

RADIOTRACER TECHNIQUE IN ADSORPTION STUDY, PART II*. ADSORPTION OF PHOSPHATE IONS ON CHROMIUM METAL POWDER

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The adsorption of phosphate ions on chromium metal powder from aqueous solutions of sodium dihydrogen phosphate labelled with ^{32}P has been studied as a function of concentration (10^{-3} to 10^{-6} mol l $^{-1}$), temperature (303--323 K), and pH (3.5--10.6) of the adsorptive solution. The time for the equilibrium establishment was found to be about 4 hours and it is dependent on the solution acidity. The smooth and continuous growth of phosphate adsorption follows the first order kinetics and the rate constants are found to be of the order of 10^{-3} min $^{-1}$. The results show that the adsorption in the system under study obeys the Freundlich isotherm. The increase in temperature from 303 K to 323 K does not effect the process markedly. The adsorption kinetics of phosphate ions is highly dependent on pH of the adsorptive solution. On the basis of the present data the nature and mechanism of the adsorption are discussed.

In recent years, studies on metal/solution interfaces¹⁻⁸ have been a subject of much interest in deciding about the qualitative and quantitative aspects of adsorption of ions which play an important role in various phenomena like corrosion, passivity or heterogeneous catalysis as well as in determining the role of metals in the double layer structure. Investigations are also in progress for the placement of monolayer of desired species onto metallic electrode surfaces⁹⁻¹¹ through adsorption enabling the electrode to carry out a specific function. However, one of the current approaches to improve fuel cell performance is to use phosphoric acid as an electrolyte¹² in which the adsorbed phosphate species on the electrode surface may be responsible for the increase of the cell performance in the energy conversion.

A literature survey reveals numerous investigations¹³⁻¹⁷ dealing with the adsorption of phosphate ions on different metals. These studies are mainly oriented towards regularity and mechanism of adsorption on metals as a function of pH and time of contact of the solution with the metal. Nevertheless, the maximum and minimum phosphate adsorption was explained on the basis of H^+ and OH^- ion adsorption in the acidic and alkaline pH ranges. A monolayer uptake of phosphate ions on iron

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surface has been reported by Thomas¹⁸ and the mechanism of oxide film formation on tantalum and niobium in phosphoric and sulphuric acids has been discussed by Randall *et al.*¹⁹. Kazarinov *et al.*²⁰ have also investigated the adsorption of H_2PO_4^- and SO_4^{2-} ions on platinized platinum surfaces and their findings were in agreement with the work of Horányi *et al.*^{16,17} who investigated the potential and concentration dependence of specific adsorption of anions (Cl^- , HSO_4^- , H_2PO_4^-) at low concentrations in 1M- HClO_4 supporting electrolyte. According to Bakirov and coworkers²¹ the sorption characteristics of orthophosphate ions on copper and nickel is suitably described by the Freundlich isotherm. While studying the kinetics of adsorption of orthophosphate ions on metal oxides and zirconium metal powder, Vissers²² observed that the process was probably diffusion controlled and made an effort to correlate the phosphate sorption with BET surface area of the adsorbent. These results further indicated that the monolayer coverage, describing a fixed stoichiometry existing between the sorbed phosphate molecules and the metal oxide sites present on the surface, exists for a fairly wide range of conditions. Yasunaga and coworkers²³ dealt with the kinetics and mechanism of the adsorption-desorption of mono- and divalent phosphate ions on $\gamma\text{-Al}_2\text{O}_3$ surface which has been classified from static and kinetic analyses on the basis of model proposed by Davis *et al.*²⁴. The latter investigations revealed that the adsorption rate of divalent phosphate is much faster than that of the monovalent ion. A recent investigation on the electrochemical adsorption of phosphoric acid on platinum and gold electrodes from the aqueous solution has been reported by Bockris *et al.*²⁵. Using the combination of radiotracer and FTIR measurements, they have discussed various aspects of adsorption and proposed a valid model.

