Adsorption Behavior of Phosphate Ion on the Iron(III) Complex of a Chelating Resin

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Phosphate ion in 0.1 M (1 M=1 mol dm^{-3}) sodium chloride solution was adsorbed selectively on the iron(III) complex of a chelating resin. Coordination unsaturated sites of the resin-bound iron(III) ion were considered to be the adsorption sites for phosphate ion, predominating species being dihydrogenphosphate ion ($H_2PO_4^-$). Adsorption capacity of the resin increased with the increasing amount of iron(III) ion loaded on the chelating resin, while the molar ratio of the adsorbed phosphate ion to the resin-bound iron(III) ion became less than unity, indicating that only a fraction of the resin-bound iron(III) ion acts as the adsorption site at higher iron content. The steric and electrostatic interactions among the phosphate ions in the resin matrix may interfere with the stoichiometric adsorption of phosphate ion on the resin-bound iron at higher iron content.

In a previous paper,[1] a report was given on the selective adsorption of arsenite and arsenate ions on the iron(III) complex of a chelating resin, with possible application to the removal of trace of arsenic from waste water of geothermal power plants.

Since the selective adsorption on such a resin is based on the coordination of anionic ligands to the coordination unsaturated sites of the resin-bound metal ion, adsorption of phosphate ion can also be expected on the iron(III) complex of the chelating resin. Such a process may be useful in the tertiary treatment of urban sewage for the effective removal of phosphate ion. This paper describes the nature of the iron(III) complex of chelating resin (Uniselec UR 10) as an adsorbent for phosphate ion.

Experimental

Materials. Uniselec UR 10 chelating resin (Unitika Ltd. Osaka) of 20—50 mesh size was used. Iron(III) complex of chelating resin was prepared by the following procedure.

An iron(III) ion solution prepared by dissolving 0.4—5.4 g of iron(III) chloride hexahydrate in 200 ml of 0.3 M sodium acetate–acetic acid buffer (pH 3.0) was mixed with 10 g of sodium form chelating resin which had been conditioned by successive washings with 2 M hydrochloric acid and sodium hydroxide solutions. The resulting iron(III) complex resin was washed with deionized water until the washings became free from iron(III) ion, sucked off, and stored in a sealed bottle in a refrigerator.

The iron content in the resin was measured on the acid eluate by EDTA titration, and expressed in terms of F (mmol/g of dry iron(III) resin). The iron contents ranged from 0.12 to 1.34. The water content was also determined on each grade of the iron(III) resin by measuring the weight loss after drying to constant weight at 110 °C. A stock solution of phosphate ion was prepared from potassium dihydrogenphosphate. All other reagents were of analytical grade.

Procedure for Adsorption Study. Adsorption equilibria were investigated by batchwise operation. A weighed amount of the iron(III) resin, *ca.* 0.5 g, was shaken with 50 ml of a buffered solution containing phosphate ion at a constant temperature for 24 h, which is sufficient to attain approximate equilibrium. For determination of partition ratio and adsorption isotherms, respectively 1.3×10^{-3} M and $(6.4\times10^{-4}$—$3.3\times10^{-2})$ M of phosphate solution were used. The ionic strength of the solution was adjusted to 0.1—0.2 with sodium chloride.

After equilibration, the phosphate ion concentrations were determined by molybdenum blue photometry on solution and resin phases, the latter being analyzed on the 2 M hydrochloric acid eluate.

The partition ratio, K_{ad}, of phosphate ion between aqueous and resin phases can be expressed by

$$K_{ad} = Q/C$$

where C and Q are the phosphate ion concentration in solution (M) and in iron(III) resin(mmol/g of dry iron(III) resin), respectively. Although wet resin was used throughout the experiment, the corrections were made for dry resin by estimating the water content of the wet resin.

Instruments. A Toa model HM-5A pH meter and Shimadzu MPS-50L spectrophotometer were used.

