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Competitive Adsorption of Ferricyanide and Ferrocyanide on γ-Al_2O_3 Surface

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In the past 3 decades, research has proven the significance of competitive adsorption in the equilibrium of pollutants between solid and liquid phases. However, studies on the competitive adsorption of complex ions are very limited in spite of its important role in transporting pollutants in the natural environment. The objective of this study is to derive the thermodynamic parameters of the competitive adsorption between ferricyanide and ferrocyanide from the modified Langmuir isotherm and the triple-layer model (TLM) to determine the location of adsorption. The effects of pH, temperature, and ion concentration on competitive adsorption onto γ-Al_2O_3 were investigated. The results demonstrate that ferrocyanide is more competitive than ferricyanide. By comparing the derived K^{app} with K^{int}, we inferred that the adsorption of ferricyanide and ferrocyanide onto γ-Al_2O_3 was achieved through outer-sphere complexation. The negative ΔH° indicated that the adsorption was exothermic. The positive entropy (ΔS°) was caused by the replacement and release of a greater number of smaller surface ions by adsorbed ferricyanide and ferrocyanide ions of larger size.

Key Words: **competitive adsorption; complexation; ferricyanide; ferrocyanide; inner sphere; outer sphere.**

INTRODUCTION

Many new pollutants are being introduced into our environment as the development of the industry continues. Among them, cyanide compounds, which are widely used in the electroplating industry, have received great attention because of their high toxicity. In nature, cyanides exist in either free form or complex forms with metal ions (i.e., Fe, Cu, and Zn). The iron-complexed cyanide compounds are unstable in the sunlight, and the free cyanide is released back into nature through photolysis (1, 2). Therefore, iron–cyanide complexes cannot be considered safe.

In the past few years, studies on competitive adsorption have focused on the behaviors of anions, cations, and organic substances on soil or metal oxides. Lopez-Hernandez *et al.* (3) examined the competition between organic chelating compounds and phosphate on the soil and discovered that phosphate adsorption was reduced, possibly due to the blocking of the surface site by low-molecular-weight aliphatic or aromatic acids. Violant *et al.* (4) conducted a similar study on oxalate and phosphate and found that the sequence of anion addition strongly influenced the adsorption of both anions. Attention has also been drawn to the competitive adsorption of pollutants on activated carbon which is an efficient adsorbent for trace contaminants in water. Gabaldon *et al.* (5), in the study of the competitive adsorption of Cd and Zn onto the granular activated carbon (GAC), found that the removal of both metals decreased in the competitive system. By applying the surface complexation constants of individual adsorbates determined with the triple-layer model (TLM), they successfully predicted the removal of Cd and Zn from solutions containing both metal ions.

The surface chemistry of aluminum oxide, Al_2O_3, has been a subject of interest, not only because it is one of the most abundant oxide minerals in the natural system but also because it constitutes the surface layer of a wide variety of industrial materials. Aluminum oxide has been used in numerous studies about adsorption because of the homogeneity and stability. In particular, the coordination chemistry approach has been successfully applied to explain the interactions between cations and anions under monolayer coverage at the aqueous/oxide interface. The TLM developed by Hayes and Leckie allows metal ions and anions to form an inner-sphere complexation at the surface layer (o-plane) or outer sphere at the compact layer (β-plane) (6–9). Kanungo (10) suggested that the location of the ion complex on the oxide surface can be determined by comparing the apparent adsorption constant (K^{app}) from the Langmuir isotherm with the intrinsic adsorption constant (K^{int}) from the TLM; the K^{app} and the K^{int} differ in an electrostatic term [$\exp(\Psi F/RT)$]. In general, for cations adsorption on a metal oxide surface, a greater K^{int} than K^{app} suggests inner-sphere complexation. The K^{int} can be calculated from the HYDRAQL developed by Papelis *et al.* (11).

