

# Thermodynamic Parameters of Iron–Cyanide Adsorption onto $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

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In this study, we describe the adsorption of ferricyanide (Fe(CN)<sub>6</sub><sup>3-</sup>) on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> by a modified Langmuir adsorption isotherm. The modified Langmuir isotherm developed herein can accurately predict the apparent equilibrium constant ( $K^{app}$ ) at different pH values and temperatures. In the experimental pH range of 5–6.5, adsorption capacity and apparent equilibrium constants decrease as the temperature increases. Because surface protonation increases as pH decrease, a more positively charged site on the surface increases the attraction force that exists between  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and the adsorbate. According to the Gibbs–Helmholtz equation, these apparent equilibrium constants at various temperatures and pH conditions can be applied to determine enthalpy changes ( $\Delta H^0$ ) for the adsorption at different pH conditions. The result indicates that enthalpy change at different pH values is near –5 kcal/mol which indicates that the enthalpy change is in the order of hydrogen bonding and confirms the exothermic nature of the adsorption process. The results also indicate that other thermodynamic parameters change of ferricyanide adsorption. The positive entropy change ( $\Delta S^0$ ) has been explained from the viewpoint of exchange reaction in this study. The negative free energy change ( $\Delta G_{ads}^0$ ) for ferricyanide adsorption shows the spontaneous nature of the adsorption process. © 1997 Academic Press

**Key Words:** adsorption; iron–cyanide; ferricyanide; aluminum oxide; free energy; entropy; enthalpy.

## INTRODUCTION

Soil and aquatic systems containing free and complexed metal cyanide at industrial sites are a major environmental concern as long as spent cyanide process solutions are generated. Distributing iron–cyanide complexes between the soil solution and the soil solid phase determines the concentration of iron–cyanide in the soil solution and its transport rate through the soil. Meeussen (1) indicated that a large fraction of the cyanide in the soil solid phase was leached from soils at a nearly constant iron–cyanide concentration in the leaching process. This finding would suggest that the dissolved iron–cyanide was in a mineral phase. In the environment, iron–cyanide exists in the form of ferricyanide and ferrocyanide.

The surface chemistry of aluminum oxide, Al<sub>2</sub>O<sub>3</sub>, is interesting not only because it is one of the most abundant oxide minerals in the natural systems, but also because it constitutes the surface layer in a wide variety of industrial material. The homogeneity and stability of the aluminum oxide surface layer are important factors to be improved to allow adsorbates to bind to the oxide surface. Consequently, numerous studies have been devoted to this field of surface science. In particular, the coordination chemistry approach has been successfully applied to account for the interactions between cations and anions under monolayer coverage at the aqueous/oxide interface (2). For more complex heterogeneous systems, the adsorption behaviors can be exactly described by the proton-competitive Langmuir isotherm with two-site affinity or site affinity distribution function (3, 4). In an aqueous solution, some factors, such as the adsorbent size, pH values, surface potential, temperature, and ionic strength, influence the adsorption or complex formation. Among these factors, temperature and pH are two major environmental factors that affect adsorption. The objectives of this study were to investigate the effects of temperature and pH on the adsorption of ferricyanide onto  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface using the modified Langmuir isotherm, and to derive the thermodynamic parameters, including free energy ( $\Delta G^0$ ), enthalpy ( $\Delta H^0$ ), and entropy ( $\Delta S^0$ ) changes during adsorption.

## EXPERIMENTAL

### Materials

$\gamma$ -Aluminum oxide, supplied by Japan Aerosol Co., was produced by the hydrolysis of AlCl<sub>3</sub> using the flame process reference to technique. The oxide diameter was smaller than 1  $\mu$ m. The aluminum oxide was treated according to the procedure of Hohl and Stumm (5). The oxide solids were mixed with 0.1 M NaOH solution overnight and then settled. The supernatant was discarded and the settled solids were washed by Milli-Q distilled water several times to remove impurities (i.e., SiO<sub>2</sub>) from the oxide surface. The solids were finally dried in an oven at 103°C overnight. Stock solutions of 0.05 M K<sub>3</sub>Fe(CN)<sub>6</sub> were prepared using supplies from Riedel de Haen without further purification.

