Surface Diffusion in Liquid-Filled Pores

Surface diffusivities of benzaldehyde in liquid-filled pores of Amberlite particles (polystyrene) were measured at 25°C using water as a solvent. For particles of different surface areas but chemically similar pore surfaces, the intrinsic surface diffusivity D_s' was about the same, but the relative importance of surface to pore-volume diffusion increased with surface area. For a single type of particle, the adsorption capacity was decreased about twenty-fold by adding up to 19 mole % methanol to the solvent. This was accompanied by an increase in D_s' from 1.2×10^{-8} to 1.2×10^{-7} cm^2/s. These results were interpreted in terms of a two-step theory for surface migration: (1) formation of a vacant site on the adsorbent surface followed by (2) movement of the adsorbate molecule into the site by breaking the surface-adsorbate bond. The theory predicts that surface transport will be large when the surface area is high and that the D_s' will be large when the heat of adsorption is low, and when the bond between solvent molecules and the surface is weak.

In our studies the surface contribution to intraparticle transport was as much as 20 times the contribution due to pore-volume diffusion. This ratio increases as the concentration of adsorbate in the liquid decreases.

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SCOPE

Adsorption processes in liquid systems, for example, purification of wastewaters, are often strongly affected by intraparticle diffusion. This is because the intrinsic rate of the physical adsorption process at an interior site in the adsorbent particle is rapid with respect to diffusion. Hence, an understanding of intraparticle transport is necessary for the design of liquid-phase adsorption systems. In porous adsorbents, such transport can occur by diffusion within the pore volume or by migration on the pore walls. Some recent investigations in this field (Hashimoto et al., 1973; Urano, 1973; Kawazoe et al., 1968; Knoblauch et al., 1969; Furusawa and Smith, 1974) have proposed that the latter process, surface diffusion, might be an important contribution. This conclusion was reached indirectly in that the surface contribution was separated from pore-volume transport by utilizing the dependency of the observed total diffusivity on the concentration of adsorbate for nonlinear adsorption steps; that is, for nonlinear adsorption isotherms. In a study of intraparticle diffusion Komiyama and Smith (1974a) used the more direct method of changing the adsorption capacity by varying the solvent in which the adsorbate is dissolved. First, the pore-volume contribution was determined using a solvent such that adsorption was negligible. Then this contribution was subtracted from the total diffusivity observed for a solvent from which the adsorbate was strongly adsorbed.

The success of this method indicated that it might be used to carry out a careful study of surface migration itself. The objectives were twofold: (1) to determine the factors that influence the magnitude of surface transport with respect to pore-volume diffusion, and (2) to separate the effect of surface area on the diffusive flux so that some of the factors influencing the intrinsic surface diffusivity could be examined. The experimental work consisted first of measuring the rate of adsorption of benzaldehyde from aqueous solution on three types of polystyrene porous particles (Amberlite particles) which had different surface areas but nearly the same surface chemically. Then in the second phase, adsorption rates were obtained for one type of particle using as solvents for the benzaldehyde various mixtures of water and methanol. The adsorption capacity, and presumably the heat of adsorption, changed with solvent composition so that these results provided information for the effect of bonding energy on the surface diffusivity.

CONCLUSIONS AND SIGNIFICANCE

A theory was developed for correlating the surface diffusivity in terms of the heat of adsorption and the free energy of activation ΔF_h^* for forming a vacant site adjacent to an adsorbed molecule. For a linear adsorption isotherm the intrinsic surface diffusivity could be expressed in terms of the adsorption equilibrium constant per unit area K/S_g and ΔF_h^*. The resulting equation showed ln D_s' to be a linear function of ln K/S_g. The theory predicts that surface diffusivities increase as the heat of adsorption decreases and as the bond becomes weaker between solvent molecules and adsorbent surface.

The results for Amberlites of different surface area showed different adsorption capacities but nearly the same intrinsic surface diffusivities in accordance with the theory. When the methanol content of the solvent was increased from 0 to $x_m = 0.19$, the adsorption capacity decreased more than one order of magnitude while the intrinsic surface diffusivity increased from 1.2×10^{-8} to 1.2×10^{-7} cm^2/s. Further increase in x_m was accompanied by a slight maximum in D_s'. While the adsorption isotherms

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were not linear, an apparent equilibrium constant could be calculated from the Freudlich representation of the isotherm. The increase in ln D_s' followed the linear relationship suggested by theory and is attributed to the decrease in bonding energy between benzaldehyde and the surface as the methanol content of the solvent increases. It is postulated that the slight maximum in surface diffusivity at higher x_m is due to increased adsorption of methanol resulting in an increase in ΔF_h^*. Data for other systems, including heats of adsorption, are needed to test further the proposed theory. Satterfield et al. (1973) in a study of diffusion of liquids in very fine pores (32 A) also concluded that the surface diffusivity was a decreasing function of the adsorption equilibrium constant. Their conclusions about surface diffusion were tentative because the results were influenced by the small size of the pores with respect to the diameter of the diffusing molecules.

The results for our range of adsorbate concentrations ($\leq$ 10 ppm) showed that the surface contribution was up to 20 times as large as the pore-volume contribution. The relative importance of surface transport increases as the adsorbate concentration decreases. This may be of practical significance in the design of equipment for removal of small concentrations of pollutants from water since the diffusion rate into the particles will be much greater than that predicted by neglecting surface transport. The correlation in Figure 8 suggests a method for predicting the surface diffusivity from well defined and easily measurable quantities.