The preceding brief review of literature shows that there is no systematic study dealing with the phosphate ion adsorption on chromium metal surface, particularly at micro and tracer concentrations. However, phosphate is always found in natural waters and in most waste waters in such low concentration ranges. Furthermore, adsorption on chromium metal was chosen because of its paramount importance in industrial applications as corrosion-resistant material and in refractories. With respect to the facts mentioned above, this paper presents some interesting results on the regularity and mechanism of the phosphate ion adsorption on chromium metal powder obtained by the study of the dependence of adsorption on various relevant factors such as concentration, temperature, and pH of the adsorptive solution.

EXPERIMENTAL

Chemicals and procedure. All stock solutions were prepared from redistilled water and A.R. grade chemicals. Chromium metal powder (99% pure) of 100 mesh was obtained from Fischer Scientific Company (U.S.A.) and used as such without any further treatment. Carrier-free ^{32}P as H_3PO_4 in the dilute HCl solution was supplied by the Bhabha Atomic Research Centre, Trombay, Bombay (India). This radioactive solution was diluted prior to labelling to obtain the

required specific activity. The adsorption solutions of required concentrations were prepared from the stock solution of $\text{NaH}_2\text{PO}_4 \cdot 2 \text{H}_2\text{O}$ (0.1 mol l^{-1}) by successive dilution. The adsorptive solutions of a particular concentration and pH were obtained by adding suitable quantity of the stock solution with the calculated amount of HCl and NaOH. The pH of these solutions was checked using the Elco pH-meter (Model LI-12T, India) with glass and calomel electrodes. The accuracy of the instrument was ± 0.01 pH. $50 \mu\text{l}$ of the radioactive solution was used to label 10.0 ml of adsorptive solution throughout the investigations.

The procedure consists of keeping weighed quantity of chromium powder (0.100 g) in 10.0 ml of the labelled adsorption phosphate solution of the required concentration and acidity in a conical glass centrifuge tube (Vensil). The whole system was thermostatted at the required temperature. Unless otherwise specified, all experiments were carried out at 303 K except in the temperature-dependence studies, where temperature was varied from 303 to 323 K . During the total period of adsorption, the solution was constantly stirred at a regular interval with uniform speed so that the sphere of the concentration gradient around one particle does not interfere with the other. Before adding the adsorbent, an aliquot of the bulk solution was withdrawn using $50 \mu\text{l}$ SIGMA micropipette for the measurement of the initial radioactivity. The progress of adsorption of phosphate ions with time was then followed by measuring the radioactivity of such withdrawals of the contact solution at definite time intervals. Special care was taken to avoid any particle coming with the solution. For this, tubes were placed in a centrifuge machine, centrifuged at 3000 rpm , and the solution was allowed to stand for 30 s before each withdrawal. To achieve the constant adsorption value and to be able to observe various steps of the adsorption, the experiments were carried out for 24 hours of contact time. Each aliquot was transferred to an aluminium planchette and dried slowly under infrared lamp. The radioactivities of all samples were measured using the end-window GM counter and the necessary corrections were made.

The relative amount of adsorption was evaluated adopting the differential method, *i.e.*, the difference between the activity (and hence concentration) before and after the addition of adsorbents, using the following relation:

$$a_d = \frac{R_0 - R_t}{R_0} c \frac{V}{m}, \quad (1)$$

where a_d is the amount adsorbed at time t (mol g^{-1}), R_0 and R_t are radioactivities of bulk at zero time and time t , respectively, c is initial concentration of the adsorptive solution (mol l^{-1}), V is the volume of the solution (l), and m is the mass of the adsorbent (g). Accuracy of the method was checked and evaluated to be $\pm 2\%$ in our experiments. For the sake of comparison, V/m ratio was kept constant throughout.

Desorption study. For the desorption study, the metal powders employed in adsorptive measurement, were washed three times with redistilled water and the radioactivity of the solution was measured after each washing. Subsequently, the desorptive solution (10.0 ml of water and non-radioactive phosphate solution of known concentration) was added to the solid. The time interval between adsorption and the beginning of desorption was about 10 minutes. After shaking for various intervals, the progress of desorption was measured during the period of 24 hours in the same way as in the adsorption experiments.