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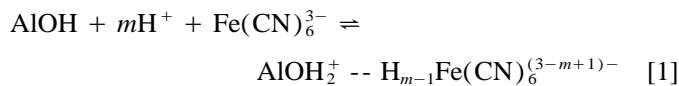
### Adsorption Isotherms

A 0.25-g sample of  $\gamma\text{-Al}_2\text{O}_3$  was immersed in 100 ml of 0.01 M NaClO<sub>4</sub>. The pH was adjusted to 5.0, 5.5, 6.0, and 6.5 by adding of HNO<sub>3</sub> or NaOH under nitrogen atmosphere for the adsorption experiments with ferricyanide. Four temperatures (10, 25, 35, and 45°C) were chosen in the study of temperature effect. Next,  $\gamma\text{-Al}_2\text{O}_3$  suspensions with initial ferricyanide concentrations ranging from  $0.5 \times 10^{-4}$  to  $4.0 \times 10^{-4}$  M were shaken on a reciprocating shaker at 150 rpm for 4 h. After 4 h the pH was readjusted to 5.0, 5.5, 6.0, and 6.5 and the shaking was repeated. At the end of 24 h of shaking, the pH values were measured and the samples were filtered through a 0.45- $\mu\text{m}$  membrane filter. Also, filtered supernatant was analyzed for residual Fe(III) by AAS on a Shimadzu 680 spectrophotometer. To investigate the possibility of releasing free cyanide during the adsorption, the concentration of free cyanide in the filtered supernatant was analyzed by polarography (Metrohm model 693) with the method of differential pulse voltammetry. The half-wave potential for cyanide was  $-0.24$  V in the 0.1 M KOH solution.

## RESULTS AND DISCUSSION

### Modified Langmuir Isotherm

The Langmuir model is expected to be approximately valid for a clean, smooth, nonporous surface, showing reversible, physical adsorption of a pure solute. The  $\gamma\text{-Al}_2\text{O}_3$  surface is an adsorbent capable of approximating to these conditions. Ferricyanide is an ion that possess high charged numbers so adsorption occurs uniformly over the  $\gamma\text{-Al}_2\text{O}_3$  surface resulting in a more negatively charged colloidal surface. Moreover, stable iron-cyanide complexes maintain their dissolved condition regardless of an increase in concentration. Therefore, the adsorption of iron-cyanide complex on the surface can form only the monolayer coverage as the hypotheses of Langmuir isotherm. As a result of our previous work (6), the ferricyanide adsorption on  $\gamma\text{-Al}_2\text{O}_3$  surface may be described by an individual step as expressed in Eq. [1].



$$K^{\text{app}} = \frac{[\text{AlOH}_2^+ \text{--} \text{H}_{m-1}\text{Fe}(\text{CN})_6^{(3-m+1)-}]}{[\text{AlOH}][\text{H}^+]^m[\text{Fe}(\text{CN})_6^{3-}]}, \quad [2]$$

where  $K^{\text{app}}$  is the apparent adsorption constant. Eaton (7) contended that there is no evidence for the conjugation of ferricyanide with proton above pH 1. Therefore, the  $m$  values in Eq. [1] are given as 1. For an exact analysis of the proton stoichiometry, Langmuir theory allows the  $m$  value to be an integral.

$C_{\text{sf}}$ ,  $C_{\text{s}}$ , and  $C_{\text{f}}$  represent  $[\text{AlOH}_2^+ \text{--} \text{Fe}(\text{CN})_6^{3-}]$ ,

$[\text{AlOH}]$ , and  $[\text{Fe}(\text{CN})_6^{3-}]$ , respectively. Also,  $C_{\text{T}}$  is equivalent to the combination of  $C_{\text{sf}}$  and  $C_{\text{f}}$  with a given molar concentration of  $\text{Fe}(\text{CN})_6^{3-}$  solution. Eq. [2] can then be rewritten as

$$C_{\text{sf}} = \frac{K^{\text{app}}C_{\text{s}}C_{\text{T}}[\text{H}^+]}{1 + K^{\text{app}}C_{\text{s}}[\text{H}^+]} \quad [3]$$

and

$$C_{\text{s}} = C_{\text{max}} - C_{\text{sf}}, \quad [4]$$

in which  $C_{\text{max}}$  represents the maximum value of  $C_{\text{sf}}$ . Combining Eqs. [3] and [4] yields Eq. [5]

$$C_{\text{sf}} = \frac{K^{\text{app}}C_{\text{f}}C_{\text{max}}[\text{H}^+]}{1 + K^{\text{app}}C_{\text{f}}[\text{H}^+]}. \quad [5]$$