Results and Discussion

Nature of the Iron(III) Chelating Resin. Uniselec UR 10 chelating resin used in the experiment has a three-dimensional network structure containing an *N*-(*o*-hydroxybenzyl)iminodiacetic acid moiety as a chelating group. Since the chelating site has phenolic oxygen in addition to the iminodiacetic acid group which is often found in the conventional chelating resin such as Dowex A-1, the coordination site of the Uniselec resin behaves as a quadridentate ligand to iron(III) ion, resulting in a more stable chelate than that by the Dowex A-1 type resins. As a result, iron(III) ion is so tightly bound to the resin that it is not easily released from the resin even in the presence of a large excess of alkali and alkaline earth cations above pH 3.

Iron(III) ion which is coordinatively hexavalent is bound to the Uniselec resin under so called "coordination unsaturated" conditions, leaving two coordination sites aquated. The sites are expected to act as adsorption sites for the coordinating anions as suggested by Helfferich.[2] A report appeared on the selective adsorption of arsenite and arsenate ions by the iron(III) chelating resin.[1]

pH *Dependence of the Partition Ratio, K_{ad}.* Figure

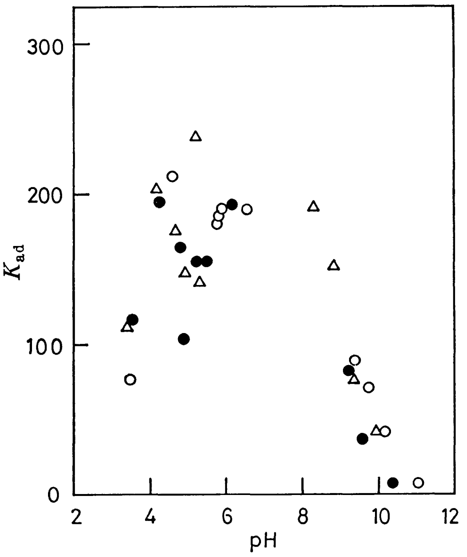

Fig. 1. pH profile of partition ratio, K_{ad}, of the iron(III) resin (F=1.25) at 35 °C. In acidic region, buffered with 0.1 M acetate buffer. In alkaline region, buffered with 0.1 M ammonia-ammonium chloride (○) or with 0.1 M ammonia-ammonium nitrate either in the presence (△) or absence (●) of 0.1 M sodium chloride.

1 shows the pH dependency of the partition ratio, K_{ad}, of phosphate ion at 35 °C. The pH of the aqueous phase was buffered with 0.1 M acetic acid–sodium acetate in the acidic region, and with 0.1 M ammonia–ammonium chloride (○) or 0.1 M ammonia–ammonium nitrate (●, △) in the alkaline region. The symbol (△) shows the partition ratio in the presence of 0.1 M sodium chloride. Though the points are scattered, the adsorption of phosphate seems to be most favorable in the pH region 4—7. The K_{ad} value decreases rapidly with variation in pH on either side of the optimum region. If we consider the acid dissociation constants of phosphoric acid (pK_a; 2.06, 7.03, 12.1), such a pH profile suggests the univalent dihydrogenphosphate ion to be responsible for adsorption. Since the presence of chloride ion gives no adverse effect on K_{ad} value, the adsorption is not due to the ion-exchange reaction.

The nature of the iron(III) resin changes with variation in pH. When pH<1, iron(III) ion may be displaced from the resin with proton, resulting in the loss of adsorption capacity. With increase in pH, the proton dissociation of coordinated water on the resin bound iron(III) ion might occur, forming monohydroxo- and dihydroxo species.

This has been discussed by Harris *et al.*[3] on the iron(III) chelate of monomeric *N*-(*o*-hydroxybenzyl)-iminodiacetic acid in aqueous solution, where the proton dissociation constants of diaquated iron(III) chelate were found to be:

$$\mathrm{FeL(OH_2)_2} \rightleftharpoons \mathrm{FeL(OH_2)(OH)^-} + \mathrm{H^+} \qquad \log K = -5.71$$

$$\mathrm{FeL(OH_2)(OH)^-} \rightleftharpoons \mathrm{FeL(OH)_2{}^{2-}} + \mathrm{H^+} \qquad \log K = -9.1$$

where H_3L denotes the free ligand. If we assume a similar proton dissociation scheme on the resin bound diaquated iron(III) ion, it may behave as a dibasic acid (Fig. 2).

