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Binding of Pb and Zn to Aluminium Oxide and Proton Stoichiometry

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ABSTRACT

The interaction of Pb and Zn with Al_2O_3 in aqueous solution was studied as a function of pH and metal ion concentration. Results indicated the complexation of metal ions by oxide surfaces is strongly pH dependent; the extent of adsorption is a function of pH with an abrupt change within approximately 2 pH units. The adsorption of Pb and Zn on aluminium oxide can be interpreted in terms of a surface complexation formed by association with one surface AlOH group, thus releasing one bound hydrogen ion. $\text{-AlOH} + M^{2+} = \text{-AlOM}^{+} + H^{+}$. It is suggested that the major surface reaction is the formation of a monodentate inner-sphere complex.

INTRODUCTION

Metallic oxides and silicas are abundant components of the earth's crust. Adsorption of metals from aqueous solution onto oxide surfaces is considered to be an important process in natural environments and in many industrial systems. Examples include the interactions between sediments and the water column, the mobility and transportation of trace metals in natural waters, leaching of metals from landfills, and the use of adsorption for removal or recovery of trace metals in wastewater and water treatment operations. It is therefore of practical and theoretical interest to obtain a detailed understanding of the sorption process at the oxide-water interface. This understanding hinges to a great extent upon elucidation of the nature of particulate surface, and the effects of pH, ionic strength, and metal concentrations. pH is probably the single most important factor influencing metal behavior in aqueous systems. Typically adsorption of metals on oxides increases from near zero to nearly 100% as pH increases through a critical range of 1-2 units wide (Lion et al., 1982; Benyahya and Garnier, 1999).

The mobility of metal ions in aquatic environment is often characterized by a distribution coefficient K_d defined as the ratio of the concentration of metal adsorbed on the solid phase (Γ) to that in solution at equilibrium (C_f). High values of K_d indicate that the metal has been retained by the solid through sorption reactions, while low values of K_d indicate that most of the metal remain in solution where it is available for transportation and geochemical reactions. Trace metal ion adsorptions at oxide/natural waters interfaces are often better described by a distribution coefficient, since their concentrations in natural aquatic systems are usually low.

Several mechanisms and models have been developed for metal ion adsorption reactions at the oxide-water interface. (1) James and Healy (1972) proposed an ion-solvent interaction model, which considers electrostatic, solvation, and specific chemical energy interactions as the ion approaches the interface and which implies that a lowering of the ionic charge of the metal species (e.g., by hydrolysis) decreases the ion-solvent interaction which presents a barrier to close approach of multiple charged ions to the surface. The pH at which adsorption of metal ions becomes significant is the pH at which the dissolved cations undergo hydrolysis to hydroxy complexes. It is because the hydrolyzed species do not have a strongly held hydration shell to prevent adsorption. (2) The ion exchange model suggested by Dugger (1964), according to which metallic cations upon adsorption on the hydrous oxide surface replace protons from hydroxyl groups -AlOH. And (3) Schindler-Stumm surface complex formation model (Stumm et al., 1970; Huang et al., 1973; Schindler et al., 1987; Hohl et al., 1976; Schindler, 1981) hypothesizes that complexes are formed at the surface of the oxide, which is composed of a hydroxyl species bound to a central cation. In this model the hydrous oxide surface groups, -AlOH, -AlO$^-$, or -Al-OH$_2$+ are treated similar to amphoteric functional groups in polyelectrolytes, as complex forming species. The fundamental concept is that adsorption takes place at defined coordination sites (the surface hydroxyl groups are present in finite number). The surface complexation model permits us to handle adsorption equilibria in the same way as equilibria in solution; adsorption is thus closely analogous to complex formation in solution, and can be described by similar equations.

Accordingly, we interpret our results of adsorption of metal ions (M^{2+}) on Al_2O_3 in terms of this latter model and characterize the amphoteric and complex forming properties by the acid-base reactions:

$$AlO^- \overset{+H^+}{<\!\!=\!\!=\!\!=\!\!>} AlOH \overset{+H^+}{<\!\!=\!\!=\!\!=\!\!>} AlOH_2+$$

and the following coordination reactions, (thus leading to the formation of either monodentate or bidentate surface complexes.)

$$Al\text{-}OH + M^{2+} = Al\text{-}OM^{+} + H^{+}$$

$$\text{or } 2Al\text{-}OH + M^{2+} = (Al\text{-}O)_2M + 2H^{+}$$

where M^{2+} is either Pb^{2+} or Zn^{2+} in this study.