Theories of surface diffusion on porous solids of high surface area have been proposed for gas-filled pores. For example, Higashi et al. (1963) related the surface diffusivity to the effective bond energy between adsorbate molecules and the adsorbent surface. They assumed that an adsorbed molecule hops instantaneously from one adsorption site until another vacant site is located. Gilliland et al. (1958) proposed a different theory based upon writing a force balance for the adsorbed layer in terms of a two-dimensional pressure. For liquid systems such theories do not appear appropriate since, unlike gaseous systems, the adsorbed molecule is closely surrounded by solvent or other adsorbate molecules. Therefore, force fields are involved between adsorbed and solvent molecules as well as those between adsorbate molecules and adsorbent surface. Surface diffusion in this situation seems more analogous to diffusion in bulk liquids than to surface diffusion in gas-filled pores. Accordingly, the theory presented here for liquid-filled pores is based upon a modification of the hole theory for molecular diffusion in liquids. In any treatment of surface diffusion, care must be taken to distinguish between the effects of extent of adsorption (adsorption capacity) and the intrinsic surface diffusivity. To separate these two factors measurements of two types were made: (1) for adsorbents of different surface area but the same chemical structure and for the same solvent-adsorbate system, and (2) for the same adsorbent but chemically different solvent-adsorbate systems.

In one of the hole theories for molecular diffusion in liquids (McLaughlin, 1959), the diffusivity is expressed as

$$D = fP_h a^2 \tag{1}$$

where f is the frequency with which a molecule attains sufficient energy to surmount the potential barrier restricting it to a given location or cell. Following Eyring's rate theory (Glasstone et al., 1941), this frequency is given by

$$f = \frac{k_B\,T}{h} \exp\left(-\Delta F_b^*/R_gT\right) \tag{2}$$

The probability P_h of a hole being available for the activated molecule to move into is postulated to be

$$P_h = \exp\left(-\Delta F_h^*/RT\right) \tag{3}$$

Combining these equations gives

$$D = a^2 \frac{k_B\,T}{h} \exp\left(-\frac{\Delta F_h^* + \Delta F_b^*}{R_gT}\right) \tag{4}$$

where a is the distance between adjacent cells.

An analogous mechanism is proposed for surface diffusion. The process is visualized to occur in two steps: the formation of a hole on the surface followed by movement of the activated, adsorbed molecule into the hole. The total Gibbs free energy of activation may be written as

$$\Delta F^* = \Delta F_h^* + \Delta F_b^* \tag{5}$$

where ΔF_h^* represents the contribution of the hole-making step so that $\exp\left(-\Delta F_h^*/RT\right)$ is the probability that a vacant site is adjacent to the activated molecule. Then ΔF_b^* represents the contribution associated with breaking the bond between the adsorbed molecule and the surface. It may be expressed as $\Delta F_b^* = \Delta H_b^* - T\,\Delta S_b^*$. Then the intrinsic surface diffusivity, following Equation (4), may be written

$$D_s' = A \exp\left(-\Delta F_h^*/R_gT\right) \exp\left(-\Delta H_b^*/R_gT\right) \tag{6}$$

where A includes the entropy of activation for the bond-breaking step. Comparison with Equation (4) indicates that A also will be a function of the distance between two adsorption sites.

In terms of Fick's law, the surface flux per unit of pore perimeter normal to the direction of diffusion is

$$N_s' = -D_s' \frac{\partial q'}{\partial l_s} \tag{7}$$

To incorporate surface transport into equations representing total mass transfer, it is convenient to define an effective surface diffusivity D_s in terms of the surface diffusion per unit cross-sectional area normal to the direction of net transport and in terms of the adsorbed concentration q based upon unit volume of the porous particle. Then

$$N_s = -D_s \frac{\partial q}{\partial x} \tag{8}$$

The relationship between D_s' and D_s depends upon pore configuration, which can be expressed in terms of a tortuosity factor γ_s for surface diffusion. With reference to the pore assembly shown in Figure 1, the surface flow, per unit cross sectional area, in the direction x of net transport is related to N_s' by

$$N_s = N_s' \frac{L_s}{A_s} \frac{dx}{dl_s} \tag{9}$$

The concentrations q' and q are related through the particle density and S_g, the pore surface area per unit mass

$$q = \rho_p\, S_g\, q' \tag{10}$$

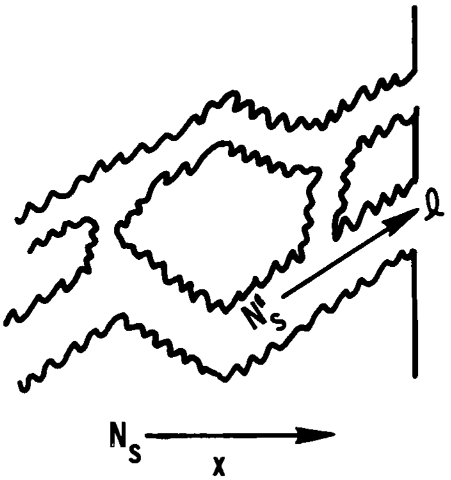

Fig. 1. Pore configuration.

The surface area is given by

$$S_g \rho_p = \frac{L_s}{A_s} \tag{11}$$

Substituting Equations (7), (10), and (11) into (9) yields

$$N_s = -\frac{D_s'}{\left(\frac{dl_s}{dx}\right)^2} \frac{\partial q}{\partial x} \tag{12}$$

Comparison of this result with Equation (8) shows that the effective diffusivity is related to D_s' by

$$D_s = \frac{D_s'}{(dl_s/dx)^2} = \frac{D_s'}{\gamma_s} \tag{13}$$

where $\gamma_s = (dl_s/dx)^2$, the tortuosity factor for surface transport.

The same type of reasoning for pore-volume diffusion lead Wheeler (1951) to a tortuosity factor γ_p given by $(dl_L/dx)^2$. Since the surface is not smooth l_s is likely to be greater than l_L. Also the tortuosity factor is actually evaluated from diffusion measurements according to the defining equation

$$D_e = \frac{\epsilon_p D}{\gamma} \tag{14}$$

This means that γ is a composite correction involving such other factors as pore interconnections as well as the directional effects used in obtaining Equation (13). Hence, γ_s is unlikely to be exactly the same as γ_L.