The objective of this study is to derive the thermodynamic parameters of the competitive adsorption between ferricyanide and ferrocyanide under various pHs temperatures, and ion concentrations using the modified Langmuir isotherm and the TLM, to determinate the location of the complex ion adsorption.

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MATERIALS AND METHODS

Materials

γ-Aluminum oxide (γ-Al_2O_3), supplied by Japan Aerosol Co., was produced from the hydrolysis of $AlCl_3$ in the flame process. The oxide particle was smaller than 1 μm in diameter and apparently uniform. The aluminum oxide was pretreated with the procedure suggested by Hohl and Stumm (12). Oxide impurities were first removed with 0.1 N NaOH and followed by washing with Milli-Q distilled water for several times. The solid was dried in an oven at 103°C overnight. Stock solutions of $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$ were prepared from analytical grade reagents (Riedel de Haen).

Batch Adsorption

In a 100-ml PE bottle, 0.125 g of γ-Al_2O_3 in 50 ml of 0.01 M $NaClO_4$ were mixed with an appropriate amount of the complex ion stock solutions. The initial concentrations of ferricyanide and ferrocyanide were ranging from 0.5×10^{-4} to 4.0×10^{-4} M. The pH was adjusted from 3 to 12 with HNO_3 or NaOH, and the reaction was carried out on a thermostat shaker for 24 h. At the end of the reaction, the pH of the samples was measured and the solid was removed by membrane filtration with a 0.2-μm filter. The filtered supernatant was analyzed for Fe(II) and Fe(III) by ion chromatography with the conductivity detector purchased from DIONEX Co. The ion pair column was MPIC-NS1, and the eluent consisted of 0.002 M TBAOH, 0.0002 M Na_2CO_3, and 35% (v/v) acetonitrile with a 1 cm^3/min flow rate.

RESULTS AND DISCUSSION

Effect of pH on Competitive Adsorption

An equal amount of ferricyanide and ferrocyanide, ranging from 5.0×10^{-5} to 2.0×10^{-4} M, were added to PE bottles containing γ-Al_2O_3 and the pH was adjusted from 3 to 10. After 24 h of adsorption, the amount of complex ions left in the solution were determined. In Fig. 1, it shows that the adsorption of both ferricyanide and ferrocyanide decreases with the increasing solution pH. This is because that at higher solution pH less $AlOH_2^+$ sites on the γ-Al_2O_3 surface are available, and the surface becomes more negatively charged which discourages the adsorption of anions on the oxide surface. When the adsorption percentage was converted to the adsorption capacity (mol/g), as shown in Fig. 2, it is obvious that ferrocyanide is much more competitive than ferricyanide under all experimental conditions due to its higher electric charge. Figure 2 also shows that the adsorption capacity of ferrocyanide increases with the adsorbate concentration, while the opposite result is observed in that of ferricyanide. This can be explained by the limited adsorption sites at a particular pH. At a higher adsorbate, more surface sites were occupied by the more competitive ferrocyanide which left ferricyanide with less available sites. This phenomenon was especially significant at low pH (<7), where the adsorption of ferrocyanide nearly reached 100%. The temperature effect on the competitive adsorption of ferricyanide and ferrocyanide was conducted with an initial concentration of 1.0×10^{-4} M under four temperatures (10, 25, 35, and 45°C). The result is presented in Fig. 3. A significant decrease in the adsorption ability of both complex ions was observed at a higher solution temperature, which suggested that the adsorption is exothermic.

