Intraparticle Mass Transport in Liquid-Filled Pores

Adsorption rate data were measured at 25° to 75°C for benzaldehyde on polymeric, porous Amberlite particles. When the benzaldehyde is dissolved in methanol, the adsorption capacity is very low. Data for methanol solutions gave reasonable values for intraparticle diffusivities based solely on transport in the pore volume. For adsorption from aqueous solution (where the adsorption capacity was high), the contribution of surface diffusion was important.

From the two sets of data it was possible to evaluate average effective surface diffusivities by using a model based upon both pore-volume and surface transport. These values were about 10^{-8} cm^2/s and were sufficiently sensitive to temperature to give activation energies of 7 to 9 k cal/mole.

For the more hydrophobic Amberlite, XAD-4, surface transport was many times as large as pore-volume diffusion.

HIROSHI KOMIYAMA
and
J. M. SMITH

University of California
Davis, California 95616

SCOPE

Most studies of intraparticle diffusion have been for gas-filled porous materials because of the importance of gas-solid catalytic reactions. Several of the investigators, Kawazoe (1965), Schneider and Smith (1968), and Reed and Butt (1971), have pointed out the significance of surface diffusion. With increasing applications of trickle-bed processing, examination of intraparticle transport in liquid-filled pores becomes important. There are a few references concerned with liquid-filled pores, but for many of these the chief objective was to determine rates of reaction; intraparticle diffusivities were obtained indirectly by separating the intrinsic kinetics from the observed global rates. In these studies (Satterfield et al., 1965; Komiyama and Inoue, 1971; Kenny and Sedriks, 1972) normal values for tortuosity factors in the pore volume were found, indicating that surface diffusion was negligible. Two references were found that were more directly concerned with intraparticle transport. Both present adsorption data. The first (Knoblauch et al., 1969) discusses the possibility of surface diffusion. In the second (Furusawa and Smith, 1973), it was found that adsorption measurements for benzaldehyde on porous Amberlite and activated carbon particles gave unreasonably high effective diffusivities. It was suggested that surface migration was the reason for the high values.

The significance of surface diffusion seems likely to depend strongly on the properties of the particular system, that is, the combination of adsorbent particle, adsorbate, and other components in the liquid phase. The purpose of the work reported here was to determine quantitatively the importance of surface transport by evaluating intraparticle diffusivities for benzaldehyde in nearby nonadsorbing and in strongly adsorbing systems and for chemically different types of adsorbents.

CONCLUSIONS AND SIGNIFICANCE

Adsorption capacities for benzaldehyde from methanol solution on Amberlite particles were found to be very low at temperatures from 25° to 75°C. These polymeric adsorbents consist of assemblies of nonporous microspheres, and, hence, have a monodispersed pore system. Dynamic desorption experiments in methanol gave effective diffusivities and tortuosities (1.5 to 2.7) that were in the expected range for an array of highly interconnected pores such as would exist in a particle assembled from microspheres.

Similar measurements for benzaldehyde in aqueous solutions gave adsorption capacities about three orders of magnitude larger than those for methanol solution. Further, the effective diffusivities of benzaldehyde in water were about one order of magnitude greater (for XAD-4 Amberlite) than diffusivities for the methanol case. These large D_e values were attributed to surface migration, due to the large capacity of XAD-4 for adsorption and to the low concentrations used in this investigation. The dynamic adsorption curves could be correlated accurately by a transport model which accounted separately for both pore-volume and surface diffusion. The effective surface diffusivities so obtained were about 10^{-8} cm^2/s, or considerably smaller than usual surface diffusivities reported for gas-solid systems. The results indicate that surface migration is the dominant transport mechanism for the strongly hydrophobic XAD-4 particles and of equal importance with pore-volume diffusion for the less hydrophobic XAD-7 Amberlite.

While XAD-4 had a larger adsorption capacity, the surface diffusivity, D_s, for XAD-7 was more than that for XAD-4. The greater importance of surface diffusion for XAD-4 at the low concentrations studied here is believed to be due solely to its adsorption capacity. The higher D_s values for XAD-7 may be related to the lower bonding energy between benzaldehyde and the less hydrophobic surface of XAD-7, as proposed by Higashi et al. (1963) for gaseous systems.

The results demonstrate that surface diffusion can dominate intraparticle mass transport in liquid-filled pores. The data also suggest that it might be possible to correlate surface diffusivities with the bond energy between the adsorbate molecule and the adsorbent surface.

Correspondence concerning this paper should be addressed to J. M. Smith.

Amberlite polymeric particles are well suited for adsorption studies since they are available (Rohm and Haas Company) over a range of hydrophobicities and their pore size distributions are uniform and known. The particles are consolidated assemblies of very small, nonporous microspheres. Adsorption is supposed to occur by van der Waal's forces. For the adsorption of benzaldehyde from an aqueous solution, hydrophobic bonding with the particles is involved. Thus, the more hydrophobic forms of Amberlite more strongly adsorb a hydrophobic adsorbate from aqueous solution than do the hydrophillic forms. Further, it is expected that the adsorption of benzaldehyde from methanol solution would be very weak, since methanol has both hydrophobic and hydrophilic groups. This dependency of the adsorption capacity of Amberlite on the solvent was used to separate the contribution of surface diffusion from the measured overall diffusivities.