Competitive complex formation equilibria (metal ion versus H^+, or anion versus OH^-) explain the strong dependence of metal ion (as well as anion) binding on pH.

Hence uptake and release of H^+ ions in solution can be described by the acidity constants. Similarly, adsorption equilibria involving metal ion are conveniently characterized by stability constants for the formation of surface complexes. According to the above equations, we assume that among other species in solution at the pH studied only free cations (Pb^{2+} or Zn^{2+}, and not another species such as $PbOH^+$ or $ZnOH^+$) form surface complexes (i.e. adsorbed) and that the pH-dependence of the association of metal ions can be explained by the pH-dependence of the surface concentration of the AlO^- group and the affinity of this group to the free metal ion.

Although experimental studies on adsorption conducted to date represents a considerable increase in knowledge, a quantitative application of this knowledge to natural aqueous environments is still inadequate. The binding stoichiometry of metal ions to the solid and suspended phase is not yet resolved satisfactorily. The focus of this study was (1) to study the effect of pH on the adsorption of metal ions (lead and zinc) on aluminium oxide, and (2) evaluate quantitatively the interaction of these cations with the surface hydroxyl group on aluminium oxide in terms of proton stoichiometry.

MATERIALS

A commercial product, Aluminium Oxide C (Fumed Alumina), supplied by Degussa Corporation (N.J.) was used without further treatment. The surface properties of this sample have been reported previously (Hachiya et al., 1979). It has a pH_{zpc} of 8.3 and a specific surface area of 100 m^2/g, with a particle size smaller than 1 μm and apparently uniform.

All chemicals used were reagent grade, and together with the reference standard solutions of Pb and Zn for atomic absorption were purchased from Fisher Scientific (N.J.). Solutions of 0.1 M NaOH and HCl were prepared and used in adjusting the pH of the experimental samples.

METHODS

Our study is aimed at: (1) The extent of cation (Pb and Zn) interactions with the Al_2O_3 surface at various pH evaluated from direct measurements of the cation uptake by the surface. And (2) the studies of proton release and stoichiometry at aluminium oxide/water interface during metal ion adsorption through a titration of suspended aluminium oxide particles with cation (lead and zinc), and the plots of K_d versus pH. Pb or Zn bound to the surface is calculated from the difference between the total Pb or Zn added to the system and that remaining in solution using AAS (Atomic Absorption Spectrophotometer, SpectrAA 20, Varian Instrument) for the measurements. The pH of the suspension is monitored as cations are titrated with the suspension of aluminium oxide using an Orion research digital ionalyzer (Model 701A) with an Orion Combination electrode.

(1) Adsorption of Lead and Zinc on Aluminium oxide - Effect of pH

(a) In the first set of adsorption runs, 0.1 g of aluminium oxide was weighed into a 250mL polycarbonate erlenmeyer flasks containing 100mL of lead of concentration 1.0 - 14 mg/L or 0.4 - 4.0 mg/L of zinc. The pH was adjusted to the required value. pH values of 5-8 were studied. Samples were sealed in nitrogen, and then shaken overnight in a shaker at 150 revolutions per minute and 25°C. After this period the pH of the samples was readjusted, equilibrated and then filtered. The filtrate was retained for metal analysis. The difference between the initial and final concentration was taken as the amount adsorbed.

(b) In the second set of adsorption runs, the adsorption edges (the pH region in which adsorption increases rapidly) of lead and zinc on aluminium oxide were determined. A suspension containing 0.5 g/L of the adsorbent (aluminium oxide) was placed in a 500mL flask and equilibrated for 1 hour under nitrogen atmosphere at pH 2 where no adsorption was anticipated. After 1 hour a 50mL aliquot was removed as a blank, and then 10 mg/L lead or 6 mg/L zinc was added. A 50mL aliquot containing the adsorbate was removed and transfered to a clean 250mL polycarbonate erlenmeyer flask. Then the pH was adjusted upward (2-11), 50mL aliquots being drawn at each pH. Samples were sealed under nitrogen, and then shaken overnight in a shaker at 150 revolutions per minute and 25°C. After this period the pH of the samples was readjusted, equilibrated and then filtered. The filtrate was retained for metal analysis.

