Adsorption Behavior of Iron–Cyanide onto γ-Al₂O₃ Interface: A Coagulation Approach

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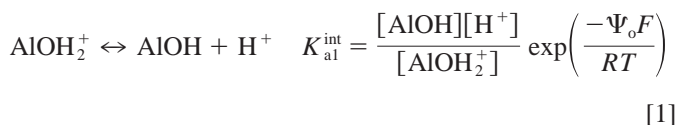
Ferrocyanide and ferricyanide ions have strong coagulation ability in a natural water system due to their high valences. Studies with aluminum oxide turbid waters showed significant differences in coagulation between simple ions (Cl^-, SO_4^{2-}, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$) and other species ($H_2PO_4^-$) that interact chemically with the oxide surface. The evidence suggested that the adsorption of ferrocyanide and ferricyanide on aluminum oxide surface is an outer-sphere reaction. The linear relationship between the logarithm of the significant coagulation concentration and Schultz–Hardy ratios indicated that the coagulation obeyed the DLVO rule. Therefore, it is concluded that the coagulation of aluminum oxide by ferrocyanide and ferricyanide is essentially caused by compression of the electric double layer rather than by charge neutralization. © 1999 Academic Press

Key Words: coagulation; ferricyanide; ferrocyanide; adsorption.
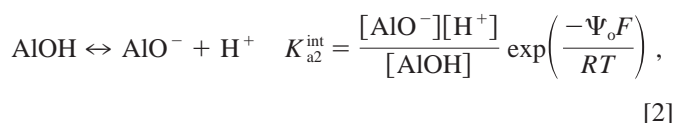
INTRODUCTION

Adsorption phenomena of inorganic ions and organic acids on hydrous oxides of aluminum, iron, manganese, and silica have been studied for over three decades. However, most research involved simple ions rather than complex ions. Cyanides released from factories readily form complexes with metal ions, e.g., iron, zinc, and nickel, which are less toxic than the original cyanides. These metal–cyanide complexes, i.e., ferrocyanide [$Fe(CN)_6^{4-}$] and ferricyanide [$Fe(CN)_6^{3-}$], can slowly decompose when exposed to light under general soil and water conditions (1, 2) and release the free cyanide back to the environment. The amount released depends upon the stability of the complex ions in soil, which rely greatly upon the adsorption on soil.

The protolysis of the hydroxyl groups on aluminum oxide surface may be simulated as a surface ionization model (3). The equilibrium reactions can be set up as

$$AlOH_2^+ \leftrightarrow AlOH + H^+ \quad K_{a1}^{int} = \frac{[AlOH][H^+]}{[AlOH_2^+]} \exp\left(\frac{-\Psi_o F}{RT}\right)$$

[1]

and

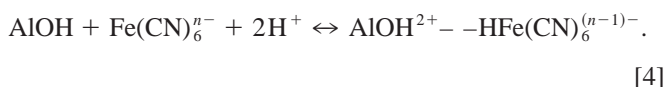$$AlOH \leftrightarrow AlO^- + H^+ \quad K_{a2}^{int} = \frac{[AlO^-][H^+]}{[AlOH]} \exp\left(\frac{-\Psi_o F}{RT}\right),$$

[2]

where R is the gas constant, F is the Faraday constant, Ψ_o is the oxide surface potential, and K_{a1}^{int} and K_{a2}^{int} are the first and second intrinsic acidity constants of the aluminum oxide surface. Surface charge and potential difference decrease with increasing distance from the oxide–solution interface to the solution phase. The adsorption of ions at the oxide–solution interface is commonly described by solution coordination chemistry. The triple layer model (TLM) developed by Hayes and Leckie (4) allows metal ions and anions to form an inner-sphere complexation at the surface layer or an outer-sphere at the compact layer (5–7). Our previous work (8, 9) concluded that the adsorption of ether ferrocyanide or ferricyanide complexes onto aluminum oxide include following equations:
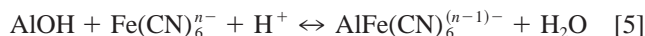
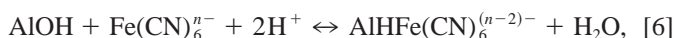The reactions in the outer-sphere complexation may include

$$AlOH + Fe(CN)_6^{n-} + H^+ \leftrightarrow AlOH^{2+} - {-}Fe(CN)_6^{n-} \quad [3]$$

and

$$AlOH + Fe(CN)_6^{n-} + 2H^+ \leftrightarrow AlOH^{2+} - {-}HFe(CN)_6^{(n-1)-}.$$

[4]

The reactions in the inner-sphere complexation may include

$$AlOH + Fe(CN)_6^{n-} + H^+ \leftrightarrow AlFe(CN)_6^{(n-1)-} + H_2O \quad [5]$$

and

$$AlOH + Fe(CN)_6^{n-} + 2H^+ \leftrightarrow AlHFe(CN)_6^{(n-2)-} + H_2O, \quad [6]$$

in which n equals 3 or 4, representing the charge of ferricyanide and ferrocyanide, respectively.