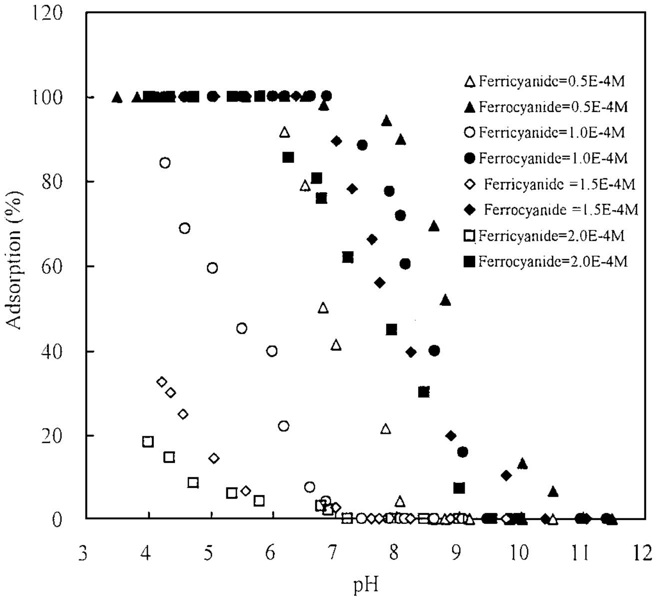

FIG. 1. Sorption percentage of ferricyanide and ferrocyanide onto γ-Al_2O_3 as a function of pH and initial concentration.

Modified Langmuir Isotherm

In our previous work (13–15), we studied the individual adsorption of ferricyanide ($Fe(CN)_6^{3-}$) or ferrocyanide ($Fe(CN)_6^{4-}$)

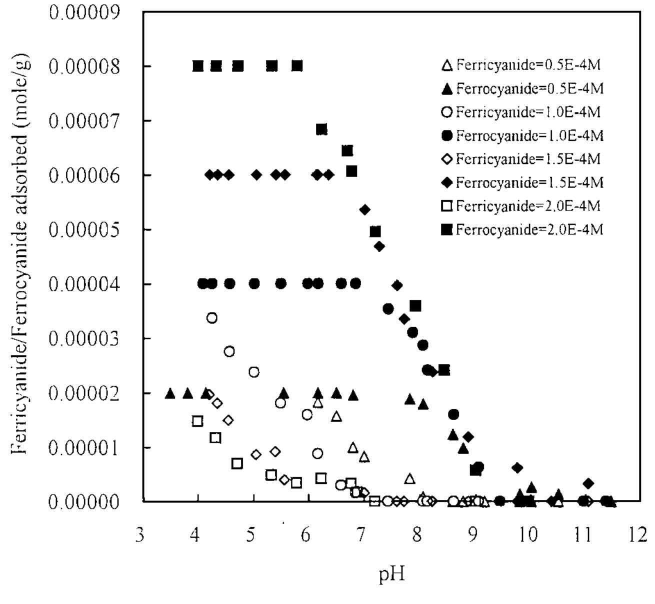

FIG. 2. Sorption capacity of ferricyanide and ferrocyanide onto γ-Al_2O_3 as a function of pH and initial concentration.

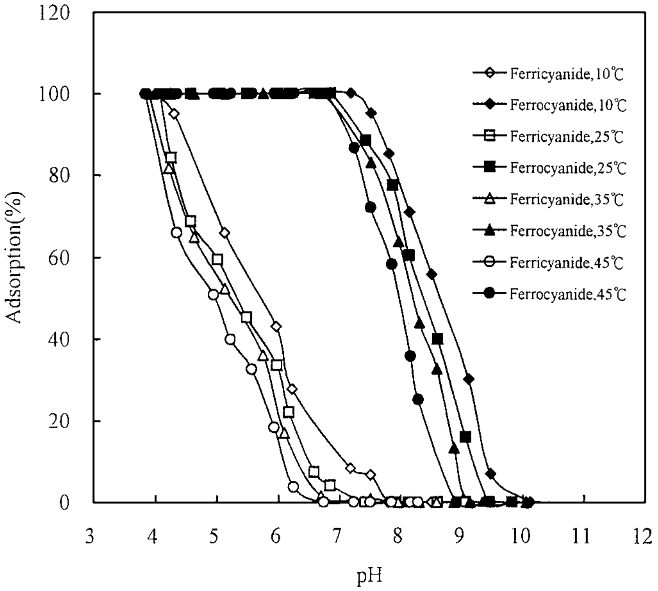

FIG. 3. Sorption percentage of ferricyanide and ferrocyanide onto γ-Al_2O_3 as a function of pH and temperature.