RESULTS AND DISCUSSION

The results reported here are the average of, at least, three independent measurements. Figs 1 to 3 show the results of the time growth of the phosphate ions adsorption

from aqueous solutions of sodium dihydrogen phosphate on chromium metal powder at various phosphate concentrations, temperature, and pH, respectively. These curves (a plot of the amount of the adsorbed phosphate ion in mol g^{-1} vs time) clearly reveal that the smooth and continuous growth of the phosphate ion adsorption is fast at the initial stages, becoming slower later on and ultimately reaching saturation. The time required to reach saturation is about 4 hours at all the concentrations studied (Fig. 1) and it varies from 4 to 8 hours with the increasing pH (Fig. 3). No further change was observed up to 24 hours of contact in all the cases. The kinetics and mechanism of the adsorption seem to be similar as the general nature of these curves is found to be essentially the same in all experiments.

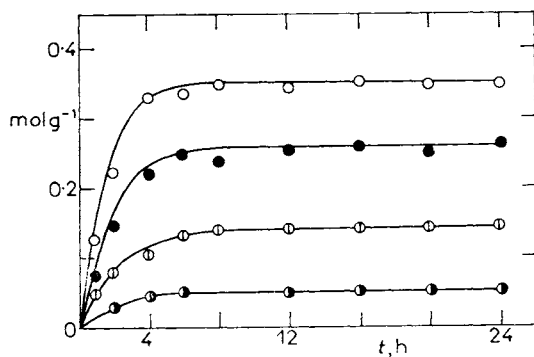


FIG. 1

Time variation of adsorption of H_2PO_4^- ions on chromium metal powder at various concentrations: ● $\cdot 10^4$; ○ $\cdot 10^5$; ● $\cdot 10^6$; ○ $\cdot 10^7$; 303 K, pH 4.0

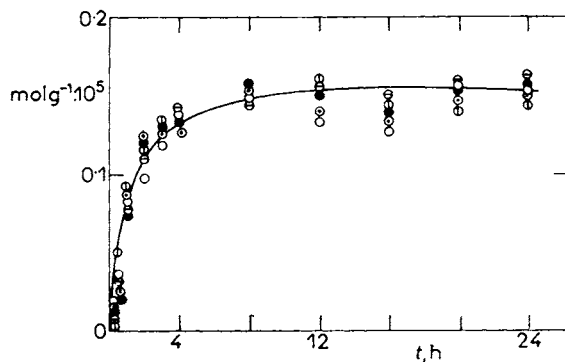


FIG. 2

Temperature effect on adsorption of H_2PO_4^- ions on chromium metal powder: ○ 323 K, ○ 318 K, ● 313 K, ○ 308 K, ○ 303 K $10^{-4} \text{ mol l}^{-1}$, pH 6.0

A steep increase of the curves at lower concentrations of adsorption (Fig. 1) clearly indicates that the relative fraction of adsorption (%) increases with an increase of dilution. Such characteristics are seemingly due to the lower number of phosphate species available at lower concentration in comparison to greater number of sorption sites on the surface of chromium. Smooth and continuous growth up to saturation, beyond which no further change is found (*vide supra*) despite long duration of the contact time (24 hours), suggests that the process involved is uniform and unaccompanied by any complication.

In the present work a simple kinetic analysis of the adsorption process has been worked out. This reveals that the adsorption on chromium metal follows the first-order adsorption rate expression (Fig. 4) of Lagergren²⁶:

$$\log(a_e - a_t) = \log a_e - \frac{k}{2.303} t, \quad (2)$$

where a_e is the amount of phosphate adsorbed at equilibrium, a_t is the amount adsorbed at time t , and k is the adsorption rate constant. The rate constants (Table I at 303 K and pH 4.0) were evaluated from the slope of the straight line applying the least squares fit procedure. It is noteworthy that the values of k are of the same

