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# Studies of the Selective Adsorption of Anions by Metal Ion Loaded Ion-exchange Resin. VI.[1] The Adsorption Behavior of the Phosphate Ion on the Iron(III) Loaded Ion-exchange Resin

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(Received June 6, 1983)

Adsorption isotherms for the phosphate ion by various iron(III)-loaded ion-exchange resins(IRC-Fe(III)), which are different in iron(III)-ion concentrations, were prepared at 5—35 °C in aqueous systems with pH values of 3 and 4.6 by means of the batch method. These isotherms could be represented by the $C_p = Q_\infty(C_p/Q) - 1/K$ equation in the phosphate-ion-concentration range from $3.23 \times 10^{-4}$ to $3.23 \times 10^{-2}$ mol dm$^{-3}$ (10 ppm to 1000 ppm as P), where $C_p$ and $Q$ are the phosphate-ion concentrations of the aqueous phase and the adsorbent respectively; $Q_\infty$ is the saturated phosphate concentration of the adsorbent, and $K$ is the equilibrium constant. From the analysis of adsorption isotherms, the values for $Q_\infty$ and $K$ were determined on each adsorbent, and the nature of the adsorbent IRC-Fe(III) was discussed, with consideration paid to these two parameters and the pH-dependency of the distribution ratio of the phosphate ion between the aqueous phase and the adsorbent.

In a previous paper,[2] we reported on the adsorption behavior of the phosphate ion on the iron(III)-loaded chelating resin(UR 10-Fe(III)) and on the evidence that the resin-bound iron(III) was the site for phosphate adsorption. While iron(III) is tightly held on UR 10 resin through the chelate formation with the *N*-(*o*-hydroxybenzyl)iminodiacetate moiety, our investigation was extended to find a better phosphate adsorbent using other types of chelating resins or cation-exchange resins. We finally found that the iron(III)-loaded weakly acidic carboxylate-type cation-exchange resins, such as Amberlite IRC-50 or diaion WK, were the most advantageous adsorbents for phosphate with regards to their adsorption capacity, thermal stability, iron-binding property, and recycling perfomances.[3] This paper describes the results of our detailed investigation of the adsorption behavior of the phosphate ion on the iron(III)-loaded Amberlite IRC-50.

## Experimental

*Materials.* The weakly acidic carboxylate-type cation-exchange resin, Amberlite IRC-50(30 to 50 mesh; proton-exchange capacity, 10.62 mequiv g$^{-1}$), was washed with 2 mol dm$^{-3}$ of sodium hydroxide and hydrochloric acid alternatively three times, and finally converted to the sodium form. Fifteen grams of the sodium-form resin was suspended for 24 h in 200 cm$^3$ of a 0.03 mol dm$^{-3}$ sodium acetate–acetic acid buffer solution of pH 3.0 containing from 0.7 to 5 g of iron(III) chloride hexahydrate. The resulting iron(III)-loaded Amberlite IRC-50(hereafter abbreviated as IRC-Fe(III)) was washed with deionized water until the washing became free from iron(III); it was then sucked and centrifuged . The IRC-Fe(III) adsorbent was sealed in a bottle and stored in a refrigerator.

The iron(III) content in the resin was determined spectrophotometrically on the acid eluate as has been described in a previous paper;[3] it was expressed in terms of $C_{Fe}$(mmol g$^{-1}$ of the dry adsorbent). The iron(III) contents ranged from 0.323 to 1.97 mmol g$^{-1}$, as is shown in Table 1. The water content of IRC-Fe(III) was determined on each batch by measuring the weight loss after drying to a constant weight at 110 °C immediately before the adsorption study.

A stock solution of phosphate was prepared from potassium dihydrogenphosphate. All the other reagents were of an analytical grade.

