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Implications of Weak Donnan Potential in Ion-Exchange Reactions. An Alternate Strategy for Modeling Sorption Processes

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ABSTRACT

Donnan potential generated during an ion-exchange process is conventionally believed to play an important role in partitioning co-ions in the resin and solution phases; most earlier studies implied near total exclusion of co-ions from the resin pores. The present work attempts to investigate implications of weak Donnan potential with specific reference to the sorption of acids on weak base resins. An alternate mathematical treatment has been proposed to describe the sorption behavior of any type of acid by assuming diffusion and sorption of single species, the composite acid molecule, in the resin pores. Fick's law is then used to characterize the diffusion process. The proposed model is validated using data reported in the literature for the sorption of a strong monobasic acid (HCl) and also for a weak monobasic acid (HCOOH). The fit of the model is excellent, and the regressed values of the effective diffusion coefficient are shown to be reasonable and correct to the order of magnitude. The model is expected to offer a simpler and unified approach for modeling sorption behavior of different types of acids and will be more useful in problems of acid separation from mixtures.

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

INTRODUCTION

Knowledge of ion-exchange equilibria and exchange dynamics is essential for the design of ion-exchange processes, especially for the prediction of behavior of industrial column operations and chromatographic separations. Although the present understanding of ion-exchange equilibria is largely incomplete, mainly due to the nonidealities associated with the resin-phase species, much progress has been achieved in describing the exchange dynamics and the diffusion process inside the resin pores. The diffusion process has been conventionally modeled using either Fick's law (1–12) or the Nernst–Planck equation (13–27). In majority of the models reported in earlier studies, the distribution of counterions was obtained by using the ion-exchange equilibria, and partitioning of the co-ions in the resin and solution was assumed to be in accordance with that predicted by the ideal Donnan equilibrium (28). The application of ideal Donnan equilibria in these cases predicts near total exclusion of co-ions from the resin pores (29). Recent studies, however, suggest the formation of an electrical double layer near the walls of resin pores and, therefore, exclusion of co-ions only from this region on the basis of the ideal Donnan equilibrium principle. The remaining part of the pore is relatively free for the diffusion of ions. This concept was originally proposed by Bhandari et al. for the sorption of acids on weak base resins (24–26). It was later successfully applied for cation-exchange kinetics by Hasnat and Juvekar (27). Recently, Jansen et al. (30) showed that neglecting co-ion exclusion i.e., incorporating the uptake of co-ion, results in a major improvement compared to conventional models. The present study attempts to examine the implications of this weak Donnan potential as experienced in the major part of resin pores for the sorption of acids on the weak base resins, especially when the double layer is compact and the exclusion of co-ions from pores is negligible. An alternate approach to mathematical modeling of the sorption processes has been proposed by assuming diffusion of a single species, the composite acid molecule, in the resin pores and by using Fick's law to characterize the diffusion. The model is validated using experimental data reported in the literature on the sorption of two different types of acids on weak base resins.

ACID SORPTION

Sorption of acid is an important problem in chemical and biochemical process industries, e.g., removal of acids during water treatment, separation/recovery of acids from "process" or "waste" streams, recovery of acids from fermentation broths, etc. (31–35). Weak base resins are most commonly employed for sorption due to their high capacity and ease of regeneration.

The mechanism of acid sorption has been well discussed since it was first postulated by Helfferich (15, 18). It essentially involves protonation of the fixed ionogenic groups of the resin (denoted by $\overline{\mathrm{R}}$) by the H^+ ions of an acid according to the following reaction:

$$\overline{\mathrm{R}} + \overline{\mathrm{H}^+} \Leftrightarrow \overline{\mathrm{RH}^+} \tag{1}$$

Anions of the acid are then strongly held by these positively charged groups of resin to form a resin salt of the acid. In effect, a complete acid molecule is sorbed on the resin surface.

$$\overline{\mathrm{RH}^+} + \overline{\mathrm{A}^-} \Leftrightarrow \overline{\mathrm{RH}^+\mathrm{A}^-} \tag{2}$$