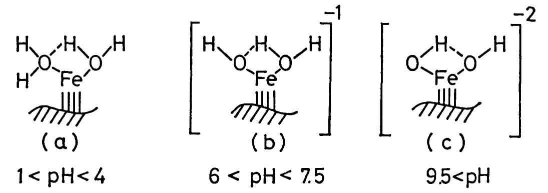

Fig. 2. Possible states of the resin bound iron(III) ion.

Species (a), (b), and (c) may predominate in the pH regions <4, 6—7.5, and >9.5, respectively. The electrostatic repulsion between the resin bound iron(III) ion and phosphate ion becomes larger in the order (a)<(b)<(c). At the same time, the resistance to the ligand exchange reaction between phosphate ion and the hydrolyzed species would become larger in the order (a)<(b)<(c). Thus, of the three states of the iron(III) resin, the most favorable one for the adsorption of phosphate ion seems to be (a), showing the optimum K_{ad} value in a weakly acidic region.

Adsorption Isotherms with the Iron(III) Resin. The effect of temperature on the adsorption isotherms of phosphate ion with the iron(III) resin is shown in Fig. 3, where the resin of F=1.34 was used at pH 6.0 with ionic strength *ca.* 0.2. The effect of iron(III) ion content on the adsorption isotherms under similar experimental conditions at 35 °C is shown in Fig. 4. The phosphate uptake by the resin, Q, increases with rise in temperature and increase in the iron(III) ion content. It also increases with increase in phosphate ion concentration in the aqueous phase, C, approaching saturation at higher phosphate ion concentration. The results suggest that the adsorption of phosphate is a chemical reaction and that the adsorption sites are the resin bound iron(III) ions.

The adsorption of phosphate ion can be considered to be the ligand exchange reaction between the coordinated water and the phosphate ion. If we assume that the reacting species of the resin bound iron(III) ion is mainly in the state (a), the reaction can be schematically written as follows.

$$\mathrm{RFe(OH_2)_2} + \mathrm{H_2PO_4^-} \overset{K_{eq}}{\rightleftharpoons} \mathrm{RFe(H_2PO_4)^-} + 2\mathrm{H_2O} \qquad (1)$$

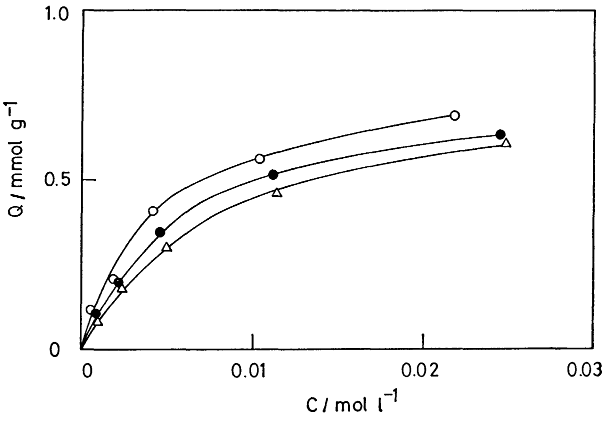

Fig. 3. Adsorption isotherms of the iron(III) resin (F=1.34) at different temperatures (pH=6.0, $\mu \approx 0.2$). —○— 35 °C, —●— 25 °C, —△— 8 °C.

