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Ion-Exchange Studies in the Removal of Polybasic Acids. Anomalous Sorption Behavior of Phosphoric Acid on Weak Base Resins

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ABSTRACT

Sorption behavior of phosphoric acid on the weak base resins Amberlite IRA-93 and Dowex WGR-2 is reported. Studies on sorption equilibria and dynamics reveal anomalous sorption behavior as compared to sorption of strong and weak monobasic acids. A mathematical treatment is developed to correlate the experimental data on sorption dynamics. An alternative type of mechanism is also proposed based on the results obtained in this work to explain the anomalous sorption behavior of phosphoric acid on weak base resins.

Key Words. Ion exchange; Acid sorption; Weak base resin; Modeling; Wastewater treatment

INTRODUCTION

It is a well-established industrial practice to employ weak base ion-exchange resins for the sorption of acids from aqueous solutions. The acid sorption mechanism involves formation of a charged surface on the pore walls of resins through protonation of the free base groups located on the pore walls. Partial or near total neutralization of this charged surface oc-

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curs due to specific adsorption of acid anions, the extent of which depends on the equilibrium characteristics of individual systems. Our work (1) has shown that the sorption can be modeled by considering the electrical double layer at the pore walls of resin. Specific adsorption of counterions, anions of the acid, occurs in this region. The model predicts a considerably lower extent of co-ion exclusion from resin pores. This theoretical framework was successfully extended to the sorption of weak monobasic acids (2) and also to the sorption of dibasic acids (3) on weak base anion-exchange resins. Recently, Hasnat and Juvekar (4, 5) successfully applied this methodology to cation-exchange kinetics.

As compared to monobasic acids, the sorption of polybasic acids on weak base resins has received much less attention so far. The main reason for the scarcity of literature on this problem is probably the fact that the behavior in the case of polybasic acids is much more complicated due to multiple dissociation equilibria and difficulty in describing sorption equilibria and dynamics of polyvalent ions.

Almost the entire work reported in the literature on the sorption of polybasic acids is concerned with sorption of sulfuric acid (3, 6–8). Large differences in sorption rates have been observed for sulfuric acid over strong monobasic acids. Helfferich and Hwang (8) attempted to explain high rates of sorption for H_2SO_4 on the basis of a "proton transfer mechanism" via diffusion of HSO_4^- ions in the resin pores. Our studies (3) have successfully explained the higher rates of sorption in the case of H_2SO_4 on the basis of a dual site sorption mechanism for dibasic acids. In this case the adsorbing anion is SO_4^{2-} which is attached to two protonated sites of resin. It was found that the extent of reversibility for dibasic acids is considerably less and there is practically negligible exclusion of H^+ ions from resin pores. This was attributed mainly to the reason that divalent ions are expected to be more strongly anchored on the resins sites than monovalent ions, thereby weakening the electrical potential of the resin surface. This increases the driving force for sorption due to suppression of the surface charge. Because of these factors, the diffusive flux in the case of dibasic acids has a significant contribution of H^+ ions.

Sulfuric acid is a strong dibasic acid for which the first dissociation of acid is essentially complete. It is instructive to study the sorption behavior of a polybasic acid for which the first and successive dissociations are not complete. Phosphoric acid is one such example since it is a weak polybasic acid and has three dissociation equilibria. However, it can be shown that the contribution due to second and third dissociation is negligible even at low concentrations. One would be then tempted to conclude that the acid is likely to behave as a weak monobasic acid. However, our experimental data on sorption equilibrium have shown that the sorbed species is not monovalent $H_2PO_4^-$ ion but divalent HPO_4^{2-} ion. Thus it is believed that phosphoric acid also follows a dual site sorption mechanism similar to that observed with sulfuric acid sorption. Therefore, phosphoric acid is expected to behave differently than other types of acids. It is the purpose of this study to investigate the sorption of phosphoric acid on two different types of weak base resins; viz., Dowex WGR-2 and Amberlite IRA-93.

