

The effect of temperature on the surface properties of α -Al₂O₃ and As(V) adsorption

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Despite a growing number of studies on surface complexation, very little is known about the effect of temperature on adsorption. It appears from theoretical and experimental data that the pH_{zpc} is mainly varying as a function of the dissociation constant of water (Schoonen, 1994; Machesky *et al.*, 1994) and that surface complexes become increasingly important at higher temperature (Renders and Seward, 1989). The purpose of this study is first to better understand the changes in the pH_{zpc} with temperature and second, to evaluate the effect of increasing temperature on adsorption. The study was conducted using α -Al₂O₃ as a substrate and As as the adsorbate. This system was selected because As forms negatively charged aqueous complexes (as opposed to the better studied heavy metals) and adsorption onto \equiv AlOH can significantly influence the behaviour of As in numerous contaminated sites.

Experiments

The aluminium oxide used was washed prior to the experiment and the dried powder had a surface of 12 m² per gram, as determined by B.E.T. Titration and adsorption experiments were conducted in closed Teflon vessels in an inert Ar-atmosphere. For titration runs, ten grams of aluminium oxide were put into 100 ml of a NaNO₃ electrolyte solution and 0.1 M NaOH or HNO₃ solutions were added with an automatic titrator. Titrations were done over several hours in 0.01, 0.1 and 1 M electrolyte solutions.

Adsorption experiments were done in a 0.1 M electrolyte solution and 1 ppm As(V). Two grams of α -Al₂O₃ were put into 200 ml of solution and subsequently split in equal aliquots into Teflon tubes. The pH was then adjusted and the system was allowed to react for 1h30 (reaction time was determined by kinetic experiments). The solid was then separated by filtration and the supernatant was analysed for its As content by atomic adsorption.

Results

Titration runs at the various ionic strengths indicate a

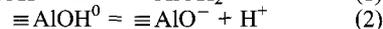
pH_{zpc} of 9.1, i.e. the value commonly accepted for α -Al₂O₃. The effect of temperature on the pH_{zpc} was determined by 'ΔT titration', i.e. by raising the temperature of the system at the pH_{zpc} and continuously recording the pH. Temperature was raised rapidly (15min) in order to avoid dissolution. The pH_{zpc} is continuously decreasing from the starting value of 9.1 at 25°C to 8.0 at 75°C. This pH decrease occurred along a perfectly straight line when plotted versus the inverse of the temperature (Fig. 1). Cooling of the system from 75 to 25°C occurred along the same path suggesting that dissolution of the aluminium oxide was negligible.

We applied the same technique to a system containing 10 g/l of aluminium oxide and 1 ppm As(V) from a starting pH of 8.19. As for the pH_{zpc} , a decrease in pH was observed with increasing temperature (Fig. 1). The rate and the magnitude of the pH change is identical to the one observed for the pH_{zpc} .

Figure 2 shows the percentage of As(V) adsorbed onto the aluminium oxide in this system at 25°C (solid line). Almost all the arsenic was adsorbed onto the aluminium powder up to a pH of 8. With further increase in pH, arsenic is progressively desorbed. Also shown (in the inset) is the effect of increasing temperature starting at a pH of 8.14. Results show an increase in the adsorption of As as pH is decreasing with increasing temperature. This does, however, not occur along the adsorption edge.

Discussion

Surface acidity is determined by the amount of H⁺ adsorbed onto the surface through reactions



Combining the two reaction yields the reaction



For this reaction, $\text{Log } K_{(3)} = -2 \text{ pH}_{zpc}$ at 25°C since the concentration at the pH_{zpc} and the activity coefficients of both surface species are equal. From

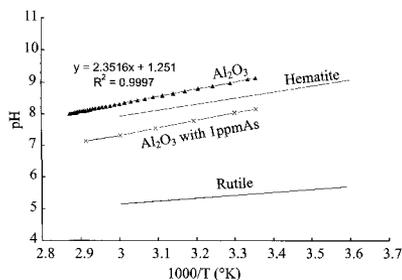


FIG. 1. Variation in the pH_{zpc} with temperature for simple oxides. Also shown is the variation in pH with increasing temperature of Al_2O_3 with 1ppm As(V).