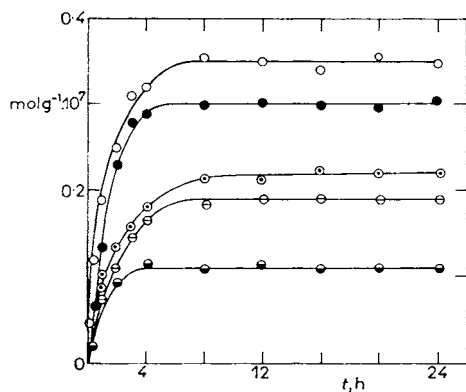


FIG. 3

Time variation of adsorption of phosphate ions on chromium metal powder at different pH: \ominus 3; \bullet 3.5; \circ 4; \odot 5; \ominus 7-10.7. $10^{-6} \text{ mol l}^{-1}$, 303 K

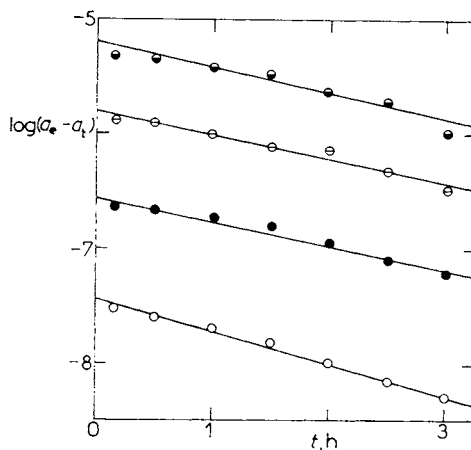


FIG. 4

Plot of $\log(a_e - a_t)$ vs time for the adsorption of H_2PO_4^- ions on chromium metal powder; concentration, mol l^{-1} : \bullet 10^{-3} ; \circ 10^{-4} ; \bullet 10^{-5} ; \circ 10^{-6} , 303 K; pH 4.0

order (10^{-3} min^{-1}) at all the concentrations studied. This would indicate that the adsorption rate is independent of the saturation value of adsorption. Similar results on the first-order adsorption kinetics have also been reported earlier²⁷⁻²⁹.

Furthermore, the concentration dependence of adsorption was analysed from the equilibrium data in the concentration range of 10^{-3} – $10^{-6} \text{ mol l}^{-1}$ (Table I). The plot of the logarithm of saturation adsorption against the logarithm of equilibrium concentration gives a straight line (Fig. 5), corroborating the validity of the Freundlich isotherm ($a_e = Kc_e^b$). The slope, b , and intercept, K , are found to be 0.68 and $6.9 \cdot 10^{-4} \text{ mol g}^{-1}$, respectively. These values were refined by applying the least squares fit method. The value of b ($0 < b < 1$) refers to the incomplete saturation of the surface together with an exponential distribution of the energy of adsorption sites^{30,31}. In the present case, the value of K would refer to the adsorption capacity of the chromium surface. The applicability of Freundlich isotherm has been reported previously^{21,32} for the phosphate ion adsorption on copper, nickel, and platinum metals.

The temperature dependence of adsorption (303–323 K) was studied with $10^{-4} \text{ mol l}^{-1}$ adsorptive solution of pH 6.0. Present results at various temperatures show that the kinetics and amount adsorbed remain unchanged from 303 K to 323 K. It is evident (Fig. 2) that both the equilibrium and pre-equilibrium values of adsorption remain almost constant at the temperatures studied. The time variation of adsorption with temperature is given in Table II. It is interesting to note that the time required to attain saturation is not affected by the corresponding variation in temperature. Similar results on temperature independence in the range 296–333 K are reported by Yap *et al.*³³ and Kulkarni³⁴. Also the effect of temperature on the trace adsorption has been found to be very small and the adsorption was nearly constant in the range 273–333 K for many systems^{35,36}. To ascertain definitively about

TABLE I

Kinetic data for the adsorption of H_2PO_4^- ions on chromium metal powder (temperature 303 K, pH 4.0): intercept $K = 6.9 \cdot 10^{-4} \text{ mol g}^{-1}$, slope $b = (0.68 \pm 0.02)$