The most representative mechanisms of the destabilization of colloids are electric-double-layer compression, adsorption

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and charge neutralization, enmeshment, and interparticle bridging. Ions induce coagulation in two ways: (1) Inert electrolytes, ions that are not specifically adsorbed, compress the double layer and thus reduce the stability of the colloid (e.g., ions that form outer-sphere complexation); (2) specifically adsorbed ions reduce the surface charge directly (e.g., species that form inner-sphere complexation).

According to the empirical valence principle of Schultz and Hardy (10), critical coagulation concentration (CCC) is proportional to z^{-6} for inert electrolytes. After simplification, the CCC of mono-, di-, tri-, and tetravalent ions vary in the ratio of 10000:156:13.7:2.44. The specifically adsorbable species, however, is able to coagulate colloids at lower concentration and redispersion may occur at higher concentration. Therefore, by assessing the coagulation profiles of various ions, we can distinguish the inner-sphere adsorption from the outer-sphere adsorption. Electrolytes affect the stability of particles by varying the surface potential and charge through chemical bonding to the surface (i.e., inner-sphere adsorption) or compressing the diffuse layer (i. e., outer-sphere adsorption). Liang and Morgan (11) have discussed the coagulation from a chemical point of view and applied it to the natural system. They used the diffusion layer model to explain the complexation on the surface of adsorption. They studied the change of surface charge and potential during coagulation in various experimental conditions to explain the destabilization of the metal oxide particle and to predict the minimum coagulant dosage. Liang and Morgan (11) have reported a CCC ratio of 10,000:2 for Cl^- and HPO_4^{2-} on Hematite at pH 6.63. This CCC ratio does not follow the Schultz–Hardy theory due to the fact that HPO_4^{2-} is specifically adsorbed on the metal oxide surface (12, 13). Conversely, for the nonspecific adsorption nature of nitrate and sulfate, Overbeek (14) found a CCC ration of 10,000:170, which is almost the same as the value predicted by the Schultz–Hardy theory. These studies suggested that the mode of the reaction of electrolytes on a colloid liquid–solid surface might be determined from the dosage of the coagulant used. The objective of this study is to discuss the adsorption mechanism of the ferrocyanide and ferricyanide on a γ-Al$_2$O$_3$ particle from a coagulation point of view.

EXPERIMENTAL PROCEDURE

Materials

Aluminum oxide (γ-Al$_2$O$_3$) purchased from the Japan Aerosol Company was produced through the process of hydrolyzing AlCl$_3$ in the flame. The size was smaller than 1 μm in diameter with uniform shape. The aluminum oxide was pretreated following the procedure suggested by Hohl and Stumm (15). Stock solutions of K$_4$Fe(CN)$_6$ were purchased from Riedel de Haen without further purification.

Jar Test

The effectiveness of the ferrocyanide and ferricyanide in removing aluminum oxide turbidity was evaluated using a
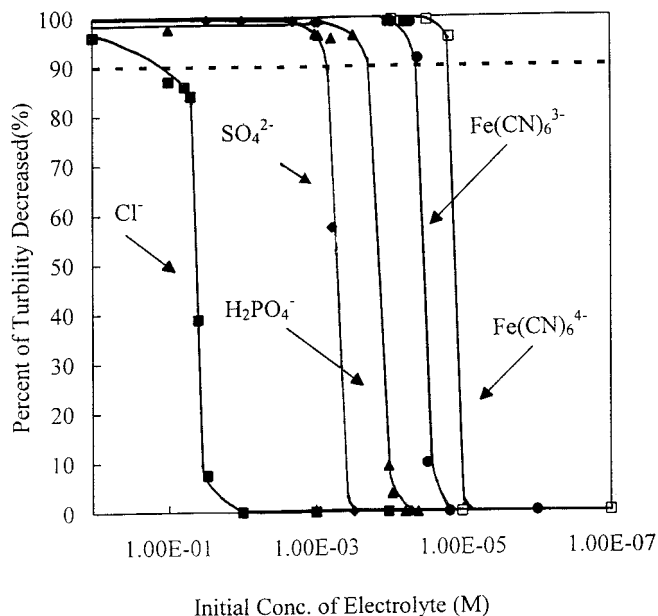
FIG. 1. The effect of charge valences and initial concentration on turbidity removal. (γ-Al$_2$O$_3$ = 1.5 g/l, pH 5)