Helfferich (15, 18), in his analysis of various ion-exchange processes involving reactions, showed that the rate laws differ considerably in such cases from those in ordinary ion-exchange processes. He postulated a shrinking core mechanism by assuming an irreversible reaction for neutralization of strong base resins, acid sorption by weak base resins (Eq. 1), and similar reactions of cation-exchange resins. The conventional approach to modeling the sorption of acids on weak base resins assumes complete dissociation of the resin salt in the resin pores (Eq. 2) and consequently a high extent of co-ion exclusion from resin pores according to the ideal Donnan equilibrium (8, 9, 11, 20, 36). Although this approach showed a fairly good fit to the experimental data, the values of the pore diffusion coefficient regressed from the model were, in general, highly unrealistic. The reasons for the failure of the conventional approach could be traced back to the mode of application of the ideal Donnan equilibrium rule for coupling concentrations between the two phases and not accounting for the reversibility of sorption. There is a need to assess the implications of the weak Donnan potential, especially in the light of recent evidence which largely indicates exclusion of co-ions well short of what is predicted by the ideal Donnan principle (24–27, 30, 37).

DONNAN EXCLUSION

Co-ion exclusion is a phenomenon wherein the co-ion (H^+ ion in this case) is excluded to a certain extent from the resin pores. Mathematically, the extent of co-ion exclusion can be defined as

$$\text{Extent of exclusion} = 1 - \overline{[\mathrm{H}^+]}/[\mathrm{H}^+] \tag{3}$$

Since the conventional models assume complete dissociation of the resin salt and uniform distribution of the counterions in the resin pore, the extent of co-ion exclusion can be demonstrated by the cases given below.

Consider a weak base resin placed in a solution containing any acid, HA. The highly mobile H^+ ions diffuse and protonate the fixed ionogenic groups of the resin, thereby creating a positively charged interface. The electrical potential buildup by this process is called the Donnan potential. An equilibrium is established between the tendency of ions to diffuse due to concentration differences and the electrical field. The equilibrium in the pore phase and the extraparticle solution yields

$$[H^+][A^-] = \overline{[H^+][A^-]} \tag{4}$$

Using the condition of electroneutrality in the extraparticle fluid ($[H^+] = [A^-]$), one can write

$$[H^+]^2 = \overline{[H^+][A^-]} \tag{5}$$

The electroneutrality condition inside the resin pore is written

$$\overline{[H^+]} + \overline{[RH^+]} = \overline{[A^-]} \tag{6}$$

Eliminating the anion term, we get

$$[H^+]^2 = \overline{[H^+]}^2 + \overline{[H^+]}\,\overline{[RH^+]} \tag{7}$$

It is clear from Eq. (7) that

$$\overline{[H^+]} \leqslant [H^+] \tag{8}$$

since both $\overline{[H^+]}$ and $\overline{[RH^+]}$ are positive. Also, the higher the concentration of the protonated species, the larger is the extent of co-ion exclusion.

Co-ion uptake and electrolyte sorption are equivalent according to this theory. The above theoretical framework therefore implies exclusion of electrolyte, at least partially, which is a unique feature of electrolyte sorption by an ion-exchange resin. As a result, while simulating the dynamics of sorption, lower H^+ concentration values in the pore force diffusivity to assume a high value in order to match the experimental rates of sorption (24). Since the above theoretical framework predicts a smaller extent of co-ion exclusion at high concentrations of acid, diffusivity values from such models (20) at high acid concentrations are closer to reality.

DEVELOPMENT OF A SIMPLIFIED APPROACH

From the above discussion it is evident that, in general, the models presented in the literature, are not reliable for the following reasons.

1. The sorption reaction is assumed to be irreversible, which is usually not the case, especially at lower acid concentrations.
2. The resin salt is assumed to be completely dissociated and the counterions are assumed to be uniformly distributed across the cross section of the pore, thereby predicting high co-ion exclusion from resin pores.

The above two drawbacks can be eliminated by using the more rigorous approach of the reversible sorption model based on double layer theory (24,

25) for the sorption of acids on weak base resins. Mathematical treatment reveals that the exclusion of co-ions from the resin pores is far from complete. Recently, Hasnat and Juvekar (27) showed that the extent of co-ion exclusion is substantially lower than that predicted from the ideal Donnan equilibrium for cation-exchange kinetics. The models of the above class assume formation of an electrical double layer in the vicinity of charged resin surfaces. The effect of an electrical potential gradient is believed to be largely restricted to this double layer region only, especially where pore size is large (e.g., macroporous resins). For this reason, the core region of a pore is more or less free from the effect of surface charge, and here a local electroneutrality condition can be applied which yields practically no exclusion of co-ions. This is schematically shown in Fig. 1.