By using a double reciprocal plot (Langmuir plot), i.e.,  $C_{\text{f}}/C_{\text{sf}}$  vs  $C_{\text{f}}$ , Eq. [5] can be rearranged as Eq. [6]

$$\frac{C_{\text{f}}}{C_{\text{sf}}} = \frac{1}{K^{\text{app}}C_{\text{max}}[\text{H}^+]} + \frac{1}{C_{\text{max}}} C_{\text{f}}. \quad [6]$$

In this plot,  $C_{\text{max}}$  and  $K^{\text{app}}$  can be obtained from the intercept and slope of the plot at constant pH. Figure 1 presents the Langmuir plots for ferricyanide adsorption isotherms on  $\gamma\text{-Al}_2\text{O}_3$  surface at four different pH and temperature values. Table 1 lists the subsequent values of  $C_{\text{max}}$  and  $K^{\text{app}}$ . According to these results,  $C_{\text{max}}$  ranges from the lowest value of  $7.63 \times 10^{-5}$  M at pH 6.5 and 318°K to the highest value of  $2.08 \times 10^{-4}$  M at pH 5 and 283°K. Obviously,  $C_{\text{max}}$  decreased with an increase in pH at constant temperature. This was because surface protonation increases with a decrease in pH; more positively charged sites on the surface increase the attraction force existing between  $\gamma\text{-Al}_2\text{O}_3$  and the adsorbate.

### Temperature Effect

Temperature is an important factor in controlling ferricyanide adsorption on  $\gamma\text{-Al}_2\text{O}_3$ . The adsorption isotherm for ferricyanide onto  $\gamma\text{-Al}_2\text{O}_3$  was measured as a function of temperature (283, 298, 308, and 318°K). Table 1 also reveals that the  $C_{\text{max}}$  values decrease as temperature increases. This decrease in maximum adsorption capacity contradicts the Langmuir model assumption. The model assumes that adsorption is limited to a monolayer and, therefore,  $C_{\text{max}}$  is a constant and is independent of temperature.

Related studies have addressed the temperature dependence of cation or anion adsorption onto metal oxide surface—cation adsorption increasing with increasing temperature (8–12) and anion adsorption decreasing with increasing temperature (13–14). The cause of these temperature effects remains unclear. At least two theories can explain why the

