Surface Diffusion of Stearic Acid on Aluminum Oxide

By means of infrared internal reflection spectroscopy we measured the time dependence of the surface concentration of stearic acid molecules over a well defined region of the surface. The molecules were diffusing into this region from a source comprising a compressed monolayer or bulk crystalline material outside the field of view. By these measurements in conjunction with solutions to the diffusion equations we determined the diffusion coefficient D_s of stearic acid on the (0001) plane of α-alumina. We also determined the dependence of D_s upon the amount of water coadsorbed on the surface. When the surface was free of reversibly adsorbed water, D_s had a value of about 2×10^{-7} cm²/s. As the surface coverage of coadsorbed water increased to about a monolayer D_s increased to a maximum value of about 4×10^{-5} cm²/s. With further additions of surface water D_s then decreased and became less than 10^{-8} cm²/s at coverages slightly less than about two monolayers. In the region of its maximum value the temperature dependence of D_s indicated an activation energy for the diffusion process of about 26 kcal/mole.

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SCOPE

An accurate experimental method is needed to measure surface diffusion rates on nonporous surfaces. Plane surfaces provide simple models for the study of the general phenomenon of surface flux which contributes to transport through catalyst pellets, adsorbent beds, and the diffusion barriers used in important separation processes. Most previous studies of surface diffusion have been based on a determination of total diffusive flow through porous materials. Gas chromatography, nuclear magnetic resonance, and neutron scattering spectroscopy have been employed for this purpose. The contribution due to Knudsen flow is then calculated and subtracted from the total. The difference is attributed to surface diffusion. Clearly, this approach is not applicable to nonvolatile species, but it is the least volatile component in any system which is most affected by surface diffusion.

The direct measurements of surface diffusion on solids previously reported were by Beischer (1951) and Rideal and Tadayon (1954). They determined the diffusion coefficient of stearic acid on mica by means of radioactive tracer techniques. Our method is also based on a direct observation of transport in adsorbed layers on planar surfaces. It uses the somewhat simpler and more generally applicable technique of Internal Reflection Spectroscopy (IRS) to measure time dependent surface concentration. The results are combined with approximate solutions of the Fick diffusion equations under appropriate boundary conditions to give surface diffusion coefficients.

Water adsorbed on a solid surface often has a dramatic effect upon the rates of interphase exchange or chemical reactions at that surface. In at least one case, where surface transport is the slow step, it has been shown that the marked effect of adsorbed water on the rate of reaction is due to its influence on the rate of diffusion (Levy and Boudart, 1974). In this paper we report the effect of coadsorbed water on the surface diffusion of stearic acid on aluminum oxide. We also present some results obtained on the surface of a mixed crystal of thallium bromide and thallium iodide (KRS-5).

CONCLUSIONS AND SIGNIFICANCE

We have successfully applied Internal Reflection Spectroscopy (IRS) to a measurement of surface diffusion rate. Our test case was the diffusion of stearic acid on aluminum oxide in the temperature range from 25° to 40°C. On a (0001) surface plane which is dry except for the water adsorbed irreversibly at 40°C, the diffusion coefficient for stearic acid has an extremely small value of about 2×10^{-7} cm²/s. As reversibly adsorbed water is added to the surface the diffusion coefficient increases. It reaches a maximum value two orders of magnitude larger when the amount of reversibly adsorbed water becomes equivalent to about a monolayer. With further increases in adsorbed water the diffusion coefficient of stearic acid decreases sharply and becomes immeasurably small when the surface coverage of water is about two monolayers. There are several examples in the literature in which the diffusion coefficient of a species varies with the surface coverage of that species (Boddenberg et al., 1972; Gilliland et al., 1958; Haul and Peerbooms, 1958; Carman and Raal, 1951). In each case the diffusion coefficient passes through a maximum at a surface coverage corresponding to a monolayer, but the overall variation is never more than a factor of five. To our knowledge, the results reported here comprise the first quantitative determination of the influence of one adsorbed species on the surface diffusion of another. They reflect by far the most pronounced effect yet reported of coverage upon surface transport.

It is possible to interpret our observations in terms of a random walk model. In this model it is assumed that the stearic acid molecules hop from adsorption site to adsorption site. The overall diffusion time is the sum of the residence time at each site and the transit time between sites. When the surface is dry, the adsorption bonds are strong. Then the residence time is long and is the main factor in determining the diffusion rate. As the amount of adsorbed water increases the more energetic sites are occupied by water molecules and become less attractive to the stearic acid molecules. Thus the average residence time of the latter becomes smaller and their diffusion rate increases (Yang et al., 1973). Meanwhile as the surface concentration of water molecules increases, the stearic acid molecules undergo an increasing number of collisions with water molecules en route from site to site. The transit time between sites grows longer and longer and finally is the major component of the diffusion time. Thus, at water coverages in the multilayer regime the stearic acid diffusion rate becomes determined by an activation energy associated with the free energy of hole formation in the second water layer. The plausibility of this model is supported by the results obtained with RS-5. The surface of this material does not have strong adsorption sites. The diffusion coefficient of stearic acid is independent of the amount of adsorbed water at coverages below a monolayer. At coverages above a monolayer the stearic acid diffusion coefficient decreases with increasing water but not as markedly as in the case of α-aluminum oxide.

The above mentioned results suggest the possibility of practical application in engineering chemical systems where mass transport is the rate limiting step in the process. Perhaps dual-functional catalysts can be made more effective by addition of a component to the reaction mixture which will increase the rate of transport between sites but not otherwise influence the catalysis. Water and alcohol have been shown to play such a role in the Pt catalyzed reduction of WO_3 (Levy and Boudart, 1974).