*Procedure for Adsorption Study.* An exactly weighed amount of IRC-Fe(III)(*ca.* 0.5 g) was shaken with 50 cm$^3$ of a buffered solution containing phosphate at a constant temperature for 48 h. This shaking time was found to be sufficient to attain an approximate equilibrium. For the observation of the adsorption isotherms, the pH of the aqueous phase was adjusted to 3.0 or 4.6 with 0.09 mol dm$^{-3}$ sodium sulfate or with 0.1 mol dm$^{-3}$ acetic acid–sodium acetate respectively. However, in the experiment at pH 3.0, the pH of the solution after equilibration deviated over the range from 2.5 to 3.3 because of the poor buffering capacity of the reagent. For the measurements of the distribution ratio, *D*, at various pHs, the pHs of the aqueous phases were adjusted with the use of 2 mol dm$^{-3}$ sodium hydroxide and 1 mol dm$^{-3}$ hydrochloric acid. The ionic strength of the aqueous phase was maintained at 0.3 and 0.15 with sodium chloride for the study of the adsorption isotherm and the distribution ratio respectively. After equilibration, the phoshate concentrations were determined spectrophotometrically by the molybdenum blue method on both aqueous and resin phases, the latter being analyzed on the eluate with 2 mol dm$^{-3}$ sodium hydroxide.[3] The percentages of the recovery of phosphate found in the adsorbent and in the aqueous phase against the initial phosphate concentration were 97.0 to 103%, with an average of 99.72±1.27% for 170 measurements.

The distribution ratio, *D*, of phosphate between the aqueous phase and the adsorbent is expressed as $D = Q/C_p$, where $C_p$ and $Q$ represent the phosphate-ion concentrations in the aqueous phase(mol dm$^{-3}$) and in the adsorbent(mmol g$^{-1}$ of dry adsorbent) respectively. While the wet adsorbent was used throughout the experiment, the corrections were made for the dry-adsorbent base by taking into account the water content of each wet adsorbent.

*Instruments.* A TOA HM-5A pH meter was used for the pH measurements, while a Shimadzu MPS-50L spectrophotometer was used for the absorbance measurements.

## Results and Discussion

*Adsorption Isotherms.* The effect of the iron(III) concentration of the resin, $C_{Fe}$, on the adsorption isotherms of phosphate at 35 °C is shown in Figs. 1(at pH

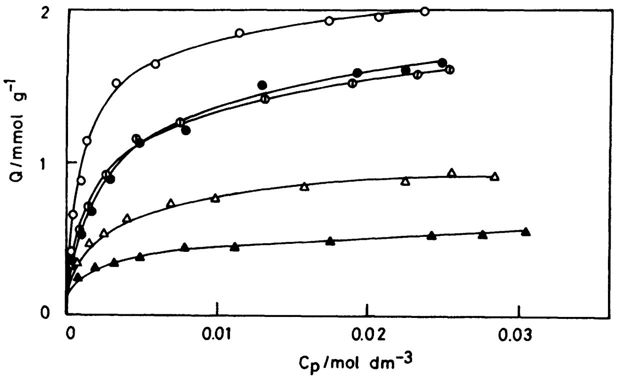

Fig. 1. Adsorption isotherms of phosphate ion by IRC-Fe(III) at 35 °C. pH 3, $I$=0.3.
—O—: $C_{\rm Fe}$=1.97 mmol g$^{-1}$, —●—: 1.81, —⦶—: 1.64, —△—: 0.950, —▲—: 0.726.

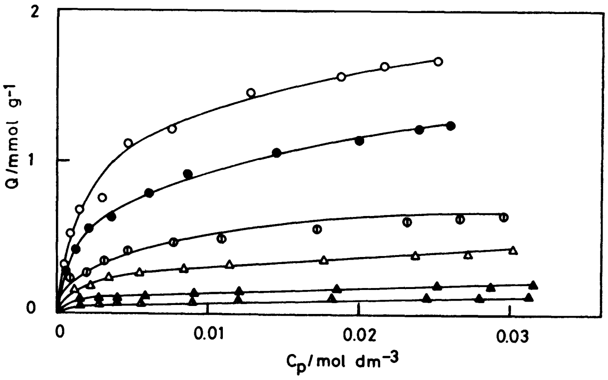

Fig. 2. Adsorption isotherms of phosphate ion by IRC-Fe(III) at 35 °C. pH 4.6, $I$=0.3.
—O—: $C_{\rm Fe}$=1.97 mmol g$^{-1}$, —●—: 1.75, —⦶—: 1.34, —△—: 0.993, —▲—: 0.469, —◭—: 0.323.