EXPERIMENTAL WORK

Experimental work was carried out on the sorption of phosphoric acid (analytical reagent grade) on two different weak base resins; viz., Dowex WGR-2 (epoxyamine resin supplied by Dow Chemical Company) and Amberlite IRA-93 (polystyrene resin supplied by Rohm and Haas Company). The characteristics of these resins are given in Table 1. The procedure for the characterization of resins and the details of experimental work on equilibrium and dynamics studies are well discussed in the literature (1, 9). The total concentration of the acid in solution was obtained from its pH by accounting for the extent of dissociation of the acid. Phosphoric acid has a first dissociation constant, K_{a1}, of 7.1×10^{-3} kmol/m^3, while the second and third dissociation constants, K_{a2} and K_{a3}, are 6.2×10^{-8} and 7.2×10^{-13} kmol/m^3, respectively. It can therefore be shown that even at very low concentrations of H_3PO_4 ($\sim 1 \times 10^{-5}$ kmol/m^3), the contribution to H^+ ions due to the second and third dissociation is negligible. Hence, the total concentration of the acid in the solution was obtained from its pH by accounting for only the first dissociation ($H_3PO_4 \rightarrow H^+ + H_2PO_4^-$; $K_{a1} = 7.1 \times 10^{-3}$ kmol/m^3) of the acid.

TABLE 1
Resin Characteristics and Operating Conditions

	Dowex WGR-2	Amberlite IRA-93
1. Polymer matrix	Epoxyamine	Polystyrene
2. Type	Microporous	Macroporous
3. Capacity based on pore volume	10.1 kmol/m^3	4.67 kmol/m^3
4. Water content	0.95 cm^3/g	1.18 cm^3/g
5. Bead size	$R_b = 2.45 \times 10^{-4}$ m	$R_b = 2.25 \times 10^{-4}$ m
6. Form	Free base	Free base
7. Temperature	27 ± 1°C	27 ± 1°C
8. Speed of agitation	450 rev/min	450 rev/min

EQUILIBRIA

Plots of the equilibrium concentrations of H^+ ions in solution vs sorbed acid concentration for resins Dowex WGR-2 and Amberlite IRA-93 are shown in Fig. 1 by dashed lines. The sorbed acid concentration is based on the pore volume of the resin and is obtained from the difference between the initial and the equilibrium extraparticle acid concentrations. Appropriate correction for the free acid present in the pores is incorporated. It can be observed that the capacity of the resins Dowex WGR-2 and Amberlite IRA-93 are approximately 5.0 and 2.3 kmol/m^3, respectively. These capacity values are similar to those obtained for H_2SO_4. Since the capacities of these resins for the sorption of monobasic acids as obtained in our previous work are 10.1 and 4.67 kmol/m^3, respectively, it can be concluded that each of the sorbed acid molecules occupies two sites on the resin surface. This means that H_3PO_4 will not be sorbed as monovalent $H_2PO_4^-$ anion but will be sorbed as divalent anion HPO_4^{2-}:

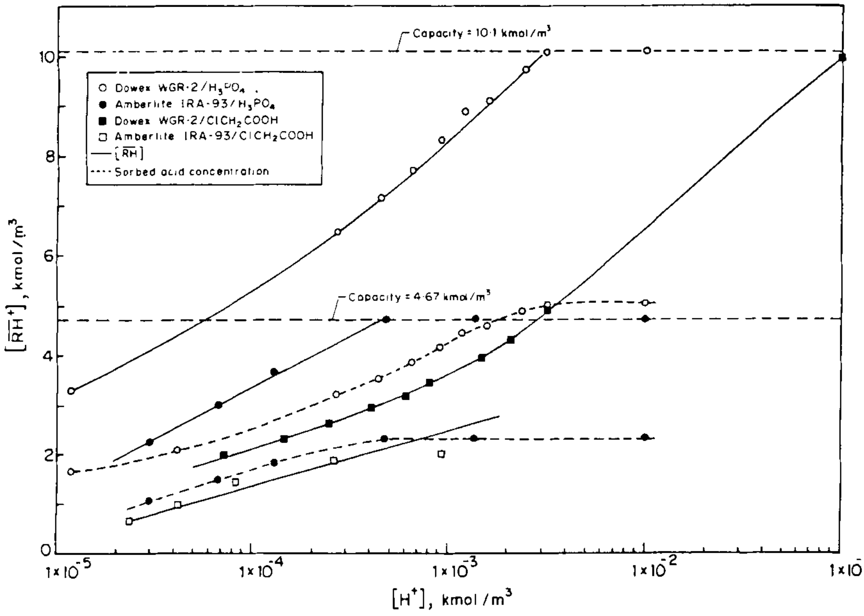
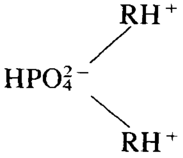


FIG. 1 Sorption equilibria of phosphoric acid on weak base resins.