In view of the above, it is possible to develop an alternate modeling strategy for the sorption of acids on weak base resins by considering the reversibility of sorption and by neglecting co-ion exclusion. (Since the core region of the pore is expected to make a major contribution to the overall diffusion flux, the assumption of negligible co-ion exclusion is justified.) Further, simplification can be achieved by considering the diffusion and sorption of a single species, the composite acid molecule. This approach, though somewhat empirical, has the advantage of being applicable to any type of acid

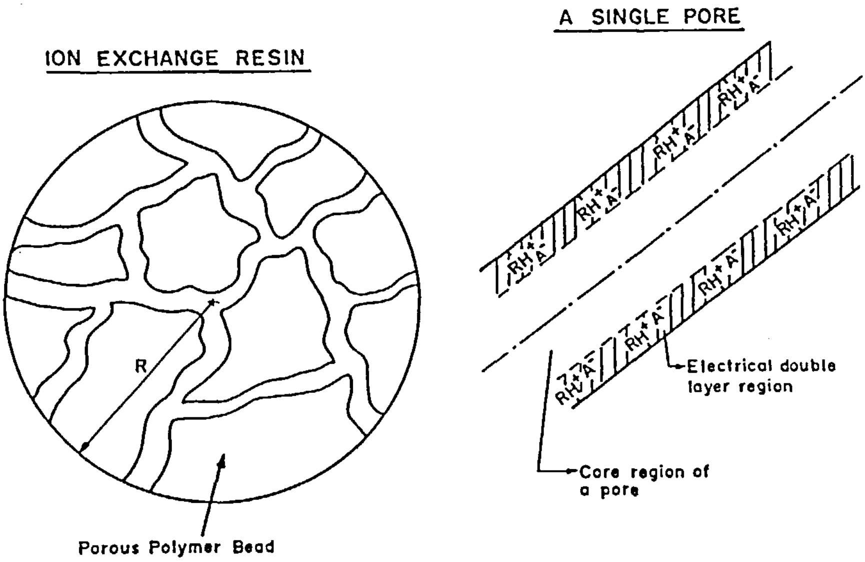

FIG. 1 Schematic representation of a pore with a compact electrical double layer.

(strong/weak/polybasic) without any change in its form as against the conventional shrinking core model, the rate controlling model of Helfferich and Hwang (20), the more rigorous reversible sorption model based on the double layer theory of Bhandari et al. (24, 25), and the modified shrinking core model (38).

In the development of the model, all the intraparticle concentrations are defined on the basis of the pore volume of the resin. Further, for simplicity in writing the equations, the following "abbreviations" are used: $\overline{[\mathrm{H}]}$ for $\overline{[\mathrm{H}^+]}$, $\overline{[\mathrm{A}]}$ for $\overline{[\mathrm{A}^-]}$, $\overline{[\mathrm{RH}]}$ for $\overline{[\mathrm{RH}^+]}$, and $\overline{[\mathrm{RHA}]}$ for $\overline{[\mathrm{RH}^+\mathrm{A}^-]}$.

Correlation of the Sorption Isotherm

The overall sorption reaction (Eqs. 1 and 2) is now represented by

$$\overline{\mathrm{R}} + \overline{\mathrm{HA}} \Leftrightarrow \overline{\mathrm{RHA}} \tag{9}$$

The sorption equilibria are correlated by defining the following empirical form:

$$K = \frac{\overline{[\mathrm{RHA}]}_e}{\overline{[\mathrm{R}]}_e \overline{[\mathrm{HA}]}_e^n} \tag{10}$$

where the subscript "e" denotes the equilibrium concentrations of the respective species, and K and n are the sorption isotherm constants for a given resin–acid system. At equilibrium:

$$[\mathrm{HA}]_e = \overline{[\mathrm{HA}]}_e \tag{11}$$

The concentration of the free base group, [R], can be calculated by subtracting $\overline{[\mathrm{RHA}]}_e$ from the resin capacity, Q. From Eq. (10), $\ln[\mathrm{HA}]_e$ and $\ln(\overline{[\mathrm{RHA}]}_e/\overline{[\mathrm{R}]}_e)$ can be linearly correlated to obtain K and n.

