

SORPTION OF BORON BY HYDROUS Al-OXIDE

S. G. DE BUSSETTI, E. A. FERREIRO, AND A. K. HELMY

Universidad Nacional del Sur, 8000 Bahía Blanca, República Argentina

Abstract—Boron sorption by hydrous Al-oxide was studied as a function of concentration, pH, temperature and in the presence of oxalate and phosphate. For comparison sorption of B was also measured with charcoal as adsorbent.

At constant pH a Langmuir type equation was found to fit the results well at pH values below 7.2 where only boric acid molecules are present in solution. B sorption was dependent on pH with maximum sorption at pH 8.5. Oxalate and phosphate ligands form strong bonds to Al and were found to reduce B sorption. Sorption of boric acid molecules decreased with increasing temperature and the isosteric heat of reaction was 13.8 kJ mol^{-1} . These results indicate that there are two mechanisms of sorption on hydrous Al-oxide, physical sorption of boric acid molecules and ligand exchange (chemisorption) of borate, and both mechanisms are favored onto the oxide.

Key Words—Boron, Hydrous Al-oxide, pH.

INTRODUCTION

Sorption of boron by soils, clays and hydrous oxides of Al and Fe has been studied by many workers (Keren and Bingham 1985). Langmuir and/or Freundlich type equations were found to describe boron sorption within certain pH ranges (Singh 1971, McPhail *et al* 1972, Prasad 1978). Sorption was found to be pH dependent with maxima that vary over a wide range of pH from 7.3–9.6 for different sorbents. The sorption maxima were found further to depend on boron concentration and the identity of the cation in the equilibrium solution (Kluge and Beer 1979).

The concept that boron sorption, above pH 7.2, involves two species, boric acid molecules and borate anions (Basset 1980), each with its own sorption characteristics does not seem to have gained the attention it deserves. In reports of B sorption data there is often no discrimination between the two species. This also explains why sorption equations derived for one species of sorbate failed to describe B sorption (McPhail *et al* 1972, Hingston 1964), since the sorption mechanism is probably not the same for both species.

The purpose of the following study is to elucidate the mechanisms involved in boron sorption as related to the participating species. Boron sorption was studied using hydrous Al-oxide and charcoal as sorbents and relating the amount of sorption to concentration, pH, presence of competing anions and temperature.

MATERIALS AND METHODS

The hydrous oxide of aluminium (Fluka, TYP 507) used was amorphous to X-rays. It had a point of zero charge, obtained by the addition method (Helmy and Ferreiro 1976), at pH 7.5. The specific surface area determined by the paranitrophenol method (Giles and Trivedi 1969) was $32,300 \text{ m}^2 \text{ kg}^{-1}$.

Preliminary experiments showed that B sorption remained constant after 24 hours. Therefore this period of reaction was adopted for all experiments.

A stock solution of 0.001 M boric acid was used for the preparation of the solutions from which sorption took place.

The sorption of B by the hydrous oxide of aluminium was determined by adding 20 ml of B solutions of different concentrations ($0.2\text{--}1.0 \text{ mmol liter}^{-1}$) to 0.4 g of adsorbent in 50 ml plastic bottles. The bottles were shaken for 2 hours and left 18 hours at $28 \pm 1^\circ\text{C}$ with occasional shaking. Filtration followed and filtrates were analyzed for B by the azomethine-H colorimetric method (Gupta and Stewart 1975). The amounts of B adsorbed were calculated from the difference between initial and final concentrations. The initial and final pH were also measured in the suspensions.

Experiments using the same procedure as given above were made using charcoal (Mallinckrodt (AR) activated charcoal) as sorbent. The objective of these experiments was to obtain data that would help in understanding the mechanisms involved in the B sorption reaction.

To determine the effect of pH on the adsorption of B by hydrous aluminium oxide the pH of the B solutions was adjusted by adding HCl or KOH (0.1 M). The range of equilibrium pH covered was from 5 to 10 at the same initial concentration of B in solution.

For the study of B adsorption as a function of pH in presence of P, 0.4 g samples of Al_2O_3 were placed in plastic bottles. Twenty ml of solution containing $0.5 \text{ mmol B liter}^{-1}$ with a known pH and containing $0.1 \text{ mmol P liter}^{-1}$ (as KH_2PO_4) were added to the powder. The rest of the procedure was as given above.

Boron sorption in the presence of oxalate was determined in an identical manner with potassium oxalate $0.5 \text{ mmol liter}^{-1}$ replacing KH_2PO_4 .