(1)

where RH$^+$ represents protonated species on the resin which is formed by the protonation reaction between H$^+$ ions of acid and free ionogenic groups of resin, $\overline{R}$.

The reason for such dual site sorption is probably the high surface charge density of these resins (3). It should be noted that for anion-exchange resins of high basicity, the sorption of H_3PO_4 as PO_4^{3-} on three sites cannot be overlooked. For the weak base resins used in this work, however, such a possibility is ruled out.

Based on this dual site sorption mechanism, the concentration of RH$^+$ can now be obtained by doubling the sorbed acid concentration. Figure 1 depicts these equilibrium plots (represented by continuous lines). It also compares these equilibrium plots with those obtained with sorption of monochloroacetic acid (2), a weak monobasic acid. It is evident that the extent of reversibility is less in the case of phosphoric acid.

SORPTION DYNAMICS

Sorption dynamics was studied in a 500-cm^3 capacity glass vessel fitted with four axial baffles and a turbine-type glass stirrer. A known weight of resin was added to a 250-cm^3 acid solution of known concentration. The stirring was started immediately after resin addition, and an average stirring speed of 450 rev/min was maintained. This stirring speed was found to be sufficient to ensure uniform suspension of resin particles in the solution and also to ensure that there is negligible film diffusion resistance. A research-grade digital pH meter with a resolution of 0.001 pH, precalibrated in the required acidic range, was employed for the measurement of pH of the solution. Acid concentration corresponding to the pH value was then obtained at different time intervals.

A generalized mathematical treatment for the sorption of dibasic acids was developed in our earlier work (3). Since equilibrium studies on the sorption of phosphoric acid reveal sorption of divalent HPO_4^{2-} anion, the generalized model for dibasic acid can be applied for this case also. In the following section the application of this model for the sorption of phosphoric acid is presented.

In development of the model, strong adsorption of divalent anions on the protonated resin surface is assumed. Consequently, the surface potential is practically reduced to zero and the co-ion can freely diffuse inside the pores. In writing the material balance equations, we have neglected the film mass transfer coefficient since the preliminary experimental work showed that the sorption process is essentially pore diffusion controlled. Further, in the derivation of the model equations we have considered fixed ionogenic groups of the resin to be located on the pore walls. Diffusion of the ions is assumed to occur along the axis of the pore which also corresponds to the radial coordinate of the spherical particle. The diffusion equation inside the pore is expressed in cylindrical coordinates while the transport equations in the pore phase are written in spherical coordinates.

Batch sorption dynamics of phosphoric acid would involve diffusion of H^+, $H_2PO_4^-$, and undissociated acid molecule H_3PO_4 species in the resin pores. Since the sorption equilibria reveal sorption of divalent anion on the resin surface, the following rate processes need to be considered (3):

$$\overline{H_3PO_4} \underset{r_2}{\overset{r_1}{\rightleftharpoons}} \overline{H^+} + \overline{H_2PO_4^-} \tag{2}$$

$$\overline{H_2PO_4^-} \underset{r_4}{\overset{r_3}{\rightleftharpoons}} \overline{H^+} + \overline{HPO_4^{2-}} \tag{3}$$

$$\overline{R} + \overline{H^+} \underset{r_6}{\overset{r_5}{\rightleftharpoons}} \overline{RH^+} \tag{4}$$

The continuity equations for the independent species are then written as

$$\frac{\partial[\overline{H^+}]}{\partial t} + (r_2 - r_1) + (r_4 - r_3) + (r_5 - r_6) = -\frac{1}{r^2}\frac{\partial}{\partial r}(r^2 J_{H^+}) \tag{5}$$

$$\frac{\partial[\overline{H_2PO_4^-}]}{\partial t} + (r_2 - r_1) + (r_3 - r_4) = -\frac{1}{r^2}\frac{\partial}{\partial r}(r^2 J_{H_2PO_4^-}) \tag{6}$$

$$\frac{\partial[\overline{H_3PO_4}]}{\partial t} + (r_1 - r_2) = -\frac{1}{r^2}\frac{\partial}{\partial r}(r^2 J_{H_3PO_4}) \tag{7}$$