Initial adsorptive concentration mol l^{-1}	Equilibrium concentration of the bulk $c_e \text{ mol l}^{-1}$	Amount adsorbed (saturation value) $a_e \text{ mol g}^{-1}$	Rate constants $k \cdot 10^3 \text{ min}^{-1}$
$1.0 \cdot 10^{-3}$	$0.95 \cdot 10^{-3}$	$0.05 \cdot 10^{-4}$	8.5 ± 0.8
$1.0 \cdot 10^{-4}$	$0.86 \cdot 10^{-4}$	$0.14 \cdot 10^{-5}$	8.1 ± 0.5
$1.0 \cdot 10^{-5}$	$0.74 \cdot 10^{-5}$	$0.26 \cdot 10^{-6}$	8.1 ± 0.4
$1.0 \cdot 10^{-6}$	$0.65 \cdot 10^{-6}$	$0.35 \cdot 10^{-7}$	10.7 ± 0.3

the observed temperature independence, low temperature studies are indeed required. Nonetheless, it seems likely that adsorption, in the present case, has a similar behaviour with respect to lower temperature (below room temperature) as reported in earlier studies. If this would be the case then adsorption should definitely decrease

TABLE II

Temperature dependence of the adsorption of H_2PO_4^- ions on chromium metal powder (concentration $1 \cdot 10^{-4} \text{ mol l}^{-1}$, pH 6.0)

Time h	Phosphate adsorbed $\cdot 10^5, \text{ mol g}^{-1}$				
	303 K	308 K	313 K	318 K	323 K
0.16	0.010	0.015	0.013	0.012	0.011
0.50	0.038	0.024	0.021	0.036	0.050
1.00	0.084	0.080	0.076	0.085	0.083
2.00	0.101	0.116	0.118	0.118	0.125
3.00	0.121	0.129	0.131	0.127	0.130
4.00	0.139	0.128	0.135	0.137	0.138
8.00	0.150	0.153	0.155	0.149	0.147
12.00	0.138	0.151	0.150	0.155	0.160
16.00	0.142	0.146	0.143	0.153	0.141
20.00	0.149	0.160	0.150	0.158	0.140
24.00	0.151	0.150	0.153	0.163	0.148

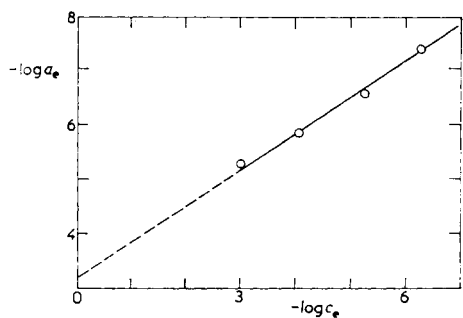


FIG. 5

Plot of $\log a_e (\text{mol g}^{-1})$ vs $\log c_e (\text{mol l}^{-1})$ for the adsorption of H_2PO_4^- ions on chromium metal powder, 303 K, pH 4.0

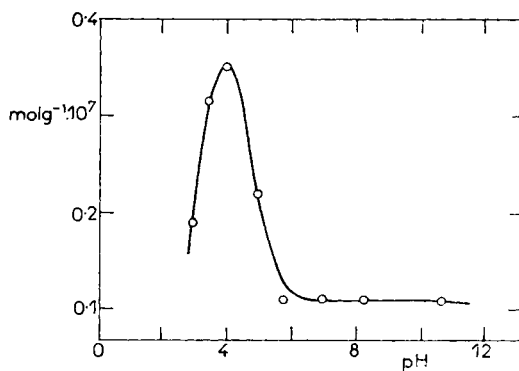


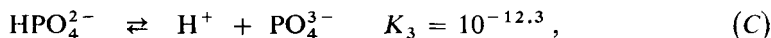
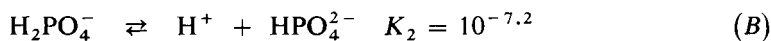
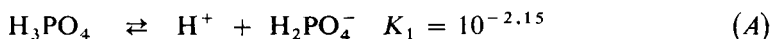
FIG. 6

Effect of pH on adsorption of phosphate ions (at equilibrium) on chromium metal powder. $1.0 \cdot 10^{-6} \text{ mol} \cdot \text{l}^{-1}$, 303 K

with reduction in temperature, which is a characteristic of either an endothermic chemical process or an activated adsorption at the surface.