For the study of B sorption as a function of temperature at pH 6.5, the same procedure was followed except that reaction vessels were left for 24 hours in an incubator at 8, 26 and 39°C, with occasional shaking.

RESULTS AND DISCUSSION

Effect of pH on boron sorption

The data for the effect of pH in the range 4–10 on B sorption onto Al-oxide and onto coal using different initial concentrations of boron in solution are shown in Figure 1. On both sorbents the curves have two well defined parts: one for pH <7 and the second for pH values >7. Since in boric acid solutions only the molecule $B(OH)_3$ is present at pH values <7.2 (Basset 1980), the first part of the curves corresponds to molecular sorption only. The second part, however, represents the sorption of both molecular and anionic boron, since these are the species present above pH 7. In systems containing alkali earth cations and/or heavy metals, cationic borate complexes could be present in solutions and could be adsorbed at pH values >7 (Kluge and Beer 1979, Mattigod *et al* 1985). Maximum adsorption occurs at pH 8.5 for the oxide and at pH 4.6 for the charcoal thus reflecting important differences in the sorption mechanisms between sorbents. As early as 1953 Phillipson suggested that B fixation on hydrous oxides occurs by the formation of H bonds between boric acid molecules and OH groups belonging to the hydroxy Al surface. We add to this idea that such bonding is facilitated by the condition that in both $B(OH)_3$ and $Al(OH)_3$, each OH group is hydrogen bonded to two others. The OH-OH distance in boric acid is 0.272 nm which is very similar to the OH-OH distance in $Al(OH)_3$ (0.278 nm) (Evans 1964). Thus boric acid molecules can H-bond to themselves and to the OH groups on the surface of Al without distortion in the OH-OH distances. Such ideal disposition explains why boric acid sorbs on hydrous Al-oxide in amounts higher than on other sorbents (Sims and Bingham 1968).

On carbon surfaces H bonding is unlikely to take place and sorption involves dispersion (van der Waals) forces (Young and Crowell 1962). This mechanism is valid for the $B(OH)_3$ molecule and the borate anion. As appears from Figure 1 less sorption occurs at pH values >7 when borate is present and can be explained on the basis that charged sorbate anions experience mutual repulsion and should maintain larger distances apart on a surface than uncharged sorbates. Hence the maximum in sorption on charcoal always occurs in the range of pH values where the $B(OH)_3$ molecule of weak electrolytes is the predominant species. Similar results viz. higher sorption of molecular than charged species has been reported for benzoic acid on coal by Miller *et al* (1985). On the hydrous oxide at pH values >7 several mechanisms of sorption are expected to oper-

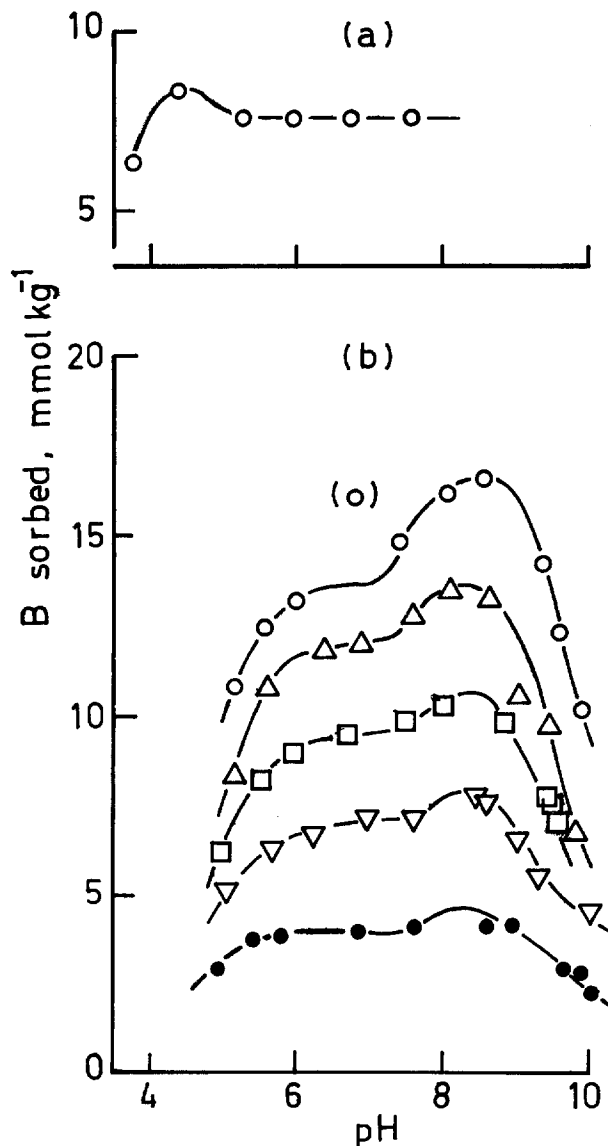


Figure 1. a) Sorption of boron onto charcoal (20 g liter⁻¹) as a function of pH. Initial boron concentration was 1 mmol liter⁻¹. b) Same as in (a) but for hydrous Al-oxide (19.47 g liter⁻¹). Initial boron concentrations were: (●) 0.205, (▽) 0.402, (□) 0.587, (△) 0.797 and (○) 0.993 mmol liter⁻¹.

