k_{ads} = adsorption rate constant, s^{-1}
k_f = mass transfer coefficient, m/s
l = $\sqrt{c^2 + d^2}$
m = $\dfrac{\epsilon}{1 - \epsilon}$
Pe = $\dfrac{zV}{D_L}$, Peclet number
$\bar{q}$ = volume averaged concentration in particles, mol/m^3
R_1 = $\dfrac{K}{m}$, distribution ratio
R_2 = $\dfrac{K_A}{\epsilon_p}$, distribution ratio
R_F = $\dfrac{b}{3k_f}$, film resistance, s
r = radial distance from center of spherical particle, m
s = Laplace transform variable, S^{-1}
t = time, s
u = C/C_0, dimensionless concentration in fluid
V = average linear pore velocity, m/s
x' = see Eq. 25, m^{-2}
y = $\dfrac{k_{ads}}{K_A} t$, contact time parameter
y' = see Eq. 26, m^{-2}
z = distance in flow direction, m

Greek Letters

γ = $\dfrac{3D_p\epsilon_p}{b^2}$, s^{-1}
δ = $\dfrac{\gamma z}{mV}$, bed length parameter
ϵ = void fraction of bed, m^3/m^3
ϵ_p = void fraction of particle, m^3/m^3
λ = variable of integration
ν = γR_F
ϕ_1 = see Eq. 31
ϕ_2 = see Eq. 32

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Measurement of Surface Self-Diffusion of Sulfur Dioxide on Porous Vycor Glass by Radioisotope Tracer Method

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When adsorbable gases flow or diffuse through microporous media, the flux is appreciably increased in the presence of the adsorbed phase. This additional flow, or surface flow, is important from the viewpoint of fundamental research or practical applications such as adsorption, catalytic reaction, gaseous separation and drying.

The models most commonly used to describe the surface flow mechanism are a hydrodynamic model (Babbit, 1950; Gilliland et al., 1958) and a hopping model (Hill, 1956; Higashi et al., 1963; Smith and Metzner, 1964; Weaver and Metzner, 1966; Gilliland et al., 1974; Ponzi et al., 1977). The authors have interpreted the surface flow from the standpoint of a random walk mechanism or a hopping mechanism rather than a viscous one and proposed a transport model (Okazaki et al., 1981; Tamon et al., 1981). The dependence of the surface flow coefficient on the amount adsorbed and the temperature for many experimental results can be correlated by this model.

The purpose of the present work is to obtain the surface self-diffusion coefficient and the surface flow coefficient of

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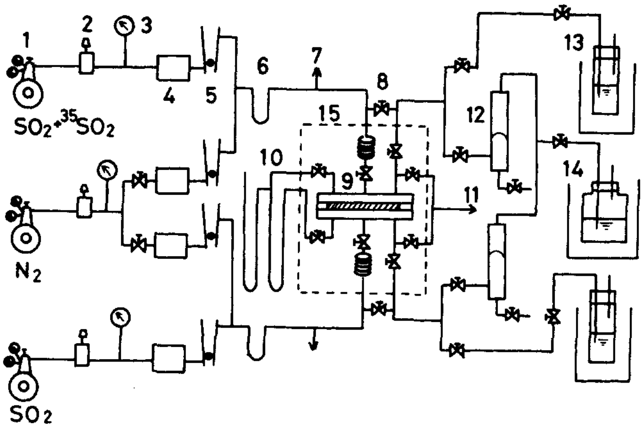

Figure 1. Experimental apparatus. 1. Gas cylinder. 2. Pressure valve. 3. Pressure gauge. 4. Flow control valve. 5. Rotameter. 6. Dryer ($CaCl_2$). 7. Sampling hole. 8. Cock. 9. Diffusion cell. 10. Manometer. 11. Diffusion pump. 12. Soap film meter. 13. Trap for sample gas. 14. Trap for waste gas. 15. Temperature-controlled bath.

sulfur dioxide through porous Vycor glass by the radioisotope tracer method. In addition, the transport mechanism of adsorbable gas is interpreted and the observed results are used to verify the previously proposed model for conditions with and without capillary condensation.

EXPERIMENTAL

Materials

The physical properties of porous Vycor glass have been reported in the previous paper (Okazaki et al., 1981).