The IRS technique for studying surface diffusion should be applicable to any diffusing species which has reasonably strong absorption bands in a region of the spectrum to which the surface bulk substrate is transparent. Of course, the diffusing molecules must have a negligible vapor pressure so that transport through the ambient gas does not intrude. Results obtained by this method should be useful in the formulation and analysis of simple models for both qualitative and quantitative description of the surface diffusion process.

EXPERIMENTAL METHOD

General Approach

In any direct measurements of diffusion one key problem is to determine a local concentration of the diffusing species and to resolve its dependence upon time and/or distance. In the case of surface diffusion this problem is particularly difficult because the amount of material on any well prescribed surface location is very small. Beischer (1951) and Rideal and Tadayon (1954) resorted to radioactive tracers to obtain the necessary sensitivity. We decided to try Internal Reflection Spectroscopy (IRS) because it can be used to detect a small fraction of a monolayer (Haller and Rice, 1970) and does not require radioactive labeled molecules. The theory and practice of this technique has been reviewed by Harrick (1967). We will briefly summarize its principal features.

A beam of radiation incident upon the interface between two media of differing refractive index can be totally reflected if the angle of incidence is greater than a critical value determined by the wavelength of radiation and the refractive indices of the two media. This total reflection is the basis for the familiar light pipe phenomenon. At the point of reflection the beam penetrates the low index region for a distance of about the wavelength of the radiation before turning back. If there is some substance in this penetration region which can absorb radiation, the reflection will not be total and the beam will be attenuated at the absorbing wavelength. In prisms of appropriate geometry the beam can be made to undergo a large number of internal reflections. Even a very small amount of absorption at each reflection can thus be integrated to give a detectable signal.

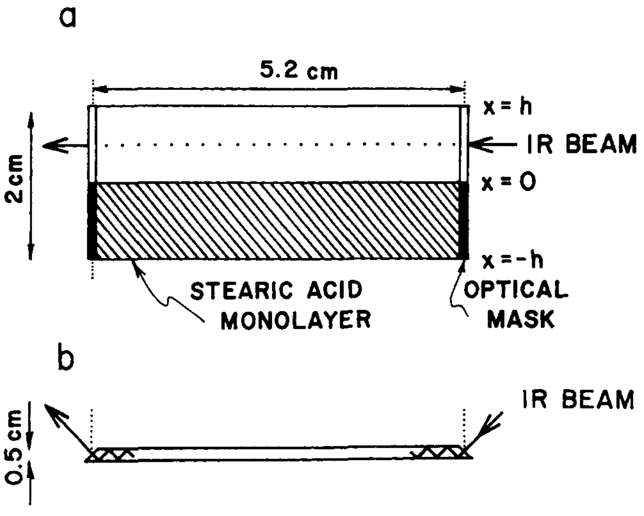

Fig. 1. (a) Projection of IRE showing a schematic of the stearic acid monolayer source. (b) Cross section through the IRE.

Figure 1a is projection of the Internal Reflection Element (IRE) showing one of the major surfaces. Figure 1b is a cross section of the IRE depicting the path of a single ray of infrared beam through the prism. The beam enters and leaves the prism at normal incidence. A source of diffusing molecules is deposited on half the area of the IRE which is optically masked so that the radiation sees only that part of the surface which is initially clean. It is necessary to mask both the entrance and exit bevels because the beam is not composed of parallel rays only, that is, the beam diverges as it passes through the IRE. Molecules which diffuse from the source region into the field of view give rise to absorption which is used to monitor the rate at which they cross the boundry at $x = 0$, the center line. This arrival rate is matched to that obtained by solving the diffusion equation with appropriate boundary conditions in order to calculate the diffusion coefficient.

Apparatus and Materials

All infrared spectra were recorded on a Beckman IR 12 spectrophotometer in the double beam mode. The IRS cell and mirror set were manufactured by Wilks Scientific Corporation. The cell consisted of a stainless steel circular chamber with gas outlet and inlet. Two sapphire windows on flange mounts with Viton "O" ring seals provided an optical access through the sides of the chamber to the IRE. The IRE was clamped into a stainless steel block suspended from the lid flange which could be sealed vacuum tight to the top of the main body of the chamber with a gold "O" ring. Also mounted on this flange were two heater wells with a thermocouple well between them which were bored through the lid into the stainless steel block from outside the chamber. A more complete description of the cell is given by Rice (1972).

The cell temperature was maintained constant within 0.05°C. Temperature gradients within the cell were not measured but were assumed to be negligibly small at temperatures near ambient. This assumption is supported by the fact that even at temperatures above 400°C the differences in temperature between the IRE and the thermocouple well and between one end of the IRE and the other were less than 5°C (Haller and Rice, 1970).

The α-aluminum oxide IRE was made from a rectangular prism of flame-fusion grown single crystal with major faces oriented parallel to the (0001) crystalographic plane. Its dimensions were 52 × 20 × 0.5-mm. The ends were beveled to 45° to form entrance and exit apertures and provided for about one-hundred 45° internal reflections. The surface was polished with diamond dust to an average roughness of 100Å. The KRS-5 IRE comprised a synthetic mixed crystal of 42 mole % thallium bromide and 58% thallium iodide (KRS-5). Its dimensions were 52 × 20 × 1 mm and it provided about fifty 45° internal reflections. Stearic acid labeled 99% + *pure* was used. All water used for washing, supporting monolayers and as a source of vapor was doubly ion-exchanged, passed through an organic removal filter and then distilled. All other chemicals were of laboratory reagent grade.