Dynamic adsorption experiments were first carried out for the adsorption of benzaldehyde from methanol solutions using a very hydrophobic Amberlite (XAD-4; polystyrene particles) and a somewhat hydrophilic Amberlite (XAD-7, acrylic ester particles). Diffusion occurred predominantly in the volume of the liquid-filled pores because the adsorption capacity was slight. From these data, tortuosity factors characteristic of pore-volume diffusion in the two Amberlite particles were obtained. Since adsorption was low and therefore difficult to measure accurately, rates of desorption were determined. The method consisted of inserting a stainless steel basket, containing Amberlite particles whose pores were filled with a known benzaldehyde concentration, into a vessel of well-stirred, pure methanol. The benzaldehyde concentration in the methanol was measured continuously. The concentration vs. time curves were analyzed to determine intraparticle diffusivities and tortuosity factors.

Subsequently, similar measurements were made using aqueous solutions. In this case benzaldehyde is strongly adsorbed by the particles. Initially, a 5.0 cm^3 solution (2100 ppm) of benzaldehyde in water was rapidly introduced into the stirred absorption vessel filled with water. The vessel contained stationary baskets holding the benzaldehyde-free particles. The concentration of benzaldehyde in the bulk water phase was measured continuously. These concentration vs. time curves were used, along with the previously established tortuosity factors, to evaluate surface diffusivities for the aqueous solution-Amberlite systems.

APPARATUS AND PROCEDURE

The Pyrex adsorption vessel (Figure 1) was equipped with an 8-bladed impeller and 4 or 8 stationary, equally spaced, baskets made of 40 mesh stainless steel screen. The baskets, used to hold the adsorbent particles, were approximately rectangular in cross section, 20 mm in height and with a 10 × 10 mm cross section. The centerline of the baskets was located at the same elevation as the centerline of the blades on the impeller.

Preliminary runs were made at impeller speeds of 400, 700, and 1050 rev./min. The three concentration vs. time curves agreed with each other within 2% and there was no trend with rotation speed. It was concluded that the effect of fluid-to-particle mass transfer resistance was negligible. The remainder of the data were obtained with impeller speeds of 600 to 800 rev./min.

The benzaldehyde concentration in the bulk liquid was measured by continuously withdrawing a small stream [2 cm^3/min. for small capacity pump and 30 to 60 cm^3/min. for large pump] from the adsorber and pumping it through an ultraviolet photometer of 0.02 cm^3 cell volume, operating with 2750 Å radiation. The flow was returned to the adsorber from the photometer. There was a small amount of dispersion in the lines from the vessel to the photometer and particularly in the pump. Depending on the adsorption time, one of two pumps was used: a relatively large capacity pump of very constant flow rate with relatively more dispersion or a small capacity unit with little dispersion.

Even a small amount of dispersion had a significant effect on the measured concentration vs. time curves for a time period at the start of a run. Hence, careful tests were made to determine the response time of the measuring system. This was done by injecting samples of benzaldehyde solutions (in water) into the agitated vessel filled with pure water. The response curve measured at the photometer could be approximated with the expression for a well-mixed vessel.

$$C_{\text{meas}} = C_0\,(1 - e^{-t/\tau}) \qquad (1)$$

where t is the time measured from the time of the initial response of the photometer, C_0 is the concentration in the vessel, and τ is a time constant for the measuring system. Tests gave values of $\tau = 30$ s and $\tau = 2.5$ s for the large capacity and small capacity pumps, respectively.

During an adsorption run, the true concentration in the liquid in the vessel can be approximated by the equation

$$C_{\text{true}} = C_\infty + (C_0 - C_\infty)e^{-t/\tau'} \qquad (2)$$

in which τ' is the time constant for the adsorption system. Approximate values of τ' can be obtained from Equation (2) for each adsorption run. With C_{true} from Equation (2) as the input to the measuring system, the concentration measured at the photometer during adsorption is related to τ and τ' by the expression

$$C_{\text{meas}} = C_\infty\,(1 - e^{-t/\tau}) + \frac{C_0 - C_\infty}{1 - \tau/\tau'}\,[e^{-t/\tau'} - e^{-t/\tau}] \qquad (3)$$

Then the relative error in the measuring system, defined as $(C_{\text{true}} - C_{\text{meas}})/(C_{\text{true}} - C_\infty)$, can be expressed in terms of τ and τ' as follows:

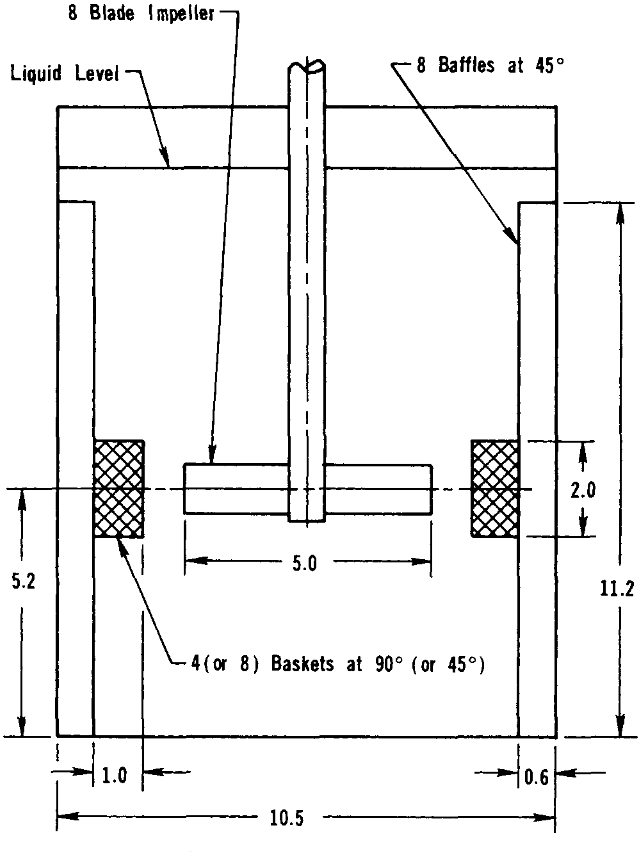

Fig. 1. Adsorption vessel (dimensions in cm).