The influence of pH (3.5–10.6) on the adsorption of phosphate ions on chromium metal surface was studied at 10^{-6} mol l⁻¹ phosphate concentration (Fig. 3). The plot of the amount adsorbed at equilibrium against initial pH is shown in Fig. 6. It would be evident from this figure that the adsorption increases rapidly with the increasing pH up to a maximum value at about pH 4.0, followed by a decrease up to pH 6.0 and thereafter with further increase in pH, it becomes practically constant. It is worth noting that the adsorption of phosphate ions on chromium metal is favoured in the acidic pH range. However, the adsorption of phosphate is found to be inhibited in aqueous and alkaline pH.

The adsorption of phosphate ions on solids is rather complex than that of other anions. While considering the adsorption of phosphate species from solutions by solids, it is well argued that pH markedly affects the states of adsorbents. The possible states of phosphate species in aqueous solution are molecules and ions, according to the following dissociation reactions³⁷:



where K_1 , K_2 , and K_3 are the respective dissociation constants at the room temperature. Owing to the presence of H^+ and OH^- ions in the solution, the amount of different forms of phosphate species differs and results in different adsorbability. Beneš *et al.*³⁸ have shown that the radiophosphorus is always present in the form of pseudocolloidal particles in trace concentrations. These colloids are negatively charged or neutral and are formed by the adsorption of H_2PO_4^- (also HPO_4^{2-}) on the colloidal impurities in the solution. They are present in fresh solution but their relative amount increases with the age of solution. The amount of colloids is also dependent on pH and exists predominantly in solutions of pH 4.

According to the aforesaid arguments, the increase in adsorption up to pH 4.0, as observed in the present case, may be due to the increasing dissociation of phosphoric acid to H_2PO_4^- or to the greater content of pseudocolloids in the solution. The decrease in adsorption between pH 4 to 6 is presumably due to the reduced amount of pseudocolloids. The constant but appreciable amount of adsorption after pH 6 is due to the presence of HPO_4^{2-} ions whose adsorbability is found to be lower on negatively charged surfaces³⁹.

Another explanation for the pH dependence of adsorption of phosphate ions is connected with the presence of metal oxide film already present on the chromium

surface. ESCA study⁴⁰ has revealed the presence of chromium-rich oxide layer in which the chromium is present in the trivalent form. Considering the presence of surface oxide layer on metals, Herczyńska¹³ has explained the adsorption of phosphate ions by ion exchange mechanism. The occurrence of two maxima is reported for the anion adsorption, one in acidic and another one in neutral pH region. The maximum adsorption on chromium metal at pH 4.0 is in good agreement with Herczyńska hypothesis⁴¹. However, second maximum was not observed in the present investigation. Further, decrease in the adsorption of phosphate beyond pH 4.0 is also explicable either by the displacement of the oxide layer on the surface during adsorption or, partly, by water desorption which would be similar to the mechanism proposed by Bockris *et al.*²⁵ for the adsorption of phosphate species on platinum and gold surfaces.

The desorption of phosphate ions from chromium powder was also studied in water and in 10^{-6} mol l⁻¹ unlabelled phosphate solution. It was observed that no appreciable activity of adsorbed species was transferred from the metal powders to the solution for a period of 24 hours of contact. This suggests that adsorbed phosphate ions are firmly held on the metal surface supporting a strong bonding between the phosphate ions and the adsorbent metal surface. It appears that as a consequence of superposition of comparatively stronger coulombic interactions, the physically adsorbed species are converted to the final stable adsorption phase. Through radio-tracer experiments and contact potential measurements, Hackerman and Powers⁴² have also concluded that the passive chromium surface may consist of a very thin and normally undetectable oxide layer overlain by a chemisorbed monolayer of anions oriented with their negative dipoles out.

Overall results on the adsorption of phosphate ions on chromium metal powder indicate that the adsorption is of the first-order and obeys the Freundlich isotherm. Temperature does not seem to affect the adsorption at and above room temperature and the process is found to be highly dependent on pH. These results together with the fact that there is no appreciable desorption indicate that the involved adsorption is of chemical nature.

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