$$\frac{\partial[\overline{RH^+}]}{\partial t} = r_5 - r_6 \tag{8}$$

Concentrations of all the species are represented by using square brackets, and an overbar above the species indicates pore phase concentration. Combining Eqs. (5) to (8), we get the following unsteady-state continuity equation for phosphoric acid sorption in the pore phase:

$$\frac{\partial[\overline{H^+}]}{\partial t} + \frac{\partial[\overline{H_2PO_4^-}]}{\partial t} + \frac{\partial[\overline{RH^+}]}{\partial t} + 2\frac{\partial[\overline{H_3PO_4}]}{\partial t}$$

$$= -\frac{1}{r^2}\frac{\partial}{\partial r}(r^2 J_{H^+}) - \frac{1}{r^2}\frac{\partial}{\partial r}(r^2 J_{H_2PO_4^-}) - \frac{2}{r^2}\frac{\partial}{\partial r}(r^2 J_{H_3PO_4}) \tag{9}$$

Since for phosphoric acid the second and third dissociations in the extraparticle solution and inside the resin pores can be neglected, the electroneutrality condition can be expressed as

$$[\overline{H^+}] = [\overline{H_2PO_4^-}] \tag{10}$$

Further, in this case the no current condition requires

$$J_{H^+} = J_{H_2PO_4^-} \tag{11}$$

Using Eq. (10) and Eq. (11), we can simplify the continuity equation, Eq. (9), as

$$\frac{\partial[\overline{H^+}]}{\partial t} + \frac{1}{2}\frac{\partial[\overline{RH^+}]}{\partial t} + \frac{\partial[\overline{H_3PO_4}]}{\partial t} = -\frac{1}{r^2}\frac{\partial}{\partial r}(r^2 J_{H^+}) - \frac{1}{r^2}\frac{\partial}{\partial r}(r^2 J_{H_3PO_4}) \tag{12}$$

The H^+ ion concentration can be related to the concentration of undissociated acid molecule with the help of the dissociation constant as

$$[\overline{H_3PO_4}] = [\overline{H^+}]^2/K_{a1} \tag{13}$$

The Nernst–Planck equation has been most appropriately used for expressing ionic flux since it was first proposed by Helfferich in 1958 (10). The Nernst–Planck equation has the following form:

$$J_i = -D_i\left(\nabla C_i + z_i C_i \frac{\mathcal{F}}{RT}\nabla\phi\right) \tag{14}$$

The flux equations for different ionic species can be solved in conjunction with the no current condition to yield the following expression for the electrical potential gradient:

$$\frac{\mathcal{F}}{RT}\nabla\phi = -\left(\frac{D_{H^+}\dfrac{\partial[\overline{H^+}]}{\partial r} - D_{H_2PO_4^-}\dfrac{\partial[\overline{H_2PO_4^-}]}{\partial r}}{D_{H^+}[\overline{H}] + D_{H_2PO_4^-}[\overline{H_2PO_4^-}]}\right) \tag{15}$$

Eliminating the $\nabla\phi$ term, we get

$$J_{H^+} = \left[\frac{-2D_{H^+}D_{H_2PO_4^-}}{D_{H^+} + D_{H_2PO_4^-}}\right]\frac{\partial[\overline{H^+}]}{\partial r} \tag{16}$$

The term in the square bracket of Eq. (16) represents the effective diffusivity obtained from the Nernst–Planck equation.

Fick's law can be used to express the flux of a molecular species, i.e., the undissociated H_3PO_4 acid molecule:

$$J_{H_3PO_4} = -D_m \frac{\partial[\overline{H_3PO_4}]}{\partial r} \tag{17}$$

where D_m is the molecular diffusivity of phosphoric acid.

Equation (12) can be rewritten as

$$\left[1 + \frac{1}{2}\frac{\partial[\overline{RH^+}]}{\partial[\overline{H}^+]} + \frac{\partial[\overline{H_3PO_4}]}{\partial[\overline{H}^+]}\right]\frac{\partial[\overline{H^+}]}{\partial t} = -\frac{1}{r^2}\frac{\partial}{\partial r}(r^2 J_{H^+}) - \frac{1}{r^2}\frac{\partial}{\partial r}(r^2 J_{H_3PO_4}) \tag{18}$$

where the derivatives inside the square bracket can be obtained from the equilibrium relation between RH^+ concentration and H^+ concentration (Fig. 1) and Eq. (13), respectively. Equation (18) requires two boundary conditions and one initial condition for its solution. The boundary conditions are given as