TABLE 1. SCOPE OF MEASUREMENTS

A. Properties of adsorbents*	Amberlite XAD-4	Amberlite XAD-7
Solid phase density, g/cm^3	1.08	1.24
Surface area (dry), m^2/g	750	450
Porosity of dry particles	0.51	0.55
Particle density (dry), g/cm^3	0.529	0.558
Particle diameter, cm		
dry	0.0778	0.0674
in water	0.0800	0.0860
in methanol	0.0816	0.0860
Volume swelling factor, S.F.		
in water	1.076	1.95
in methanol	1.15	1.95
Nominal pore diameter, Å	50	80

B. Volume of liquid in adsorber, V, cm^3 = 1000

C. Volume of solid, v, cm^3 = 0.72 to 10

D. Initial concentration of benzaldehyde in bulk liquid, ppm = 10.5

E. Impeller speed, rev./min. = 400 to 1050

[*] From Summary Bulletin on Amberlite Polymeric Adsorbents, IE-172, Rohm and Haas, Philadelphia, Pa. 19105.

$$\frac{C_{\text{true}} - C_{\text{meas}}}{C_{\text{true}} - C_\infty} = \frac{-\tau/\tau'}{1-\tau/\tau'} + \left[\frac{C_\infty}{C_0 - C_\infty} + \frac{1}{1-\tau/\tau'}\right] e^{t\left(\frac{1}{\tau'} - \frac{1}{\tau}\right)} \qquad (4)$$

The measured values of τ/τ' were less than 0.1 in all but one run. The second term of Equation (4) is negligible for $t > 5\tau$. Also, the magnitude of the correction becomes relatively large for time values less than 5τ so that the data before 13 s with the small capacity pump and before 2.5 min. with the large pump were not used in the analysis. For the period after 5τ, the measured concentration was corrected to give C_{true} by using Equation (4). The magnitudes of the relative error ranged from 0.02 to 0.08 except for two runs where the error was as high as 0.15. It is believed that with this correction method the error due to the measuring system was reduced to the level of the normal experimental uncertainty in the data. For example, if the error in the correction method is as high as 20%, the resulting uncertainty in C_{true} is no more than 3% of $(C_{\text{true}} - C_\infty)$.

The physical properties of the adsorbents and some operating conditions are given in Table 1. Amberlite particles swell in water or in methanol. This effect was evaluated by measuring diameters of the particles, in prints (3.7 magnification) of photographs taken of a sample of particles placed on black paper. Approximately 100 particles were measured from the photographs of the dry, wet with methanol, and wet with water, particles. Swellng factors (S.F.) are included in Table 1.

METHANOL SOLUTION RESULTS

Adsorption isotherms at 25°C were measured by introducing known samples of benzaldehyde solution into a flask containing a slurry of the particles in pure methanol and shaking until equilibrium was achieved. The results, shown in Figure 2, indicate that the amounts adsorbed are small; they are about three orders of magnitude less than the adsorption from aqueous solutions at the same liquid concentration (Figure 4). For these small adsorptions the isotherms can be represented by the linear relation:

$$q = K\,C \qquad (5)$$

where

$K = 1.3$ (g/cm^3 of adsorbent)/(g/cm^3 of liquid) for XAD-4

$K = 0.29$ for XAD-7

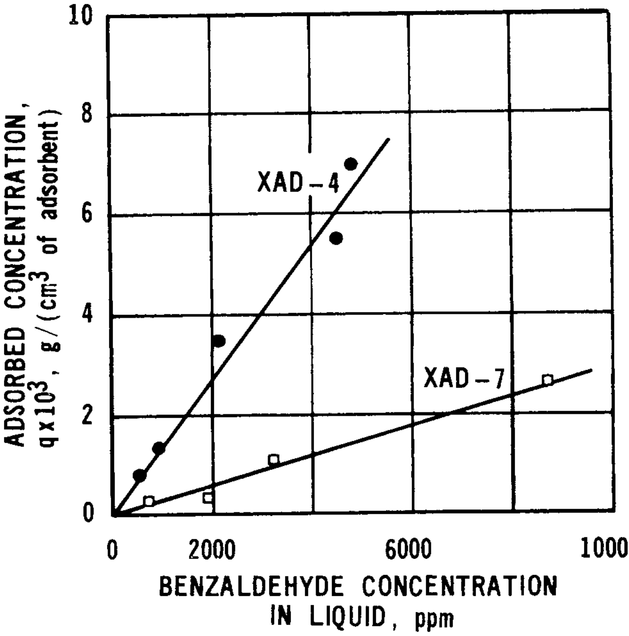

Fig. 2. Adsorption isotherms for benzaldehyde (in methanol) on amberlite XAD-4 and XAD-7 at 25°C.

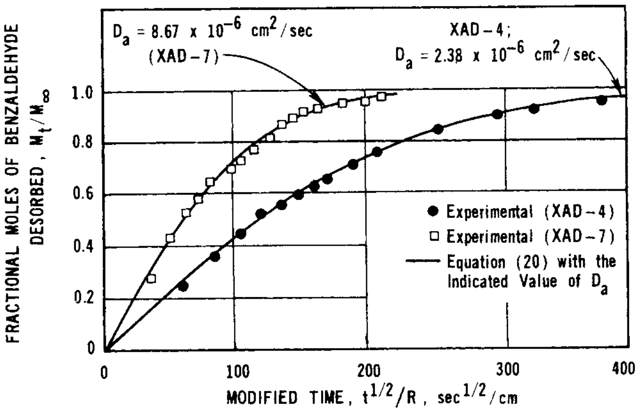

Fig. 3. Desorption curves of benzaldehyde from amberlite particles into methanol.