Radioactive sulfur dioxide [6.6 mcurie in about 1.1 cm^3 (s.t.p.)] was obtained from the Radiochemical Centre, Amersham, England. The radioactive nuclide is S^{35}. The radioactive sulfur dioxide was diluted by a factor of 4×10^6 with commercial inactive sulfur dioxide whose purity was above 99.9%, and poured into a gas cylinder.

Apparatus and Procedure

Figure 1 shows a schematic drawing of the experimental apparatus, which is a constant-pressure and countercurrent diffusion apparatus (Wicke-Kallenbach type). Two kinds of sulfur dioxide containing SO_2 and $SO_2 + {}^{35}SO_2$ were mixed with nitrogen. Each mixed gas was regulated at a constant flow rate by flow control valves and then passed through a calcium chloride tube to remove water. The two streams, called sides 1 and 2, were introduced into a diffusion cell. During a tracer experiment, the difference in pressure between the two sides of the cell was kept within 0.5 mm on the oil manometer. The diffusion cell was immersed in a temperature-controlled liquid bath at 30°C or −10°C.

The composition of gas at the inlet to the cell was analyzed with the thermal conductivity detector of a gas chromatograph (Shimadzu GC-3AH). Radioactive sulfur dioxide was absorbed into a solution of monoethanolamine. The radioactivity was measured by counting β-rays with a liquid scintillation counter (Nuclear Chicago ISOCAP/300), where a toluene scintillator containing PPO($C_{15}H_{11}NO$) and POPOP($C_{24}H_{16}N_2O_2$) was used. The flow rates of the outlet gases from the diffusion cell were measured by soap film meters.

After steady state was achieved, the total transport rate was determined from the above measured quantities. When side 1 contains $^{35}SO_2$ at the inlet to the diffusion cell, the total transport rate N^*_{t1} from side 1 to side 2 is given by

$$N^*_{t1} = I_2 L_1 y_1/(I_1 + I_2) \tag{1}$$

where I_1 and I_2 are the counting rates of β-rays on sides 1 and 2 at the outlets from the cell, respectively. $L_1 y_1$ is the flow rate of sulfur dioxide on side 1. When side 2 contains $^{35}SO_2$ at the inlet to the diffusion cell, N^*_{t2} from side 2 to side 1 is similarly given by

$$N^*_{t2} = I_1 L_2 y_2/(I_1 + I_2) \tag{2}$$

Surface Self-Diffusion. The total transport rate was measured for the condition that the concentrations of sulfur dioxide on both sides of the diffusion cell were equal to each other. In this case N^*_{t1} is equal to N^*_{t2}.

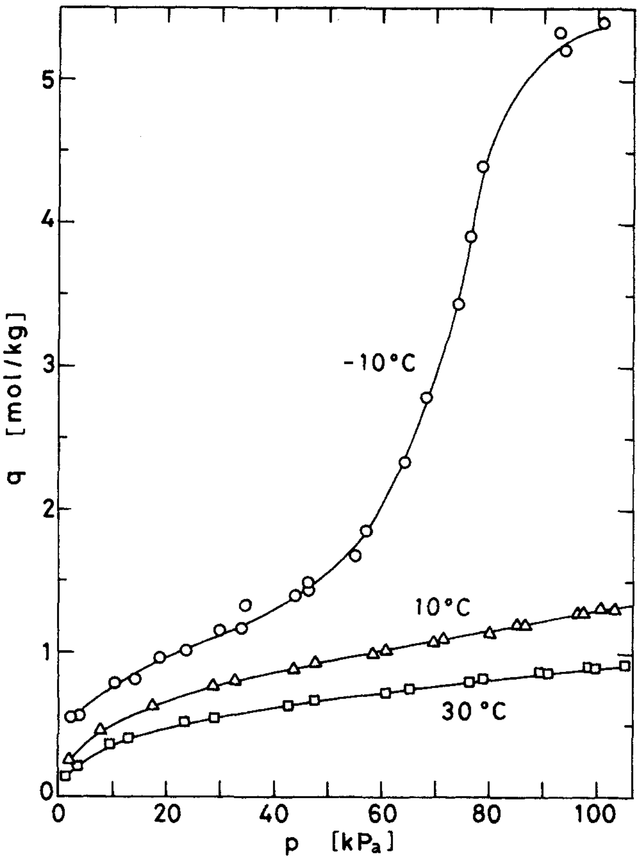

Figure 2. Adsorption isotherms of SO_2 on porous Vycor glass.