Sorption Dynamics

The following assumptions have been made in deriving the model equations for the sorption dynamics.

1. The resin particles are assumed to be spherical in shape and uniform in size.
2. The pore phase is assumed to consist of cylindrical pores of uniform radius. Further, a pore is assumed to run straight from the surface of a resin bead to the center. The tortuous nature of pores is accounted for in the tortuosity factor.
3. Diffusion of ions is assumed to occur along the pore axis, which corresponds to the radial coordinate of the spherical particle (r-coordinate).

The transport equations in a pore are written using cylindrical coordinates while those in the pore phase are written in spherical coordinates.

4. Acid is assumed to diffuse as a single species, the composite acid molecule HA.
5. The extraparticle film resistance is assumed to be negligible since in most cases particle diffusion is controlling even at very low concentrations. Also, the data used in the present study confirmed the absence of film diffusion control (24, 25).
6. An equilibrium between the sorbed species and the unsorbed acid, as described in Eq. (10), is assumed to exist at all locations in the resin.

The unsteady-state continuity equation in the pore phase can be written

$$\frac{\partial\overline{[\mathrm{HA}]}}{\partial t} + r_{\mathrm{HA}} = D_{\mathrm{HA}}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\overline{[\mathrm{HA}]}}{\partial r}\right)\right\} \tag{12}$$

where r_{HA} is the rate of acid sorption per unit pore volume. In writing Eq. (12), Fick's law has been employed for expressing the flux of acid in the pore phase and D_{HA} is the effective diffusivity of the composite acid molecule. The boundary conditions to Eq. (12) are

$$\frac{\partial\overline{[\mathrm{HA}]}}{\partial r} = 0, \qquad \text{at } r = 0 \tag{13}$$

$$\overline{[\mathrm{HA}]} = [\mathrm{HA}], \qquad \text{at } r = R_{\mathrm{b}} \tag{14}$$

while the initial condition is

$$\overline{[\mathrm{HA}]} = \overline{[\mathrm{HA}]}_{\mathrm{i}}, \qquad \text{at } t = 0 \tag{15}$$

where $\overline{[\mathrm{HA}]}_{\mathrm{i}}$ is the initial concentration of the sorbed acid in the resin. For the free base form of resin, $\overline{[\mathrm{HA}]}_{\mathrm{i}} = 0$.

The balance of total ionogenic sites at any point yields

$$\overline{[\mathrm{R}]} + \overline{[\mathrm{RHA}]} = Q \tag{16}$$

The continuity equation for the sorbed species, RHA, may be written as

$$\frac{\partial\overline{[\mathrm{RHA}]}}{\partial t} = r_{\mathrm{HA}} \tag{17}$$

Elimination of $\overline{[\mathrm{R}]}$ from Eq. (10) by using Eq. (16) and subsequent rearrangement gives

$$\overline{[\mathrm{RHA}]} = \frac{KQ\overline{[\mathrm{HA}]}^{\mathrm{n}}}{1 + K\overline{[\mathrm{HA}]}^{\mathrm{n}}} \tag{18}$$

Differentiation of Eq. (18) with respect to time with subsequent elimination of $\partial\overline{[\mathrm{RHA}]}/\partial t$ yields

$$r_{\mathrm{HA}} = \frac{nKQ[\overline{\mathrm{HA}}]^{n-1}}{(1 + K[\overline{\mathrm{HA}}]^{n})^2} \frac{\partial[\overline{\mathrm{HA}}]}{\partial t} \tag{19}$$

Substituting for r_{HA} from Eq. (19) into Eq. (12) and rearranging the resulting equation, we get

$$\frac{\partial[\overline{\mathrm{HA}}]}{\partial t} = \frac{D_{\mathrm{HA}}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial[\overline{\mathrm{HA}}]}{\partial r}\right)\right\}}{\left(\frac{nKQ[\overline{\mathrm{HA}}]^{n-1}}{(1 + K[\overline{\mathrm{HA}}]^{n})^2} + 1\right)} \tag{20}$$