It will be assumed that the enthalpy difference ΔH_b^* between activated and adsorbed states is a certain fraction of the normal heat of adsorption, or

$$\Delta H_b^* = \frac{-1}{n} \Delta H_{\mathrm{ads}} \tag{15}$$

where n is a constant greater than unity. If heat of adsorption data are unavailable, Equation (15) and hence Equation (6) can be expressed in terms of the adsorption equilibrium constant. For a linear adsorption isotherm this equilibrium constant is

$$K' = q'/C \tag{16}$$

The relationship between K' and ΔH_{ads} is given by the van't Hoff equation, which may be written for constant ΔH_{ads}, as

$$K' = K^0 \exp(-\Delta H_{\mathrm{ads}}/R_g T) \tag{17}$$

Substituting Equations (15) and (17) in the expression for D_s' [Equation (6)] gives

$$\ln \frac{D_s'}{A} = -\frac{1}{n} \ln \frac{K'}{K^0} - \Delta F_h^*/R_g T$$

or

$$\ln D_s' = -\frac{1}{n} \ln K' - \frac{\Delta F_h^*}{R_g T} + B \tag{18}$$

where

$$B = \frac{1}{n} \ln K^0 + \ln A \tag{19}$$

Since experimental adsorption data are usually expressed in terms of mass of adsorbent, it is convenient to define the isotherm in terms of q, that is,

$$K = \frac{q}{\rho_p C} \tag{20}$$

From Equations (20), (16), and (10), $K' = K/S_g$. Then Equation (18) for D_s' can be written in terms of the usual adsorption equilibrium constant and D_s as

$$\ln D_s' = \ln \gamma_s D_s = -\frac{1}{n} \ln \frac{K}{S_g} - \frac{\Delta F_h^*}{R_g T} + B \tag{21}$$

Since Equations (18) and (21) are based upon a linear isotherm, they include the assumption of homogeneous adsorption sites. Actually, the surface is expected to be heterogeneous for most systems, including the benzaldehyde-Amberlite one studied here. The variation of K or K' with adsorbed concentration is lessened because of the small concentration range ($0 < C < 10$ ppm). However, the need to use a Freundlich isotherm (Figure 2) to represent the equilibrium adsorption is evidence that heterogeneity exists. Therefore, Equations (18) and (21) are not expected to represent exactly the data for benzaldehyde. These equations are valuable in showing how the effects of bonding energy (through K or K') and hole probability on surface diffusivity can be separated. In our research the nonlinearity of the system was accounted for by using an apparent equilibrium constant K_{app} defined in terms of the Freundlich isotherm [Equation (32)]. Then D_s and K_{app} were determined from experimental data. First, measurements were made for the adsorption of benzaldehyde in aqueous solution on three Amberlite particles of about the same chemical nature (polystyrene) but widely different surface areas. The purpose of these data was to test the independence of intrinsic diffusivity D_s' on S_g, as postulated by Equations (18) or (21). Second, the dependence of $\gamma_s D_s$ or D_s' on K_{app} was determined from adsorption data for benzaldehyde on the same Amberlite particles but using as solvents mixtures of water and methanol containing 0 to 100% methanol.

METHOD OF DETERMINING SURFACE DIFFUSION

The adsorption experiments consisted of rapidly injecting a sample of known concentration of benzaldehyde in solvent into a Pyrex vessel containing the solvent and the Amberlite particles. The liquid was well mixed with an impeller while the particles were held stationary in stainless steel, 40 mesh baskets attached to the vessel wall. Rates of adsorption were determined from curves of the concentration of benzaldehyde in the solution as a function of time. These curves were obtained by withdrawing a stream from the vessel and subsequently returning it after its absorbance at 2540 Å was continuously recorded in an ultraviolet photometer (cell volume = 0.017 cm^3). The adsorption vessel and method of operation were the same as described in detail earlier (Komiyama and Smith, 1974a). Impeller speeds of 600 to 800 rev./min. were employed since it was found in the prior work that fluid-to-particle mass transfer resistances were negligible at these speeds. It was necessary in a few runs at low times to correct the observed concentration at the photometer for the dispersion in the line from vessel to photometer. When this was necessary the concentration in the vessel was obtained by the correction method described in the earlier paper. The adsorption experiments were carried out using as a solvent water and water-methanol mixtures. For these solvents benzaldehyde is adsorbed on Amberlite particles so that the effective intraparticle diffusivity includes the contributions of both surface and pore-volume transport. Data were obtained in the low concentration range; initial concentrations of benzaldehyde in the vessel were 8.75 to 10.5 ppm.

The contribution of surface diffusion was separated from the total in the following way. First, desorption rates into pure methanol were made. In these runs the wire-mesh baskets, containing Amberlite particles whose pores were filled with a known solution of benzaldehyde in methanol, were inserted into the vessel of well-stirred pure methanol. Then the benzaldehyde concentration in the liquid was measured continuously. Since the adsorption capacity of the Amberlite particles for benzaldehyde in methanol is slight, the contribution of surface diffusion to the overall desorption rate was negligible. Hence, the effective intraparticle diffusivity obtained from such data could be used to calculate the porosity-tortuosity ratio ϵ_p/γ_L for the pore-volume transport. For this calculation the following form of Equation (14) was used

$$D_{LM} = \left(\frac{\epsilon_p}{\gamma_L}\right) D_{BM} \tag{22}$$

Then these ϵ_p/γ_L values were used with the data for adsorption from the water-methanol solutions to obtain the pore-volume transport. Finally, the surface diffusion contribution was evaluated by subtracting from the measured effective diffusivity the pore-volume part. Since swelling of Amberlite particles was not very large and about the same in either water or methanol, it seems reasonable to assume that ϵ_p/γ_L is the same for methanol as for water-methanol mixtures. Separate values of the tortuosity factor, while not required for separation of the surface transport, were evaluated using the known porosities for the dry Amberlite particles.