conventional jar test. A six-beaker jar test apparatus was set up with 300 ml of aluminum oxide solution in each jar. Aluminum oxide concentration was kept at 1.5 g/l, while various amount of different salts, namely Cl^-, SO_4^{2-}, $Fe(CN)_6^{3-}$, and $Fe(CN)_6^{4-}$, were added and the optimum dosage was determined. The pH of the suspension was kept constant by adding either HNO$_3$ or NaOH. The suspension was mixed for 2 min at 100 rpm, followed by 20 min of flocculation at 30 rpm. At the end of the flocculation, the suspension was allowed to settle for a period of up to 10 min and the sample was taken from the 3-cm level below the liquid surface for turbidity measurement.

Turbidity was measured with turbidity meter (Model 2100A, Hach Camlab). Because of the difficulty in obtaining CCC experimentally, we used significant coagulation concentration (SCC) in our study, which is the amount of the electrolyte achieving 90% turbidity removal.

RESULT AND DISCUSSION

The Effect of Valence Charge on Adsorptions

The effect of five different anions on the stability of the positively charged aluminum oxide (pH 5.0) is illustrated in Fig. 1. It shows that the SCC of phosphate (predominantly $H_2PO_4^-$ at pH 5) is much smaller than that of chloride (Cl^-). This result contradicts the Schultz–Hardy rule that the same SCC was required by ions of the same valence charge. The SCC of [$H_2PO_4^-$] is 10^3 times lower than that of a chloride ion bearing the same charge, which demonstrates that the mechanism of aluminum oxide coagulation by phosphate ion is specific adsorption as previously studied (12, 13). Therefore, a chemical model (inner-sphere reaction) can better explain the strong adsorption of the phosphate species. It is also observed
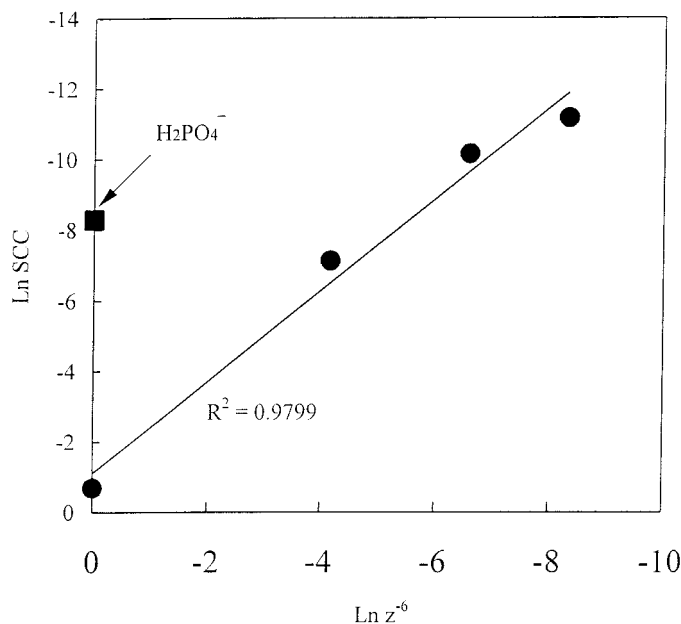
FIG. 2. The relationship between the logarithms of SCC and valence charge of the counterion.

that at higher concentration, phosphate does not alter or reverse the surface charge of aluminum oxide. By triple-layer assumption, at lower solution pH values, surface reaction of phosphate [$H_2PO_4^-$] on the o-plane may be written as

