

ADSORPTION OF PHOSPHATE BY VARIOUS OXIDES: THEORETICAL TREATMENT OF THE ADSORPTION ENVELOPE

F. CABRERA, L. MADRID AND P. DE ARAMBARRI

(Centro de Edafología y Biología Aplicada del Cuarto, C.S.I.C., Apartado 1052, Sevilla, Spain)

Summary

An explanation is put forward for the shape of adsorption envelopes found for phosphate adsorption by various metallic oxides. The equation $x_m = C_1 (\mu_{H_3PO_4} + \mu_{\Sigma anions})$ is proposed, where $\mu_{H_3PO_4}$ is the chemical potential of undissociated H_3PO_4 ; $\mu_{\Sigma anions}$ is the chemical potential of all phosphate anions considered as one component; C_1 is a constant that includes influences of surface charge, chemical affinity of the metal for phosphate, specific surface area, etc., and x_m is the calculated Langmuir maximum adsorption of P at each pH. The dependence of C_1 on the metal present in the oxide is shown.

Introduction

ANIONS that can be specifically adsorbed on certain mineral surfaces are held in amounts which are different at each pH value of the medium (Hingston *et al.*, 1967). Most experimental data can be fitted to a Langmuir equation (Muljadi *et al.*, 1966; Hingston *et al.*, 1968, 1970, 1972; Obihara, 1969), which allows a maximum value for the adsorption to be calculated. Such values are related to pH by curves which have been termed 'adsorption envelopes'.

For phosphate, the adsorption envelope commonly shows breaks in the slope at pH values close to the second and third pK values of phosphoric acid. This shape has been recently interpreted by Bowden *et al.* (1973) using the Stern double-layer theory.

The main intention of the present paper is to suggest an explanation for the shape of the envelope for phosphate adsorption by different oxides based upon chemical potentials of species in solution. This explanation involves fewer parameters to be determined than the model proposed by Bowden *et al.* (1973).

Materials and methods

Gibbsite: a commercial sample supplied by Reynolds Metals Co., BET specific surface area $13.1 \text{ m}^2 \text{ g}^{-1}$, and zero point of charge (ZPC) at pH 7.80 (method given by Herrman and Boehm, 1969).

Boehmite: supplied by British Aluminium Co. ('Cera Hydrate'), BET specific surface area $2.9 \text{ m}^2 \text{ g}^{-1}$, and ZPC at pH 7.24.

Corundum: obtained by heating commercial aluminium oxide at

1200° C for 5 h, BET specific surface area $6.0 \text{ m}^2 \text{ g}^{-1}$, and ZPC at pH 3.55.

Goethite: obtained from $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ by the method given by Taylor *et al.* (1964), BET specific surface area $87.4 \text{ m}^2 \text{ g}^{-1}$, and ZPC at pH 8.45.

Lepidocrocite: obtained from $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ by the method given by Brauer (1958), BET specific surface area $128.0 \text{ m}^2 \text{ g}^{-1}$, and ZPC at pH 6.20.

Hematite I: obtained by precipitating 0.5 M solution of FeCl_3 at boiling point with 1:1 NH_4OH . After filtering and washing the amorphous solid, it was heated at 1000° C for 1 h. BET specific surface area $1.2 \text{ m}^2 \text{ g}^{-1}$, and ZPC at pH 6.45.

Hematite II: obtained by heating $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ at 150° C for 1 h, BET specific surface area $17.3 \text{ m}^2 \text{ g}^{-1}$, and ZPC at pH 6.77.

Pyrolusite: obtained by dissolving metallic Mn in HNO_3 and subsequently evaporating the solution. The solid was washed with boiling conc. HNO_3 in order to dissolve oxides of lower valency; BET specific surface area $2.3 \text{ m}^2 \text{ g}^{-1}$, and ZPC at pH 5.63.

Anatase: supplied by Bayer Hispania (Commercial name Bayertitan AN-2), BET specific surface $13.8 \text{ m}^2 \text{ g}^{-1}$, and ZPC at pH 7.54.

Adsorption isotherms

Suspensions of 0.2 to 1 g oxide in 50 ml of 0.1 M NaCl solutions containing KH_2PO_4 with initial P concentrations ranging from 0 to 100 parts 10^{-6} were shaken at 25° C for 24 h. Small quantities of 0.1 M NaOH or HCl solutions were added to obtain the desired pH. After shaking, pH was measured in the suspensions, and P concentration was measured in the clear supernatant solutions (Murphy and Riley, 1962). Adsorbed P was taken to be that lost from solution during shaking.