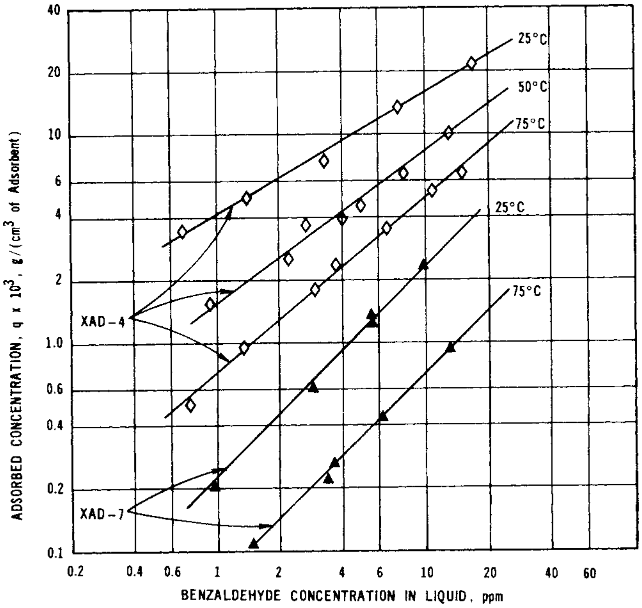

Fig. 4. Adsorption isotherms for benzaldehyde (in water) on amberlite XAD-4 and XAD-7.

In treating the dynamic desorption data, it was assumed that the physical adsorption step at an interior site in the particle was rapid with respect to intraparticle diffusion. This means that the concentration in the liquid and on the solid are in equilibrium and related by Equation (5). Hence

$$\frac{\partial q}{\partial t} = K \frac{\partial C}{\partial t} \tag{6}$$

Particle-to-fluid mass transfer resistance has been eliminated in the adsorber by stirring. Then, if it is assumed that the benzaldehyde concentration in the vessel is uniform, conservation equations for benzaldehyde in the bulk fluid and in the particles are

$$V \frac{dC}{dt} = - D_e\, S_s \left| \frac{\partial C_r}{\partial r} \right|_{r=R} \tag{7}$$

$$\epsilon_p \frac{\partial C_r}{\partial t} + \frac{\partial q}{\partial t} = D_e \left(\frac{\partial^2 C_r}{\partial r^2} + \frac{2}{r} \frac{\partial C_r}{\partial r} \right) \tag{8}$$

In writing Equation (8) it is supposed that surface diffusion is negligible since the adsorption is low. The volume v of the particles is calculable from the measured mass of adsorbent, the density of the dry particles, and the swelling factor, according to the equation

$$v = \frac{m}{\rho_p} \,(\mathrm{S.F.}) \tag{9}$$

It is this volume upon which the concentration q is based. Since Amberlite particles are smooth spheres, the outer surface area is given by

$$S_s = \frac{3v}{R} \tag{10}$$

Since v and R have been measured S_s can be calculated from Equation (10).

For the desorption experiments, the initial and boundary conditions are

$$\text{at} \quad t = 0: \quad C = 0, \;\; C_r = C_0 \; (0 \leqq r \leqq R) \tag{11}$$

$$\text{at} \quad t > 0: \quad \left(\frac{\partial C_r}{\partial r} \right)_{r=0} = 0 \tag{12}$$

$$C = C_r \quad \text{at} \quad r = R \tag{13}$$

Equations (7), (8), and (11) to (13) may be written in the form

$$\frac{\partial C_r}{\partial t} = D_a \left(\frac{\partial^2 C_r}{\partial r^2} + \frac{2}{r} \frac{\partial C_r}{\partial r} \right) \tag{14}$$

$$\text{at} \quad t = 0: \quad (C_r)_{r=R} = 0, \;\; C_r = C_0 \; (0 \leqq r \leqq R) \tag{15}$$

$$\text{at} \quad t > 0: \quad \left(\frac{\partial C_r}{\partial r} \right)_{r=0} = 0 \tag{16}$$

$$\frac{\partial C_r}{\partial t} = - \frac{3\, D_a\, \alpha (\epsilon_p + K)}{R} \frac{\partial C_r}{\partial r} \quad \text{at} \quad r = R \tag{17}$$

where

$$D_a = \frac{D_e}{\epsilon_p + K} \tag{18}$$

$$\alpha = v/V \tag{19}$$

The solution of Equation (14) with (15) to (17) is given by Crank (1956) as

$$\frac{M_t}{M_\infty} = 1 - \sum_n \frac{6\, \phi (\phi + 1) \exp\left[-(D_a t/R^2) \lambda_n^2\right]}{9 + 9\phi + \lambda_n^2\, \phi^2} \tag{20}$$

where λ_n are the nonzero roots of

$$\tan \lambda_n = \frac{3\lambda_n}{3 + \phi\, \lambda_n^2} \tag{21}$$

and

$$\phi = \frac{\epsilon_p + K}{\alpha} \tag{22}$$

For desorption M_t is the total amount of adsorbate in the bulk liquid in the vessel after time t, while M_∞ is the corresponding quantity at infinite time. From the known volume of liquid and the measured concentration vs. time data, a curve of M_t/M_∞ vs. time can be obtained. Comparison of this experimental curve with Equation (20) determines D_a. Figure 3 shows the results for XAD-4 and XAD-7 and indicates that the model resulting in Equation (20) agrees well with the data. The D_a values are given in Table 2.