$$\partial[\overline{H^+}]/\partial r = 0 \qquad \text{at } r = 0 \tag{19}$$

$$[\overline{H^+}] = [H^+] \qquad \text{at } r = R_b \tag{20}$$

The initial condition can be written for representing the free base form of the resin at time $t = 0$:

$$[\overline{H^+}]_i = 0 \qquad \text{at } t = 0 \tag{21}$$

Batch sorption dynamics also involves concentration changes in the extraparticle acid concentration with time. The material balance in the extraparticle fluid yields

$$-\frac{d[H^+]}{dt} - \frac{d[H_3PO_4]}{dt} = 4\pi R_b^2 \epsilon_p N(-J_{H^+}|_{r=R_b} - J_{H_3PO_4}|_{r=R_b}) \tag{22}$$

The above equation can be expressed in terms of resin loading, W, which is now defined as

$$W = \frac{\text{total resin capacity}}{\text{total initial acid content}} = \frac{NV\frac{4}{3}\pi R_b^3 \epsilon_p Q}{V([H_3PO_4]_0)_i} \tag{23}$$

Substitution of Eq. (23) in Eq. (22) yields

$$-\frac{d[H^+]}{dt} - \frac{d[H_3PO_4]}{dt} = \frac{3W([H_3PO_4]_0)_i}{R_b Q}(-J_{H^+}|_{r=R_b} - J_{H_3PO_4}|_{r=R_b}) \tag{24}$$

where $[H_3PO_4]_0$ represents the total acid concentration. The concentration of undissociated acid species can be obtained by the equilibrium relation given by

$$[H_3PO_4] = [H^+]^2/K_{a1} \tag{25}$$

The initial condition of Eq. (24) is given by

$$[H^+] = [H^+]_i \qquad \text{at } t = 0 \tag{26}$$

METHOD OF SOLUTION

The following dimensionless variables have been defined.

$$\tau = tD_H/R_b^2; \qquad y = r/R_b; \qquad \bar{a} = [\overline{H^+}]/[H^+]_i; \qquad a = [H^+]/[H^+]_i \tag{27}$$

Equations (18) and (24) were converted into dimensionless form by using the above transformation. The orthogonal collocation technique (11) was used to convert the PDEs into a set of ODEs which were then solved using the IMSL routine IVPAG.

The values of diffusion coefficients for the H^+ and $H_2PO_4^-$ ions in solution are 9.31×10^{-9} m^2/s and 0.88×10^{-9} m^2/s, respectively (12, 13). The value of solution diffusivity for H_3PO_4 is not known; we assumed it to be equal to 1×10^{-9} m^2/s. However, sensitivity analysis showed that the variation of D_m, i.e., the diffusivity of H_3PO_4, within ±30% had no effect on the simulated results. This is mainly due to the fact that an appreciable amount of the acid dissociates in the pore phase and therefore the contribution of the molecular species in the overall diffusion process is small. As before, the tortuosity factor of 2 derived from Wheeler's correlation (14) was used for both resins in order to obtain the pore diffusivity values for individual ionic and molecular species (3). The value of effective diffusivity was not regressed. Instead, the value of effective diffusivity obtained by the Nernst–Planck equation, Eq. (16), was directly used in predicting the sorption rate.

RESULTS AND DISCUSSION

The fit of the model to the sorption data was found to be extremely poor (a typical case is shown by the dashed line in Fig. 2). The experimentally observed rate of sorption was very much higher than the rate predicted by the model.

However, it was observed that the initial portion of the sorption data is a good fit if we assume that the initial sorption is due to species