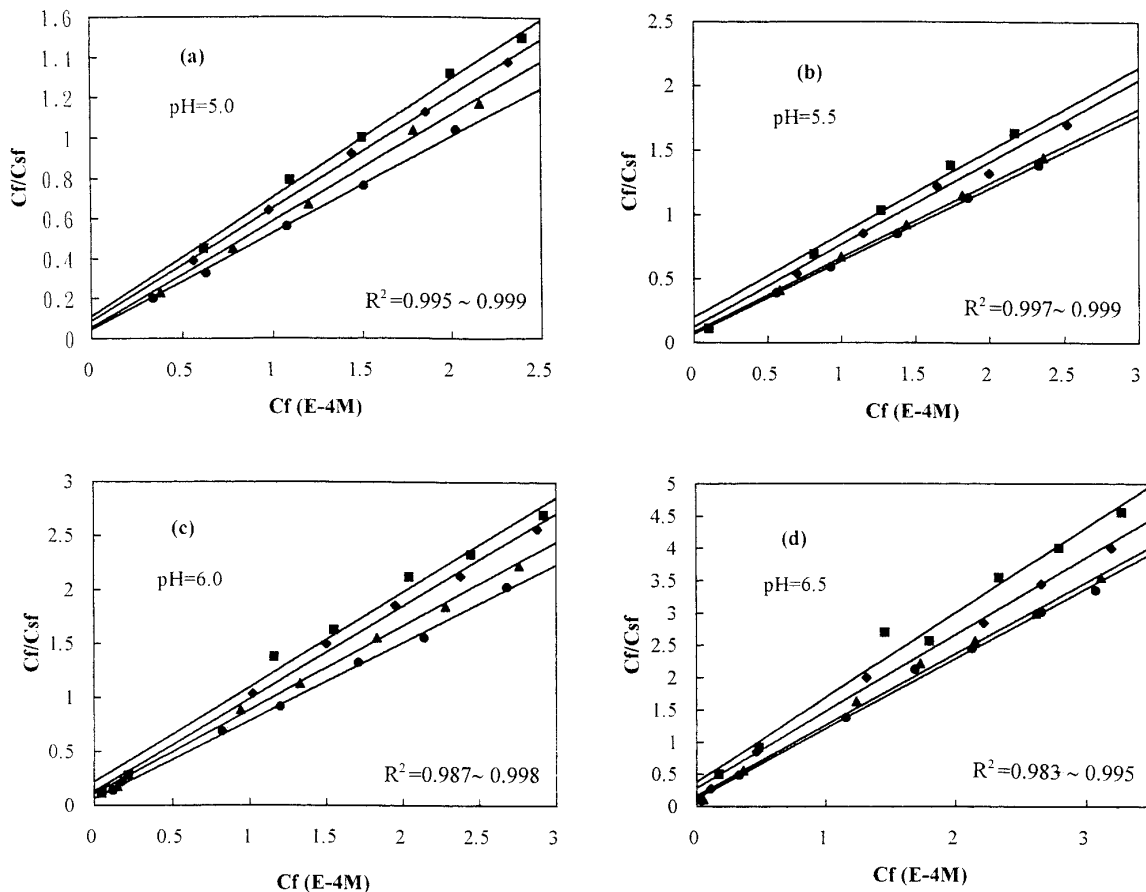


FIG. 1. Langmuir plots for ferricyanide adsorption in the expression of ferricyanide concentration in the solution ( $C_f$ )/ferricyanide concentration adsorbed ( $C_{sf}$ ) vs ferricyanide concentration in the solution ( $C_f$ ) under various pH and temperature conditions. (■) 318, (◆) 308, (▲) 298, and (●) 283°K.

adsorption decreases (or increases) as the temperature increases. The first theory is that of the point of zero charge ( $\text{pH}_{\text{pzc}}$ ). Zeltner *et al.* (13) have demonstrated that the proton dissociation on an oxide surface is an endothermic reaction. Thus, increasing the temperature will reduce  $\text{pH}_{\text{pzc}}$  (15). It was evident that the amount of  $\text{AlOH}_2^+$  decreases with increasing solution temperature at the same pH. If adsorption of ferricyanide onto hydrous  $\gamma\text{-Al}_2\text{O}_3$  is favorable at the  $\text{AlOH}_2^+$  sites, a decrease in temperature will enhance ferricyanide adsorption reaction. The second theory is thermodynamics—some studies have suggested that adsorption reactions for many cations are endothermic (16–17). The equilibrium constants for such reactions increase with temperature. By contrast, Zeltner *et al.* (13) observed that the exothermic reaction exists on the surface complex formation of some anions on the oxide.

#### Description of Thermodynamic Parameters

As indicated in Table 1,  $K^{\text{app}}$  is related to the standard enthalpy of adsorption  $\Delta H^0$  and the relationship can be described by the Gibbs–Helmholtz equation as

$$\frac{\partial \ln K^{\text{app}}}{\partial (1/T)} = \frac{-\Delta H^0}{R}, \quad [7]$$

where  $R$  and  $T$  are gas constant and absolute temperature, respectively. Thus, from  $\ln K^{\text{app}}$  versus  $1/T$  plots, the values of enthalpy ( $\Delta H^0$ ) were calculated from the slope of the plot at different pH. Figure 2 presents such a plot. The relative values of thermodynamic parameters, including free energy ( $\Delta G^0$ ) and entropy ( $\Delta S^0$ ), were calculated at different pH values or temperatures using Eqs. [8] and [9], Table 2 summarizes these results.

$$\Delta G^0 = -RT \ln K^{\text{app}} \quad [8]$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0. \quad [9]$$

The values of enthalpy change ( $\Delta H^0$ ) at different pH values were found to be negative, thereby confirming the exothermic nature of the adsorption process. As indicated in Table 2, the enthalpy change of adsorption is close to  $-5$  kcal/mol. If the major contribution to adsorption originated from a change in the hydrogen bonding energy, enthalpy