Procedure

The aluminum oxide IRE was cleaned with warm chromic acid and distilled water. Further treatment with concentrated nitric acid assured the removal of any chromium ions attached to the surface. The crystal was then flushed with distilled water and dried in an oven. After this treatment, the absorbance of hydrocarbons left on the surface was always less than 1% of the absorbance due to a deposited compressed stearate monolayer. The KRS-5 IRE was cleaned with nearly boiling methyl ethyl ketone and chloroform. Under the best conditions with this cleaning method the amount of hydrocarbon left on the surface corresponded to about 5% of a deposited stearate monolayer. Because KRS-5 is slightly soluble in water, it was not possible to deposit stearic acid monolayers by the Langmuir-Blodgett technique. Therefore, it was necessary to use a bulk stearic acid source as described below for all experiments on KRS-5.

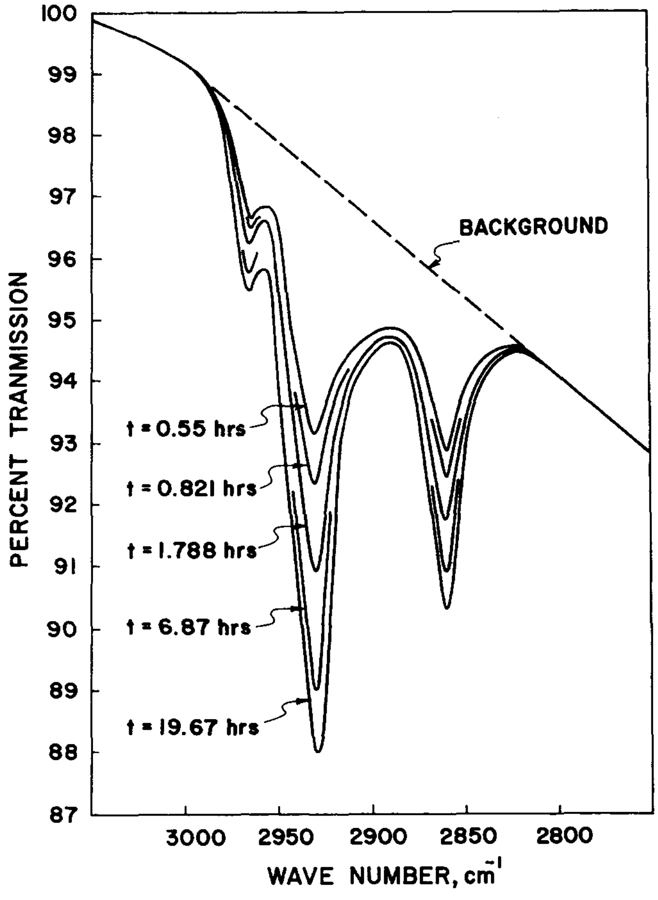

Fig. 2. Typical set of spectra showing the increase in absorption by C-H bonds of stearic acid as a function of time.

In experiments where a monolayer source was used, the monolayers were deposited by the method of Langmuir-Blodgett described by Blodgett (1935). Half the surface (52 × 10 mm area) of the IRE was submerged in a Langmuir trough containing water with enough hydrochloric acid to reduce the *p*H to 4.0 as suggested by previous workers (Bagg et al., 1964). Stearic acid was spread on the water surface from a hexane solution, compressed with an oleic acid piston. The IRE crystal was slowly withdrawn through the compressed monolayer. It was then clamped into the holding block and the half carrying the monolayer optically masked with aluminum foil in such a way that the mask did not touch the surface. Figure 1 shows the arrangement schematically.

In experiments where a bulk source was used, the long (52 mm) edges of the IRE were dipped into a concentrated solution of stearic acid in *n*-hexane. The volatile solvent was vaporized and a layer of bulk stearic acid comprising a line source was left along each side of the surface.

After the IRE was in place, the cell was filled with helium having a controlled water vapor content. It was then sealed and IR spectra were recorded throughout the diffusion process over a period of up to 20 hours. The absorption by C-H bands of stearic acid was normally amplified 10 times by using the expanded scale of the spectrophotometer. Spectra were recorded at intervals ranging from 15 min. to several hours. The shorter intervals were used in the initial period.

RESULTS AND DISCUSSION

Development of IRS Method

Figure 2 shows a typical set of IRS spectra recorded in this work. The decrease in transmission through the IRE with time is associated with the absorbance at the carbon-hydrogen stretching frequencies of stearic acid molecules diffusing from a bulk source on the surface of (0001) α-Al_2O_3. This transmisson, neglecting reflection losses at the entrance and exit to the IRE, follows an exponential law:

$$\frac{I}{I_0} = e^{-C\alpha} \tag{1}$$

The absorption coefficient α is a function of the number of reflections, an electric field amplification factor at the internally reflecting interface and the molecular extinction coefficient (Rice and Haller, 1973). Note that I/I_0 on Figure 2 is usually expressed in terms of its logarithm which is called the *absorbance.* In this paper we use the natural logarithms. The absorbance for the most intense band of oriented monolayer of stearic acid on an aluminum oxide IRE giving 103 reflections at 45° is 0.92 (Haller and Rice, 1970). Assuming a stearic acid monolayer concentration of 5.0×10^{14} molecules/cm^2 (Gaines, 1966), α is 1.8×10^{-15} cm^2/molecule. Early in the process, when the concentration of molecules which have diffused out of the source region into the field of view does not exceed 5×10^{13} molecules/cm^2, we can make the approximation $e^{-C\alpha} \simeq 1 - C\alpha$. Over the time that this linear approximation holds, the absorbance will be a measure of the average concentration per unit surface area independent of the actual concentration profile. The actual concentration distribution is not known but it is reasonable to assume the symmetric profile illustrated in Figure 3. This profile is known to obtain for the case of stearic acid diffusing out of a monolayer at an air-water interface (Good and Schechter, 1972). An alternative limiting case, which could be considered as a two-dimensional analog to evaporation, would show a gradually receding sharp boundary (surface) between the monolayer source and the diffusing molecules. This evaporation model would require that the difference in energy between a molecule in the monolayer and one alone on the surface be large with respect to kT. The fact that the activation energy for diffusion exceeds 20 kcal/mole suggests that this possibility is unlikely. Such a high activation energy would also be consistent with the random walk or hopping of individual molecules between adsorption sites, a mechanism which would result in the symmetric concentration profile shown in Figure 3.

In the early stages when the concentration changes near the boundaries are negligible we can treat our finite system as an infinite plane. We solve Fick's law:

$$\frac{\partial C}{\partial t} = D_s \frac{\partial^2 C}{\partial t^2} \tag{2}$$

for the initial distribution of concentration given by

$$C = C_0 \quad \text{for} \quad x < 0, \quad \text{and} \quad C = 0 \quad \text{for} \quad x > 0, \quad \text{at} \quad t = 0$$

for the IRE geometry and coordinate system shown in Figure 3. The solution is usually written in the form (Crank, 1956):

$$C(x, t) = \frac{C_0}{2} \operatorname{erfc} \frac{x}{2\sqrt{D_s t}} \tag{3}$$

We follow Jost (1960) and calculate the total amount of material diffusing across a unit cross section into a unit area to obtain the average concentration.

At short times all the material found in a one cm² area between $x = 0$ and $x = 1$ cm has come there by diffusion across a 1-cm line at $x = 0$ during the time t and

$$C_{av} = \frac{1}{\text{cm}} \int_0^t D_s \left(\frac{\partial C}{\partial x}\right)_{x=0} dt = C_0 \sqrt{\frac{D_s t}{\pi}} \tag{4}$$

When a monolayer source is used C_0 is known and C_{av} can be calculated from Equation (1). Hence D_s can be determined from the slope of a plot of the fraction of the monolayer which has diffused out of the source region, $C_{av}/C_m = A/A_m$ vs. $\sqrt{t}$.

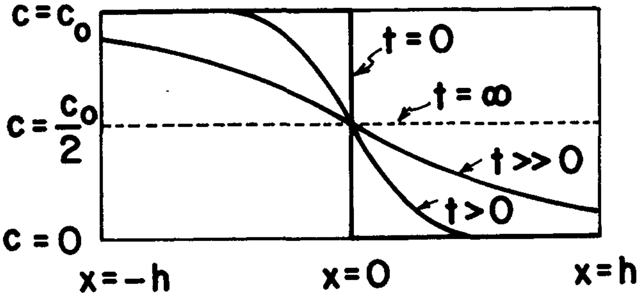

Fig. 3. The concentration profile and coordinate system appropriate to the monolayer source.

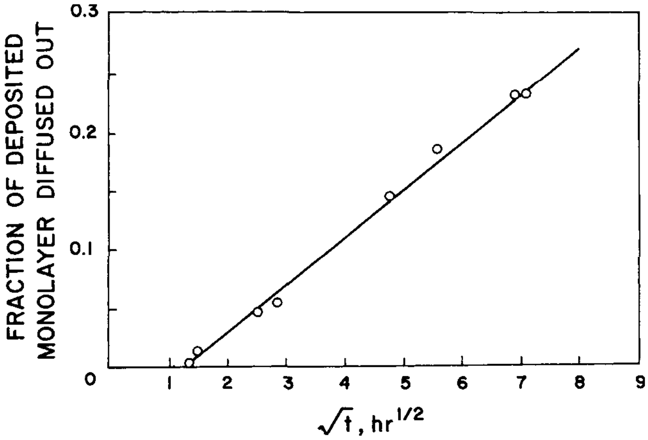

Fig. 4. A plot of fraction of the monolayer that has diffused out of the source region vs square root of time.

Figure 4 is a typical plot used to calculate D_s from the recorded spectra. The absorbance at 2918 cm^{-1}, the absorption band due to antisymmetric stretching of the 16 methylene groups of stearic acid, is used in the calculation of the fraction of the monolayer diffused out of the source region. In this case the diffusion coefficient is 1.4×10^{-6} cm²/s at 25°C when the surface is in equilibrium with several mm pressure of water vapor. The effect of coadsorbed water on the diffusion coefficient is discussed in detail below. It should be noted in Figure 4 that the apparent fraction diffused out is not zero at zero time. This discrepancy arises from the experimental difficulty in exactly masking off the source region. In the case shown in Figure 4 the mask did not quite cover the source region and a positive absorbance was measured at zero time defined as the time at which the source was deposited.