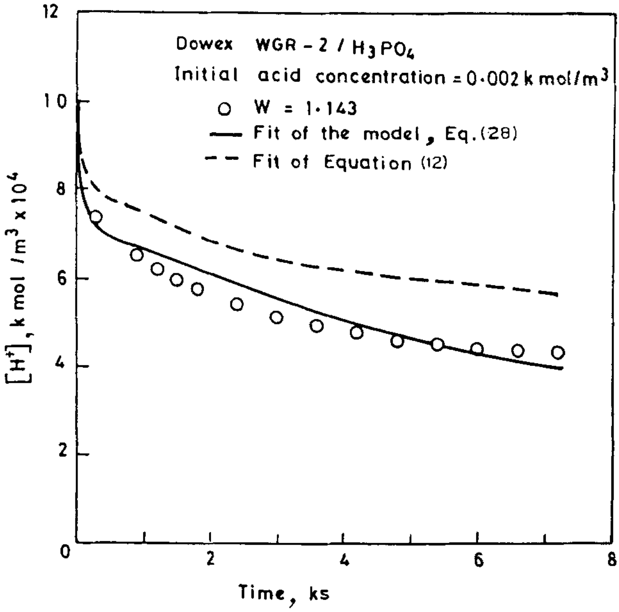


FIG. 2 Fit of the model using experimental data on sorption dynamics.

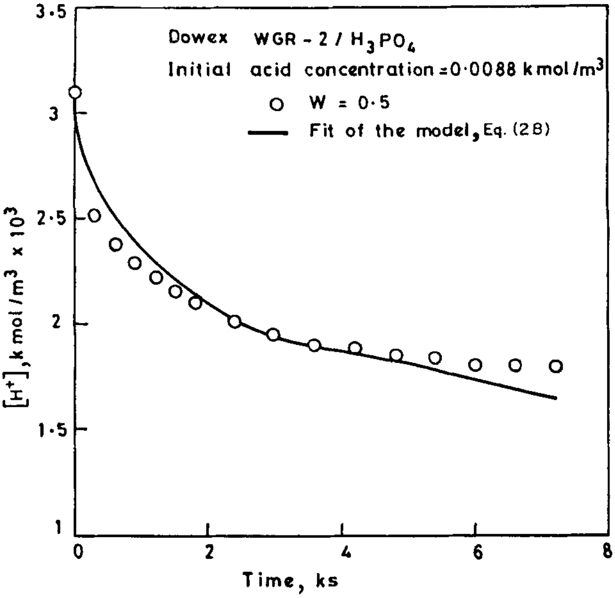


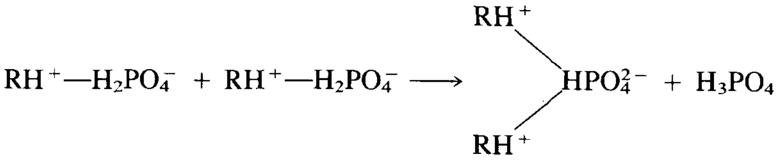
FIG. 3 Fit of the model using experimental data on sorption dynamics.

$H_2PO_4^-$. In such a case the continuity equation, Eq. (12), will have to be modified to

$$\frac{\partial\overline{[H^+]}}{\partial t} + \frac{\partial\overline{[RH^+]}}{\partial t} + \frac{\partial\overline{[H_3PO_4]}}{\partial t} = -\frac{1}{r^2}\frac{\partial}{\partial r}(r^2 J_{H^+}) - \frac{1}{r^2}\frac{\partial}{\partial r}(r^2 J_{H_3PO_4}) \tag{28}$$

Figures 2 through 6 compare the results of simulation with the experimental data of H^+ ion concentration vs time using Eq. (28) in the model in place of Eq. (18). The plots support the above argument. If the sorption were to proceed entirely in the form of $H_2PO_4^-$, then the concentration profile as shown by the solid line in Figs. 2 through 6 will be obtained. It can be seen that the actual sorption rate is much slower in the latter portion of the curve.

It is proposed that equilibrium is established when two adjacent sites of the resin react in the following manner:



$$RH^+{-}H_2PO_4^- + RH^+{-}H_2PO_4^- \longrightarrow \begin{matrix} RH^+ \\ \quad\diagdown \\ \quad\; HPO_4^{2-} \\ \quad\diagup \\ RH^+ \end{matrix} + H_3PO_4 \tag{29}$$