To obtain tortuosity information for the porous particles it is necessary first to calculate D_e from Equation (18). It is difficult to measure ϵ_p directly for the particles (swollen) filled with methanol. However, $(\epsilon_p + K)$ can be established by equating the total benzaldehyde in both phases at the beginning of each desorption experiment to that at the end of the run:

$$0 + v\, C_0\, (\epsilon_p + K) = V\, C_\infty + v\, C_\infty\, (\epsilon_p + K)$$

or

$$\epsilon_p + K = \frac{C_\infty}{\alpha (C_0 - C_\infty)} \tag{23}$$

Eliminating $(\epsilon_p + K)$ from Equations (18) and (23) gives

$$D_e = D_a \frac{C_\infty}{\alpha (C_0 - C_\infty)} \tag{24}$$

Values of D_e computed from this expression are given in Table 2. Since all the diffusion is in the pore volume (no surface diffusion), D_e is related to the pore-volume tortuosity factor τ by the defining expression

$$D_e = \frac{\epsilon_p\, D_{BM}}{\gamma} \tag{25}$$

where D_{BM} is the molecular diffusivity of benzaldehyde in methanol at 25°C. An experimental diffusivity is available at 15°C (Bruins, 1929). Using the temperature dependency given by the Othmer-Thakar equation (Reid and Sherwood, 1966), the diffusivity at 25°C was predicted to be 1.95×10^{-5} cm^2/s. With this value of D_{BM}, ϵ_p/γ was calculated from Equation (25). The results are given in Table 2.

These values of ϵ_p/γ were used later to determine the pore-volume diffusion when benzaldehyde was adsorbed from aqueous solution. It is not necessary to know the tortuosity factor separately for this purpose. However, approximate values can be obtained by estimating ϵ_p. For XAD-4 Amberlite the swelling was slight (see Table 1) so that ϵ_p is close to 0.51. For XAD-7, where swelling is

TABLE 2. TRANSPORT PROPERTIES OF BENZALDEHYDE (IN METHANOL SOLUTION) IN AMBERLITE PARTICLES

	XAD-4	XAD-7
D_a, cm^2/s	2.38×10^{-6}	8.67×10^{-6}
D_e, cm^2/s	3.66×10^{-6}	8.02×10^{-6}
D_{BM}, cm^2/s	1.95×10^{-5}	1.95×10^{-5}
ϵ_p/γ	0.188	0.414
γ	2.72	1.54

TABLE 3. ADSORPTION ISOTHERMS FOR AQUEOUS SOLUTIONS

Temp.	Amberlite XAD-4	Amberlite XAD-7
25°C	$q = 3810C^{0.578}$	$q = 205C$
50°C	$q = 1670C^{0.731}$	
75°C	$q = 700C^{0.829}$	$q = 71C$

C in g/cm³ of water; q in g/cm³ of wet adsorbent.

large, ϵ_p was calculated from $\epsilon_p + K$. From Equation (23), $\epsilon_p + K$ was found to be 0.925 so that $\epsilon_p = 0.925 - 0.29 = 0.63$, in comparison with 0.55 for the dry particles (Table 1). Using these porosities, the approximate tortuosity factors are 2.72 for XAD-4 and 1.54 for XAD-7. These relatively low tortuosities are anticipated for large-porosity assemblies of nonporous microspheres. As expected, τ is less for XAD-7 particles because the porosity is larger.

AQUEOUS SOLUTION RESULTS

Adsorption Isotherms

Adsorption isotherms for benzaldehyde in aqueous slurries of Amberlite were measured at 25° to 75°C and the results are given in Figure 4. For XAD-7 the isotherms were linear (slope of lines in Figure 4 is unity) but for XAD-4 the Freundlich equation was needed to correlate the data. Although the surface area for XAD-4 is less than twice that of XAD-7, its adsorption capacity is nearly an order of magnitude larger due to the greater hydrophobicity of XAD-4. The isotherm equations are given in Table 3.

Evidence for Surface Diffusion

The dynamic adsorption experiments were first analyzed by the method used for the methanol-solution data. That is, curves of M_t/M_∞ were predicted from Equations (7) and (8) and (11) to (13) except that the following initial condition for adsorption was used, rather than Equation (11):

$$\text{at } t = 0: \quad C = C_0, \quad C_r = 0 \quad (0 \leq r \leq R) \qquad (26)$$

The diffusivity D_e was calculated from Equation (25) employing ϵ_p/γ, values obtained from the methanol results (Table 2) and replacing D_{BM} with D_{BW}. This is based upon the absence of surface diffusion so that $D_e = D_L$ where D_L is the effective diffusivity in the pore volume. Since the swelling factors in water and in methanol are about the same (Table 1), the assumption that ϵ_p/γ is the same for both solutions should be a reasonable one. The molecular diffusivities for benzaldehyde-water were calculated using the Othmer-Thaker equation (Reid and Sherwood 1966). These values and those for D_L are given in Table 4.

The solution of Equations (7), (8), (26), (12), and (13) can be put in the form of M_t/M_∞. The results are different than Equation (20) because for XAD-4 the isotherms were nonlinear, requiring a numerical solution, and because adsorption experiments were made rather than desorption. The dotted lines in Figures 5 to 7 give the predicted M_t/M_∞ curves. In all cases the experimental points are not in agreement with the predicted curves, but for XAD-4 (Figures 6 and 7) the differences are striking.