Table 1. Scope of Measurements

A. Properties of adsorbents*	XAD-1	XAD-2	XAD-4
Solid phase density, g/cm³ of solid phase	1.07	1.07	1.08
Surface area (dry), m²/g	100	330	750
Porosity of dry particles	0.37	0.42	0.51
Particle density (dry), g/cm³	0.674	0.621	0.529
Particle diameter, cm			
dry	0.0778	0.0778	0.0778
in water	0.0800	0.0800	0.0800
in methanol	0.0816	0.0816	0.0816
Volume swelling factor**, S.F.			
in water	1.076	1.076	1.076
in methanol	1.15	1.15	1.15
Nominal pore diameter, Å	200	90	50

B. Volume of liquid in adsorber, V, cm³ = 1000 ~ 1200

C. Volume of particles v, cm³ = 0.85 ~ 6.80

D. Initial concentration of benzaldehyde in bulk liquid, ppm = 8.75 ~ 10.5

E. Impeller speed, rev./min. 600 ~ 800

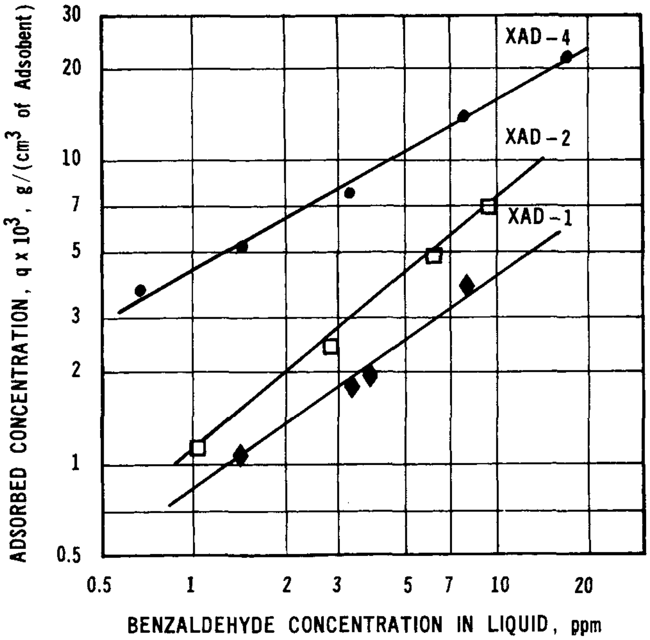

Fig. 2. Adsorption isotherms for benzaldehyde (in water) on Amberlite XAD-1, XAD-2, and XAD-4.

To carry out the procedures just described, molecular diffusivities of benzaldehyde in methanol-water mixtures are required at 25°C and atmospheric pressure. These data are available (Komiyama and Smith, 1974b).

Amberlite particles consist of a consolidated assembly of nonporous microspheres. Surface area (S_g) and average pore diameter varies with the size of the microspheres. The effect of surface area was studied by using XAD-1, XAD-2, and XAD-4 polystyrene particles which covered a range of 100 to 750 m²/g. Physical properties of the adsorbents and also operating conditions for the experiments are given in Table 1.

RESULTS

Effect of Surface Area

Equilibrium isotherms were measured at 25°C for the adsorption from aqueous solutions for the three Amberlite particles. The data were obtained by adding known samples of benzaldehyde solution into the adsorber containing agitated water and particles. The amount adsorbed was calculated from the steady state concentration of benzaldehyde in the liquid. The results, shown in Figure 2, are well correlated by the Freundlich equation. While the adsorption capacity increases with surface area for all three Amberlites, XAD-1 has a rather greater capacity than suggested by its area. The direct proportionality is more nearly followed for XAD-2 and XAD-4. This suggests that the intrinsic adsorption properties of XAD-1 are not exactly the same as for the other particles.

In analyzing the data it was assumed that the adsorption step (physical adsorption) at an interior site was rapid with respect to intraparticle diffusion. This means that the concentrations in the liquid and on the adsorbent

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

** The swelling factors for XAD-1 and XAD-2 were assumed to be same as that for XAD-4.

TABLE 2. TRANSPORT PROPERTIES OF AMBERLITE ADSORBENTS

	XAD-1	XAD-2	XAD-4
D_{LM}, cm^2/s	2.15×10^{-6}	2.80×10^{-6}	3.66×10^{-6}
D_{BM}, cm^2/s	2.25×10^{-5}	2.25×10^{-5}	2.25×10^{-5}
ϵ_p/γ_L	0.0956	0.124	0.163
ϵ_p	0.37	0.42	0.51
γ_p	3.87	3.39	3.13

at any location are related by the equilibrium isotherm. For Freundlich isotherms this relation is

$$q = \rho_p\, k\, C^p \tag{23}$$

It is further assumed that the benzaldehyde concentration in the liquid is uniform throughout the vessel. Then, mass conservation equations for benzaldehyde in the bulk liquid and within the particles are

$$V\frac{dC}{dt} = -S_s\left[D_L\left(\frac{\partial C_r}{\partial r}\right)_{r=R} + D_s\left(\frac{\partial q}{\partial r}\right)_{r=R}\right] \tag{24}$$

and

$$\epsilon_p\frac{\partial C_r}{\partial t} + \frac{\partial q}{\partial t} = D_L\left(\frac{\partial^2 C_r^2}{\partial r^2} + \frac{2}{r}\,\frac{\partial C_r}{\partial r}\right) + D_s\left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r}\,\frac{\partial q}{\partial r}\right) \tag{25}$$

with boundary and initial conditions

$$\text{at}\quad t = 0:\quad C = C_0 \tag{26}$$

$$C_r = 0\quad (0 \leqq r \leqq R) \tag{27}$$

$$\text{at}\quad t > 0:\quad \left(\frac{\partial C_r}{\partial r}\right)_{r=0} = 0 \tag{28}$$

$$C = C_r \quad \text{at} \quad r = R \tag{29}$$

Since the particles are spherical, their total outer surface area is given by

$$S_s = \frac{3v}{R} \tag{30}$$

The volume of the particles is obtained from their measured mass, density of dry particles, and swelling factor (S.F.) according to the expression

$$v = \frac{m}{\rho_p}\,(\text{S.F.}) \tag{31}$$

Equations (24) and (25) with the boundary and initial conditions and with Equation (23) can be solved numerically in terms of D_L and D_s to give a predicted relationship between amount adsorbed and time. Then the measured curve of amount adsorbed vs. time can be compared with the predicted curve to identify the diffusivities.