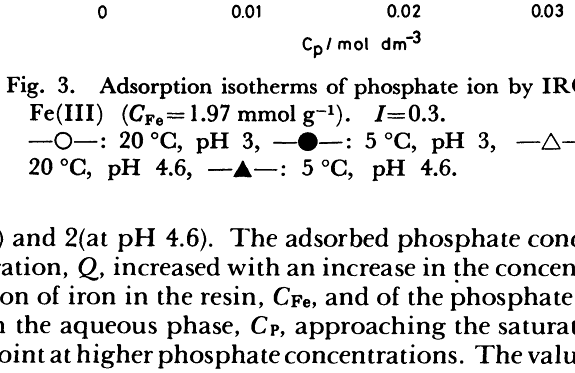

Fig. 3. Adsorption isotherms of phosphate ion by IRC-Fe(III) ($C_{\rm Fe}$=1.97 mmol g$^{-1}$). $I$=0.3.
—O—: 20 °C, pH 3, —●—: 5 °C, pH 3, —△—: 20 °C, pH 4.6, —▲—: 5 °C, pH 4.6.

3) and 2(at pH 4.6). The adsorbed phosphate concentration, $Q$, increased with an increase in the concentration of iron in the resin, $C_{\rm Fe}$, and of the phosphate ion in the aqueous phase, $C_{\rm P}$, approaching the saturation point at higher phosphate concentrations. The value of $Q$ also increased with a rize in the temperature in the range from 5 to 35 °C as is shown in Figs. 1 to 3.

Thus, the adsorption of phosphate is attributable to the ligand-exchange reaction of phosphate with the coordinated water on the resin-bound iron(III), as has been reported previously.2) Accordingly, the adsorp-

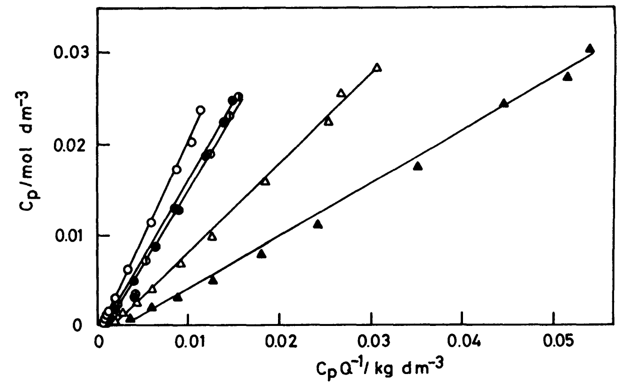

Fig. 4. $C_{\rm p}$ *vs.* $C_{\rm p}/Q$ plots on the adsorbent of different iron(III) concentration at 35 °C. pH 3, $I$=0.3.
—O—: $C_{\rm Fe}$=1.97 mmol g$^{-1}$, —●—: 1.81, —⦶—: 1.64, —△—: 0.950, —▲—: 0.726.

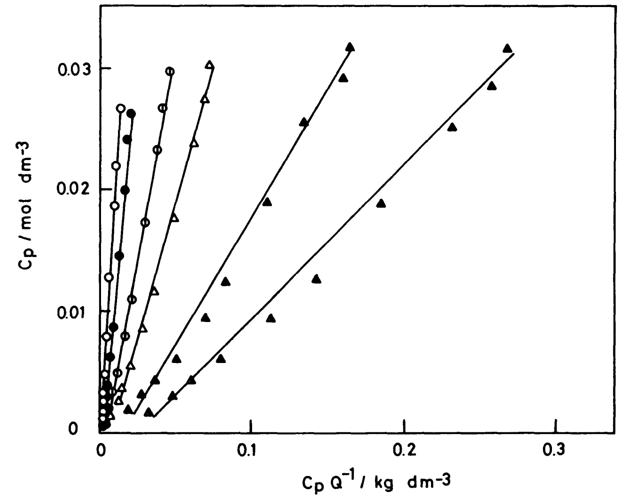

Fig. 5. $C_{\rm p}$ *vs.* $C_{\rm p}/Q$ plots on the adsorbent of different iron(III) concentration at 35 °C. pH 4.6, $I$=0.3.
—O—: $C_{\rm Fe}$=1.97 mmol g$^{-1}$, —●—: 1.75, —⦶—: 1.34, —△—: 0.993, —▲—: 0.469, —◭—: 0.323.