ate. In addition to H bonding of boric acid molecules and van der Waals dispersion forces (Singh 1971), chemisorption of borate takes place (Singh and Mattigod 1992, Beyrouthy *et al* 1984, Goldberg and Glaueberg 1985). In this type of anion sorption on hydrous oxides ligand exchange takes place between borate and surface hydroxyls. A general characteristic of this reaction on oxides is that sorption decreases as pH increases (Figure 1) due to the fact that the sorbent surface acquires progressively greater negative charge thus reducing an-

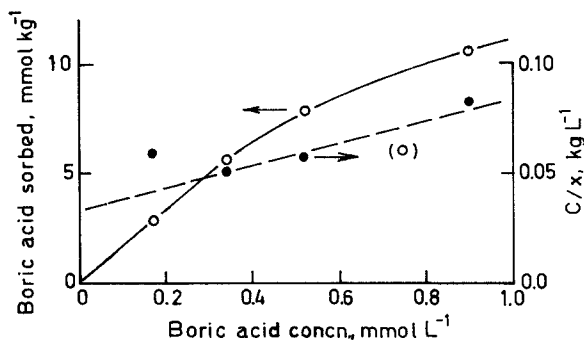


Figure 2. Sorption isotherm of boric acid onto charcoal (20 g liter⁻¹) at pH 6.5 (O). The straight line is the Langmuir plot of the data (●).

ion sorption through electrostatic repulsion (Peinemann and Helmy 1977).

The sorption maximum for borate on aluminium oxide occurs at pH 8.5. Literature values vary widely between pH 7.2 to 9.6 depending on sorbent properties, and is more frequently in the pH range where borate/boric acid ratios are greater than one. This fact may be explained on the basis of the reaction mechanisms involved since higher free energies are associated with chemi than with physical sorption (Young and Crowell 1962) leading to higher sorption values for the borate anion. We end this section by stating that the trends observed in the curves of Figure 1 show that the sorption values of boron are a result of a combined effect of pH on sorbent and sorbate.

Effect of boric acid concentration at constant pH

The effect of boric acid concentration on sorption at pH 6.5 where only boric acid molecules are present in solution is shown in Figure 2 for the sorption on carbon and in Figure 3 for the sorption on the Al-oxide. Both

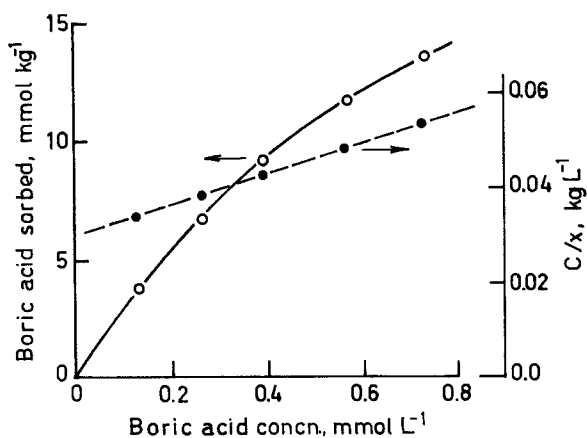


Figure 3. Sorption isotherm of boric acid onto hydrous Al-oxide (19.47 g liter⁻¹) at pH 6.5 (O). The straight line is the Langmuir plot of the data (●).