This procedure was followed first for the desorption data with methanol as solvent. Since the adsorption of benzaldehyde is negligible for this solvent, $D_s = 0$ and the comparison of measured and predicted curves gives D_L. By the procedure described earlier ϵ_p/γ_L was then calculated using Equation (22). The results are shown in Table 2. The ratio ϵ_p/γ_L increases significantly with porosity of the Amberlite since γ_L should decrease with porosity. These values of ϵ_p/γ_L were then used to calculate D_{LW} for the adsorption runs with water as the solvent, using Equation (22) with D_{BW} substituted for D_{BM}. The results are given in the second column of Table 3.

The experimental data points for adsorption from water are shown for the three Amberlites in Figures 3 to 5. The solid lines represent the predicted curves with the D_s values given in the third column of Table 3. These results are discussed later, but two points need be mentioned here. First, the surface diffusivities for XAD-2 and XAD-4 are nearly the same, as predicted from Equation (18) or (21) for chemically similar adsorbents (constant K'). For XAD-1 D_s is somewhat less, but it was shown (Figure 2) that its surface is chemically different from XAD-2 and XAD-4. Second, surface diffusion is a major contribution to the intraparticle mass transport. This is evident

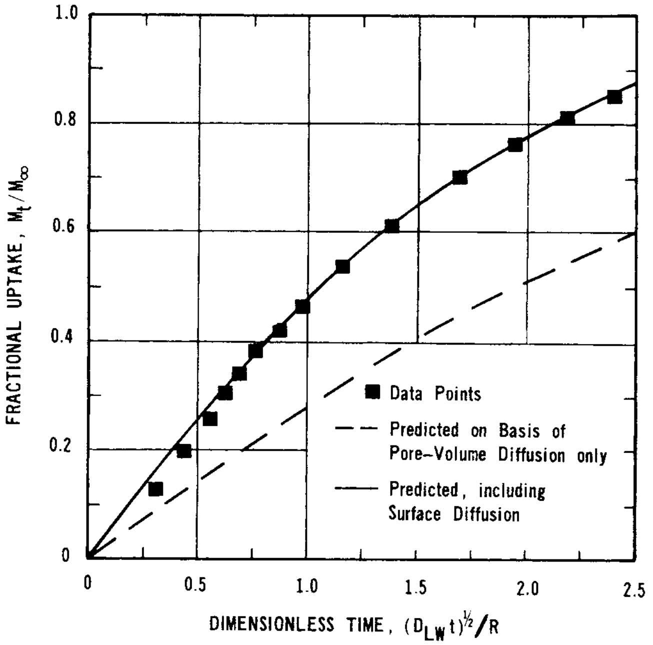

Fig. 3. Adsorption of benzaldehyde from aqueous solution on XAD-1. $S_g = 100$ m^2/g; $C_0 = 9.55$ ppm; $C_x/C_0 = 0.385$; $v = 3.26$ cm^3; $V = 1100$ cm^3.

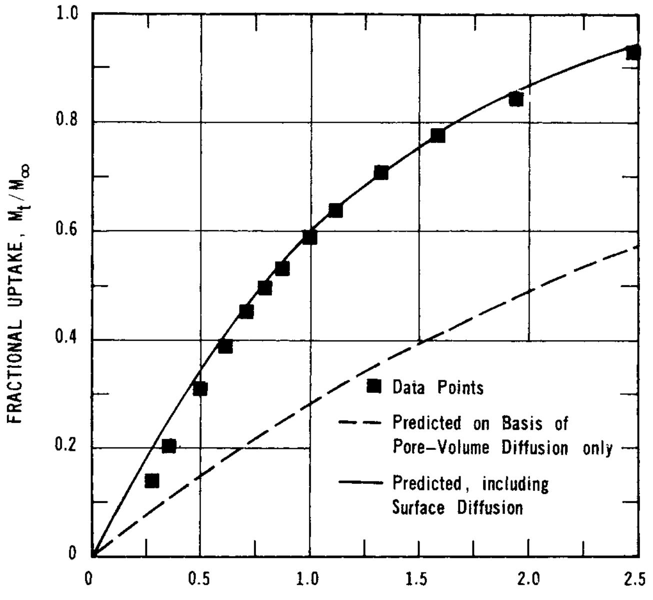

Fig. 4. Adsorption of benzaldehyde from aqueous solution on XAD-2. $S_g = 330$ m^2/g; $C_0 = 9.55$ ppm; $C_x/C_0 = 0.306$; $v = 3.00$ cm^3; $V = 1100$ cm^3.