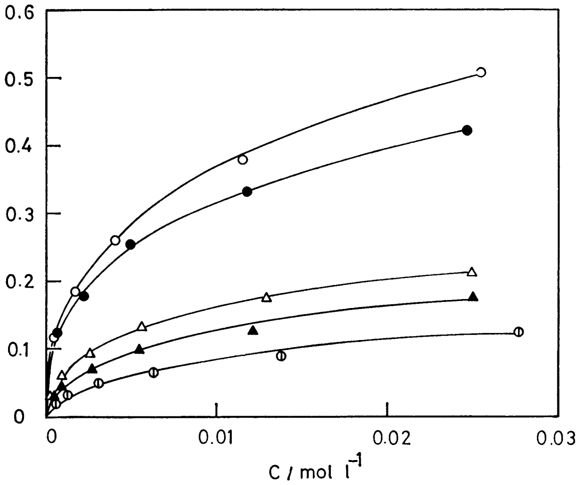

Fig. 4. Adsorption isotherms of the iron(III) resin of various iron contents at 35 °C (pH=6.0, $\mu \approx 0.2$). —○— F=0.88, —●— 0.64, —△— 0.31, —▲— 0.23, —⦶— 0.12.

where $RFe(OH_2)_2$ denotes the resin bound iron(III) ion. The equilibrium constant of this reaction can be given by

$$K_{eq} = \frac{X_{RFe(H_2PO_4)^-}}{X_{RFe(OH_2)_2}} \cdot \frac{1}{C} \tag{2}$$

where the mole fractions of unadsorbed and adsorbed sites in the resin, and the molar concentration of phosphate ion in the aqueous phase are expressed as $X_{RFe(OH_2)_2}$, $X_{RFe(H_2PO_4)^-}$, and C, respectively.

The mole fraction of adsorbed site can be written as

$$X_{RFe(H_2PO_4)^-} = \frac{A}{WQ_\infty} = \frac{Q}{Q_\infty} \tag{3}$$

where A is the amount of phosphate adsorbed (mmol) on W g of the iron(III) resin ($Q=A/W$), and Q_∞ is the saturated adsorption capacity of the resin.

By means of the relation

$$X_{RFe(OH_2)_2} + X_{RFe(H_2PO_4)^-} = 1, \tag{4}$$

Eq. 2 can be written as

$$C = -\frac{1}{K_{eq}} + Q_\infty\left(\frac{C}{Q}\right). \tag{5}$$

Thus, the plots of C against C/Q should give a straight line, from which $-1/K_{eq}$ and Q_∞ can be obtained from the intercept and slope, respectively.

The isotherms of the resins of various iron(III) ion contents at various temperatures were treated by means of Eq. 5 where the phosphate ion concentrations of the aqueous phase were in the range (3.2×10^{-4}—2.9×10^{-2}) M after equilibration. The results are shown in Figs. 5 and 6, respectively. The values for K_{eq} and Q_∞, obtained from the intercept and slope of each line drawn by the method of least squares, are summarized in Table 1.

Equilibrium constant, K_{eq}, increased with increase in temperature, indicating that the adsorption is a

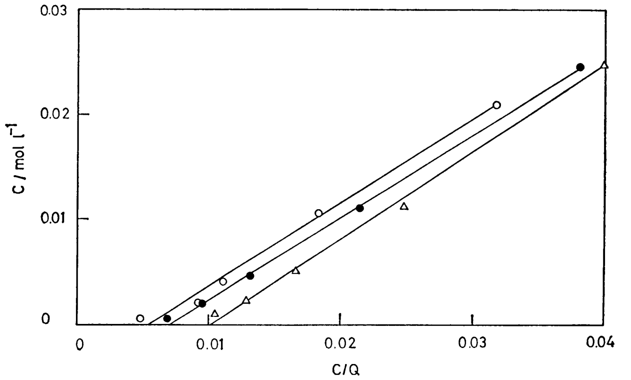

Fig. 5. C vs. C/Q plots at different temperatures. —○— 35 °C, —●— 25 °C, —△— 8 °C.