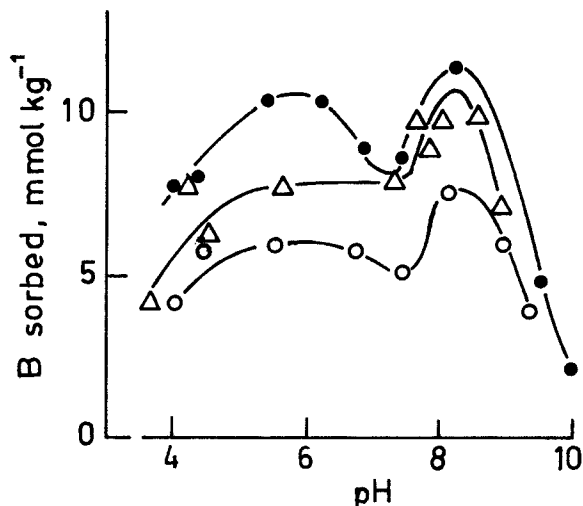


Figure 4. Sorption of boron onto hydrous Al-oxide (9.43 g liter⁻¹) as a function of pH in absence (●) and in the presence of oxalate (Δ) and phosphate (O). Initial boron concentration was 0.5 mmol liter⁻¹.

sorption isotherms could be described by a Langmuir type equation, which is a further evidence for the physical adsorption mechanism already mentioned for boric acid. The calculated sorption maxima are 0.022 mol kg⁻¹ for the carbon and 0.033 mol kg⁻¹ for the oxide (for a suspension concentration of 9 g liter⁻¹). The K parameters are also of the same order for the two sorbents being 1730 liters mol⁻¹ for the carbon and 1033 liters mol⁻¹ for the oxide.

It is worth mentioning that B sorption as a function

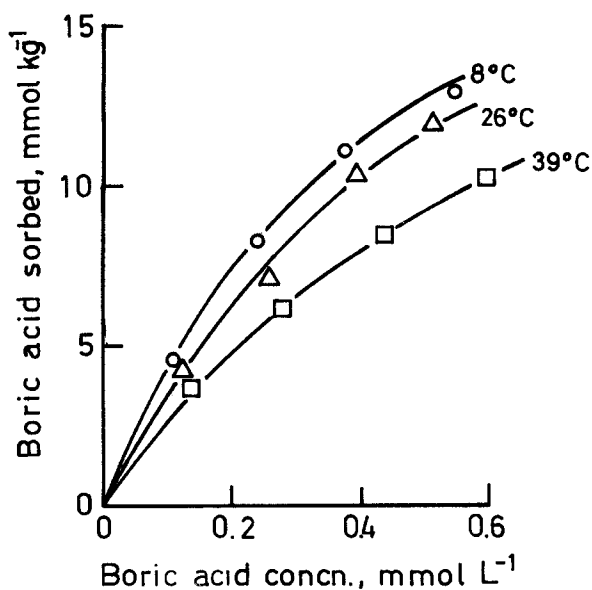


Figure 5. Boric acid sorption isotherms onto hydrous Al-oxide at different temperatures.

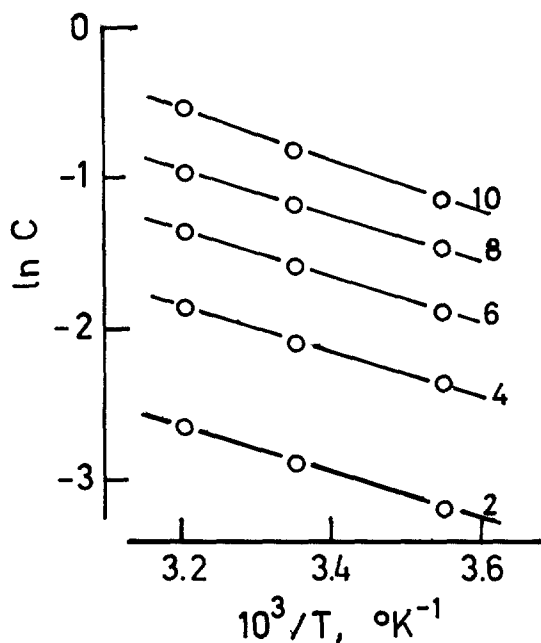


Figure 6. Plots of the logarithms of the equilibrium concentration of boric acid at constant amounts adsorbed against the reciprocal of the absolute temperatures. Numbers on the lines represent adsorbed amounts (mmol kg^{-1}).

of concentration obtained at pH values greater than 7.2 could not be described either by the Langmuir or the Freundlich type equations; probably because, as stated earlier, more than one mechanism is involved in the boron sorption reaction, a condition not contemplated by the equations.

Effect of oxalate and phosphate on boron sorption

The effect of oxalate and phosphate on B sorption was studied as a function of pH at constant initial concentration of boric acid of $0.5 \text{ mmol liter}^{-1}$. The data depicted in Figure 4 show that phosphate and oxalate effectively reduce boron sorption at all pH values between 4 and 10. Thus oxalate and phosphate interfere in the sorption of both the boric acid and the borate anion. These results are not unexpected since phosphate and oxalate are ligands that bond strongly to Al viz. chemisorb to Al atoms on hydrous oxide surfaces (Peinemann and Helmy 1977) and hence compete strongly with borate for the chemisorption sites. The above results are a further demonstration of the mechanism of borate sorption on hydrous Al-oxide, namely a ligand exchange reaction in which borate displaces a surface hydroxyl and bonds to an Al atom.