The flux of acid at the outer surface of the resin particle ($r = R_b$) can be obtained from

$$J_{\mathrm{HA}}|_{r=R_b} = -D_{\mathrm{HA}}\frac{\partial[\overline{\mathrm{HA}}]}{\partial r}\Big|_{r=R_b} \tag{21}$$

Here the flux is based on the part of the area of the outer surface occupied by the pores. If we assume this area is the ε_p fraction of the total outer surface area, then the acid balance in the extraparticle fluid may be written as

$$-\frac{d[\mathrm{HA}]}{dt} = 4\pi R_b^3\varepsilon_p N(-J_{\mathrm{HA}}|_{r=R_b}) \tag{22}$$

where N is the number of particles per unit volume of the extraparticle fluid.

Dimensionless resin loading, W, can be defined on the basis of resin capacity and the initial acid concentration in the solution by the following relation:

$$W = \frac{4\pi R_b^2 N \epsilon_p Q}{3[\mathrm{HA}]_i} \tag{23}$$

By eliminating N from Eqs. (23) and (22) and substitution of $J_{\mathrm{HA}}|_{r=R_b}$ from Eq. (21) into the resulting equation, we get

$$-\frac{d[\mathrm{HA}]}{dt} = \frac{3D_{\mathrm{HA}}W[\mathrm{HA}]_i}{R_b Q}\frac{\partial[\overline{\mathrm{HA}}]}{\partial r}\Big|_{r=R_b} \tag{24}$$

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

$$[\mathrm{HA}] = [\mathrm{HA}]_i, \qquad \text{at } t = 0 \tag{25}$$

Equations (20) and (24) have to be solved simultaneously along with the respective boundary and initial conditions in order to obtain the extraparticle acid concentration [HA] as a function of time. The only unknown parameter in these equations is D_{HA}, which has to be regressed from the experimentally observed [HA] vs time relationship.

DIMENSIONLESS TRANSFORMATION

Equations (20) and (24) along with the boundary and initial conditions can be transformed to dimensionless forms by using the following transformations:

$$\tau = \frac{tD_{\mathrm{HA}}}{R_{\mathrm{b}}^{2}}; \qquad u = \left(\frac{r}{R_{\mathrm{b}}}\right)^{2}; \qquad a = \frac{[\mathrm{HA}]}{[\mathrm{HA}]_{\mathrm{i}}}; \qquad \bar{a} = \frac{\overline{[\mathrm{HA}]}}{[\mathrm{HA}]_{\mathrm{i}}}$$

Further, the following constants have been defined.

$$\alpha = KQ[\mathrm{HA}]_{\mathrm{i}}^{n-1}; \qquad \beta = K[\mathrm{HA}]_{\mathrm{i}}^{n}$$

The transformed form of equations along with the boundary and initial conditions are

$$\frac{\partial \bar{a}}{\partial \tau} = \frac{\left\{4u\frac{\partial^{2}\bar{a}}{\partial u^{2}} + 6\frac{\partial \bar{a}}{\partial u}\right\}}{\left\{\frac{\alpha n(\bar{a})^{n-1}}{(1 + \beta \bar{a}^{n})^{2}} + 1\right\}} \tag{26}$$

$$-\frac{da}{d\tau} = \frac{6W\beta}{\alpha}\left.\frac{\partial \bar{a}}{\partial u}\right|_{u=1} \tag{27}$$

$$\bar{a} = \text{finite}, \qquad \text{at } u = 0 \tag{28}$$

$$\bar{a} = a, \qquad \text{at } u = 1 \tag{29}$$

$$a = 1 \text{ and } \bar{a} = 0, \qquad \text{at } \tau = 0 \tag{30}$$

METHOD OF SOLUTION

The data reported on the sorption of hydrochloric acid (24) and formic acid (25) on two weak base resins (Dowex WGR-2 and Amberlite IRA-93) were used for validating the proposed model. The capacities of the two resins were reported as 10.1 and 4.67 kmol/m^3, respectively, based on pore volume. The average radius of the resin beads was 490 μm for Dowex WGR-2 and 450 μm for Amberlite IRA-93. For the sorption isotherm, Eq. (10) was fitted using the sorption equilibrium data. The regressed values of the constants K and n for different systems are listed in Table 1. In all cases the correlation coefficient of the fit was greater than 0.99, indicating that Eq. (10) satisfactorily correlates the sorption isotherm data.