(2) Proton Release and Stoichiometry during adsorption of metal ions:

(a) Titration - proton release during adsorption

Suspended particles were titrated with cations (lead and zinc) while pH change as a result of titration was measured. 0.1 g of aluminium oxide was weighed into a 250mL flask containing 100mL of distilled deionized water. The solution of metal ion whose pH was adjusted to the same as that of the aluminium oxide suspension was introduced through a burette while the suspension was stirred using a Teflon-coated magnetic stirrer. The pH change of the suspension was measured using a glass electrode as the cations were titrated with the suspension. A blank titration containing no metal ion was performed for comparison.

(b) Proton stoichiometry estimated from the plots of K_d versus pH.

We assume that surface complexation is the major interaction during adsorption. The association of aluminium oxide with metal ions (M^{2+}) can be represented in a general form as follows:

$$(AlOH)_\alpha + M^{2+} = (AlO)_\alpha M^{2-\alpha} + \alpha H^+$$

where M^{2+} is a divalent aqueous metal ion such as Pb^{2+} or Zn^{2+} in this study. α is the number of hydrogen ions replaced from surface hydroxyl groups. This equation implies generally that one metal ion can associate with one or more surface AlOH groups, where $(AlO)_\alpha M^{2-\alpha}$ denotes bound metal ion. The value of α can be obtained from the equilibrium of the mass action law reaction.

$$K = ((AlO)_\alpha M^{2-\alpha})(H^+)^\alpha/((AlOH)_\alpha)(M^{2+}) \qquad (1)$$

where K is the equilibrium constant of the surface interaction. And

$$K_d = ((AlO)_\alpha M^{2-\alpha})/(M^{2+}) = \Gamma/C_f \qquad (2)$$

where Γ is the amount of adsorbate adsorbed per gram of adsorbent, and C_f is the equilibrium solution concentration. K_d is, therefore, equal to the slope of a straight line on a Γ versus C_f plot. As seen in the Fig. 1 and 2, the plots of Γ versus C_f are nearly linear in the portion where the concentrations of metal ions (C_f) in solution are low. Thus, K_d values at various pH can be derived by linear regression from the measurements made at low concentrations.

Therefore, $$K = K_d(H^+)^\alpha/(AlOH)_\alpha$$

$$\log K_d = \alpha pH + \log(K(AlOH)_\alpha) \qquad (3)$$

From the above equation a plot of log K_d versus pH should give a positive slope α.

RESULTS AND DISCUSSION

In all cases, the data represent a measurement precision of ±2 relative standard deviation.

(1) Effect of pH on Adsorption of Lead and Zinc

As seen from Figures 1-3, adsorption of lead and zinc is strongly pH dependent; adsorption increased markedly as pH increased. For the pH range (5-8) studied the adsorption of Pb (Fig. 1) and Zn (Fig. 2) was highest at pH 8.

The pH region in which adsorption increases rapidly (the "adsorption edge") for lead and zinc is demonstrated in Fig. 3. The abscissa is the pH of the suspension and