The more rapid uptake shown by the experimental data suggests that intraparticle diffusion resistance is less than predicted by D_L. We interpret this to mean that surface diffusion is significant. The differences in these figures between predicted and experimental curves is much more (for example, Figure 7) than could be accounted for by the possible uncertainty in using ϵ_p/γ values obtained from the methanol data. Also the deviation is in the opposite direction from that expected if the adsorption step at the interior site did not occur at near-equilibrium conditions, as assumed. Another potential explanation is that surface migration is not involved, but that the pore-volume diffusivity varies with concentration. However, concentrations were highest for the methanol system (desorption runs), but the higher intraparticle mass transport occurred for the runs with water as the solvent. Also in all runs the concentrations were so low (maximum value = 0.5 wt %) that little variation of molecular diffusivities with concentration is expected.

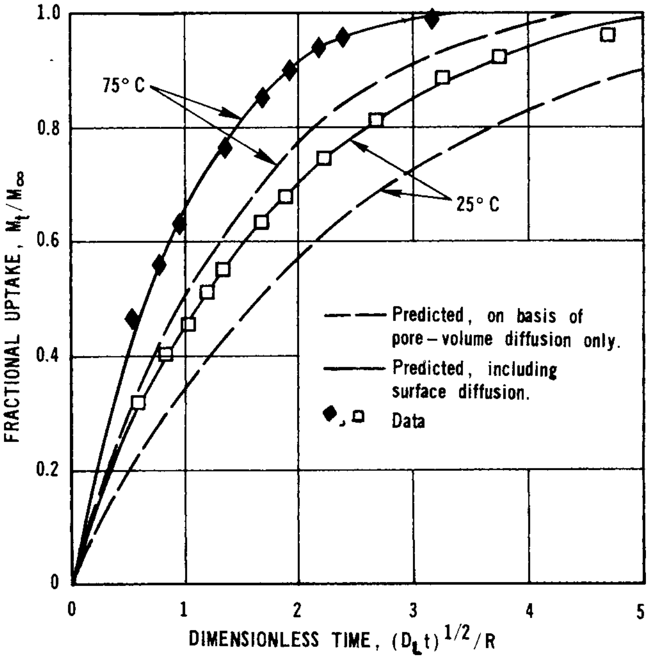

Fig. 5. Adsorption curve of benzaldehyde (in water) for amberlite (XAD-7): v = 3.89 cm³ (25°C) or 10.0 cm³ (75°C); and C_∞/C_0 = 0.523 (25°C) or 0.585 (75°C).

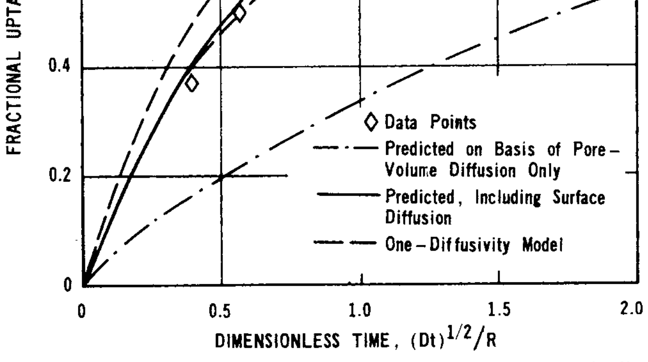

Fig. 6. Adsorption curve of benzaldehyde (in water) for amberlite (XAD-4) v = 2.57 cm³; C_∞/C_0 = 0.0804.

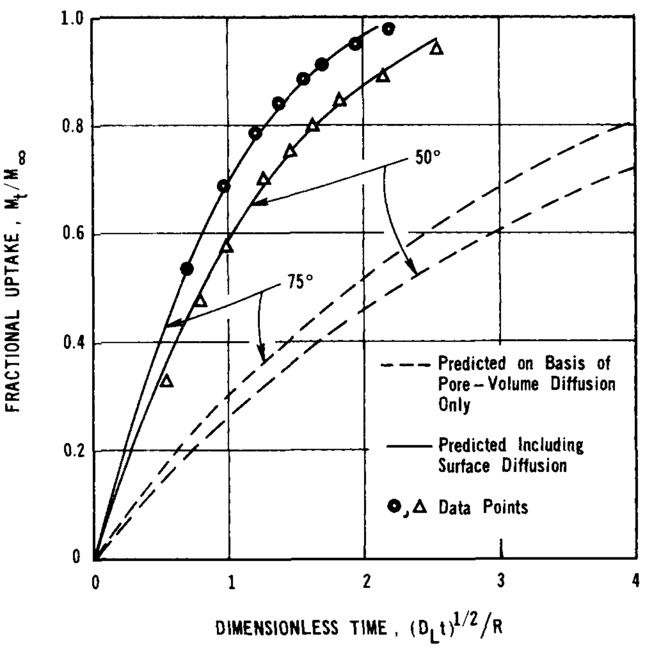

Fig. 7. Adsorption curve of benzaldehyde (in water) for amberlite (XAD-4): v = 2.05 cm³ (50°C) or 2.96 cm³ (75°C); and C_∞/C_0 = 0.261 (50°C) or 0.337 (75°C).