Table 3. Surface Diffusivity Results

	$D_{LW} \times 10^6$ cm^2/s	$D_s \times 10^8$ cm^2/s	$\gamma_s\ (= \gamma_p)$	$D_s' \times 10^7$ cm^2/s	Relative importance, $(\rho_p k p C^{p-1})\ D_s/D_L$ at 1 ppm	at 10 ppm
XAD-1	0.848	0.0509	3.87	0.196	3.38	1.61
XAD-2	1.104	0.0938	3.39	0.318	7.74	5.05
XAD-4			3.13			
x_m						
0	1.45	0.115		0.360	19.7	7.47
0.0113	1.42	0.156		0.488	15.2	6.11
0.0229	1.39	0.257		0.804	16.9	7.12
0.100	1.36	0.557		1.743	13.5	9.02
0.193	0.925	1.16		3.63	14.4	14.4
0.308	0.922	1.30		4.07	2.54	2.54
0.572	1.26	0.993		3.11	0.61	0.61

from the dotted lines in Figures 3 to 5. These are predicted curves obtained by setting $D_s = 0$. The increasing difference between the data points and the dotted lines in proceeding from XAD-1 to XAD-2 to XAD-4 shows that surface transport becomes more important as surface area increases. This is due predominantly to the increase in adsorption with surface area since the shape of the isotherms and the diffusivities are about the same.

Effect of Bonding Energy

As mentioned, the bonding energy between surface sites and benzaldehyde molecules in the liquid was changed by varying the methanol content of the methanol-water mixture used as solvent. This changed the adsorption capacity by about 100 fold for $x_m = 0$ to 0.572 as indicated by the adsorption isotherms shown in Figure 6. For these measurements XAD-4 particles were used. As the methanol content was increased, the slopes of the isotherms increased toward unity so that at $x_m \geqq 0.19$ the isotherm was essentially linear.

Adsorption rate data were obtained for the same solvent compositions as used for the isotherm measurements. Then D_s was evaluated by the same procedure as employed for the effect of surface area. For methanol contents equal or greater than $x_m = 0.308$, adsorption capacities were too low for reliable rates due to the small concentration change in the liquid phase. The previously-described desorption procedure was used for $x_m \geqq 0.308$. Adsorption vs. time data points typical of the data are shown in Figure 7 for $x_m = 0.308$ and $x_m = 0.100$. Also shown are the predicted curves used to fit the data. The D_s values so determined for various x_m are given in the lower part of the third column of Table 3 and are seen to increase significantly with increasing methanol content. This increase is attributed to the variation in adsorption equilibrium constant K' since the same particles were used for all these data. Satterfield et al. (1973) also proposed that the surface diffusivity increased with decreasing adsorption, based upon data obtained in fine pores.

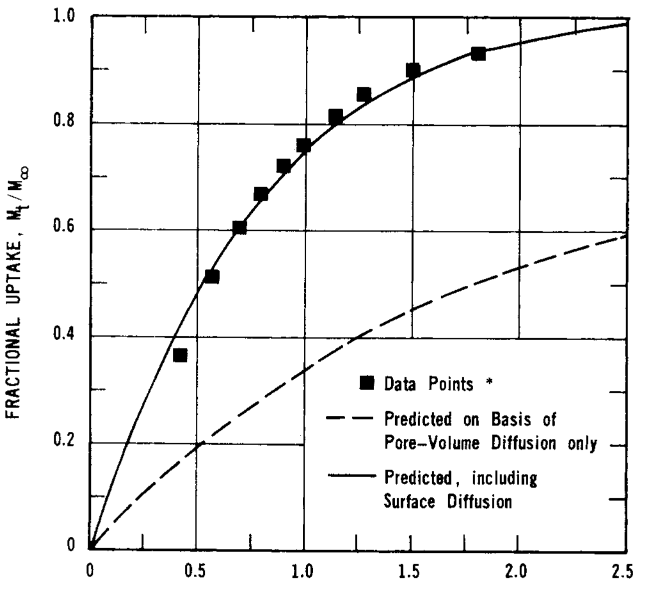

Fig. 5. Adsorption of benzaldehyde from aqueous solution on XAD-4. $S_g = 750$ m^2/g; $C_0 = 10.5$ ppm; $C_\infty/C_0 = 0.0804$; $v = 2.57$ cm^3; $V = 1000$ cm^3. *Data from Komayama and Smith (1974a).

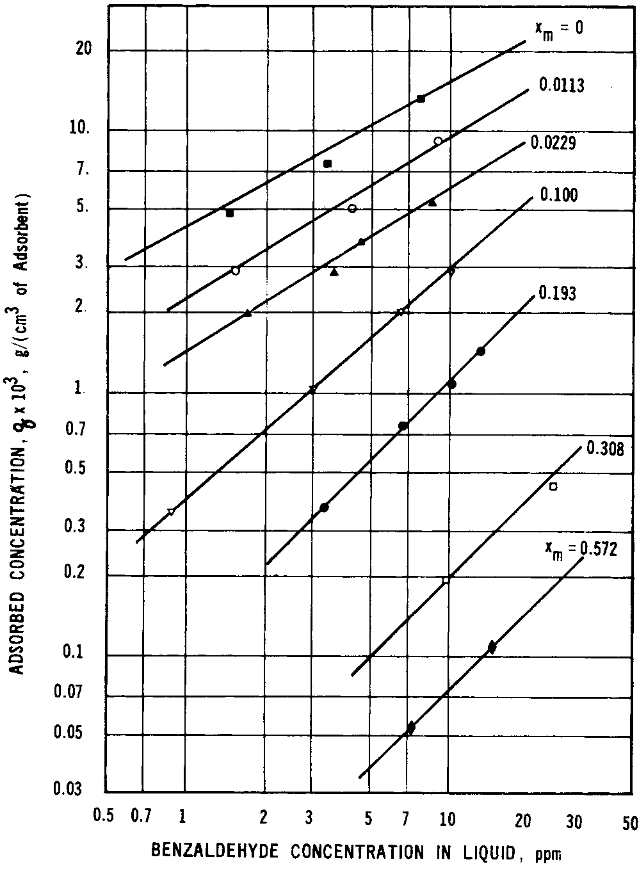

Fig. 6. Adsorption isotherms for benzaldehyde (in water-methanol mixtures) on Amberlite XAD-4.