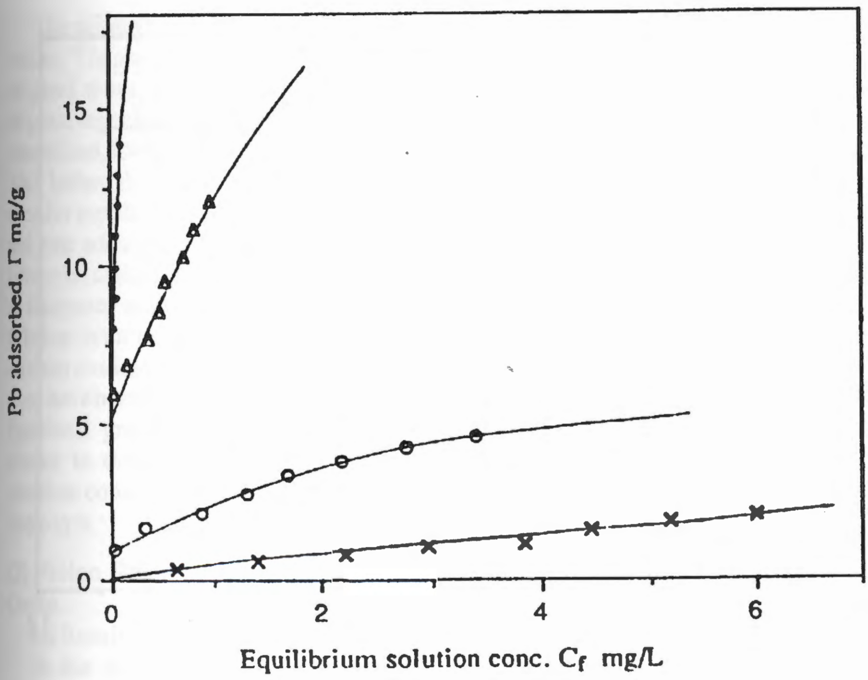

FIGURE 1. Plot of Γ versus Cf for the adsorption of Pb on aluminium oxide at pH 5 (x), PH 6 (o), pH 7 (Δ) and pH 8 (.) at 25°C.

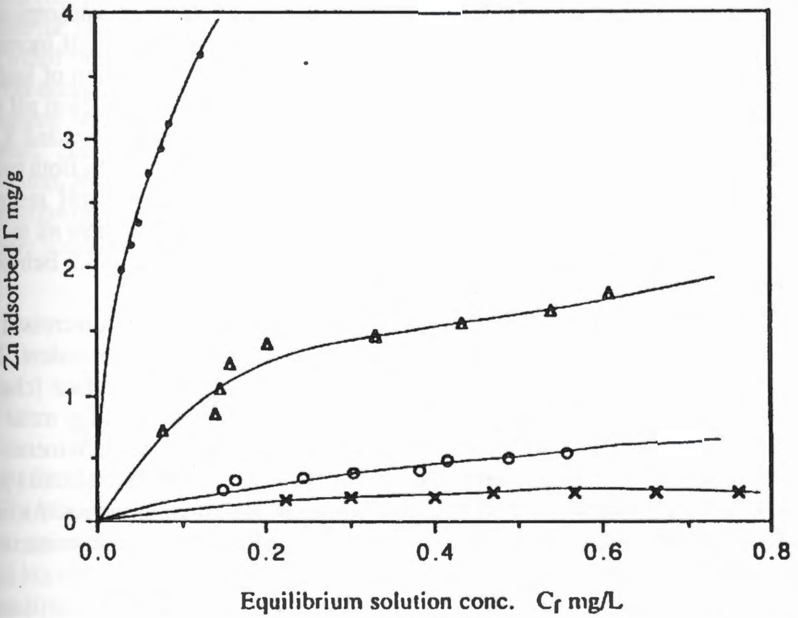

FIGURE 2. Plot of Γ versus Cf for the adsorption of zinc on aluminium oxide at pH 5 (x), pH 6 (o), pH 7 (Δ) and pH 8 (.) at 25°C.