on γ-Al_2O_3 and developed the modified Langmuir isotherm to accurately predict the equilibrium partition between the metal oxide and liquid phases. The adsorption of ferricyanide and ferrocyanide on γ-Al_2O_3 can be described as

$$\begin{aligned}&\mathrm{AlOH} + \mathrm{Fe(CN)}_6^{n-} + m\mathrm{H}^+\\ &\quad\leftrightarrow \mathrm{AlOH}_2^+\text{---}\mathrm{H}_{m-1}\mathrm{Fe(CN)}_6^{3(n-m+1)-}, \qquad [1]\end{aligned}$$

$$K^{\mathrm{app}} = \frac{\left[\mathrm{AlOH}_2^+\text{---}\mathrm{H}_{m-1}\mathrm{Fe(CN)}_6^{3(n-m+1)-}\right]}{[\mathrm{AlOH}]\left[\mathrm{Fe(CN)}_6^{n-}\right][\mathrm{H}^+]^m}. \qquad [2]$$

where n is 3 and 4 for ferricyanide and ferrocyanide, respectively, and K^{app} is the apparent adsorption constant. Since the ferrocyanide ($\mathrm{Fe(CN)}_6^{4-}$) ion can form conjugate acids, i.e., H $\mathrm{Fe(CN)}_6^{3-}$, while no conjugate acid of ferricyanide ($\mathrm{Fe(CN)}_6^{3-}$) was found above pH 1 (16), the m values in Eq. [1] for ferrocyanide and ferricyanide are defined as 2 and 1, respectively.

With C_{SF}, C_{S}, C_{F}, and C_{T} representing $[\mathrm{AlOH}_2^+\text{---}\mathrm{H}_{m-1}\mathrm{Fe(CN)}_6^{3(n-m+1)-}]$, $[\mathrm{AlOH}]$, $[\mathrm{Fe(CN)}_6^{n-}]$, and the sum of C_{SF} and C_{F}, Eq. [2] can be rewritten as

$$C_{\mathrm{SF}} = \frac{K^{\mathrm{app}} C_{\mathrm{S}} C_{\mathrm{T}} [\mathrm{H}^+]^m}{1 + K^{\mathrm{app}} C_{\mathrm{S}} [\mathrm{H}^+]^m}. \qquad [3]$$

Let $C_{\max}$ be the maximum adsorption capacity of C_{SF};

$$\text{therefore,} \quad C_{\mathrm{S}} = C_{\max} - C_{\mathrm{SF}}. \qquad [4]$$

Combining Eqs. [3] and [4] yields

$$C_{\mathrm{SF}} = \frac{K^{\mathrm{app}} C_{\mathrm{F}} C_{\max} [\mathrm{H}^+]^m}{1 + K^{\mathrm{app}} C_{\mathrm{F}} [\mathrm{H}^+]^m}. \qquad [5]$$