The use of a monolayer source is simple in concept, but the experimental procedure is rather intricate and time consuming. A second approach which is experimentally easier is to deposit a bulk source of stearic acid on the edges of the diffusion surface. The edges are then maintained at constant concentration C_0 and the concentration of diffusing stearic acid is initially zero throughout the plane. In the same coordinate system shown in Figure 3 the plane of diffusion is $-h \leqq x \leqq h$ with symmetry about $x = 0$, the boundary conditions may be written

$$C = C_0, \quad x = h, \quad t \geqq 0$$

$$\frac{\partial C}{\partial x} = 0, \quad x = 0, \quad t \geqq 0$$

The general solution to Equation (2) for these boundary conditions is a series of error-function complements to be considered below, but for the moment we consider an approximate solution valid for short times where the concentration at $x = 0$ is always zero. For each single edge source at $x = -h$,

$$C(x, t) = C_0 \left[1 - \operatorname{erf} \frac{h + x}{2\sqrt{Dt}} \right] \tag{5}$$

Again, all material from the source at $-h$ found in a 2-cm area between $x = h$ and $x = -h$ has come there by diffusion during time t across a 1 cm line at $x = -h$.

Averaging over the 2-cm width gives

$$C_{av} = \frac{1}{2\ \text{cm}} \int_0^t - D_s \left(\frac{\partial C}{\partial x}\right)_{x=-h} dt = C_0 \sqrt{\frac{D_s t}{\pi}} \tag{6}$$

Figure 5 is a typical plot of results from an experiment using a single bulk source.

There remains the problem of determining C_0 which is not known a priori. It can be evaluated by comparing results for monolayer and bulk sources under identical conditions. Results in Figures 4 and 5 were obtained at 25°C on the same crystal surface and the same equilibrium water vapor pressure so the D_s is expected to be identical in each case. C_0 is found to be equivalent to an absorbance of 0.132. We have calculated above an absorption coefficient of 1.8×10^{-15} cm²/molecule for a compressed and oriented monolayer of stearic acid. The hydrocarbon chain of the diffusing molecules will have random orientation which would lower the absorbance by about 20% (Haller and Rice, 1970). Thus, the effective bulk source concentration is 9.0×10^{13} molecules/cm² or approximately one-fifth that of a compressed and oriented monolayer. We may make a crude estimate of the surface concentration from the bulk density of stearic acid as the 2/3 power of number density per cm^3. Using a bulk density of 0.9408 g/cm^2 at 20°C, we calculate 1.6×10^{14} molecules/cm^2. Given the many assumptions implicit in both calculations, the agreement may be considered reasonable.

When the above procedure for evaluating the effective source concentration at a bulk source was repeated at 40°C, a value 9% smaller than that at 25°C was obtained. An opposite temperature effect might be expected if the evaporation model were appropriate. Because the experimental uncertainty is also about 10% we conclude that the effective bulk source concentration is roughly constant and equal to 9×10^{13} molecules/cm^2 in the temperature range 25° to 40°C.

D_s is affected by temperature. The activation energy for surface diffusion of stearic acid on (0001) Al_2O_3 was estimated from the Arrhenius plot in Figure 6 to be 26 kcal/mole. Note that the water coverage as determined by the 3400 cm^{-1} band was held constant at about one monolayer during these measurements because of the strong effect coadsorbed water has on D_s. This value of activation energy is reasonable if stearic acid is chemisorbed on the surface. The only other values to which it can be compared are for stearic acid on mica reported to be 8.6 kcal/mole and 40 kcal/mole by Beischer (1951) and Rideal and Tadayon (1954), respectively. In neither case was the amount of coadsorbed water controlled.

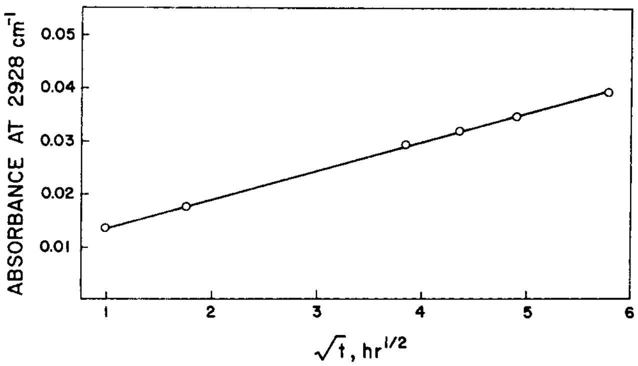

Fig. 5. A plot of absorbance of stearic acid diffused from a single bulk source vs square root of time.

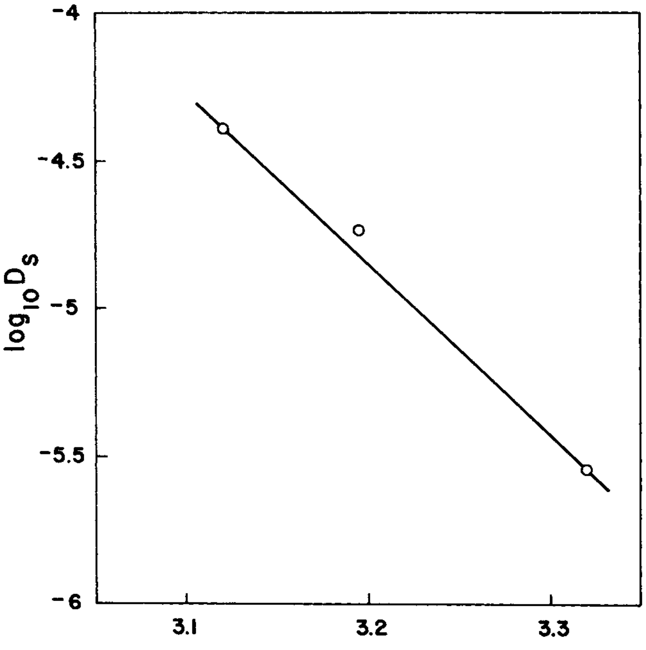

Fig. 6. An Arrhenius plot of stearic acid on (0001) plane of aluminum oxide.