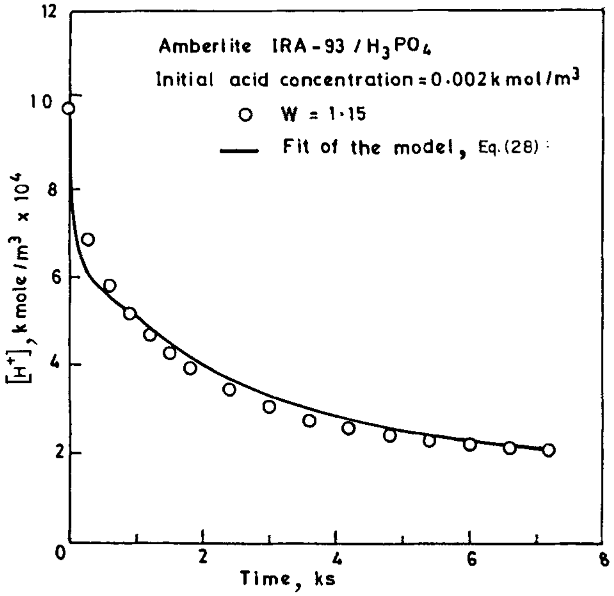


FIG. 4 Fit of the model using experimental data on sorption dynamics.

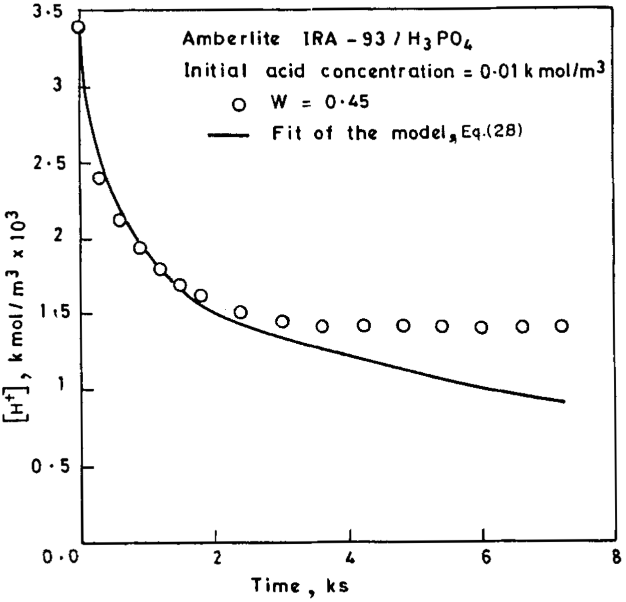


FIG. 5 Fit of the model using experimental data on sorption dynamics.

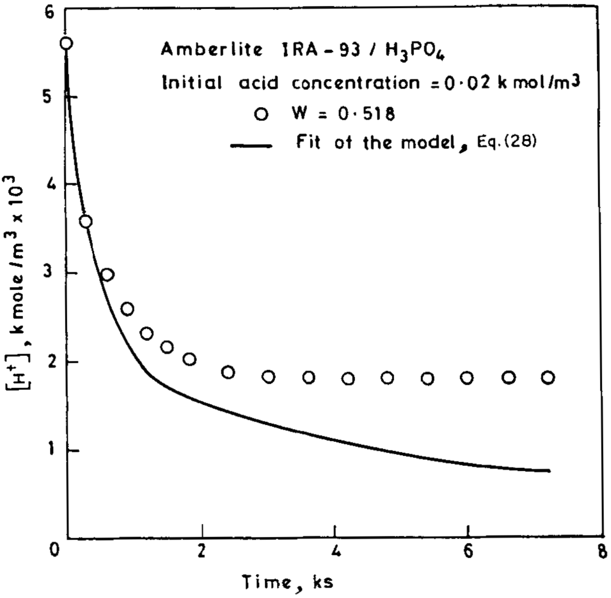


FIG. 6 Fit of the model using experimental data on sorption dynamics.

Thus, it is felt that the acid generated due to the above reaction reduces the driving force for the diffusion of acid from the extraparticle solution and thereby decreases the rate of acid uptake from the extraparticle solution. The reaction of Eq. (29) seems to have a time constant comparable to that of diffusion, and therefore its rate also needs to be considered for accurately predicting the sorption behavior. Further, as a result of this reaction, the capacity of the resin to sorb phosphoric acid appears to change during the course of sorption. It is also interesting to note that in this case, application of the conventional shrinking core model using the condition of irreversible sorption (3), or the modified shrinking core model which accounts for the reversibility of sorption (15), would be difficult.

As a consequence of the proposed mechanism (Eq. 29), it is possible to have the following three extreme cases, depending upon the type of resin. These are schematically shown in Fig. 7 in the form of a time–concentration profile of the acid in the extraparticle solution.