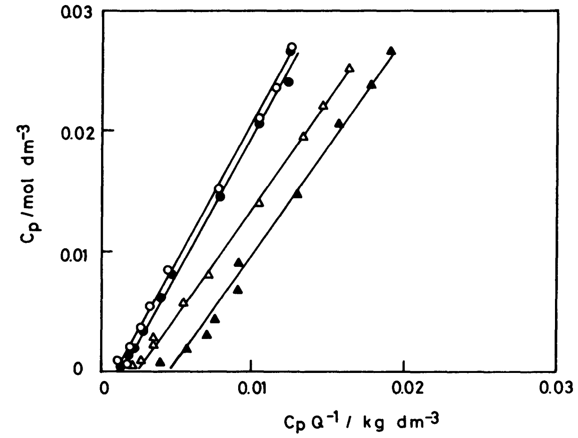

Fig. 6. $C_{\rm p}$ *vs.* $C_{\rm p}/Q$ plots on the adsorbent of $C_{\rm Fe}$= 1.97 mmol g$^{-1}$. $I$=0.3.
—O—: 20 °C, pH 3, —●—: 5 °C, pH 3, —△—: 20 °C, pH 4.6, —▲—: 5 °C, pH 4.6.

TABLE 1. ADSORPTION PARAMETERS FOR PHOSPHATE BY VARIOUS IRC-Fe(III)

| Temp °C | pH | $C_{Fe}$ mmol $g^{-1}$ | $Q_\infty$ mmol $g^{-1}$ | $K$ $dm^3$ $mol^{-1}$ | $Q_\infty C_{Fe}^{-1}$ |
|---|---|---|---|---|---|
| 35 | 3 | 1.97 | 1.97±0.04 | 618±41 | 1.00±0.02 |
| 20 | 3 | 1.97 | 1.99±0.04 | 478±19 | 1.01±0.02 |
| 5 | 3 | 1.97 | 2.19±0.09 | 240±11 | 1.11±0.05 |
| 35 | 3 | 1.81 | 1.78±0.05 | 400±12 | 0.983±0.03 |
| 35 | 3 | 1.64 | 1.69±0.02 | 548±14 | 1.03±0.01 |
| 35 | 3 | 0.950 | 0.979±0.016 | 518±18 | 1.03±0.02 |
| 35 | 3 | 0.726 | 0.578±0.010 | 481±18 | 0.796±0.014 |
| 35 | 4.6 | 1.97 | 1.87±0.03 | 294±25 | 0.949±0.015 |
| 20 | 4.6 | 1.97 | 1.76±0.03 | 239±15 | 0.893±0.015 |
| 5 | 4.6 | 1.97 | 1.81±0.06 | 111±10 | 0.918±0.03 |
| 35 | 4.6 | 1.75 | 1.39±0.03 | 265±24 | 0.793±0.015 |
| 35 | 4.6 | 1.34 | 0.692±0.012 | 309±30 | 0.516±0.009 |
| 35 | 4.6 | 0.993 | 0.440±0.010 | 293±38 | 0.443±0.010 |
| 35 | 4.6 | 0.469 | 0.204±0.000 | 292±35 | 0.435±0.000 |
| 35 | 4.6 | 0.323 | 0.123±0.003 | 285±34 | 0.381±0.009 |

tion isotherms can be treated by the linearized adsorption equation 1(in this equation, $Q_\infty$ and $K$ are the concentration of the saturated adsorbed phosphate and the equilibrium constant for the adsorption reaction respectively):

$$C_p = Q_\infty(C_p/Q) - 1/K. \tag{1}$$

Thus, the plots of $C_P$ against $C_P/Q$ should give a straight line with an intercept of $-1/K$ and a slop of $Q_\infty$. Such plots, corresponding to Figs. 1 to 3, are shown in Figs. 4 to 6 respectively. The values of $K$ and $Q_\infty$ were evaluated from these plots by the least-squares method; the results are summarized in Table 1.

In the experiment at pH 3, the concentration, $Q_\infty$, increased with the increase in the iron(III) concentration, $C_{Fe}$, while the molar ratio $Q_\infty/C_{Fe}$ was nearly equal to unity over the range from $C_{Fe}$=0.726 to 1.97, indicating that the resin-bound iron(III) is the adsorption site for phosphate. The adsorption equilibrium constant, $K$, was found to be from 400 to 618 at 35 °C, irrespective of the value of $C_{Fe}$.

In the experiment at pH 4.6, the value of $Q_\infty$ also increased with the increase in $C_{Fe}$, but the molar ratio of $Q_\infty/C_{Fe}$ was smaller than unity at lower iron concentrations and approached unity with the increase in the iron concentration. The value of $K$ was, in this case, evaluated as from 265 to 309 at 35 °C, irrespective of the value of $C_{Fe}$.