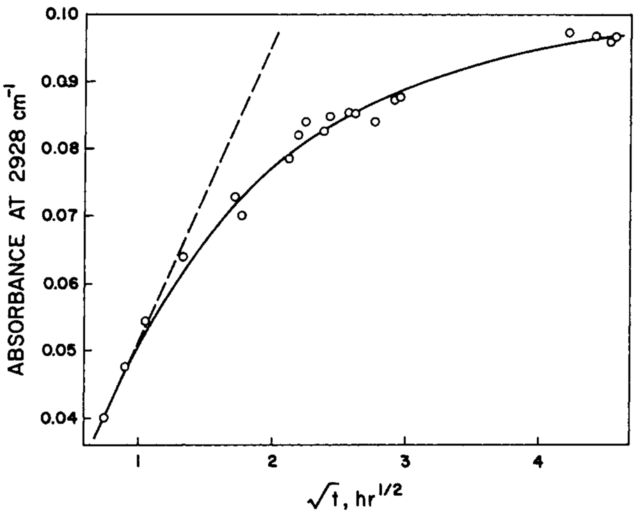

Fig. 7. A plot of absorbance of stearic acid diffused from bulk sources at both edges of an IRE where D_s is too large to use the short time approximation beyond a one-hour period.

Figure 7 is an example of a case for which the approximate solution is clearly inappropriate. We therefore consider the more general solution for a bulk source at both edges. For the boundary conditions,

$$C = C_0, \quad x = h, \quad t \geq 0$$

$$\frac{\partial C}{\partial x} = 0, \quad x = 0, \quad t \geq 0$$

The solution is given by Crank (1956) as

$$C = C_0 \sum_{n=0}^{\infty} (-1)^n \left\{ \operatorname{erfc} \frac{(2n+1)h - x}{2\sqrt{Dt}} + \operatorname{erfc} \frac{(2n+1)h + x}{2\sqrt{Dt}} \right\} \quad (7)$$

This series converges very rapidly except for large values of Dt/h^2. For example, the concentration at the center line ($x = 0$) when $Dt/h^2 = 0.25$ is in error by about 0.032% when only the $n = 0$ term is used. The series-expression to ($\partial C/\partial x$) is also converging when Dt/h^2 is small. For the case where $D_s \leq 5 \times 10^{-5}$ cm^2/s and $h = 1$ cm the one term approximation of Equation (6) will be a good approximation for diffusion times less than one hour. Thus we can use Equation (6) (modified by a factor of 2 to account for sources at both edges) and the initial slope of Figure 7 to calculate $D_s = 2.3 \times 10^{-5}$ cm^2/s. In cases where D_s is much larger than 10^{-5} cm^2/s it will be necessary to resort to curve fitting of a solution of the diffusion equation involving several terms.

Effect of Water on Surface Diffusion

The infrared absorption band of water adsorbed on crystalline oxide surfaces occurs in the same spectral region as for bulk water, 3400 cm^{-1} (Rice and Haller, 1973). This water band is well resolved from the absorbance band due to the asymmetric stretch of the methylene groups (2918 cm^{-1}) which was used to monitor the concentration of stearic acid. Therefore, the absorbance at 3400^{-1} can be used as a measure of the amount of water adsorbed on the surface over which stearic acid is diffusing.

Table 1 gives the measured values for the diffusion coefficient for stearic acid on the (0001) surface of α-Al_2O_3 at several different coverages of adsorbed water. These measurements were all performed at 40°C using a bulk source of stearic acid on both edges of the IRE. They assume an effective source concentration of 9×10^{13} molecules/cm^2 calculated above. The amount of adsorbed water was varied by changing the partial pressure of water vapor in the ambient gas which was helium. The total pressure was maintained at one atmosphere.

The experiment in which the absorbance at 3400^{-1} is 0.0357 represents a dry surface with respect to reversibly adsorbed water. That is the minimum absorbance at 3400 cm^{-1} which could be obtained by evacuation at 40°C of a surface previously saturated by immersion in liquid water. The residual absorbance is due to water irreversibly adsorbed which is probably in the form of surface hydroxyl groups. The increase in absorbance at 3400 cm^{-1} certainly represents a monotonic increase in the reversibly held water, but it is unlikely that there is a linear relation between the increase in water coverage and the increase in absorbance at 3400 cm^{-1}. The relation between absorbance and water coverage is discussed in more detail below, but it can be immediately concluded from Table 1 that reversibly adsorbed water increases the diffusion rate dramatically at low coverages and inhibits it at high coverages.

In the case of stearic acid there is very little interaction between the aliphatic end of the molecule and the surface. Therefore, a well defined monolayer can be deposited which makes possible the conversion of measured absorbances of surface stearic acid into equivalent surface coverages (Haller and Rice, 1970). Adsorbed water interacts strongly with the surface through hydrogen bonding. There is no known method of preparing a well defined water monolayer so a quantitative determination of surface coverage is much more difficult for water. Even if it were possible to obtain a known amount of surface water it is probable that the degree of hydrogen bonding changes with coverage. Variation in hydrogen bonding can lead to order of magnitude change in the stretching vibration intensities (Vinogradov and Linnel, 1971). Thus several calibration points would be required.