(a) In the first case, the sorption can entirely proceed in the form of monovalent $H_2PO_4^-$ ion followed by a slow reaction of Eq. (29),

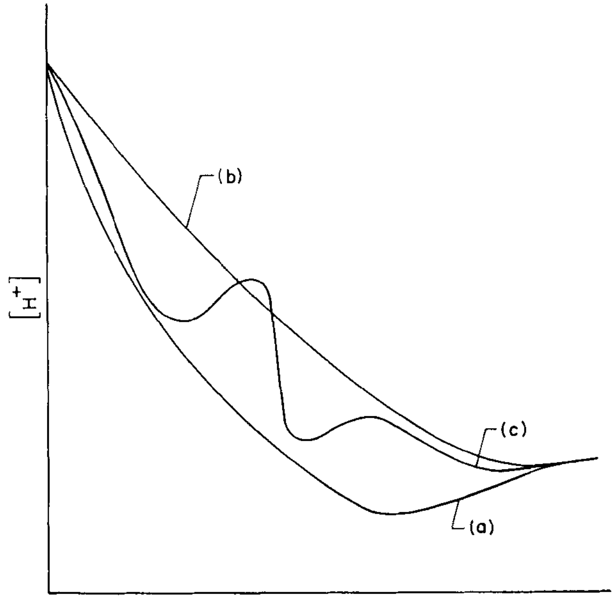


FIG. 7 Schematic representation of concentration profiles on the basis of rate of reaction, Eq. (29). See text for explanations of curves.

ultimately yielding sorption of divalent anion HPO_4^{2-} and release of one acid molecule. Here, initially there would be a sharp decrease in the solution acid concentration. Once the resin is exhausted and is completely in the monovalent $H_2PO_4^-$ form, the acid concentration would slowly start increasing as the resin converts itself from the monovalent to the divalent form, subsequently releasing acid in solution.

(b) Second, the rate of reaction of Eq. (29) can be comparable to that of diffusion. With this, the reaction proceeds simultaneously as the acid species diffuse in the pores. The acid released by the rearrangement reaction then would reduce the driving force affecting the sorption rate.

(c) If the reaction of Eq. (29) is fast enough, then there could be oscillations in the solution concentration with time due to intermittent reversals in acid diffusion inside the resin pores and the release of acid from the pore phase. The relative rates of the two would decide the frequency of oscillations and, therefore, the sorption behavior.

This phenomenon needs further detailed investigation.

CONCLUSIONS

Sorption studies on polybasic acids have indicated a strong adsorption of divalent anion, HPO_4^{2-}, in the case of H_3PO_4 on the surface of resin pores. The results obtained in this work show anomalous sorption behavior of phosphoric acid on weak base resins. The sorption dynamics here seem to follow a two-step process. In the first step, sorption of monovalent anion $H_2PO_4^-$ occurs on the surface of the resin whereas in the second step there is an interaction between two reacted resin sites, resulting in a strong anchoring of a divalent anion HPO_4^{2-} simultaneously on two resin sites. The second step generates an acid molecule which consequently reduces the driving force for the uptake of acid from solution. The theoretical framework developed in the present work attempts to explain this anomalous sorption behavior of phosphoric acid which clearly indicates an alternative mechanism for sorption.

NOMENCLATURE

a	$[H]/[H]_i$
C_i	concentration of species i (kmol/m^3)
D_i	pore diffusivity of species i (m^2/s)
D_m	pore diffusivity of acid molecule (m^2/s)

$\mathcal{F}$	Faraday's constant (C/mol)
J_i	flux of species i (kmol/m^2·s)
K_{a1}	first dissociation constant of acid (kmol/m^3)
K_{a2}	second dissociation constant of acid (kmol/m^3)
K_{a3}	third dissociation constant of acid (kmol/m^3)
N	number of resin particles per unit volume of extraparticle fluid
Q	resin capacity based on pore volume (kmol/m^3)
R_b	radius of resin bead (m)
R	gas constant (J/mol·K)
r_1–r_6	rates of reaction presented in Eqs. (2) to (4)
r	radial distance measured from the center of bead (m)
T	absolute temperature (K)
t	time (s)
V	volume (m^3)
y	dimensionless radius
W	dimensionless resin loading
Z_i	valence of ion

Greek Letters

ϵ_p	fractional pore volume based on total resin volume
ϕ	electrical potential (V)
τ	tortuosity factor

Subscript

i	initial value
i	any species

Bar Above the Species Refers to Pore Phase

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