Surface Diffusivities

To incorporate surface diffusion into the mass conservation equation, it is convenient to define a surface diffusivity D_s (based upon the total void plus nonvoid area) in terms of Fick's equation for the diffusive flux

$$N_s = -D_s \frac{\partial q}{\partial r} \tag{27}$$

Then conservation Equations (8) and (9) become

$$V\frac{dC}{dt} = -S_s\left[D_L\left(\frac{\partial C_r}{\partial r}\right)_{r=R} + D_s\left(\frac{\partial q}{\partial r}\right)_{r=R}\right] \tag{28}$$

and

$$\epsilon_p \frac{\partial C_r}{\partial t} + \frac{\partial q}{\partial t} = D_L\left(\frac{\partial^2 C_r}{\partial r^2} + \frac{2}{r}\frac{\partial C_r}{\partial r}\right) + D_s\left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r}\frac{\partial q}{\partial r}\right) \tag{29}$$

with boundary and initial conditions given by Equations (12), (13), and (26). The relations between q and C are those given by the isotherm equations in Table 3.

Since D_L is known (Table 4), Equations (28) and (29), with the boundary and initial conditions, may be solved to determine M_t/M_∞ vs. time. For a nonlinear isotherm (XAD-4) a numerical solution is required. The predicted curves can then be compared with the experimental points in Figures 5 to 7 to establish the most appropriate values of D_s. The solid curves in Figures 5 to 7 show that the model including surface diffusion fits the data well over the entire time period. The values of D_s corresponding to the solid curves are given in Table 4.

If the adsorption isotherm is linear, Equation (6) is applicable so that Equation (29) reduces to the single expression:

$$\frac{\partial C}{\partial t} = \frac{D_L + K\,D_s}{\epsilon_p + K}\left(\frac{\partial^2 C_r}{\partial r^2} + \frac{2}{r}\frac{\partial C_r}{\partial r}\right) \tag{30}$$

Equation (30) is the same as Equation (14) if $D_a = (D_L + K\,D_s)/(\epsilon_p + K)$ or $D_e = D_L + K\,D_s$. This means that a one-diffusivity model should represent the experimental results in Figures 5 to 7 if the isotherm is linear. This is not the case for XAD-4 particles as illustrated by the dashed curves in Figure 6. Regardless of the choice of D_e, these curves do not fit the data.

An Arrhenius plot of the surface diffusivities is given in Figure 8. The diffusivities are moderately strong functions of temperature corresponding to activation energies of 7.1 k cal/mole for XAD-4 and 9.6 k cal/mole for XAD-7.

DISCUSSION

The difference between the experimental data and the predicted curves assuming pore-volume diffusion only (dotted lines) in Figures 5 to 7 shows the large effect of surface diffusion in a pictorial way. A more direct, quantitative measure can be obtained by noting that the total diffusive flux at any radial position is given by

$$\text{Total mass flux} = -D_L\frac{\partial C}{\partial r} - D_s\frac{\partial q}{\partial r} = -\left(D_L + D_s\frac{\partial q}{\partial C}\right)\frac{\partial C}{\partial r} \tag{31}$$

Hence, the relative importance of surface diffusion to pore-volume diffusion is given by $\left(D_s\frac{\partial q}{\partial C}\right)\Big/ D_L$. If the constraints in the Freundlich isotherm are k and p, according to the form,

$$q = k\,C^p \tag{32}$$

and Equation (5) is used for the linear isotherm, the relative importance may be described by the ratios in the last column of the following table:

Isotherm type	Amberlite	Relative Importance of surface diffusion
Linear	XAD-7	$K\,D_s/D_L$
Nonlinear	XAD-4	$(k\,p\,c^{p-1})D_s/D_L$

Table 4. Transport Properties of Benzaldehyde (Aqueous Solution) in Amberlite Particles

	XAD-4			XAD-7	
	25°	50°C	75°C	25°C	75°C
D_{BW}, cm²/s	0.913×10^{-5}	1.54×10^{-5}	2.22×10^{-5}	0.913×10^{-5}	2.22×10^{-5}
D_L, cm²/s	1.69×10^{-6}	2.85×10^{-6}	4.10×10^{-6}	3.78×10^{-6}	9.19×10^{-6}
D_s, cm²/s	1.10×10^{-8}	2.22×10^{-8}	5.90×10^{-8}	1.50×10^{-8}	1.51×10^{-7}
$k\,p\,C^{p-1}\,D_s/D_L$					
$C = 1$ ppm	14.3	9.5	8.4		
$C = 10$ ppm	5.6	5.1	5.6		
$K\,D_s/D_L$				0.93	1.17

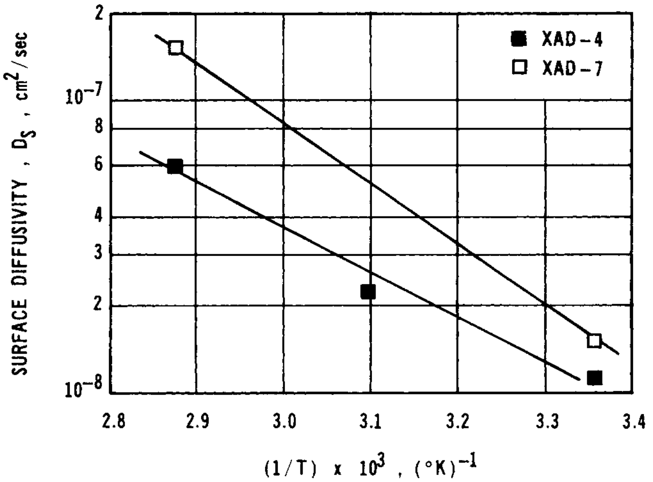

Fig. 8. Temperature dependency of surface diffusivity.

The ratios were evaluated at two concentration levels (1 and 10 ppm) and the results are given in Table 4. It is concluded that surface diffusion is dominant for XAD-4 (5 to 14 times the contribution of pore-volume transport) and about of equal importance to pore-volume diffusion for XAD-7.