As a first approximation, we use the monolayer absorbance of 0.092 calculated by Rice and Haller (1973) which assumes that both the irreversibly and reversibly adsorbed water have an extinction coefficient equal to that of bulk water. Another approximation of the absorbance to be expected from a monolayer can be obtained from water adsorption isotherms. The isosteric heat of adsorption of reversibly adsorbed water on (0001) α-aluminum oxide is 11 ± 1 kcal/mole (Rice and Haller, 1973). Since this value is within experimental error equal to the heat of condensation for bulk liquid we may consider the reversibly adsorbed water to be physically adsorbed. A monolayer equivalent can then be obtained using the BET formalism for surface area measurements (Gregg and Sing, 1967). On this basis we arrive at an absorbance of 0.036 for a BET monolayer of physically adsorbed water (Yang, 1971). The total absorbance observed will thus be the sum of that due to the irreversibly adsorbed water and physically adsorbed water, $0.036 + 0.0375 = 0.074$. It should be noted that the absorbance calculated in this manner is necessarily a lower limit with respect to the absorbance expected when every site is covered. This is so since the BET method calculates the number of molecules sufficient to cover every site if they were so distributed but assumes that multilayer adsorption occurs on some sites before every site in the first layer is in fact covered (Gregg and Sing, 1967). Given the uncertainties of both approximations the only justified conclusion is that the maximum diffusion rate occurs at water surface coverages in the vicinity of a monolayer. For purposes of discussion below we will refer to an absorbance of 0.092 as that due to a monolayer. The data in Table 1 are plotted in Figure 8 as a function of water coverage using this definition of a monolayer.

TABLE 1. VALUES OF D_s FOR THE SYSTEM STEARIC ACID ON (001) α-Al_2O_3 AT VARIOUS SURFACE COVERAGES OF WATER AT 40°C

Absorbance at 3400 cm^{-1}	D_s cm^2/s
0.0375	2.41×10^{-7}
0.04	2.13×10^{-7}
0.0625	6.55×10^{-6}
0.0766	1.683×10^{-5}
0.095	4.103×10^{-5}
0.0952	3.21×10^{-5}
0.1173	8.11×10^{-6}
0.135	9.48×10^{-7}
0.145	2.733×10^{-7}
0.163	≈ 0
0.1713	≈ 0

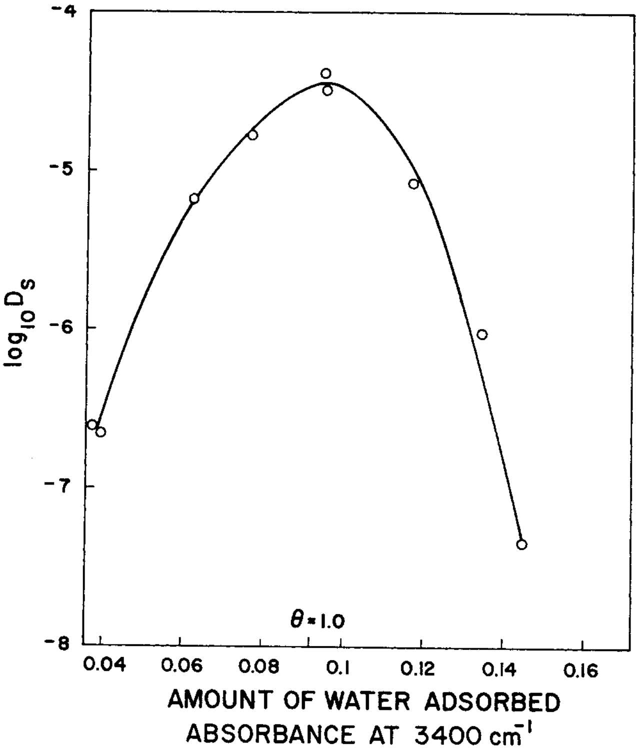

Fig. 8. A logarithmic plot of stearic acid D_s as a function of water coverage on (0001) α-Al_2O_3.

Because a theoretical expression is not available for surface diffusion involving more than one adsorbed species, we will resort to a generalized expression obtained from absolute rate theory.

$$D_s = \frac{kT}{h} d^2 f \exp - (\Delta G^*)$$

$$= \frac{kT}{h} d^2 f \exp\left(\frac{\Delta S^*}{R}\right) \exp - \left(\frac{\Delta H^*}{R}\right) \quad (8)$$

As we have pointed out earlier (Yang et al., 1973), the factor f can be considered a constant. That is, a diffusing stearic acid molecule that approaches an adsorption site occupied by a molecule of adsorbed water may also adsorb on that site, but the adsorption energy will probably be lower than that associated with a bare site. Qualitatively then we expect that the activation energy for diffusion of stearic acid molecules to decrease with increased coverage of water even if the surface is energetically homogeneous.

In fact, Al_2O_3 is known to be heterogeneous with respect to site adsorption energies. The heat of adsorption of water on a predominately (0001) crystalline surface falls from a high of about 32 kcal/mole on a surface outgassed at high temperature to 17 kcal/mole in the monolayer region. The irreversibly adsorbed water at 23°C reported by Yao (1965) is 0.4 of a monolayer in good agreement with our value of 0.41 obtained at 40°C. The change in the heat of adsorption which she found in the region $0.4 < \theta < 1$ is about 8 kcal/mole. Although we do not have heats of adsorption of stearic acid on Al_2O_3, results for other oxygen containing organic molecules indicate that they compete with water for the same adsorption sites (Yao, 1965; Rice, 1972) and that organic acids are strongly adsorbed (Rice, 1972). Thus, it is reasonable to expect that stearic acid competes with water for the high energy sites and to attribute the increase in surface diffusion rate to a lowering of the activation energy as these high energy sites become occupied by water.