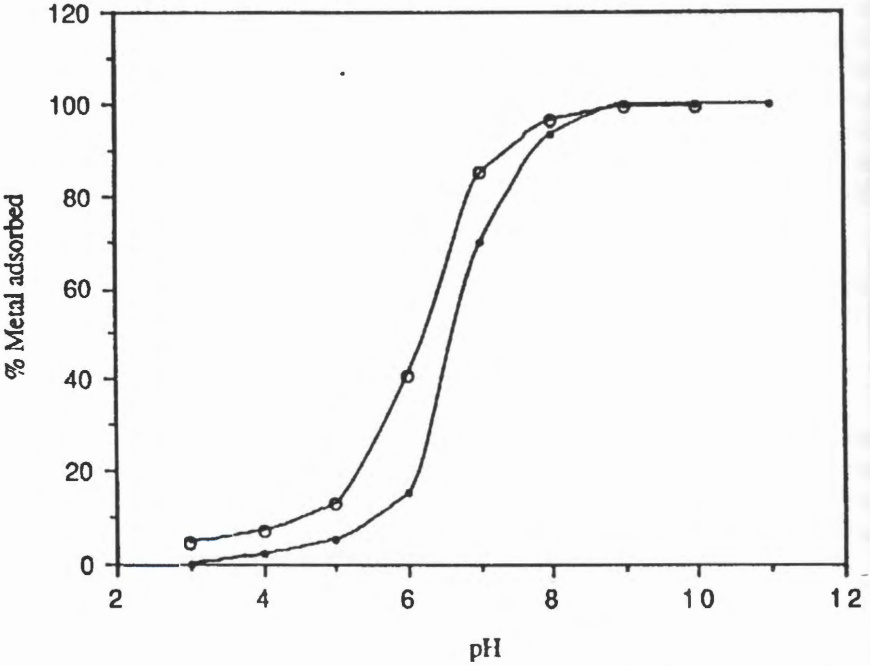

FIGURE 3. Plot of % metal adsorbed versus pH of the suspension for the adsorption of Pb (o) and Zn (.) on aluminium oxide at 25°C. The initial concentration of Pb used was 10 mg/L and that of Zn was 6 mg/L.

the ordinate is the percentage metal (lead or zinc) adsorbed. From Fig. 3 adsorption of lead increased from about 7% at pH 4 to almost 98% at pH 8, while it increased markedly between pH 5 and 7. At approximately pH 6.2 the adsorption of lead on aluminium oxide was 50%. Adsorption of zinc increased from about 4% at pH 4 to nearly 95% at pH 8, while a marked increased occurred between pH 6 and 8. At approximately pH 6.5 the adsorption of zinc on aluminium oxide was 50%. Both results show the bulk of the adsorption occurring over a relatively narrow pH range of approximately 2 unit wide where fractional adsorption increases from near nil to near 100%, and are in good agreement with literatures results (Lion et al., 1982; Benyahya and Garnier, 1999; Johnson, 1990; Tewari and Lee, 1975).

These results conform with the trend of increasing adsorption with increased pH and suggest further that adsorption of metal ions on oxides is pH dependent. This dependence can be attributed to the properties of both, the oxide surface (charge, potential, and/or surface composition) and the solution composition (e.g. metal ion speciation) change with pH. In aquatic environments, oxides and oxide minerals are covered with surface hydroxyl groups, AlOH. The presence of two lone electron pairs and a dissociable hydrogen ion indicates that these groups are ampholytes. As mentioned above, depending on the pH of the system, the surface of the oxide exists in the following forms.

$$AlO^- \overset{+H^+}{\Longleftrightarrow} AlOH \overset{+H^+}{\Longleftrightarrow} AlOH_2+$$

The pH dependent charge of a hydrous oxide results from proton transfer at the surface. The zero point of charge (pzc) of the aluminium oxide used in this study is 8.3 as stated above. At pH values well below the pzc, the majority of the surface sites will be positively charged ($AlOH_2+$). As the pzc is approached, increasing numbers will be neutralized, forming AlOH, and a small number will acquire a negative charge, forming AlO^- before the pzc is reached. At higher pH values, the number of available active sites for metals increases. Given that the adsorbed species are positively charged, lead and zinc adsorption will occur most readily on neutral and negatively charged sites. However, cations of Pb and Zn can be strongly adsorbed against electrostatic repulsion as illustrated in this study, whereby adsorption of lead and zinc occurred at the pH of solution even below the pH_{pzc}. Therefore, the interactions of metal ions with aluminium oxides cannot be explained by electrostatic interaction only; specific interactions have been interpreted in recent years in terms of surface coordination with surface functional groups, -AlOH, whose acid-base and other coordinative properties are similar to their counterparts in soluble compounds. Adsorption of metal ions is therefore considered as competitive complex formation involving one or more surface hydroxyls.

(2) Proton Release and Stoichiometry during Metal Adsorption on Aluminium Oxide.

(a) Results from titration of aluminium oxide suspension with metal ions.

In this study surface complexation process in aluminium oxide is investigated through a titration of suspended aluminium oxide particles with metal ions (lead and zinc). The pH of the suspension is monitored as the suspension is being titrated.

