer(I) and the surface of α-Fe_2O_3, the zeta potential of α-Fe_2O_3 corresponding the adsorp-

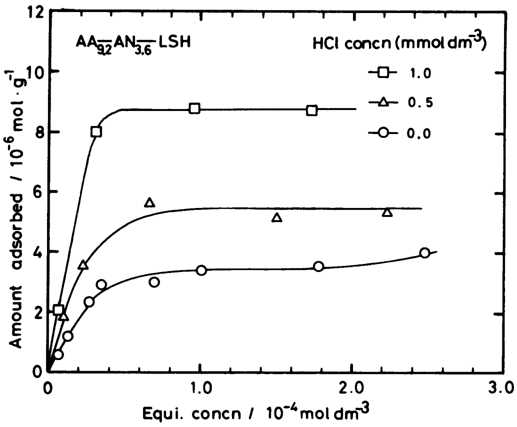


Fig. 1. Adsorption isotherms of oligomer type surfactant(I) on α-Fe_2O_3 in the absence and in the presence of HCl at 25 °C.

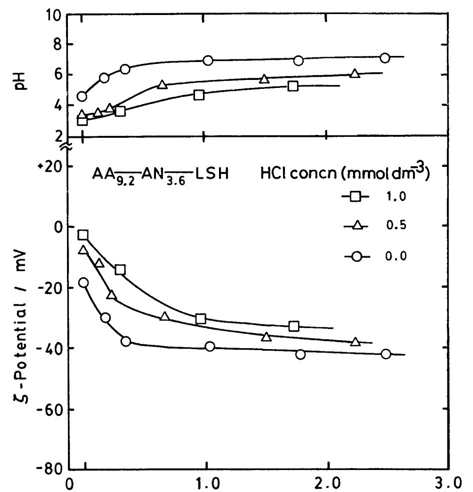


Fig. 2. Zeta potentials of α-Fe_2O_3 and pH values of suspension shown in Fig. 1.

tion isotherm was measured; the result is shown in Fig. 2. It can be seen that the zeta potential value decreases as a function of the equilibrium concentration of oligomer(I) in the absence and in the presence of HCl. The magnitude of zeta potential in the presence of higher concentrations of HCl was less negative than that in lower concentration of HCl. The above results can be interpreted as follows: since the pH of oligomer(I) aqueous solution without adding HCl is about 6, some -COO^-K^+ groups in oligomer(I) molecule are likely to dissociate easily. When such an oligomer is adsorbed on the surface of α-Fe_2O_3, an appreciable negative charge at the surface is provided in spite of the fact that less oligomer(I) is adsorbed; this may be due to repulsion of dissociable -COO^-K^+ groups in the molecule. On the other hand, with an increase of the concentration of HCl added, some -COO^-K^+ groups in oligomer(I) molecule are changed to undissociated -COOH groups, resulting in a decrease of negative charge density of the oligomer molecule. Accordingly, though the amount adsorbed with adding HCl is relatively large, the magnitude of zeta potential of α-Fe_2O_3 in the presence of HCl is less negative than that without HCl. Thus, the change in charge density of oligomer(I) molecule in the presence of various concentrations of HCl exhibits a different adsorption behavior. So, it seems interesting to study the adsorption behavior by different chemical structures of the oligomer.

Figure 3 demonstrates the adsorption isotherms of oligomer(II) containing no acrylonitrile groups on α-Fe_2O_3. This oligomer(II) has less surface active than oligomer(I). These isotherms are different from those of oligomer(I); the amount adsorbed of oligomer(II) in the presence of HCl increases with an increase of the concentration of oligomer(II), reaches a maximum, and then decreases. The isotherm is changed much remarkably in the presence of higher concentrations of HCl than in lower concentrations of HCl. This phenomenon might be explained by changes in the solubility of oligomer(II) with adding HCl and in the interaction between oligomer(II) molecules and surface of α-Fe_2O_3. That is, some -COO^-K^+ groups in oligomer(II) molecule at lower concentration are converted by addition of HCl to -COOH groups, which reaction decreases the solubility of oligomer(II), resulting in an increase of amount adsorbed. Further, with an increase of the concentration of oligomer(II) in the presence of HCl, the conversion ratio from -COO^-K^+ to -COOH declines. As a result, the increment of solubility of oligomer(II) reduces the amount adsorbed. Also, as it is expected that repulsion forces between oligomer(II) molecule and surface of α-Fe_2O_3 charged negatively increase with an increase of the suspension's pH, so the amount adsorbed would decrease. Further, the zeta potential of α-Fe_2O_3 by the adsorption of oligomer(II) in the absence and in the presence of HCl was measured. These changes in zeta potential corresponded to those of the adsorption isotherms as shown in Fig. 3. The adsorption of oligomer(II) provided more negative charge on the surface of α-Fe_2O_3 than that of oligomer(I).

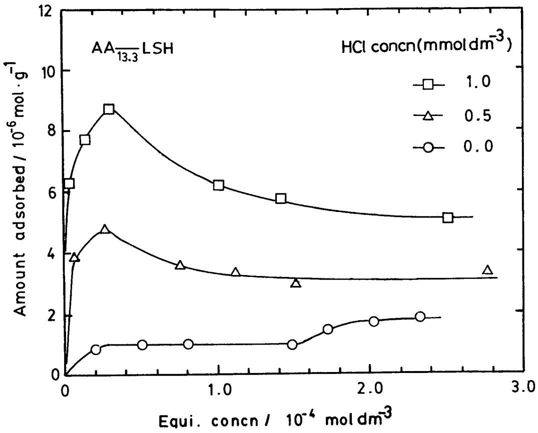


Fig. 3. Adsorption isotherms of oligomer type surfactant(II) on α-Fe_2O_3 in the absence and in the presence of HCl at 25 °C.

The occupied area per molecule at 2×10^{-4} mol dm^{-3} of the equilibrium concentration for two oligomers was calculated as a function of pH of the suspension. For both oligomers, the calculated area increases with an increase of pH of the suspension. The calculated area for oligomer(II) is larger than that for oligomer(I) in the region of above pH=6.

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