Effect of temperature on boric acid sorption

The heat of adsorption determined at constant amounts of sorbate is known as the isosteric heat of adsorption and is given by (Young and Crowell 1962):

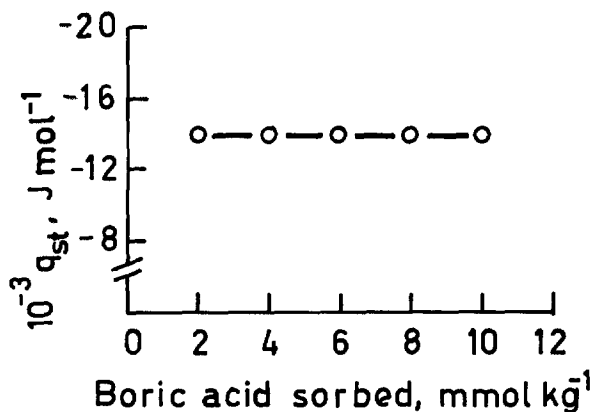


Figure 7. The isosteric heat of boric acid adsorption plotted as a function of amounts adsorbed.

$$q_{st} = -R[d \ln p/d(1/T)]_{\text{adsorbate}} \quad (1)$$

where q_{st} is the difference between the heat contents in the gas and adsorbed states, p is the pressure, R is the gas constant and T is the absolute temperature. Eq. (1) is valid for ideal gases. For adsorption from solutions p can be replaced by the concentration, as an approximation. This replacement makes possible the calculation of q_{st} for boric acid adsorption on hydrous Al-oxide. For this purpose the equilibrium concentration at constant amount of adsorbed boric acid is obtained from adsorption isotherms at different temperatures (Figure 5). The logarithm of the equilibrium concentrations are then plotted against $1/T$ and q_{st} is then calculated from the slope of the lines (Figure 6). The

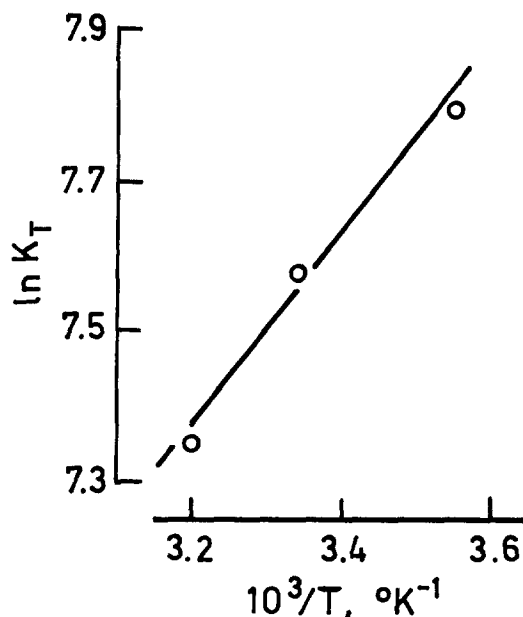


Figure 8. Plot of the logarithms of the constants of the Langmuir equation as a function of $(1/T)$.

procedure was repeated for different amounts of sorbate. The q_{st} values are shown in Figure 7 as a function of the amounts of adsorbed boric acid. The value of q_{st} is 13.8 kJ mol^{-1} and was independent of surface coverage as may be seen in Figure 7. The order of magnitude of the value indicates a physical mechanism for the adsorption of boric acid on hydrous Al-oxide (Young and Crowell 1962). The constancy in q_{st} with surface coverage is usually attributed to the absence of lateral interactions between sorbed molecules.

Even though the K parameter of the Langmuir equation is not a thermodynamic equilibrium constant, its temperature dependence may throw light on the nature of the boric acid surface reaction on the oxide. In Figure 8 $\ln K$ values obtained at different temperatures are plotted as a function of $1/T$. As seen from the figure a straight line is obtained, thus demonstrating a behavior similar to a real equilibrium constant (Graham 1953). Furthermore, the slope of the line in Figure 8 gives a value of $-10.7 \text{ kJ mol}^{-1}$; a value similar to the enthalpies of physical adsorption reactions. Hence a further substantiation for the mechanism of boric acid adsorption on the hydrous oxide.

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