Results and discussion

Linear correlation coefficients between the equilibrium P concentration and the quotient (P concentration/adsorbed P) for each adsorption isotherm were all highly significant ($P < 0.001$ for 65 isotherms and $P < 0.01$ for 23, out of 95 isotherms determined), allowing Langmuir adsorption maxima (x_m) to be calculated. As an example, Fig. 1 shows experimental x_m values for goethite plotted against the corresponding pH values. The dashed line will be referred to later. The corresponding graphs for the other oxides studied are similar and are not presented here.

Theoretical considerations

According to Hingston *et al.* (1970, 1972) the mechanism of specific adsorption of anions on oxides implies the exchange of H_2O molecules on the surface of the oxides for the dissociated anion. As the species on the surface of the oxides, OH^- and/or H_2O , depend on the ZPC (zero

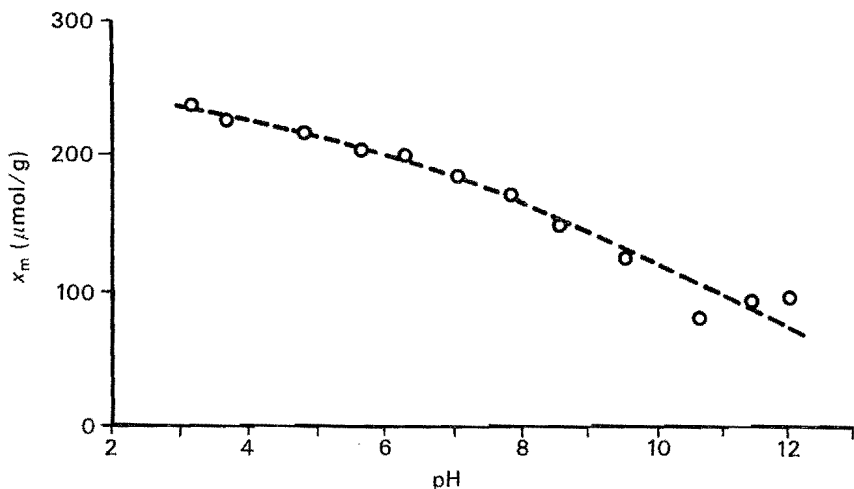


FIG. 1. Typical relationship (goethite) between experimental adsorption maxima and pH values of adsorption, with theoretical curve calculated using equation (8).

point of charge), the specific adsorption at pH higher than ZPC is only possible if the undissociated acid gives a proton to the OH^- group on the surface to form H_2O , which is readily displaced by the anion.

For monoprotic acids the maximum amount of anion adsorbed, x_m , at any pH is given by the expression

$$x_m = \frac{\Delta G}{RT} \alpha(1 - \alpha) \quad (1)$$

where ΔG is the maximum free energy of adsorption of the anion and α is the degree of dissociation.

This expression gives a maximum at $\text{pH} = \text{p}K_a$, when $\alpha = 0.5$. If such a maximum is identified with the experimental value, V_m , of maximum x_m , it can be written

$$x_m = 4V_m \alpha(1 - \alpha). \quad (2)$$

However, this function produces a curve which clearly falls below the experimental envelope (Hingston *et al.*, 1970), and the authors believe that this arises from the assumption that ΔG is constant and independent of pH.

According to Hingston *et al.* (1972), a similar treatment can only be applied to polyprotic acids (e.g. phosphoric acid) if the $\text{p}K_a$ values are sufficiently far apart, so that the effect of simultaneous existence of different proton donor species is avoided.

Nevertheless, if it is supposed that H_3PO_4 is the only species able to provide protons to the surface, a value of $(1 - \alpha)$ can be defined as

$$(1 - \alpha) = \frac{1}{1 + \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2} + \frac{K_1 K_2 K_3}{[H^+]^3}}$$

where K_1 , K_2 , and K_3 are dissociation constants for phosphoric acid. Then

$$\alpha = \frac{\frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2} + \frac{K_1 K_2 K_3}{[H^+]^3}}{1 + \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2} + \frac{K_1 K_2 K_3}{[H^+]^3}}$$

If the numerator is called N ,

$$\alpha(1 - \alpha) = \frac{N}{(1 + N)^2} = \frac{[H_3PO_4]}{[P]} \times \frac{[H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]}{[P]} \quad (3)$$

where $[P] = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$.