$$AlOH_2^+ + H_2PO_4^- \leftrightarrow AlH_2PO_4 + H_2O. \qquad [7]$$

Therefore, the adsorption of phosphate species decreases the number of positive charges on the oxide surface immediately. A further increase of phosphate in solution would not reverse the surface potential. The aluminum oxide particle becomes coagulated because of the attraction between neutrally charged surfaces [AlH_2PO_4]. A linear relationship exists between the logarithm of the SCC and the valence number of the counterion, as shown in Fig. 2. The classical Schultz–Hardy rule relates the CCC to the valence of counterion (z) as CCC $\propto$ $1/z^6$, in which a linear relationship exists between the logarithm of the molar CCC and that of $1/z^6$. Therefore, it is concluded that simple electrolytes such as Cl^-, SO_4^{2-}, $Fe(CN)_6^{3-}$, and $Fe(CN)_6^{4-}$ destabilize the aluminum oxide colloids by compressing the electric double layer. This corresponds to the finding that simple electrolyte ions such as Cl^- and possibly SO_4^{2-} are not specifically bound to the oxide surface (11, 14). From Figs. 1 and 2, it is evident that there is a dramatic difference in the coagulation abilities of simple ions, e.g., Cl^-, SO_4^{2-}, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, and other species that interact chemically with the oxide surface, e.g., $H_2PO_4^-$. From the triple-layer model, illustrated in Eqs. [3] to [6], we can conclude that the adsorptions of ferrocyanide and ferricyanide ions are outer-sphere reactions. This conclusion is the same as our previous works; the adsorption mechanism of ferrocyanide and ferricyanide ions on an aluminum oxide sur-

face has been proved by the thermodynamic theory and a HYDRAQL program simulation (7, 8).

The effect of aluminum oxide concentration on the SCC of ferrocyanide and ferricyanide at pH 5 is illustrated in Fig. 3. The result shows that the SCC is independent of the concentration of the aluminum oxide. For ions not specifically adsorbed on the oxide surface, there is no stoichiometrical relationship between the SCC and the concentration of the colloid (16), which further confirms that the mechanism of iron–cyanide ion adsorption on an aluminum oxide surface is either outer-sphere reaction or double-layer compression.

pH Effect

pH is an important factor in controlling ferrocyanide or ferricyanide adsorption on γ-Al_2O_3. To study the effect of pH on the coagulation efficiency, the 1.5 g/l γ-Al_2O_3 suspension was adjusted to pH 2, 3, 4, 5, and 6.6. Figures 4 and 5 shows that charge reversal did not occur at any pH no matter how much coagulant was added, which implies that the destabilization of γ-Al_2O_3 by ferrocyanide or ferricyanide was caused by the compression of the electric double layer. The increase in SCC with the decreasing pH is a result of more positive sites on the aluminum oxide surface at lower pH, which requires more salt to destabilize the aluminum oxide through double-layer compression.

Figure 6 shows that for each pH studied, the SCC of ferrocyanide is lower than that of the ferricyanide, but the difference increases with increasing pH. This is due to the higher valance number of ferrocyanide, which makes the compression of the double layer easier. Ferrocyanide, $Fe(CN)_6^{4-}$, can form two conjugate acids, i.e., $HFe(CN)_6^{3-}$ and $H_2Fe(CN)_6^{2-}$ with
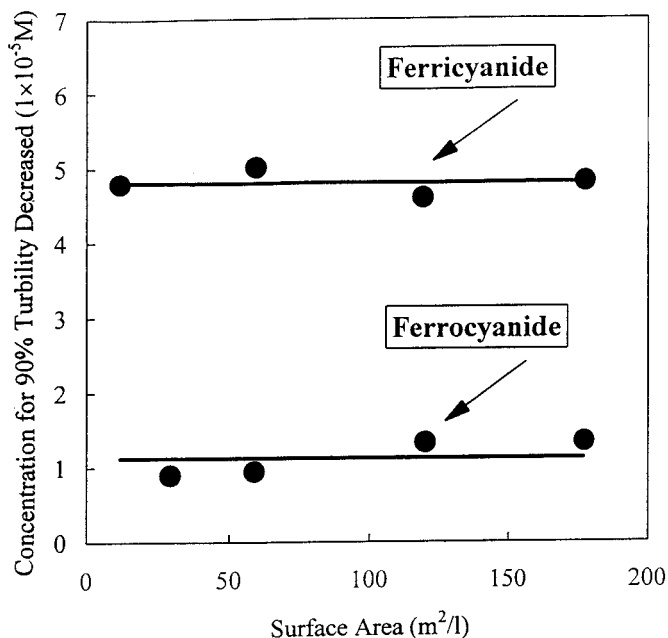

FIG. 3. The effect of the aluminum oxide concentration on the SCC of the ferrocyanide and ferricyanide at pH 5.