Fig. 1 it is apparent that pH_{zpc} of reaction (3) varies linearly with $1/T$ and it is likely that $\text{Log } K_{(3)}$ follows the same trend, i.e. that the ratio of the surface activity coefficients for reaction (3) remains one at any temperature (departure from one would induce a curvature of the line). The same is presumably true for reactions (1) and (2).

This linear dependence of $\text{Log } K$ with $1/T$ is well known from isocoulombic reactions since the ΔCp of such reactions is constant and generally close to zero over a very wide temperature range. Reaction (3) is far from isocoulombic, yet the linearity of $\text{Log } K_{(3)}$ vs $1/T$ suggests that its ΔCp is constant and the line is given by the equation

$$\text{Log } K_{(3)} = \frac{-\Delta G_{\text{T}}^0(2.303RT) - [\Delta G_{298}^0 - \Delta S(T - 298) + \Delta\text{Cp}(T - 298 - T\ln(T/298))]}{(2.303RT)}$$

From this reaction, ΔS and ΔCp can be calculated and yield values of B10.95 and 0 respectively. Consequently, $\text{Cp}_{\equiv\text{AlOH}_2^+}$ and $\text{Cp}_{\equiv\text{AlO}^-}$ are equal ($\text{Cp}_{\text{H}^+} = 0$) and the pH_{zpc} of reaction (3) can be predicted for higher temperatures using the linear regression in Fig. 1. Since the change in Cp of a reaction is mainly related to the change in charge of the species, $\text{Cp}_{\equiv\text{AlOH}}$ should also be equal to the Cp of the charged surface species.

Also shown in Fig. 1 are the results of similar experiments conducted on rutile and hematite (Fokkink *et al.*, 1989). Again, the changes in pH_{zpc} with the inverse of the temperature is linear. Using the same approach as for Al_2O_3 , calculated ΔCp are also equal to zero and the same conclusion as those drawn for $\alpha\text{-Al}_2\text{O}_3$ can be applied to these two minerals and presumably to other simple oxides and hydroxides ($\Delta\text{Cp} = 0$ for hydrogen adsorption, ratio of surface activity coefficients equals 1 at any temperature). Extrapolation of pH_{zpc} for higher temperatures from the lines in Fig. 1 tend to indicate

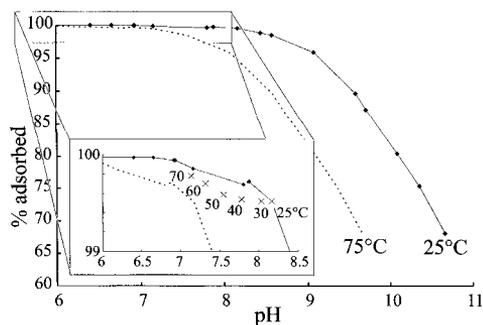


FIG. 2. Adsorption edge for As adsorption onto Al_2O_3 . Solid line is at 25°C and the dashed line is the estimated adsorption edge at 70°C . Crosses in the inset show the variation in As adsorption with increasing temperature.

that the pH_{zpc} is continuously decreasing with increasing temperature. This contrasts with extrapolation obtained with true isocoulombic reaction (Schoonen, 1994) which show an increase in the pH_{zpc} with temperature above 200°C , similar to the change in the dissociation constant of water.

In Fig. 2 the solid line is the adsorption edge of As(V) onto $\alpha\text{-Al}_2\text{O}_3$ in the system described above. Since As(V) is present as a negatively charged aqueous complex in solution, adsorption is highest at low pH and decreases with increasing pH above 8. The crosses in the inset shows the effect of the pH change on the adsorption of As(V) in the system starting from a pH of 8.14. The pH shift between 25 and 70°C is approximately 1 and if the adsorption edge is moved accordingly, this temperature increase could have a significant effect on the adsorption of As(V) at constant pH.

In this system, the decrease in pH with increasing temperature is identical to that of the pH_{zpc} (Fig. 1) suggesting that this pH change is also controlled by reaction (3). At these conditions, the As(V) adsorption reaction is likely to be



The change in the As(V) concentration of the solution is therefore only controlled by the pH, i.e. by the variation of the pH_{zpc} with increasing temperature.

Important to note is that the surface is not neutral in the presence of As at a pH of 8.14. The similar magnitude in pH change could therefore suggest that the effect of change with temperature of the electrostatic contribution to adsorption is small for these inner sphere complexes. A similar conclusion could be drawn from the temperature congruence of titration curves observed by Fokkink *et al.* (1989).