If one considers the molecular structure of Amberlite IRC-50, which is a cross-linked poly(acrylic acid), the different behavior of the adsorbent at pH 3 and 4.6 may be explained by the presence of free carboxyl groups in the adsorbent of a lower iron concentration. In the pH 3 region, these carboxyl groups remained undissociated, having little interaction with the resin-bound iron. At pH 4.6, however, the carboxyl groups, after deprotonation, became available for coordination to the resin-bound iron, giving the negatively charged tetracoordinated iron sites, which are not capable of ligand exchange with phosphate. The lower the iron concentration in the resin, the larger the fraction of inactivated adsorption sites in this pH region.

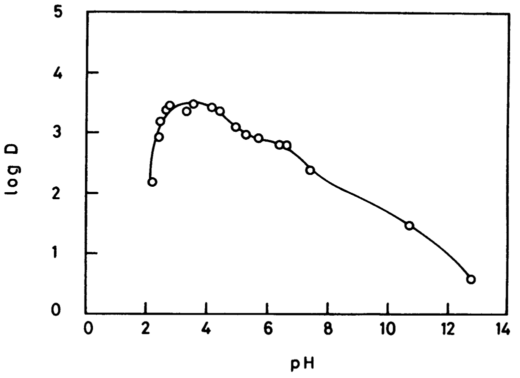

Fig. 7. pH profile of distribution ratio, $D$, of phosphate ion by IRC-Fe(III)($C_{Fe}$=1.97 mmol $g^{-1}$) at 35 °C. $I$=0.15.

*Effect of Temperature.* It may be seen from Figs. 1 to 3 that the $Q$ value increases with the rize in the temperature, while the $Q_\infty$ value remains almost constant over the temperature range from 5 to 35 °C, as shown in Table 1. Thus, the increase in the $Q$ value may be said to be due to the increase in the $K$ value in this temperature range.

*Effect of pH on the Distribution Ratio.* The distribution ratio of phosphate, $D$, at 35 °C on IRC-Fe(III)($C_{Fe}$=1.97 mmol $g^{-1}$) was markedly dependent upon the pH of the aqueous phase, as is illustrated in Fig. 7. In this experiment, the pH of the aqueous phase was adjusted with hydrochloric acid and sodium hydroxide, while the concentration of the phosphate ion in the aqueous phase, $C_p$, was kept in the range from $9.04\times10^{-5}$ to $1.90\times10^{-3}$ mol $dm^{-3}$ (2.8 to 59 ppm) after equilibration to make $Q$ considerably less than $Q_\infty$.

It may be seen from Fig. 7 that the adsorption of the phosphate ion is most appreciable in the pH range from 2.5 to 4.0. The $D$ value rapidly decreases beyond this optimum pH range. The pH profile of the distribution ratio is similar to that of UR10-Fe(III) reported previously,[2] whereas the $D$ values of IRC-Fe(III) are about twenty times larger than those of UR10-Fe(III).

The decrease in the $D$ value in the pH region below 2.5 may be ascribed to the increasing concentration of phosphoric acid($H_3PO_4$, $pK_{a1}=2.1$), which is not adsorbed on the resin, while that in the pH range above 4.0 may be due to the protolysis of hydrated water on the resin-bound iron.

*Comparison of Adsorption Behavior of IRC-Fe(III) with That of UR10-Fe(III).* In both adsorbents, the $Q_\infty$ value increased with an increase in the $C_{Fe}$ value, indicating that the resin-bound iron is the adsorption site of the phosphate ion. However, in the case of UR10-Fe(III), $Q_\infty/C_{Fe}$ decreased from 1.08 to 0.61 when $C_{Fe}$ increased from 0.12 to 1.34 mmol $g^{-1}$ at pH 6; this behavior was explained by the electrostatic and spatial interaction of the phosphate ion in the adsorbent with high $C_{Fe}$ value. On the other hand, $Q_\infty/C_{Fe}$ remained unity regardless of the $C_{Fe}$ value(0.726 to 1.97 mmol $g^{-1}$) at pH 3, while it increased from 0.381 to 0.949 with an increase in the $C_{Fe}$ value from 0.323 to 1.97 mmol $g^{-1}$ at pH 4.6. This behavior is opposite to that of UR10-Fe(III) at pH 6. The different behavior of IRC-Fe(III) in comparison with that of UR10-Fe(III) is presumably caused by the different nature of the resin matrices; that of the former and that of the latter being MR-type and gel-type respectively.

## References

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