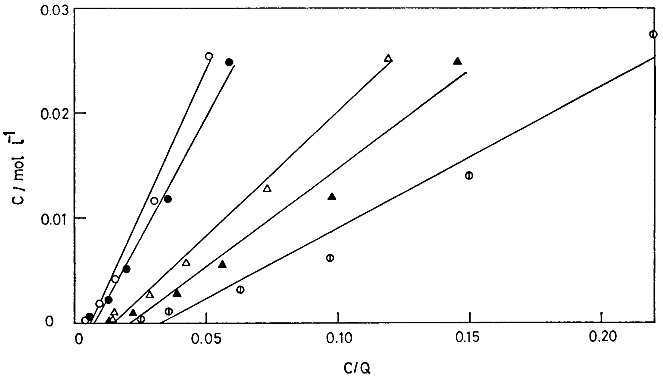

Fig. 6. C vs. C/Q plots on the resin of different iron contents. —○— F=0.88, —●— 0.64, —△— 0.31, —▲— 0.23, —⦶— 0.12.

TABLE 1. PARAMETERS FOR THE ADSORPTION ON PHOSPHATE ION BY IRON(III) COMPLEX OF CHERATING RESIN (pH=6.0, μ=0.2)

Resin			Parameters for Eq. 5		
Iron content F/mmol g⁻¹	Water content %	Temp °C	Q_∞ mmol g⁻¹	$K_{eq}\times10^{-2}$ l mol⁻¹	Q_∞/F
0.12	110.0	35	0.13±0.02	2.2±1.1	1.08±0.17
0.23	90.1	35	0.19±0.02	2.7±0.9	0.83±0.09
0.31	89.1	35	0.23±0.02	3.0±0.8	0.74±0.06
0.64	84.9	35	0.46±0.05	3.2±1.6	0.72±0.08
0.88	79.9	35	0.54±0.06	3.0±1.6	0.61±0.07
1.34	72.5	35	0.82±0.07	2.7±0.6	0.61±0.05
1.34	72.5	25	0.77±0.02	2.0±0.2	0.57±0.01
1.34	72.5	8	0.82±0.03	1.2±0.1	0.61±0.02

chemical process as shown by Eq. 1. Saturated capacity, Q_∞, does not change with temperature. It increases with increase in iron(III) ion content in the resin, indicating that the resin bound iron(III) ions act as the adsorption sites for phosphate ion.

We could expect a 1:1 binding ratio for phosphate ion: the resin bound iron(III) ion, since we found a 1:1 complex formation in the spectrophotometric study on the interaction of phosphate ion with the iron(III) chelate of *N*-(*o*-hydroxybenzyl)iminodiacetic acid in aqueous solution at pH 6.0.[4] However, as shown in Table 1, the stoichiometric ratio, Q_∞/F, indicates that only one half of the resin bound iron(III) ions act as adsorption sites at higher iron(III) ion content, the value approaching unity with the decreasing iron(III) ion content. This suggests that, at higher iron(III) ion content, the electrostatic and steric repulsions among the phosphate ions in the resin matrix may interfere with the stoichiometric adsorption of phosphate to the resin-bound iron(III) ion, while at lower iron(III) ion content, the adsorption becomes more stoichiometric due to the smaller interaction among adsorbed phosphate ions.

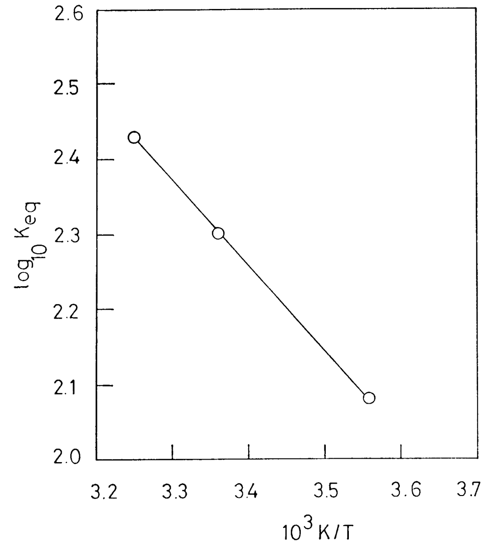

Fig. 7. Arrhenius plots for the standard heat of adsorption. Data from Table 1.

The equilibrium constant, K_{eq}, increases with increase in temperature. Thus we can estimate the apparent standard heat of adsorption from the Arrhenius plots (Fig. 7). The value $\Delta H=21.8$ kJ mol^{-1} is reasonable for the complex formation.

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References

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