TABLE 1

$C_{\max}$  and  $\ln K^{\text{app}}$  Values in the Langmuir Isotherm of Ferricyanide Adsorption on  $\gamma\text{-Al}_2\text{O}_3$  Surface at Four Different pH Values and Temperatures

Temperature (°K)	pH	$C_{\max}$ ( $10^{-4} M$ )	$\ln K^{\text{app}}$
283	5.0	2.08	23.25
298	5.0	1.89	22.97
308	5.0	1.78	22.56
318	5.0	1.69	22.39
283	5.5	1.89	24.12
298	5.5	1.73	23.80
308	5.5	1.60	23.48
318	5.5	1.51	23.16
283	6.0	1.38	25.42
298	6.0	1.28	24.99
308	6.0	1.16	24.89
318	6.0	1.14	24.41
283	6.5	0.93	26.30
298	6.5	0.91	26.06
308	6.5	0.84	25.58
318	6.5	0.76	25.41

change in the range of  $-5$  to  $-10$  kcal/mol would be expected to be the same as those having been observed in other studies (18–19). While considering the acidic conjugation constant, ferricyanide is still stable with protons even at solution pH lower than 1 (7). Therefore, ferricyanide may not conjugate with proton ions on  $\gamma\text{-Al}_2\text{O}_3$  surface by forming hydrogen bonding. However, a highly charged ion such as ferricyanide raises a significant electrostatic attractive

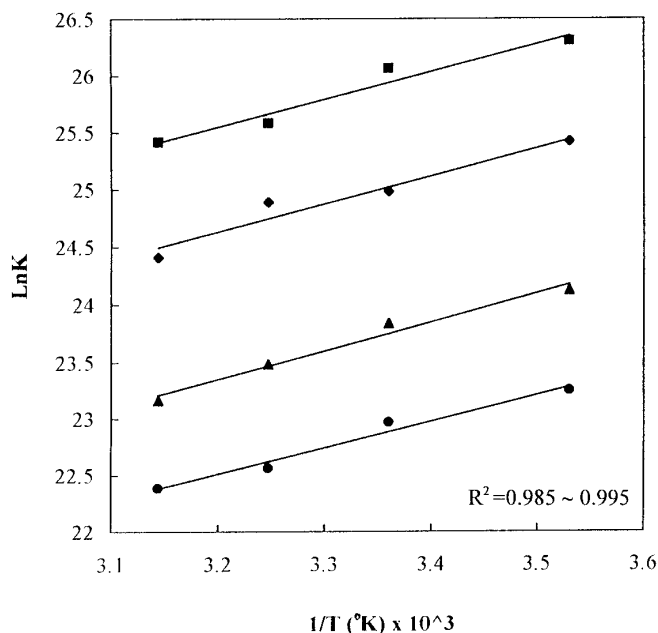


FIG. 2. Plots of  $\ln K^{\text{app}}$  vs  $1/T$  for ferricyanide adsorption on  $\gamma\text{-Al}_2\text{O}_3$  at various pH values. (■) pH 6.5, (◆) pH 6.0, (▲) pH 5.5, and (●) pH 5.0.

TABLE 2  
Thermodynamic Parameters of Ferricyanide Adsorption on  $\gamma\text{-Al}_2\text{O}_3$

$T$ (°K)	pH	$\Delta H^\circ$ (kcal/mol)	$\Delta S^\circ$ (cal/mol)	$\Delta G_{\text{ads}}^\circ$ (kcal/mol)
283	5.0	-4.64	29.6	-13.03
298			29.9	-13.55
308			29.6	-13.76
318			29.7	-14.10
283	5.5	-4.92	30.4	-13.52
298			30.6	-14.04
308			30.5	-14.32
318			30.4	-14.58
283	6.0	-4.83	33.3	-14.24
298			33.3	-14.75
308			33.6	-15.18
318			33.1	-15.37
283	6.5	-4.88	34.8	-14.74
298			35.2	-15.38
308			34.8	-15.60
318			35.0	-16.00