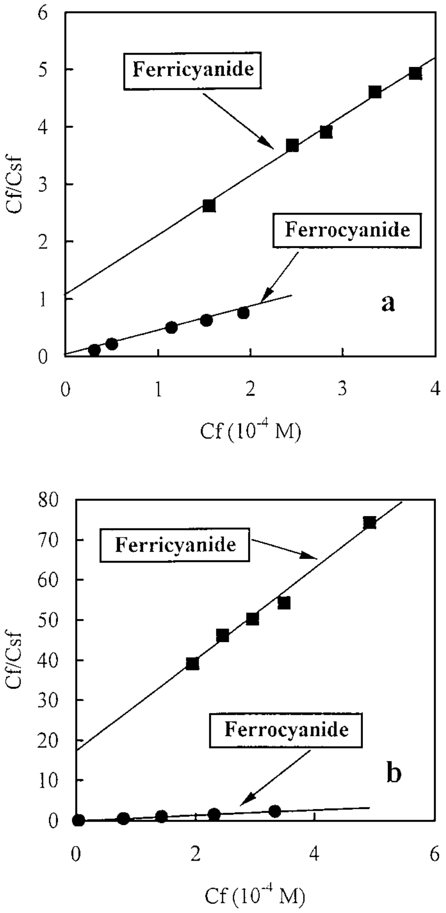

FIG. 4. Langmuir plots for ferrocyanide and ferricyanide adsorption isotherms on the γ-Al_2O_3 surface at two difference temperatures: (a) 283 K and (b) 298 K.

Equation [5] can be rearranged to

$$\frac{C_{\mathrm{F}}}{C_{\mathrm{SF}}} = \frac{1}{K^{\mathrm{app}} C_{\max} [\mathrm{H}^+]^m} + \frac{1}{C_{\max}} C_{\mathrm{F}}. \qquad [6]$$

By use of a double-reciprocal plot, i.e., $C_{\mathrm{F}}/C_{\mathrm{SF}}$ vs C_{F}, $C_{\max}$, and K^{app} can be obtained from the intercept and the slope for each pH. Figure 4 is the Langmuir plot for the competitive adsorption of ferricyanide and ferrocyanide on the γ-Al_2O_3 surface at the difference solution temperature. The $C_{\max}$ and K^{app} values obtained from the linear regression for this competitive adsorption system are presented in Table 1. Obviously, $C_{\max}$ values of

TABLE 1

$C_{\max}$ and $\log K^{\mathrm{app}}$ of the Langmuir Model for Competitive Adsorption of Ferricyanide and Ferrocyanide at pH 6.5, 283 K, and 298 K

		Ferricyanide		Ferrocyanide	
T (K)	pH	$C_{\max}$ (10^{-4} M)	$\log K^{\mathrm{app}}$	$C_{\max}$ (10^{-4} M)	$\log K^{\mathrm{app}}$
283	6.5	1.08	10.40	2.88	17.71
298	6.5	0.091	10.27	1.92	17.50

TABLE 2
Parameters Used in the TLM for γ-Al_2O_3[a]

Specific surface areas (m^2/g)	118
Site density (sites/nm^2)	1.3
Capacitance C_1, C_2 (F/m^2)	1.4, 0.2
pK_{a1}^{int}, pK_{a2}^{int}	7.2, 9.5
$pK_{Na^+}^{int}$, $pK_{ClO_4^-}^{int}$	9.1, 8.2

[a] Source. Hohl and Stumm (12), C_1 and C_2 were from Zhang *et al.* (17).

ferrocyanide and ferricyanide decrease with increasing temperature. Previous studies suggested that the dehydrogenation on the oxide surface was an endothermic reaction (14, 17). Thus, increasing the temperature will reduce the amount of the surface $AlOH_2^+$ sites at the same pH. If the adsorption of ferrocyanite and fericyanide onto hydrous γ-Al_2O_3 favors the $AlOH_2^+$ sites, a decrease in temperature will enhance the adsorption capacity and K^{app}. The much greater C_{max} and K^{app} of ferrocyanide, as shown in Table 1, also indicate competitiveness in adsorption than the ferricyanide.