DISCUSSION

While the tortuosity factor for pore-surface and pore-volume diffusion may be different, our work provided no means for evaluating this difference. Therefore, γ_s was assumed to be the same as γ_L. All the data for varying methanol content of the solvent were obtained with one adsorbent, XAD-4. For these data, γ_s/γ_L would be a constant. Further, all the data were obtained with Amberlite polymeric particles which should have similar pore structures. Hence, γ_s/γ_L should be nearly constant. Then any errors involved in calculating the intrinsic diffusivity from D_s by assuming $\gamma_s = \gamma_L$ in Equation (13) would affect all the data equally. It is anticipated that the magnitude of this effect would be small in comparison with the influence of S_g and K'. Intrinsic diffusivities so calculated are given in Table 3 and plotted vs. an apparent adsorption equilibrium constant in Figure 8.

An ideal test of the theory proposed for surface diffusion is Equation (6) with Equation (15) used for ΔH_b^*. However, heat of adsorption data were unavailable so that Equation (21) in terms of the equilibrium constant K was presented. Unfortunately, the requirement of a linear isotherm included in Equation (21) is not satisfied. This suggests that the heat of adsorption varies with surface coverage and the Freundlich isotherms in Figures 2 and 6 confirm this. The difficulty can be partially overcome by defining an apparent equilibrium constant in terms of the Freundlich equation:

$$K_{\text{app}} = k\,C^{p-1} \tag{32}$$

If this K_{app} is used in place of K, Equation (21) indicates that a plot of D_s' vs. $k\,C^{p-1}/S_g$ on logarithmic coordinates should be linear as long as ΔF_h^* is constant. Figure 8 shows all the data plotted in this way for a concentration corresponding to 10 ppm. The points for XAD-4 and XAD-2 with pure water as solvent nearly coincide, indicating that the surface area effect is accounted for adequately. Amberlite XAD-1 has both a different surface area and a somewhat different surface chemically, and these two effects seem to be correlated in Figure 8. The point for XAD-7 from Komiyama and Smith (1947a) is displaced from the curve. These Amberlite particles are made from polymeric acrylic esters, while XAD-1, XAD-2, and XAD-4 are all of polystyrene. Both ΔF_h^* and ΔF_b^* are expected to be different for XAD-7, thus explaining its deviation in Figure 8.

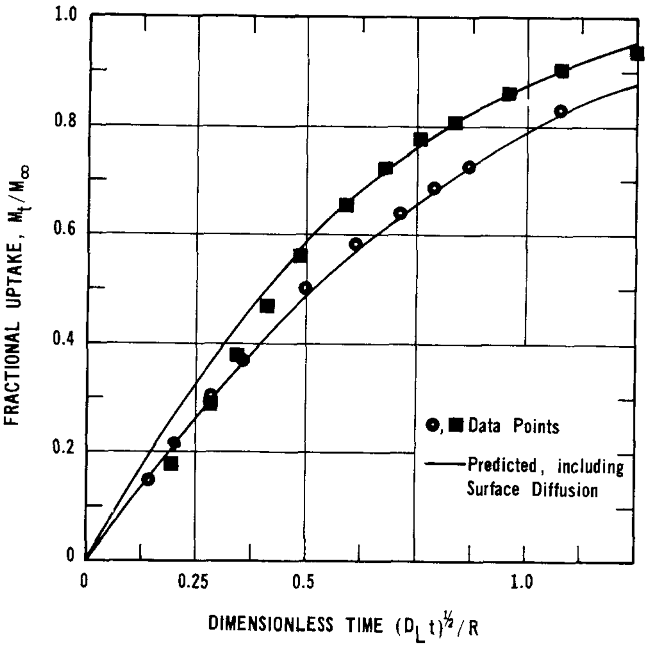

Fig. 7. Adsorption (or desorption) curves for Amberlite XAD-4. ○ Desorption: Mole fraction of methanol = 0.308; C_0 (in pores) = 500 ppm; v = 1.02 cm^3; V = 1200 cm^3. ■ Adsorption: Mole fraction of methanol = 0.100; C_∞/C_0 = 0.336; v = 6.80 cm^3; V = 1200 cm^3.

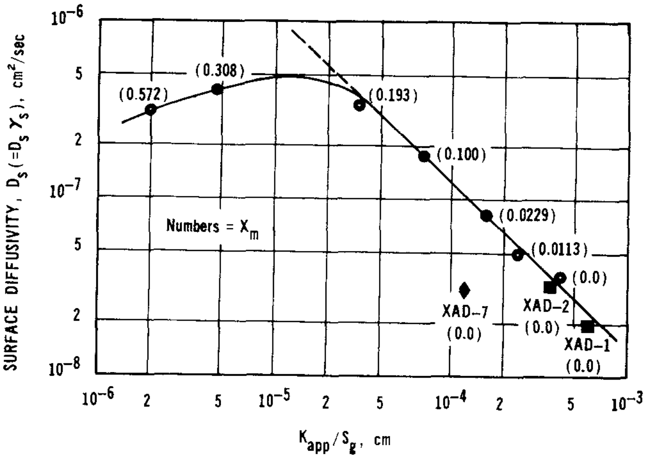

Fig. 8. Surface diffusivity vs. adsorption capacity (C = 10 ppm).

Interpreted in terms of Equation (21), the straight line in Figure 8 up to $x_m = 0.193$ indicates that the surface diffusivity on the chemically similar sites of XAD-4, -2, and -1 is primarily a function of the energy of breaking the bond between the surface and the benzaldehyde molecule. Increasing the methanol content in this range increases the bonding energy between solvent and benzaldehyde. This decreases the energy required to break the bond with the adsorbent surface and leads to a larger D_s.