The importance of surface diffusion in aqueous solution for XAD-4 at the low concentrations studied is due to the high adsorption capacity for benzaldehyde for this hydrophobic adsorbent rather than due to large values of D_s. As Figure 8 shows, surface diffusivities, defined by Equation (27), are somewhat larger for XAD-7. These relative values suggest that the surface diffusivity is a decreasing function of the binding energy between adsorbate molecule and adsorbent surface; that is, the attraction is stronger for benzaldehyde and the more hydrophobic XAD-4 than between benzaldehyde and XAD-7. This is in qualitative agreement with the model introduced by Higashi et al. (1963) to relate surface diffusion to the binding energy for gaseous molecules adsorbed on surfaces. Surface diffusivities can vary significantly with surface coverage. Since adsorbed concentrations varied during a run, the D_s results (Table 4) are average values.

ACKNOWLEDGMENT

Financial support of the American Chemical Society, through PRF Grant #4155-AC7 and the National Science Foundation, Grant GK 38881 is gratefully acknowledged. Also appreciation is expressed to Rohm and Haas Company for the Amberlite materials.

NOTATION

C = concentration of benzaldehyde in bulk liquid, g/cm^3; C_{meas} = concentration observed at the measuring device (photometer); C_{true} = true concentration in bulk liquid in adsorber; C_0 = concentration at $t = 0$; C_∞ = concentration at infinite time.
C_r = concentration of benzaldehyde in pore volume of Amberlite particles, g/cm^3
D_a = apparent diffusivity, defined by Equation (18), cm^2/s
D_{BM} = molecular diffusivity of benzaldehyde in methanol; D_{BW} = diffusivity in water, cm^2/s
D_e = effective diffusivity in porous particles, cm^2/s
D_L = effective pore-volume diffusivity, cm^2/s
D_s = effective surface diffusivity, cm^2/s
M_t = amount of adsorbate on adsorbent (for adsor tion) or in bulk liquid (for desorption) at time g; M_∞ is the amount at infinite time
K = adsorption equilibrium constant for linear isother [Equation (5)]
k = coefficient in Freundlich isotherm [Equatic (32)], (g/cm^3)$^{p-1}$
m = mass of Amberlite particles in adsorber, g
N_s = surface flux through total area perpendicular diffusion, g/s cm^2
p = exponent in Freundlich equation, Equation (32
q = concentration of adsorbed benzaldehyde, g/(cm of wet particles)
r = radial coordinate, cm
R = radius of particle, cm
S.F. = swelling factor, defined as ratio of volumes of we and dry Amberlite particles
S_s = total external area of particles in adsorber, cm^2
T = absolute temperature, °K
t = time, s
V = volume of particle-free liquid in adsorber, cm^3
v = total volume of wet particles in adsorber, cm^3

Greek Letters

α = v/V
ϵ_p = porosity of wet particles
γ = tortuosity factor
λ_n = nonzero roots of Equation (21)
ϕ = defined by Equation (22)
ρ_p = density of dry particles, g/cm^3
τ = time constant for the response of the measuring system, s
τ' = time constant of the adsorption system, s

LITERATURE CITED

Bruins, H. R., *International Critical Tables*, **5**, 73 (1929).

Crank, J., *The Mathematics of Diffusion*, p. 88, Clarendon Press, Oxford (1956).

Furusawa, T., and J. M. Smith, "Fluid-Particle and Intraparticle Mass Transport in Slurries," *Ind. Eng. Chem. Fundamentals*, **12**, 197 (1973).

Furusawa, T., and J. M. Smith, "Intraparticle Mass Transport in Slurries by Dynamic Adsorption Studies," *AIChE J.*, **20**, 88 (1974).

Higashi, K., H. Ito, and J. Oishi, "Surface Diffusion Phenomena in Gaseous Diffusion, (I) Surface Diffusion of Pure Gas," *J. Atomic Energy Soc. Japan*, **5**, 846 (1963).

Kawazoe, K., "Investigation into Mass Transfer in Adsorption Columns," Ph.D. dissertation, University of Tokyo, Japan (1965).

Knoblauch, K., H. Juntgen, and W. Peters, "Adsorption en Wasser geluster Substanzen an Adsorptionskoksen," *Chem. Ing. Techn.*, **41**, 798 (1969).

Kenny, C. N., and W. Sedriks, "Effectiveness Factors in a Three-Phase Slurry Reactor," *Chem. Eng. Sci.*, **27**, 2029 (1972).

Komiyama, H., and H. Inoue, "Performance of a Packed Bed Reactor of a Supported Liquid Phase Catalyst," *Catalyst (Japan)*, **13**, 143p (1971).

Reed, E. M., Jr., and J. B. Butt, "Surface diffusion of Single Sorbate at Low and Intermediate Surface Coverage," *J. Phys. Chem.*, **75**, 133 (1971).

Reid, R. C., and T. K. Sherwood, *The Properties of Gases and Liquids*, Second Edit., p. 548, McGraw-Hill New York (1966).

Satterfield, C. N., Y. H. Ma, and T. K. Sherwood, "The Effectiveness Factor in a Liquid-Filled Porous Catalyst," *Chem. Eng. Symp. Ser. (Br.)*, No. 28, 22 (1968).

Schneider, P., and J. M. Smith, "Chromatographic Study of Surface Diffusion," *AIChE J.*, **14**, 886 (1968).

Manuscript received February 5, 1974; revision received April 2 and accepted April 6, 1974.