Summary

An explanation is put forward for the shape of adsorption envelopes found for phosphate adsorption by various metallic oxides. The equation \( x_m = C_1 (\mu_{H_3PO_4} + \mu_{\text{anions}}) \) is proposed, where \( \mu_{H_3PO_4} \) is the chemical potential of undissociated \( H_3PO_4 \), \( \mu_{\text{anions}} \) 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 m² 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 m² 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 m² g⁻¹, and ZPC at pH 3.55.

Goethite: obtained from Fe(NO₃)₃.9H₂O by the method given by Taylor et al. (1964), BET specific surface area 87.4 m² g⁻¹, and ZPC at pH 8.45.

Lepidocrocite: obtained from FeCl₂.4H₂O by the method given by Brauer (1958), BET specific surface area 128.0 m² g⁻¹, and ZPC at pH 6.20.

Hematite I: obtained by precipitating 0.5 M solution of FeCl₃ at boiling point with 1:1 NH₄OH. After filtering and washing the amorphous solid, it was heated at 1000°C for 1 h. BET specific surface area 1.2 m² g⁻¹, and ZPC at pH 6.45.

Hematite II: obtained by heating Fe(NO₃)₃.9H₂O at 150°C for 1 h, BET specific surface area 17.3 m² g⁻¹, and ZPC at pH 6.77.

Pyrolusite: obtained by dissolving metallic Mn in HNO₃ and subsequently evaporating the solution. The solid was washed with boiling conc. HNO₃ in order to dissolve oxides of lower valency; BET specific surface area 2.3 m² g⁻¹, and ZPC at pH 5.63.

Anatase: supplied by Bayer Hispania (Commercial name Bayerititan AN–2), BET specific surface 13.8 m² 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 KH₂PO₄ 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 (xₘ) to be calculated. As an example, Fig. 1 shows experimental xₘ 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 H₂O molecules on the surface of the oxides for the dissociated anion. As the species on the surface of the oxides, OH⁻ and/or H₂O, depend on the ZPC (zero
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 H2O, 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

\[
x_m = \frac{\Delta G}{RT} \alpha (1 - \alpha)
\]

where \(\Delta G\) is the maximum free energy of adsorption of the anion and \(\alpha\) is the degree of dissociation.

This expression gives a maximum at \(pH = pK_a\), when \(\alpha = 0.5\). If such a maximum is identified with the experimental value, \(V_m\), of maximum \(x_m\), it can be written

\[
x_m = 4V_m \alpha (1 - \alpha).
\]

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 \(\Delta G\) 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 \(pK_a\) 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
where \( K_1, K_2, \) and \( K_3 \) are dissociation constants for phosphoric acid. Then

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

If the numerator is called \( N \),

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

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

\[
P_a = C_1(\mu_{H_3PO_4} + \mu_{\Sigma \text{anions}})
\]

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

\[
\ln(\alpha(1 - \alpha)) = \ln [H_3PO_4] + \ln ([H_2PO_4^- + HPO_4^{2-} + PO_4^{3-}]) - 2 \ln [P] = \ln [H_3PO_4] + \ln [\Sigma \text{anions}] - 2 \ln [P].
\]

And, multiplying by \( RT \),

\[
RT \ln(\alpha(1 - \alpha)) = \mu_{H_3PO_4} + \mu_{\Sigma \text{anions}} - \mu_{H_3PO_4} - \mu_{\Sigma \text{anions}} - 2RT \ln [P]
\]

\[
= \mu_{H_3PO_4} + \mu_{\Sigma \text{anions}} - \mu_{\text{total}}
\]

where \( \mu_{\text{total}} = \mu_{H_3PO_4} + \mu_{\Sigma \text{anions}} + 2RT \ln [P] \).

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

\[
x_m = C_1(\mu_{H_3PO_4} + \mu_{\Sigma \text{anions}})
\]

where \( C_1 \) is a constant whose meaning will be discussed later.
Substituting the value of $\mu_{H_3PO_4} + \mu_{E_{\text{anions}}}$ taken from equation (6),

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

where $\alpha(1 - \alpha)$ is a function of $[H^+]$, $C_2 = 2.303 R C_1$, 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 $\mu_{\text{total}}^0$ 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.
**TABLE 1**
Linear correlation coefficients and constants calculated from equation (8) for the oxides studied here

<table>
<thead>
<tr>
<th>Oxide</th>
<th>$r$</th>
<th>$C_1$</th>
<th>$\mu^0_{\text{Total}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gibbsite</td>
<td>0.9467***</td>
<td>4.99 x 10^{-3}</td>
<td>13,986</td>
</tr>
<tr>
<td>Boehmite</td>
<td>0.8145*</td>
<td>2.94 x 10^{-4}</td>
<td>16,562</td>
</tr>
<tr>
<td>Corundum</td>
<td>0.9213***</td>
<td>1.31 x 10^{-3}</td>
<td>21,508</td>
</tr>
<tr>
<td>Goethite</td>
<td>0.9786***</td>
<td>8.38 x 10^{-3}</td>
<td>29,269</td>
</tr>
<tr>
<td>Lepidocrocite</td>
<td>0.9913***</td>
<td>1.66 x 10^{-2}</td>
<td>18,294</td>
</tr>
<tr>
<td>Hematite I</td>
<td>0.8604**</td>
<td>1.65 x 10^{-4}</td>
<td>30,652</td>
</tr>
<tr>
<td>Hematite II</td>
<td>0.9573***</td>
<td>2.80 x 10^{-3}</td>
<td>18,669</td>
</tr>
<tr>
<td>Anatase</td>
<td>0.9442***</td>
<td>5.07 x 10^{-3}</td>
<td>11,055</td>
</tr>
<tr>
<td>Pyrolusite</td>
<td>0.9736***</td>
<td>1.90 x 10^{-4}</td>
<td>20,234</td>
</tr>
</tbody>
</table>

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)

<table>
<thead>
<tr>
<th>Reference</th>
<th>r</th>
<th>$C_1$</th>
<th>$\mu_{\text{total}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1967</td>
<td>0.9940***</td>
<td>$3.40 \times 10^{-3}$</td>
<td>27,671</td>
</tr>
<tr>
<td>1968</td>
<td>0.9993***</td>
<td>$2.58 \times 10^{-3}$</td>
<td>28,374</td>
</tr>
<tr>
<td>1971</td>
<td>0.9978***</td>
<td>$5.07 \times 10^{-3}$</td>
<td>31,325</td>
</tr>
</tbody>
</table>

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Aluminium oxides

Iron oxides

- Gibbsite
- Goethite A (Hingston et al., 1971)
- Corundum
- Goethite (Hingston et al., 1968)
- Boehmite
- Hematite II
- Lepidocrocite
- Hematite I
- Goethite

**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.

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REFERENCES


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