For simulating the sorption dynamics results, the partial differential equations in dimensionless form were first converted into ordinary differential equations using the orthogonal collocation method (39). The resulting ODE's

TABLE 1
Values of K and n in Eq. (10) of Sorption Isotherm

Resin	Acid	K	n
Dowex WGR-2	HCl	6.01	0.291
	HCOOH	6.50	0.307
Amberlite IRA-93	HCl	182	0.605
	HCOOH	2360	0.984

were then solved using the IMSL routine, IVPAG. Sensitivity to solution was analyzed by increasing the number of collocation points, and it was found that the solution became practically insensitive to the number of collocation points above eight nodes. Hence, nine collocation nodes were used for all the simulations. Use of the respective equilibrium relationships was made using values of K and n from Table 1. The diffusivity values for different runs were regressed using the experimental data on sorption dynamics.

RESULTS AND DISCUSSION

Figures 2 and 3 show typical fits of the model to the experimental data on sorption dynamics for the two acids. It is observed that the fit of the model is very good over practically the entire range of concentration. The average deviation from the experimental data for most of the runs was less than ±7%. The best fit values of the effective diffusion coefficient are reported in Table 2. From a comparison of these values with those reported in the literature (20, 24, 25, 40), it is evident that the diffusivity values are reasonable and correct to the order of magnitude [the value of the Nernst–Planck effective diffusivity for HCl using Wheeler's tortuosity factor of 2 (41) is 1.67×10^{-9} m^2/s and for formic acid is 0.63×10^{-9} m^2/s]. From Table 2 it is also seen that the regressed values of the diffusion coefficient at low concentrations are somewhat different from those obtained at higher concentrations. The reason for this can be attributed to the diffused nature of the double layer at lower concentrations. At low concentrations the double layer may extend substantially into a pore, at times covering the entire cross section of a pore. The core region of a pore in such cases may have little or no existence, and the distribution of ions in the pore is largely affected by the Donnan potential. At higher concentrations, however, the electrical double layer region is expected to be compact and, therefore, the values of the effective pore diffusion coefficient are nearly constant. The results of present study, therefore, are in accordance with those of reversible sorption theory based on double layer theory.

It may be noted that the effective diffusivity D_{HA}, as described by Eq. (12), represents a lumped parameter without actually describing the mechanism of sorption and the true diffusion process. Further, it is difficult to compare the diffusivity values for different acid species on the basis of their molecular weights. D_{HA}, as used here, is not the same as molecular diffusivity since it is the diffusivity of the composite acid molecule which is not same as the undissociated acid molecule. In the former, coupling between the anion and the cation is purely electrostatic in nature. Hence, the diffusivity of this ion pair need not be equal to that of an undissociated acid molecule. The use of Fickian diffusion in the present study can also be justified in view of the fact that although Fick's law and the Nernst–Planck equation differ from each other, both in the definition and the form, both employ effective diffusivity