TLM Modeling

The HYDRAQL program was applied to simulate the TLM for the competitive adsorption. The parameters used in the simulation are listed in Table 2. By the assumption of TLM, cations or anions if present in the solution are allowed to form surface complexes at either the o-plane (inner-sphere complexation) or β-plane (outer-sphere complexation). The surface reaction of ferrocyanide and ferricyanide ions at the β-plane were written as follows:

$$AlOH + H^+ + Fe(CN)_6^{3-} \leftrightarrow AlOH_2^+\text{---}Fe(CN)_6^{3-}, \quad [7]$$

$$AlOH + 2H^+ + Fe(CN)_6^{4-} \leftrightarrow AlOH_2^+\text{---}HFe(CN)_6^{3-}. \quad [8]$$

Figure 5 indicates that the experimental data fit the model of outer-sphere complexation, as suggested by Eqs. [7] and [8], very well. The K^{int} values in the simulation using the HYDRAQL program were set as $10^{12.5}$ and $10^{23.0}$ for ferricyanide and ferrocyanide, respectively. These K^{int} values from the competitive adsorption agree well with those from the individual adsorption previously obtained ($K^{int} = 10^{11.0}$ for ferricyanide and $K^{int} = 10^{21.1}$ for ferrocyanide) (13). The simulation results suggested that the individual adsorption of ferricyanide and ferrocyanide on the γ-Al_2O_3 occur in outer-sphere complexation, which also implied that the competitive adsorption of ferrocyanide and ferricyanide on the γ-Al_2O_3 surface used the outer-sphere complexation. Figure 5d shows that, at the initial concentration of 2×10^{-4} M, the experimental data are slightly less than the simulated values. The discrepancy may result from the coagulation by a high concentration of ions during shaking.

The K^{app} values derived from Table 1 are $10^{10.27}$ for ferricyanide and $10^{17.50}$ for ferrocyanide at 298 K, consistent with

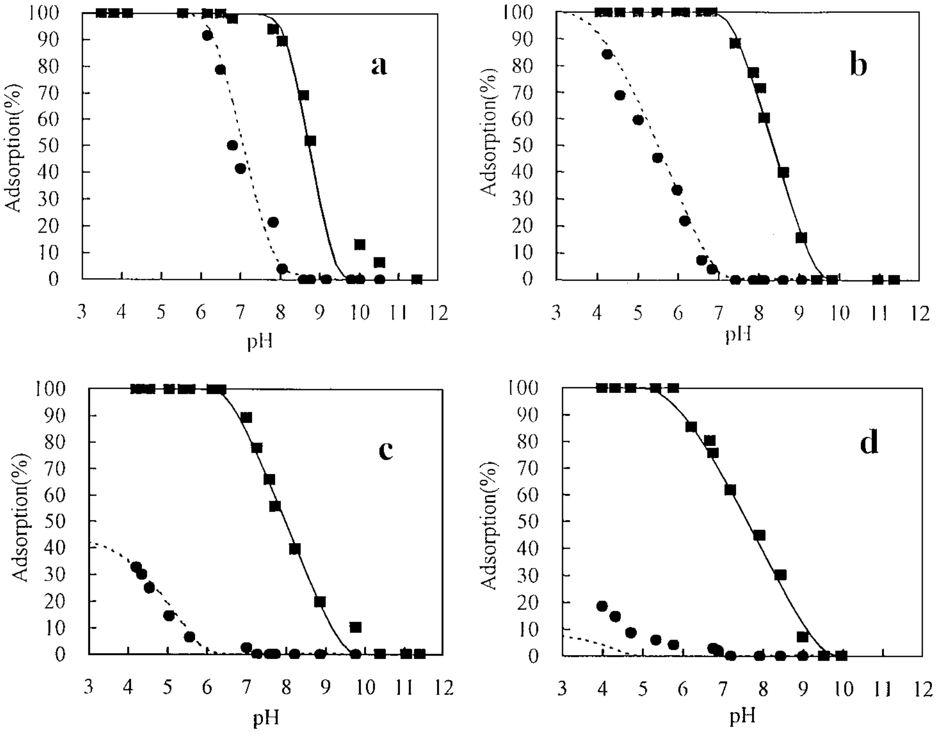

FIG. 5. HYDRAQL simulation of competitive adsorption edges of ferrocyanide (solid lines) and ferricyanide (dotted lines) as a function of pH and four different initial concentrations: (a) 0.5×10^{-4} M, (b) 1×10^{-4} M, (c) 1.5×10^{-4} M, and (d) 2×10^{-4} M (using the outer-sphere complexation model with $K_{Ferrocyanide}^{int} = 10^{23}$ and $K_{Ferricyanide}^{int} = 10^{12.5}$).