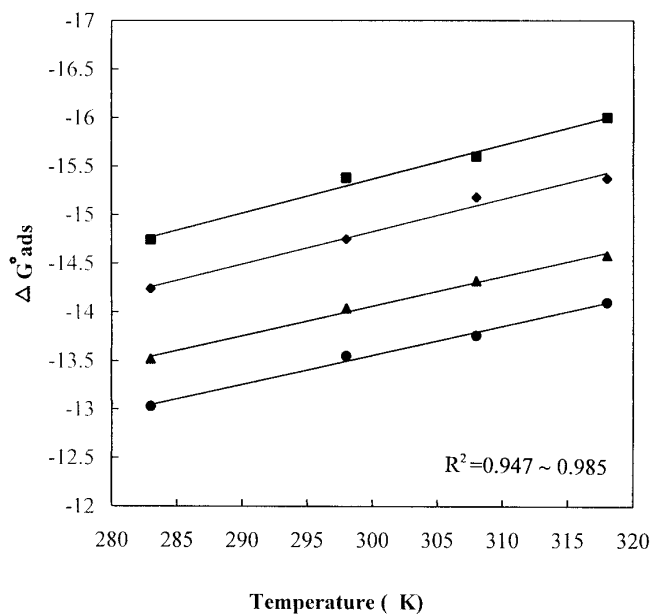
force between ferricyanide and hydroxyl groups under acidic condition, thereby resulting in a high enthalpy change near the range of hydrogen bonding in this result.

Table 2 also displays positive values of standard entropy change ( $\Delta S^\circ$ ), which may be explained by exchange reactions. During exchange reactions, the bound counter ions or water molecules on the adsorbent's surface is replaced by the adsorbate (20). Because of its large size and high charge, ferricyanide ions attach to the surface by removing more counterions or water molecules, so the entropy change ( $\Delta S^\circ$ ) of reaction becomes positive. Table 2 also reveals that  $\Delta S^\circ$  increases with pH. At lower pH values, the  $\gamma\text{-Al}_2\text{O}_3$  surface brings highly protonated sites and the affinity between the adsorbent and counter ions or water molecules increases. This increase of affinity causes a decrease in the number of counter ions or water molecules desorbed during ferricyanide adsorption.

From Table 2, it can be seen that adsorption free energy increases with pH at the same temperature. Assuming that the various adsorption mechanisms act independently, the free energy of adsorption ( $\Delta G_{\text{ads}}^0$ ) can be expressed as the sum of the individual contributions as (21)

$$\Delta G_{\text{ads}}^0 = \Delta G_{\text{coul}}^0 + \Delta G_{\text{solv}}^0 + \Delta G_{\text{chem}}^0 \quad [10]$$

The subscripts coul, solv, and chem represent the contribution of coulombic energy change, solvation energy, and a specific chemical adsorption energy. A detailed quantitative model for the adsorption of ions at the oxide-water interface is presented in accordance with the competition between the free energy changes (i.e.,  $\Delta G_{\text{coul}}^0$  and  $\Delta G_{\text{chem}}^0$ ) favorable to adsorp-



**FIG. 3.** Plots of free energy change ( $\Delta G_{ads}^{\circ}$ ) vs temperature for ferricyanide adsorption on  $\gamma$ - $\text{Al}_2\text{O}_3$  at various pH values. (■) pH 6.5, (◆) 6.0, (▲) 5.5, and (●) 5.0.

tion and the unfavorable change in solvation energy ( $\Delta G_{solv}^{\circ}$ ).

Figure 3 illustrates the similar slopes between free energy and temperature at different pH values. This relationship suggests that the reaction mechanism does not change between pH 5 and 6.5 and over temperatures from 283 to 318°K. Therefore, we infer that the  $\Delta G_{chem}^{\circ}$  values are a constant independent of the experimental conditions.

Because the  $\Delta G_{coul}^{\circ}$  is equivalent to  $ze\psi_0$ , in which  $\psi_0$  depends on the difference between the  $\text{pH}_{iep}$  of the oxide and the pH of the solution, the value of  $\Delta G_{coul}^{\circ}$  becomes more negative as pH decreases. Similarly for the solvation energy term, it increases with decreasing pH with anion adsorption on the oxide surface. The solvation energy term depends on the difference between the inverse of dielectric constant in the bulk solution ( $\epsilon_b$ ) and the inverse of that on the interface ( $\epsilon_{int}$ ) (21). If the electric field at the interface is small, i.e., at the pH values near the  $\text{pH}_{zpc}$ , there is only a slight dielectric saturation of the adsorbed water molecules ( $\epsilon_{int}$  values near  $\epsilon_b$ ), and hence, the change in solvation energy is minimal. When pH increases from 5.0 to 6.5 which is still below the  $\text{pH}_{zpc}$  of  $\gamma$ - $\text{Al}_2\text{O}_3$  (5), the solvation energy decreases. By considering the two terms of  $\Delta G_{solv}^{\circ}$  and  $\Delta G_{coul}^{\circ}$ , the values of  $\Delta G_{solv}^{\circ}$  and  $\Delta G_{coul}^{\circ}$  become less positive and less negative, respectively, as pH increases. If the solvation energy is a dominating term in the adsorption energy change of highly charged ions as suggested by James and Healy (21), the adsorption free energy will increase as pH increases as shown in Table 2.