A plot of pH versus cumulative volume of the cations is shown in Fig. 4, which reflects the interactions of Pb and also Zn with the Al_2O_3 surface. From Fig. 4 it can be seen the pH of the aluminium oxide suspension decreased as lead or zinc solution was added through a burette. The decreasing pH of the suspensions indicated that a process occurred which decreased the pH (increased H^+), as compared with the blanks containing no metal ions, which remained essentially at the same initial pH during titration. The results support the interpretation that lead and zinc adsorption on aluminium oxide can be represented in terms of a surface complexation formed by association of Pb or Zn ion with a number of surface AlOH groups thus replacing one or more bound H^+ ions (α).

$$(AlOH)_\alpha + Pb^{2+} = (AlO)_\alpha Pb^{2-\alpha} + \alpha H+$$

and

$$(AlOH)_\alpha + Zn^{2+} = (AlO)_\alpha Zn^{2-\alpha} + \alpha H^+$$

(b) Plots of K_d versus pH - Proton Stoichiometry

The resulting plots of log K_d versus pH (Eq. 3) are shown in Fig. 5. The slope of these curves demonstrated that α which give the equivalent number of H^+ released per metal ion adsorbed was determined and found to be close to unity. This suggests that for each metal ion adsorbed, approximately one H^+ is released, indicating that the major

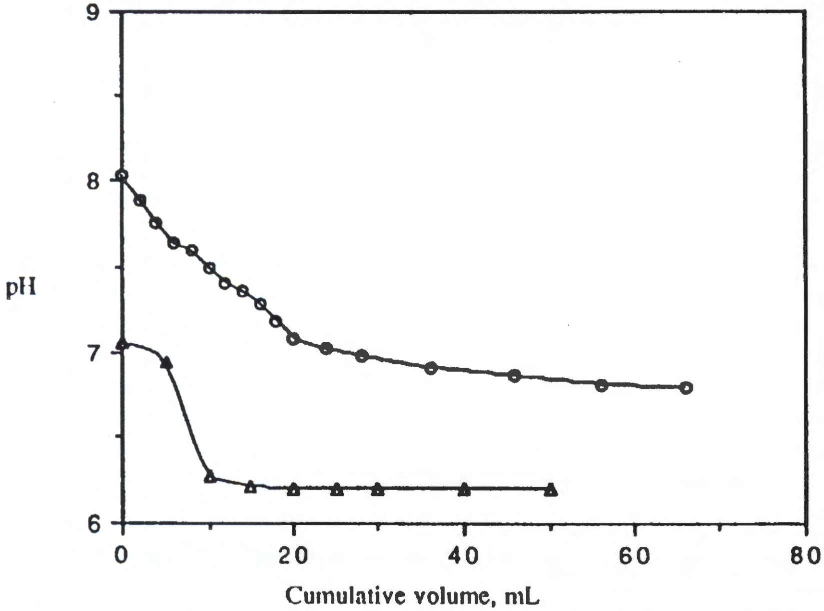

FIGURE 4. Plot of pH versus cumulative volume for the titration of 10 mg/L Pb(o), 2 mg/L Zn (Δ) with aluminium oxide suspension at 25°C.

surface reaction is the formation of monodentate inner-sphere complex over the experimental pH range.

Therefore the adsorption of lead and zinc on aluminium oxide in general can be represented:

$$AlOH + Pb^{2+} = AlOPb^{+} + H^{+}$$

and

$$AlOH + Zn^{2+} = AlOZn^{+} + H^{+}$$

This is a surface complexation formed by association of one surface AlOH group, thus replacing one bound H^+ ion. A similar mass action approach to adsorption equilibria is outlined in Kurbatov, et al. (1951), and also described for the distribution coefficient of trace metals on soils in Anderson and Christensen (1988). Based on the investigation of Pb(II) complexes at the Al_2O_3/water interface, using X-ray absorption spectroscopy, Chisholm-Brause et al. (1990) demonstrated that Pb(II) bonded directly to the Al_2O_3 surface as an inner-sphere complex and the adsorption site is monodentate, which is in direct support of our results.