The deviation from linearity at higher methanol contents may be interpreted by a change in the free energy of activation associated with providing a vacant site on the surface. Methanol has a stronger attraction than water for the hydrophobic surface of the Amberlite particles. As the methanol content increases, more energy is required to produce a vacant site so that ΔF_h^* increases and D_s decreases. This type of reasoning could also explain the low surface diffusivity for XAD-7. The surface of this polyacrylic ester is more hydrophilic than that of XAD-4. Hence a water molecule is more strongly attached to the surface and more energy is required to produce a vacant site.

An alternate explanation for the effect of methanol content on the XAD-4 adsorption capacity could be preferential adsorption of methanol. From this standpoint the decrease in adsorption, K_{app}/S_g, with increasing methanol content would be due to fewer vacant adsorption sites, rather than due to a decrease in the heat of adsorption of benzaldehyde. However, the preferential adsorption concept does not explain the increase in surface diffusivity with increasing methanol in the solvent.

The relative importance of surface to pore-volume diffusion may be evaluated by the ratio $(\rho_p\,k\,p\,C^{p-1})D_s/D_L$ (Komiyama and Smith, 1974a). The last column in Table 3 gives this ratio. Results for XAD-1, -2, and -4 in water show that surface diffusion becomes more important because surface area increases even though D_s' is about the same. For XAD-4 with low methanol contents the decrease in adsorption capacity is about balanced by the increase in surface diffusivity.

Comparison of the adsorption data points with the solid curves in Figures 3 to 5 and 7 all show poorer agreement during the initial time period of a run. Further, the deviation was greater the more nonlinear the isotherm. The reason may be the variation of surface diffusivity with concentration of adsorbate, or surface coverage. A constant diffusivity is used for the predicted curves, yet the results shown in Figure 8 suggest an increasing diffusivity with decreasing heat of adsorption. The heat of adsorption would be expected to decrease with increasing coverage. This is in agreement with the lower D_s' values at low times indicated by the deviations in the figures. Also it is consistent with this explanation that the desorption data points and predicted curve in Figure 7 do not show such deviations. Such deviations are not expected because for the desorption runs, which were at high methanol contents, the isotherms were linear. Then the heat of adsorption would be independent of surface coverage.

ACKNOWLEDGMENT

The financial support of National Science Foundation Grant G-38881 for this work is gratefully acknowledged.

NOTATION

A = pre-exponential constant in Equation (6), cm²/s
A_s = total (void plus nonvoid) cross-sectional area in the particle normal to direction of diffusion, cm²
B = constant defined by Equation (19)
C = concentration of benzaldehyde in bulk liquid; g/cm³; C_0 = concentration at $t = 0$; C_∞ = concentration at infinite time
C_r = concentration of benzaldehyde in the liquid in the pores, g/cm³
D = molecular diffusivity, cm²/s; D_{BM} and D_{BW} represent diffusivities of benzaldehyde in methanol and in water, respectively
D_e = effective intraparticle diffusivity, cm²/s
D_{LM}, D_{LW} = effective intraparticle diffusivities of benzaldehyde in methanol and in water in the pore volume, cm²/s
D_s' = intrinsic surface diffusivity, defined by Equation (7), cm²/s
D_s = effective surface diffusivity based upon adsorbed concentration per unit volume of particle, defined by Equation (8), cm²/s
ΔF^* = total Gibbs free energy of activation for surface diffusion, cal/g mole; ΔF_h^* and ΔF_b^* are contributions for forming vacant sites and for bond breaking, respectively
f = frequency in Equation (1), s^{-1}
ΔH_b^* = contribution of bond breaking to the total enthalpy of activation, cal/g mole
h = Planck's constant, cal s
K = adsorption equilibrium constant for a linear isotherm and based upon unit mass of particle, Equation (20), cm³/g
K' = adsorption equilibrium constant for a linear isotherm and based upon q', Equation (16), cm
K_{app} = apparent adsorption equilibrium constant in terms of the Freundlich isotherm; Equation (32), cm³/g
K^0 = constant in Equation (17), cm
k = constant in Freundlich isotherm, Equation (23), $(\text{g/cm}^3)^{-p}$
k_B = Boltzmann's constant, cal/°K
L_s = total perimeter of pores in cross-sectional area normal to direction of net diffusion, cm
l = path length in actual diffusion path, cm; l_s refers to surface diffusion and l_L to pore-volume diffusion
M_t = amount of benzaldehyde on adsorbent (for adsorption) or in bulk liquid (for desorption) at time t, g; M_∞ = amount at infinite time
m = mass of particles in adsorption vessel, g
N_s = surface diffusion normal to x direction and based upon adsorbed concentration q, g/cm² s
N_s' = surface diffusion in direction of l and based upon adsorbed concentration q', g/cm s
p = exponent in Freundlich isotherm, Equation (23)
P_h = probability of a hole being available for migration of an activated molecule
q = concentration of adsorbed benzaldehyde, g/cm³ of particle
q' = concentration of adsorbed benzaldehyde, g/cm² of pore structure
r = radial coordinate in spherical particle, cm
R = radius of particle, cm
R_g = gas constant, cal/g mole °K
S.F. = swelling factor defined as the ratio of the volumes of wet and dry particles
S_s = total external surface of particles in adsorption vessel, cm²
S_g = surface area of particles per unit mass, cm²/g
T = temperature, °K
t = time, s
V = volume of particle-free liquid in the adsorption vessel, cm³
v = total void plus solid volume of particles in adsorption vessel, cm³
x = coordinate in direction of net diffusion, cm
x_m = mole fraction methanol in methanol-water solvent

Greek Letters

ϵ = porosity of adsorbent particles
γ = tortuosity factor; γ_L = tortuosity factor for pore-volume diffusion; γ_s = tortuosity factor for surface diffusion
ρ_p = density of dry particles, g/cm³

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Manuscript received May 9, 1974; revision received and accepted July 8, 1974.