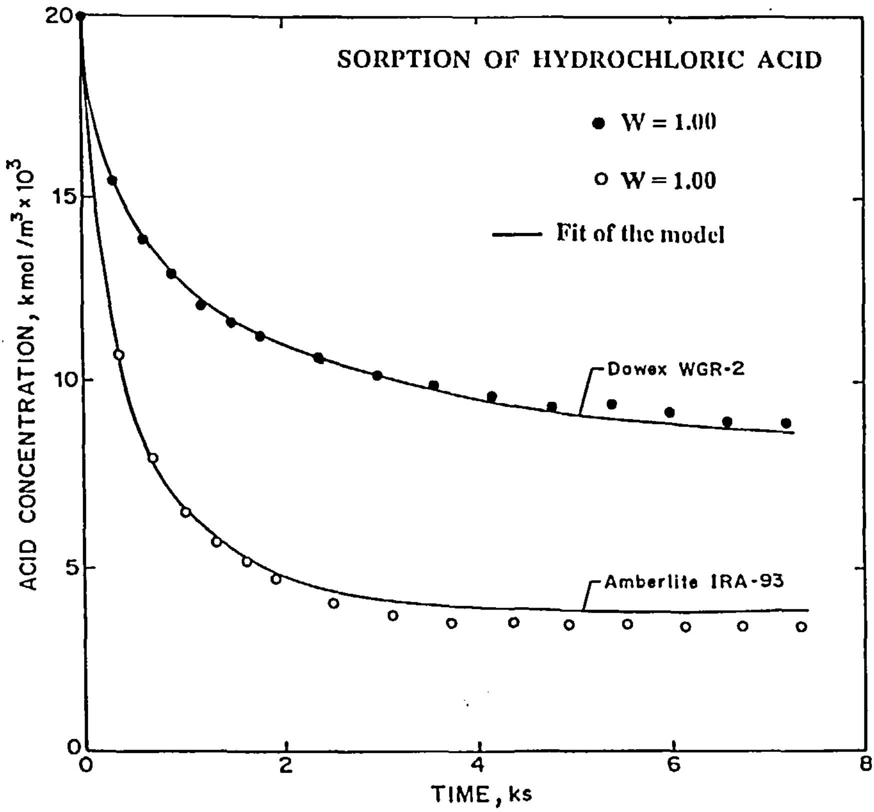

FIG. 2 Fit of the model using the experimental data on sorption dynamics.

for binary exchange. Hering and Bliss (5) compared the two models using their experimental data. Their results reveal that since the diffusivity of one ion is in general dependent on the other ion present, the Nernst–Planck model is capable of no more generality of results than is the Fick's law model. A similar view was expressed by Turner (12), according to whom the Nernst–Planck equation is only theoretically more "correct" than Fick's law.

The results of the proposed model and the excellent fit to the experimental data, therefore, clearly substantiate the methodology of the present work.

The approach developed in this work is expected to be more useful for practical systems mainly because it offers a uniform approach to different types of acids; this is particularly important if the system involves a mixture

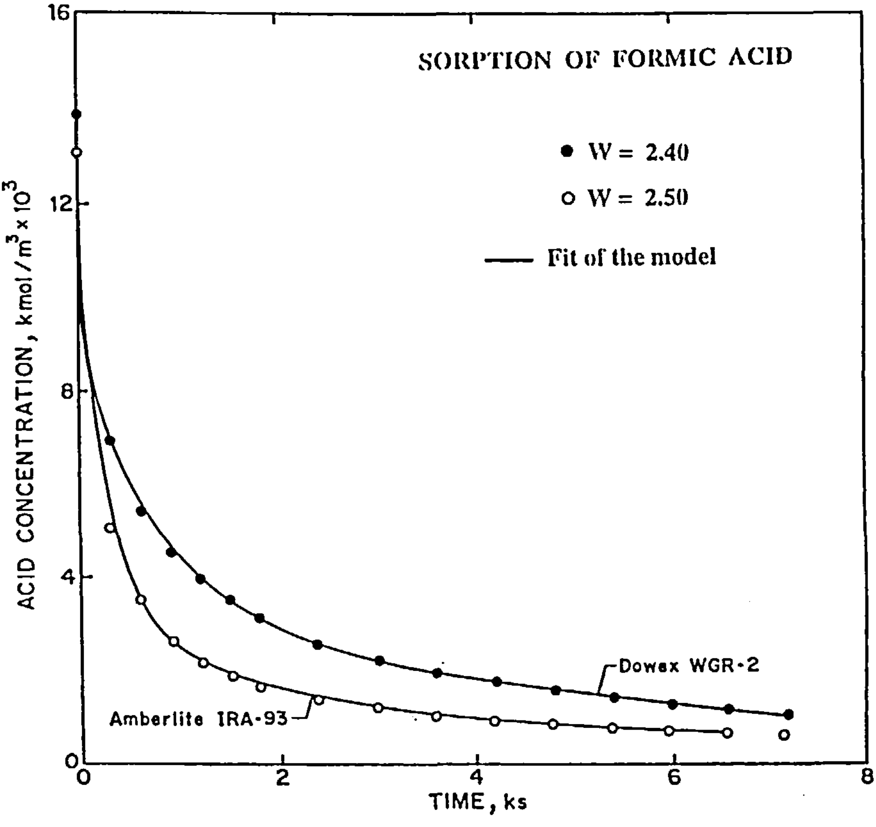

FIG. 3 Fit of the model using the experimental data on sorption dynamics.