At coverages beyond the monolayer region the measured heats of adsorption become independent of the amount of coverage (Yao, 1965) and the surface has become energetically homogeneous. The bond energy between the stearic acid molecule and the surface must still be large because the activation energy for diffusion in the region of monolayer coverage (Figure 6) is 26 kcal/mole. This activation energy is fairly high. Moreover, at high water coverages the diffusion coefficient is smaller than for stearic acid on the surface of bulk water, 2 to 3 $\times 10^{-6}$ cm²/s (Good and Schechter, 1972). These observations suggest that the diffusion in the multilayer region still involves hopping between sites on the aluminum oxide surface. As the water coverage moves into the multilayer region, a stearic acid molecule in transit between adsorption sites will suffer an increasing flight time because of the increasing number of collisions with water molecules. At some coverage the flight time between sites may become comparable to the residence time on a site.

In terms of absolute rate theory we can write

$$\Delta G^*(\theta) = \Delta G_R{}^*(\theta) + \Delta G_F{}^*(\theta)$$

where $\Delta G_R{}^*$ is the free energy of activation associated with the breaking of a bond between the diffusing molecule and the site and $\Delta G_F{}^*$ as the free energy of formation of a hole in the second layer of adsorbed water which will be negligible below monolayer coverage. Formally, we can write

for $0 < \theta < 1$;

$$\Delta G_R{}^*(\theta) \geqq \Delta G_R{}^*(\theta = 1) \quad \text{and} \quad \Delta G_F{}^* = 0$$

for $1 < \theta < 2$;

$$\Delta G_R{}^* = \Delta G_R{}^*(\theta = 1) \quad \text{and} \quad \Delta G_F{}^* \; \alpha \; \overline{G}_F{}^*$$

Since for

$1 < \theta < 2$;

$$D_s = \frac{kT}{h} d^2 f \exp\left(\frac{-G_R{}^*(\theta = 1)}{RT}\right) \exp - \left(\frac{\theta \overline{G}_F{}^*}{RT}\right) \tag{9}$$

we expect and find a plot of ln D_s vs. θ for $\theta > 1$ to be linear as is shown, within experimental error, in Figure 8. The implicit assumption that θ is proportional to absorbance should be a good approximation since the extent of hydrogen bonding can be expected to be independent of coverage for $\theta > 1$. Using the points beyond a monolayer in Figure 1 we estimate the energy of hole formation in a completed second layer of adsorbed water $\overline{G}_F{}^* = 7$ kcal/mole.

It does not seem possible at the present to interpret the effect of coadsorbed water on the diffusion of stearic acid in a more quantitative manner. Qualitatively, an interpretation reasonably consistent with experimental results indicates that the diffusion rate is determined by residence time at adsorption sites in the submonolayer region and by transit time between sites at coverages above a monolayer. Residence time depends upon energy of adsorption. Transit time is governed by the number of collisions a molecule undergoes between sites.

The behavior observed for aluminum oxide cannot be expected to hold for all surfaces. For example, stearic acid diffusion on the surface of KRS-5 is independent of the amount of water at coverages less than a monolayer. As coverage increases to the monolayer region the diffusion coefficient indeed decreases by a factor of 5 but then remains constant in the region between 2 and 6 layers of water. This behavior is at least consonant with the absence of strong adsorption sites but more quantitative interpretation is not possible. In fact we cannot even provide absolute values for the surface diffusion coefficient on KRS-5 because the experiments can only be performed with a bulk source for which the effective source concentration is unknown. The effective source strength cannot readily be determined by the deposited stearic acid monolayer method because KRS-5 is partially soluble in water.

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NOTATION

A = ln I_0/I = absorbance
A_m = absorbance of a stearic acid monolayer
C_{av} = average concentration, molecules/cm²
C_m = stearic acid monolayer concentration
C_0 = initial source concentration
d = distance between adjacent sites
D_s = activation energy for diffusion
E_a = surface diffusion coefficient
f = number of accessible sites adjacent to adsorbed molecule
$\Delta G_R{}^*$ = free energy of activation for breaking surface bond
$\Delta \overline{G}_F{}^*$ = $\theta \overline{G}_F{}^*$ = free energy of activation of hole formation in second layer
ΔG^* = free energy of activation
$\overline{G}_F{}^*$ = $\left(\frac{\partial G_F{}^*}{\partial \theta}\right)$; $\theta > 1$
h = Planck's constant
ΔH^* = enthalpy of activation
I = radiation intensity at exit of IRE
I_0 = radiation intensity at entrance of IRE
J = diffusion flux, molecules/cm-s
k = Boltzmann constant
R = ideal gas constant
ΔS^* = entropy of activation
t = time
T = absolute temperature
x = distance normal to initial line source

Greek Letters

α = IRS absorption coefficient
θ = fractional surface coverage of water

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Analysis and Optimization of the Williams-Otto Process by Geometric Programming

This paper applies the principles of geometric programming to the optimization of the well-known Williams-Otto process. Following the trend of the articles published on this subject, two different objective functions are considered and the results are compared to those of other investigators.

The dual geometric program is used to provide an answer to the question of why the optimal value of the objective function remains unchanged for perturbations in a certain variable.

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SCOPE

In this paper geometric programming is used to optimize the well-known Williams-Otto process. This process consists of a stirred-tank reactor and a separation system involving a cooler, a decanter, and a distillation column and has served as an example for a multitude of optimization studies.