## CONCLUSION

The effect of temperature and pH on the adsorption of ferricyanide onto  $\gamma$ - $\text{Al}_2\text{O}_3$  was investigated. Adsorption capacity ( $C_{max}$ ) obviously decreases as pH or temperature increases. The standard enthalpy change ( $\Delta H^{\circ}$ ) of adsorption is close to  $-5$  kcal/mole, indicating that the enthalpy change is equivalent to the order of hydrogen bonding. This finding also confirms the exothermic nature of the adsorption process. Due to the large size and high valence of one ferricyanide ion, it attaches to the oxide surface by removing more counterions or water molecules, thereby resulting in a positive value for the entropy change ( $\Delta S^{\circ}$ ). At the same temperature, the standard free energy change ( $\Delta G_{ads}^{\circ}$ ) for ferricyanide adsorption on  $\gamma$ - $\text{Al}_2\text{O}_3$  is dominated by solvation energy ( $\Delta G_{solv}^{\circ}$ ).

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## REFERENCES

- Meeussen, J. C. L., Keizer, M. G., and de Haan, F. A. M., *Environ. Sci. Technol.* **26**, 1832 (1992).
- Stumm, W., "Chemistry of the Solid-Water Interface." Wiley, New York, 1992.
- Kinniburgh, D. G., Barker, J. A., and Whitfield, M., *J. Colloid Interface Sci.* **95**, 370 (1983).
- Huang, C., Huang, C. P., and Morehart, A. L., *Water Res.* **25**, 1365 (1991).
- Hohl, M., and Stumm, W., *J. Colloid Interface Sci.* **55**, 281 (1976).
- Cheng, W. P., and Huang, C., *J. Colloid Interface Sci.* **181**, 627 (1996).
- Eaton, W. A., George, P., and Hanania, G. I. H., *J. Phys. Chem.* **71**, 2016 (1967).
- Tewari, P. H., and Lee, W., *J. Colloid Interface Sci.* **52**, 77 (1975).
- Srivastava, A., and Srivastava, P. C., *Environ. Pollut.* **68**, 171 (1990).
- Fokkink, L. G., De Keizer, A., and Lyklema, J., *J. Colloid Interface Sci.* **135**, 118 (1990).
- Johnson, B. B., *Environ. Sci. Technol.* **24**, 112 (1990).
- Rodda, D. P., Johnson, B. B., and Wells, J. D., *J. Colloid Interface Sci.* **161**, 57 (1993).
- Zeltner, W. A., Yost, M. L., and Machesky, M. I. T., in "Geochemical Process at Mineral Surface," p. 142. American Chemical Society, Washington, DC, 1986.
- Barrow, N. J., *J. Soil Sci.* **43**, 37 (1992).
- Lyklema, J., *Chem. Ind.* 741 (1987).
- Tewari, P. H., Campbell, A. B., and Lee, W., *Can. J. Chem.* **50**, 1642 (1972).
- Hodgson, J. F., Geering, H. R., and Fellow, M., *Soil Sci. Soc. Am. Proc.* **28**, 39 (1964).
- Maiety, N., Payne, G. F., and Chipchosky, J. L., *Ind. Eng. Chem. Res.* **30**, 2456 (1991).
- Sanders, N. D., and Keweshan, C. F., *J. Colloid Interface Sci.* **124**, 606 (1990).
- Davinder, S. G., David, J. R., and Richard, C. W., *J. Colloid Interface Sci.* **167**, 1 (1994).
- James, R. O., and Healy, T. W., *J. Colloid Interface Sci.* **40**, 42 (1972).