If a 'chemical potential of phosphate anions in solution' is defined as

$$\mu_{\Sigma \text{ anions}} = \mu_{\Sigma \text{ anions}}^0 + RT \ln [\Sigma \text{ anions}],$$

and it is assumed that the phosphate adsorbed at any pH, P_a , is determined by the chemical potentials of species in solution according to the equation

$$P_a = C_1(\mu_{H_3PO_4} + \mu_{\Sigma \text{ anions}}) \quad (4)$$

then P_a can be related to the logarithm of expression (3), since

$$\begin{aligned} \ln \alpha(1 - \alpha) &= \\ &= \ln [H_3PO_4] + \ln ([H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]) - 2 \ln [P] \\ &= \ln [H_3PO_4] + \ln [\Sigma \text{ anions}] - 2 \ln [P]. \end{aligned} \quad (5)$$

And, multiplying by RT ,

$$\begin{aligned} RT \ln \alpha(1 - \alpha) &= \\ &= \mu_{H_3PO_4} + \mu_{\Sigma \text{ anions}} - \mu_{H_3PO_4}^0 - \mu_{\Sigma \text{ anions}}^0 - 2RT \ln [P] \\ &= \mu_{H_3PO_4} + \mu_{\Sigma \text{ anions}} - \mu_{\text{total}}^0 \end{aligned} \quad (6)$$

where

$$\mu_{\text{total}}^0 = \mu_{H_3PO_4}^0 + \mu_{\Sigma \text{ anions}}^0 + 2RT \ln [P].$$

If the total P concentration in solution is constant and high enough such that $P_a = x_m$ (the maximum adsorption at a given pH), equation (4) changes to

$$x_m = C_1(\mu_{H_3PO_4} + \mu_{\Sigma \text{ anions}}) \quad (7)$$

where C_1 is a constant whose meaning will be discussed later.

Substituting the value of $\mu_{\text{H}_3\text{PO}_4} + \mu_{\Sigma \text{anions}}$ taken from equation (6),

$$x_m = [RT \ln \alpha(1 - \alpha) + \mu_{\text{total}}^0] C_1 = C_2 \log \alpha(1 - \alpha) + C_3 \quad (8)$$

where $\alpha(1 - \alpha)$ is a function of $[\text{H}^+]$, $C_2 = 2.303 RT C_1$, and $C_3 = \mu_{\text{total}}^0 \cdot C_1$. Plotting experimental x_m values against $\log \alpha(1 - \alpha)$ calculated for the corresponding pH values, a straight line should be obtained, whose slope should be C_2 and the intercept C_3 .

Tests of hypothesis

Fig. 2 shows one typical relationship between x_m and $\log \alpha(1 - \alpha)$, again using the results for goethite as an example. The linear correlation coefficients for all the oxides studied are shown in Table 1, which also shows the values of C_1 and μ_{total}^0 calculated from the slopes and intercepts according to equation (8).

Equation (8) has also been applied to x_m read from the phosphate adsorption envelopes for three synthetic goethites given by Hingston *et al.* (1967, 1968, 1971). As an example, Fig. 3 shows the relationship between x_m and $\log \alpha(1 - \alpha)$ for one of them (Hingston *et al.*, 1968). Calculated constants and linear correlation coefficients are given in Table 2.

From equation (8), and with constants given in Table 1, theoretical envelopes have been calculated for each oxide. The curve for goethite is shown in Fig. 1 (dashed line). The envelopes calculated were in close agreement with the experimental points, and all of them showed a change in the slope at a pH value close to 7.

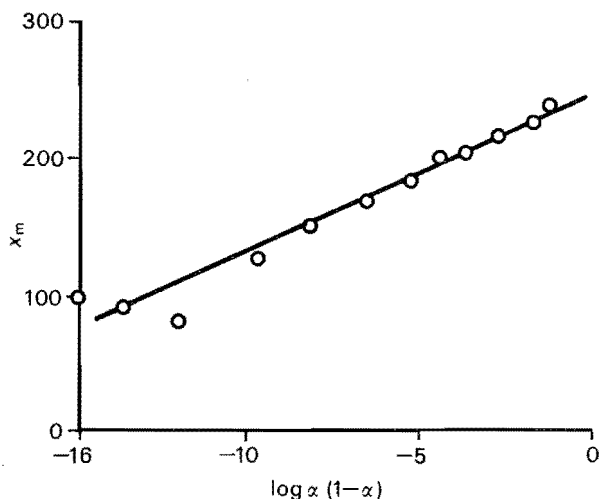


FIG. 2. Typical relationship (goethite) between experimental x_m and $\log \alpha(1 - \alpha)$ calculated for each pH value using equation (3).