the K^{int} values derived from HYDRAQL ($10^{12.5}$ and $10^{23.0}$ for ferricyanide and ferrocyanide, respectively). In solution, the charges of ferricyanide and ferrocyanide ions would not change within the experimental pH range. Therefore, the m values in Eq. [1] remain constant. The K^{int} and K^{app} can be written as follows:

$$\begin{aligned} K^{\text{int}}_{\text{ferri}} &= \frac{\left[\text{AlOH}_2^+\text{–Fe(CN)}_6^{3-}\right]}{[\text{AlOH}]\left[\text{Fe(CN)}_6^{3-}\right][\text{H}^+]}\exp\left\{\frac{[\Psi_o - 3\Psi_\beta]F}{RT}\right\} \\ &= K^{\text{app}}_{\text{ferri}}\exp\left\{\frac{[\Psi_o - 3\Psi_\beta]F}{RT}\right\}, \end{aligned} \qquad [9]$$

$$\begin{aligned} K^{\text{int}}_{\text{ferro}} &= \frac{\left[\text{AlOH}_2^+\text{–HFe(CN)}_6^{3-}\right]}{[\text{AlOH}]\left[\text{Fe(CN)}_6^{4-}\right][\text{H}^+]^2}\exp\left\{\frac{[\Psi_o - 3\Psi_\beta]F}{RT}\right\} \\ &= K^{\text{app}}_{\text{ferro}}\exp\left\{\frac{[\Psi_o - 3\Psi_\beta]F}{RT}\right\}. \end{aligned} \qquad [10]$$

The difference between the K^{int} and K^{app} is by a charge factor of $\exp([\Psi_o - 3\Psi_\beta]F/RT)$. This result demonstrates that the $\Psi_o - 3\Psi_\beta$ values can be determined by $\ln K^{\text{int}} - \ln K^{\text{app}}$. The calculated values of $\Psi_o - 3\Psi_\beta$ are 0.132 V for ferricyanide and 0.325 V for ferrocyanide (by ferricyanide, $K^{\text{app}} = 10^{10.27}$ and $K^{\text{int}} = 10^{12.50}$; ferrocyanide, $K^{\text{app}} = 10^{17.50}$ and $K^{\text{int}} = 10^{23.0}$). For comparison, the oxide surface potential were simulated by applying the HYDRAQL program under the assumption of the competitive outer-sphere complexation. The simulated result is shown in Table 3. The $\Psi_o - 3\Psi_\beta$ values determined by $\ln K^{\text{int}} - \ln K^{\text{app}}$ are in the range of results listed in Table 3.

Thermodynamic Parameters

The relationship between the reaction constant (K^{app}) and temperature (T) can be expressed with the Gibbs–Helmholtz equation,

$$\frac{\partial \ln K^{\text{app}}}{\partial(1/T)} = \frac{-\Delta H^\circ}{R}, \qquad [11]$$

where R and T are the gas constant and absolute temperature.

TABLE 3

Surface Potential of Aluminum Oxide in the Presence of Ferricyanide and Ferrocyanide Adsorption (Outer-Sphere Reaction Model, Data Simulated by HYDRAQL Program)

Initial concentration (ferricyanide and ferrocyanide)	pH	Ψ_o	Ψ_β	$\Psi_o - 3\Psi_\beta$
0.5×10^{-4} M	5	0.143	0.0599	−0.0367
	6	0.0843	0.00235	0.07725
	7	0.0355	−0.0282	0.1201
1.0×10^{-4} M	5	0.108	−0.03	0.198
	6	0.0687	−0.0404	0.1899
	7	0.0238	−0.0607	0.2059
1.5×10^{-4} M	5	0.103	−0.0405	0.2245
	6	0.0619	−0.0582	0.2365
	7	0.020	−0.0722	0.2366
2.0×10^{-4} M	5	0.0726	−0.0922	0.3492
	6	0.0406	−0.106	0.3582
	7	0.0111	−0.0969	0.3018