As suggested by Benjamin and Leckie (1981), over a wide pH range extending at least ± 3 pH units from the point of zero charge, the surface proton density is 1.0 ± 0.1 proton per surface site on oxides. In other words -AlOH is the most abundant site for adsorption over this wide pH range. Thus, if all surface sites are equivalent under the condition of low surface coverage, on the average one surface proton would be released per site occupied when a trace metal adsorbs. Thus, bidentate or multidentate com-

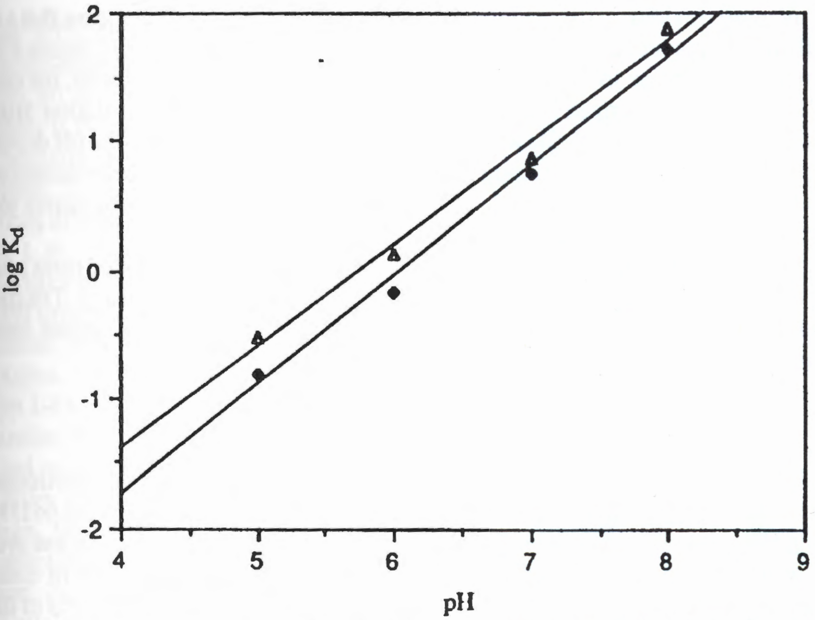

FIGURE 5. Plot of log K_d versus pH for the adsorption of Pb (Δ) and Zn (o) on aluminium oxide at 25°C.

plexes which can not be ruled out are formed only to a very small extent in comparison to the 1:1 compolexes.

Honeyman (1984) discussed the limitations of this approach, including the requirement for an excess of surface binding sites and the dependence of proton release on system pH. As we have seen from the above plotted isotherms, K_d is better described at low adsorption density where unoccupied sites are in great excess, but not at high surface coverage. Below some sufficiently low adsorption density there must exist a condition where unoccupied sites of all types are in excess. Under these conditions the adsorption density (Γ) should be a linear function of equilibrium dissolved adsorbate concentration. In the region where the surface coverage is high, the tendency for a metal ion to adsorb decreases because of three possible reasons (Schindler and Stumm, 1987; Benjamin and Leckie, 1981): (1) the coulombic attraction between the solid and the adsorbate decreases as the metal ions adsorb, because the surface charge becomes more positive. (2) There are unfavorable interactions between adjacent adsorbed species. (3) There are a variety of site types on the solid, of varying affinity for the adsorbate. As suggested by Chisholm-Brause et al. (1990), while Pb(II) surface complexes on Al_2O_3 were predominantly monodentate, some Pb was sorbed as small multinuclear complexes and the number and size of these complexes apparently increased with increasing surface coverage.

CONCLUSIONS

The experimental results obtained in this study provide some understanding of the nature and extent of adsorption of metal ions (lead and zinc) on aluminium oxide at different values of pH. It is interesting to note that the adsorption edges of Pb and Zn occur approximately in the pH range of natural water (pH 5-8). This means that a small shift in pH in aqueous system, as may occur in rivers and estuaries, causes a sharp increase or decrease in dissolved metal levels. For most natural surfaces, the electrostatic state of the interface is determined primarily by the pH of the solution. High pH facilitated the adsorption of lead and zinc. This is in agreement with the pH dependent charge characteristics of oxide surface. As the pH decreases, surface protonation will create a positively charged entity and thereby allow electrostatic interaction to take place in addition to the specific reaction.

Significant adsorption of Pb and Zn on to hydrous aluminium oxide from aqueous solutions is observed even at pH values far below the zero point of charge. The specific binding of Pb or Zn on Al_2O_3 in aqueous solution is interpreted as surface complex formation, which can be quantified by the equation:

$$\text{-AlOH} + M^{2+} = \text{-AlOM}^{+} + H^{+}$$

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