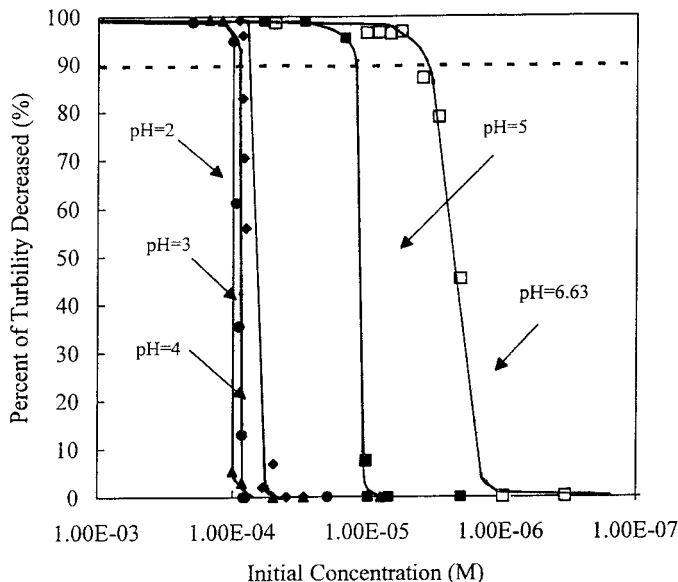**FIG. 4.** The relationship between the ferrocyanide concentration and residual turbidity at different pH conditions.

FIG. 6. The relationship between the logarithm of the SCC and the solution pH values.

pKa1 = 2.1 and pKa2 = 4.3 in solution. Ferricyanide, on the other hand, does not form any conjugate acid above pH 1 (17). Therefore, the valence difference between ferrocyanide and ferricyanide at lower pH is insignificant, resulting in little difference in SCC, as shown in Fig. 6. Moreover, when the solution pH is substantially lower than the pHzpc of oxide, nearly all of the surface groups are protonated (AlOH$_2^+$), and therefore, similar amounts of ferrocyanide and ferricyanide are adsorbed onto the aluminum oxide surface.
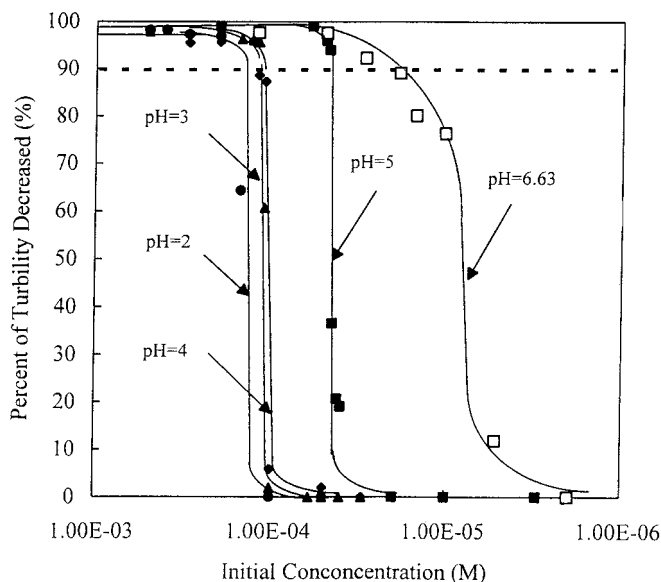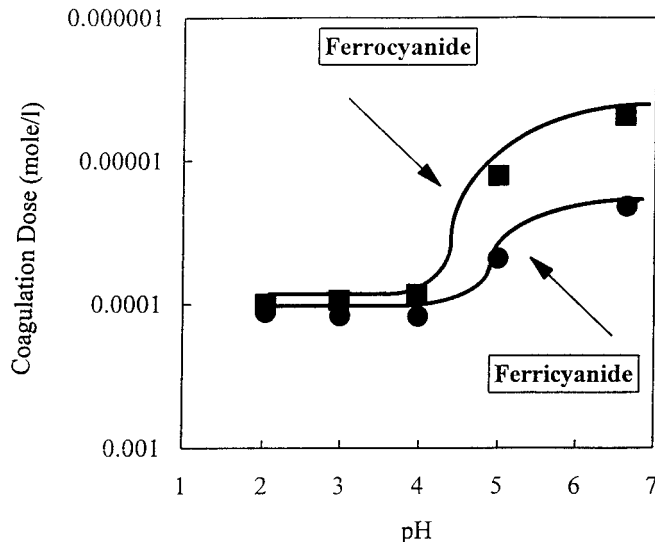
CONCLUSION

The linear relationship between the logarithm of the SCC and the valence number of the counterion suggests that the destabilization of aluminum oxide is by compression of the double layer rather than by charge neutralization. The result that the SCC of either ferrocyanide or ferricyanide is independent of the colloid concentration further proves that the adsorption of both ions on aluminum occurs in outer-sphere.

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FIG. 5. The relationship between the ferricyanide concentration and residual turbidity at different pH conditions.