TABLE 2
Values of Effective Diffusion Coefficient Regressed from the Model

Resin	Acid	$[HA]_i \times 10^3$ kmol/m^3	W	$D_{HA} \times 10^9$ m^2/s
Amberlite IRA-93	HCl	5.10	1.04	1.00
		10.0	1.00	1.60
		20.0	1.00	1.50
Dowex WGR-2	HCl	5.11	1.43	2.12
		9.50	1.11	0.80
		20.0	1.00	0.75
Amberlite IRA-93	HCOOH	1.35	2.35	0.24
		13.0	2.50	0.42
		24.6	2.00	0.52
Dowex WGR-2	HCOOH	1.46	2.50	1.50
		13.9	2.40	1.02
		28.0	1.50	0.90

of acids. The application of the Nernst–Planck equation in such cases could lead to a complex set of equations involving the electrical potential. Also, conventional models require accounting for each ionic as well as undissociated species with the extent of dissociation and individual diffusion coefficients of all the species. Further, simplifications in these models (for example, the rate-controlling ion model which assumes the co-ion is the rate-controlling ion in the case of a strong acid and the undissociated acid molecule in the case of weak acid) can lead to unrealistic values of the effective diffusion coefficient. Since no model is capable of predicting the sorption behavior without regressing the value of the effective diffusion coefficient (given either by Fick's law or the Nernst–Planck equation), a simple approach fitting the experimental data reasonably well and also giving realistic values of the diffusion coefficient can be most useful from a practical point of view. The approach developed in this work incorporates the above aspects and therefore can have wide applicability for practical systems.

CONCLUSIONS

The present work successfully attempts to simplify the mathematical treatment involved in characterizing the sorption behavior of different types of acids by taking advantage of the weak Donnan potential as predicted by the electrical double layer theory and by incorporating the reversibility of sorption. The values of the effective diffusivity of the composite acid molecule are shown to be reasonable and correct to the order of magnitude. Since the model accounts for the weak Donnan potential and the reversibility of sorption, it has wider applicability than most models reported earlier and can be used as a generalized approach for predicting column behavior without much loss in accuracy. Further, the approach developed is better suited for predicting sorption behavior in mixtures, especially mixtures involving two different types of acids.

NOMENCLATURE

A^-	anion species of acid
a	$[HA]/[HA]_i$
$\bar{a}$	$\overline{[HA]}/[HA]_i$
D_{HA}	effective pore diffusivity of the composite acid molecule (m^2/s)
H^+, H	hydrogen ion species
HA	composite acid species in the extraparticle solution
[H]	concentration of H^+ in extraparticle fluid ($kmol/m^3$)
[HA]	concentration of acid in extraparticle solution ($kmol/m^3$)
$[HA]_i$	initial acid concentration in solution ($kmol/m^3$)
J_{HA}	flux of composite acid species ($kmol/m^2 \cdot s$)
K	equilibrium constant as defined in Eq. (10)
N	number of resin particles per unit volume of extraparticle fluid
n	equilibrium constant as defined in Eq. (10)
Q	resin capacity based on pore volume ($kmol/m^3$)
R_b	radius of resin bead (m)
$\overline{R}$	free base group of resin
$\overline{RH^+}$	protonated species on the resin surface
$\overline{RHA}$	sorbed species on resin
r	radial distance measured from center of bead (m)
r_{HA}	rate of acid sorption per unit volume ($kmol/m^3 \cdot s$)
$[\overline{R}]$	concentration of free base group of resin ($kmol/m^3$)
$[\overline{RHA}]$	concentration of sorbed species ($kmol/m^3$)
t	time (s)
u	$(r/R_b)^2$
W	dimensionless resin loading

Greek Letters

α	$KQ[HA]_i^{n-1}$
β	$K[HA]_i^n$
ϵ_p	fractional pore volume based on total resin volume
τ	tD_{HA}/R_b^2

Subscripts

i initial value

Bar above a Species Refers to the Pore Phase

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