TABLE I

Linear correlation coefficients and constants calculated from equation (8) for the oxides studied here

Oxide	r	C_1	μ_{total}^0
Gibbsite	0.9467***	4.99×10^{-3}	13,986
Boehmite	0.8145*	2.94×10^{-4}	16,562
Corundum	0.9213***	1.31×10^{-3}	21,508
Goethite	0.9786***	8.38×10^{-3}	29,269
Lepidocrocite	0.9913***	1.66×10^{-2}	18,294
Hematite I	0.8604**	1.65×10^{-4}	30,652
Hematite II	0.9573***	2.80×10^{-3}	18,669
Anatase	0.9442***	5.07×10^{-3}	11,055
Pyrolusite	0.9736***	1.90×10^{-4}	20,234

From Figs 1, 2, and 3, it can be stated that the assumptions made to deduce equation (8) agree with experimental results, which means that chemical potentials in solution of the three phosphate ions considered together as one component, and of undissociated phosphoric acid as another, determine the amount of phosphate adsorbed. The proportionality constant C_1 includes the influence of chemical affinity of the metal and surface area effects.

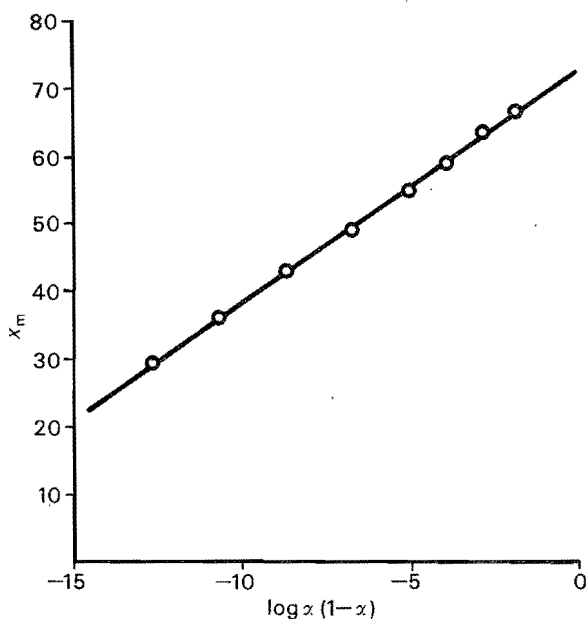


FIG. 3. Relationship between x_m given by Hingston *et al.* (1968) for goethite and $\log \alpha(1 - \alpha)$ calculated for the corresponding pH values using equation (3).

TABLE 2

Linear correlation coefficients and constants calculated from equation (8) for three goethites of Hingston et al. (1967, 1968, 1971)

Reference	r	C_1	μ_{total}^0
1967	0.9940***	3.40×10^{-3}	27,671
1968	0.9993***	2.58×10^{-3}	28,374
1971	0.9978***	5.07×10^{-3}	31,325