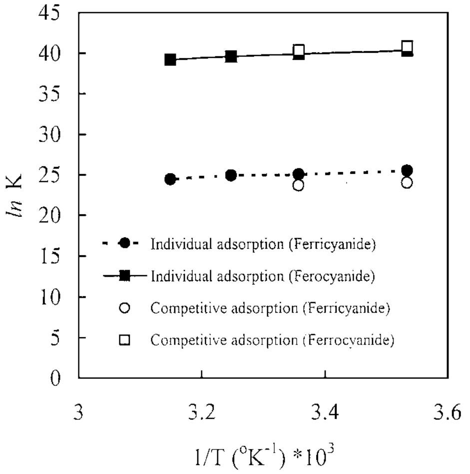

FIG. 6. Plots of $\ln K^{\text{app}}$ vs $1/T$ for ferrocyanide and ferricyanide adsorption on γ-Al_2O_3.

Thus, from the $\ln K^{\text{app}}$ versus $1/T$ plots, the values of enthalpy (ΔH°) can be determined from the slope. The $\Delta H^\circ$of the individual adsorption of ferricyanide and ferrocyanide on γ-Al_2O_3 calculated in our previous work are −4.88 and −5.96 kcal/mol, respectively (14). We plotted the data of the competitive adsorption on the regression line of individual adsorption, as shown in Fig. 6. The agreement between the two sets of data suggests that the calculated ΔH° of individual and competitive adsorption are the same. The negative ΔH° indicates the exothermic nature of the competitive adsorption process. Other thermodynamic parameters, including free energy (ΔG°) and entropy (ΔS°), can be calculated by using Eqs. [12] and [13]. Table 4 summarizes the results.

$$\Delta G^\circ = -RT \ln K^{\text{app}}, \qquad [12]$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ. \qquad [13]$$

The positive standard entropy (ΔS°), as shown in Table 4, indicates the increase in disturbance during the adsorption

TABLE 4

Thermodynamic Parameters of Competitive Adsorption on γ-Al_2O_3

	pH	T (K)	ΔH° (kcal/mol)	ΔS° (cal/mol)	ΔG° (kcal/mol)
Ferricyanide	6.5	283	−3.34	35.79	−13.47
		298	−3.34	35.84	−14.02
Ferrocyanide	6.5	283	−5.16	62.79	−22.93
		298	−5.16	62.75	−23.86

process. When the adsorbate was adsorbed onto the oxide surface, the counterions or water molecules on the surface were replaced and released. Because of the larger size and higher charge of both ions, adsorption of each complex ion will release a greater number of counterions or water molecules, resulting in a positive value of ΔS°.

CONCLUSION

The results in this study demonstrated that the adsorption of ferrocyanide on γ-Al_2O_3 is more competitive than that of ferricyanide due to its greater charge. The effects of pH and adsorbate concentration on the competitive adsorption are the same as those on the individual adsorption. Applying the modified Langmuir isotherm in competitive adsorptions, we derived the $C_{\max}$, K^{app}, and thermodynamic parameters, from which the thermodynamic characteristics was deducted. The difference between the K^{int} and K^{app} can be expressed by the electrostatic charge term, $\exp(\Psi F/RT)$. The success in substituting K^{int} with K^{app} in the TLM modeling was due to the fact that the charges of both complex ions do not change within the pH range (pH 6–10) of the experiment. The prediction from the TLM simulation with the HYDRAQL program agrees well with the experimental results, suggesting that the competitive adsorption exists in outer-sphere complexation.

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