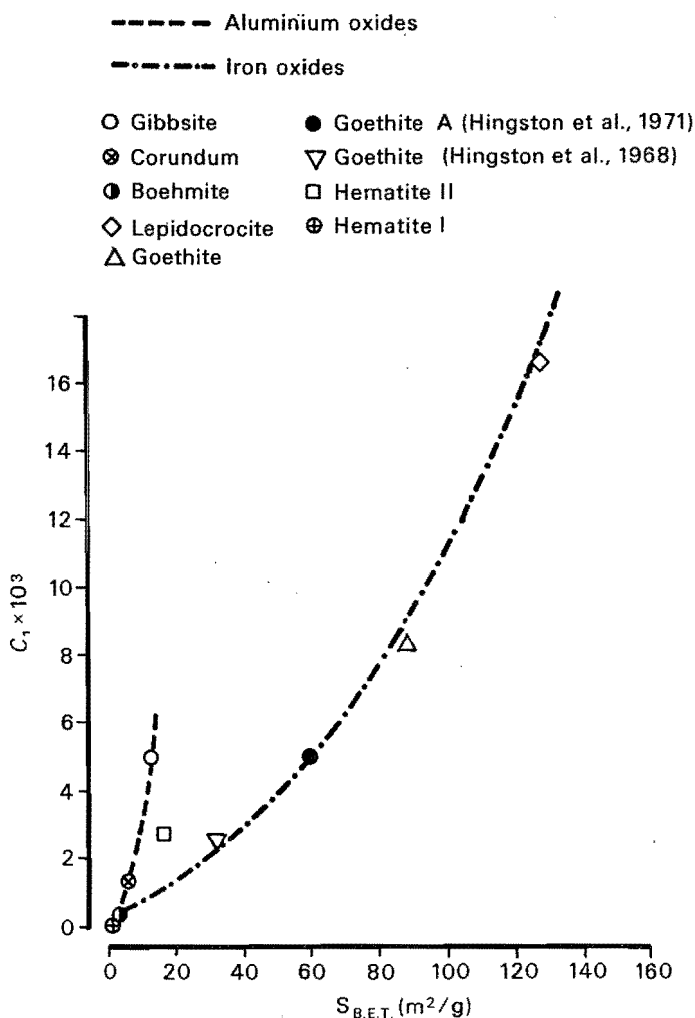


FIG. 4. Relationships between C_1 and specific surface area for aluminium and iron oxides.

Some deviations from linearity of the plots of $\log \alpha(1 - \alpha)$ against x_m at very low or very high pH values could be due to influences of very high positive or negative surface charge, that are not considered if C_1 is supposed to be constant over the entire pH range.

Fig. 4 shows the relationship between C_1 and the specific surface area for aluminium and iron oxides. Two goethites from Hingston *et al.* (1968, 1971) have been included. It is shown that C_1 is greater for aluminium than for iron oxides for a given value of the specific surface area. This conclusion agrees with results of other authors (Gastuche *et al.*, 1963; Taylor *et al.*, 1964; Arambarri and Madrid, 1971), that aluminium oxides are more reactive than iron oxides of similar specific surface areas.

Acknowledgement

Authors are grateful for the technical help they received from Miss M. F. Osta, Dr. J. Cornejo, and Mr. J. Muñoz.

REFERENCES

- ARAMBARRI, P., and MADRID, L. 1971. Reacción de óxidos de hierro y aluminio con fosfato dicálcico dihidrato. *An. Edaf. Agrob.* 30, 1083-94.
- BOWDEN, J. W., BOLLAND, M. D. A., POSNER, A. M., and QUIRK, J. P. 1973. Generalized model for anion and cation adsorption at oxide surfaces. *Nature, Lond. (Phys. Sci.)* 245, 81-3.
- BRAUER, G. 1958. "Química Inorgánica Preparativa". Reverté. Barcelona.
- GASTUCHE, M. C., FRIPIAT, J. J., and SOKOLSKI, S. 1963. Fixation du phosphore par les hydroxydes de fer et d'aluminium amorphes et cristallisés. *Pedologie* 13, 155-80.
- HERRMANN, M., and BOEHM, M. P. 1969. Über die Chemie der Oberfläche des Titandioxids. II. Saure Hydroxygruppen auf der Oberfläche. *Z. Anor. Allgem. Chem.* 336, 73.
- HINGSTON, F. J., ATKINSON, R. J., POSNER, A. M., and QUIRK, J. P. 1967. Specific adsorption of anions. *Nature, Lond.* 215, 1459-61.
- 1968. Specific adsorption of anions on goethite. *Trans. 9th int. Cong. Soil Sci.* 1, 669-78.
- POSNER, A. M., and QUIRK, J. P. 1970. Anion binding at oxide surfaces. The adsorption envelope. *Search* 1, 324-7.
- 1971. Competitive adsorption of negatively charged ligands on oxide surfaces. *Disc. Faraday Soc.* no. 52, 334-42.
- 1972. Anion adsorption by goethite and gibbsite. I. The role of the proton in determining adsorption envelopes. *J. Soil Sci.* 23, 177-92.
- MULJADI, D., POSNER, A. M., and QUIRK, J. P. 1966. The mechanism of phosphate adsorption by kaolinite, gibbsite and pseudoboehmite. *J. Soil Sci.* 17, 212-47.
- MURPHY, J. and RILEY, J. P. 1962. A modified single solution method for the determination of phosphate in natural waters. *Analytica chim. Acta* 27, 31-6.
- OBIHARA, C. C. H. 1969. Interactions between soluble silica and phosphate in soils. Ph. D. thesis, Univ. Reading.
- TAYLOR, A. W., GURNEY, E. L., and MORENO, E. C. 1964. Precipitation of phosphate from calcium phosphate solutions by iron oxide and aluminum hydroxide. *Proc. Soil Sci. Soc. Am.* 28, 48-52.

(Received 10 May 1976)