The flow term in N^*_{t1} or N^*_{t2} is neglected and only the self-diffusion term should be considered because the overall concentration gradient is not formed. When side 1 contains $^{35}SO_2$ at the inlet to the cell, N^*_{t1} is given by Eq. 3 since I_2 is much smaller than I_1.

$$N^*_{t1} = -P^*_t A p_1/l' \tag{3}$$

where p_1 is the partial pressure of sulfur dioxide on side 1. In Eq. 3, P^*_t includes the self-diffusion in the gas phase and in the adsorbed phase. As the transport mechanism in the gas phase is Knudsen flow in the present study, the permeability of the surface self-diffusion of adsorbed gas P^*_s is determined by subtracting a gas-phase permeability P'_g from P^*_t. The detailed procedure to calculate P'_g was reported in a previous paper (Okazaki et al., 1981). The surface self-diffusion coefficient D^*_s is

$$D^*_s = (P^*_s/\rho_{app})\,(dp/dq) \tag{5}$$

where (dp/dq) can be determined from the adsorption isotherm.

Surface Flow. The surface flow rate was measured from the apparent transport rate of $^{35}SO_2$ used as a tracer for the condition that the concentration of SO_2 on side 1 is a little higher than that on side 2. The total flow rate N_T containing the gas-phase flow rate and surface flow rate is given by

$$N_T = N^*_{t1} - N^*_{t2} \tag{6}$$

where N^*_{t1} and N^*_{t2} are calculated by Eqs. 1 and 2, respectively. The calculation procedures of surface flow permeability P_s and surface flow coefficient D_s from N_T were reported in a previous paper (Okazaki et al., 1981).

Adsorption isotherms are necessary to calculate surface flow coefficients, surface self-diffusion coefficients and isosteric heats of adsorption. The isotherms were determined using a standard volumetric apparatus.

RESULTS AND DISCUSSION

Adsorption Equilibrium

Adsorption isotherms for sulfur dioxide at −10°C, 10°C and 30°C are shown in Figure 2. The isotherm at −10°C indicates

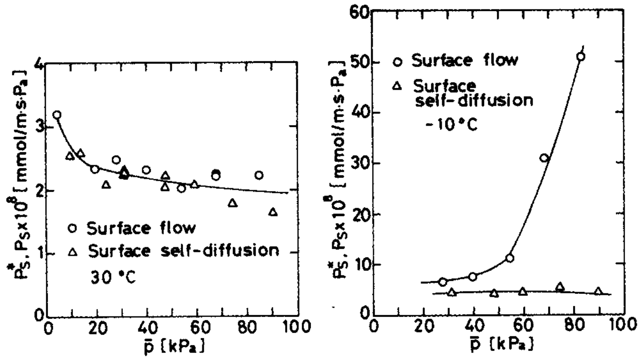

Figure 3. Permeabilities for surface flow and surface self-diffusion of SO_2 on porous Vycor glass.

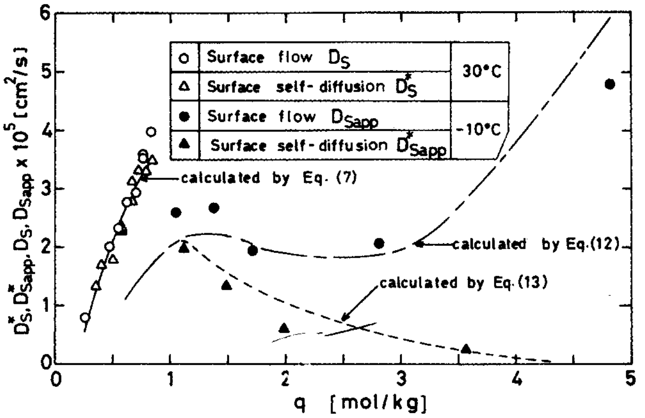

Figure 4. Surface flow coefficients and surface self-diffusion coefficients of SO_2 on porous Vycor glass.

that capillary condensation takes place when the amount adsorbed is large. The isosteric heat of adsorption can be calculated using the Clausius-Clapeyron equation, and the heat of adsorption was reported in the previous paper (Okazaki et al., 1981). This heat decreases with the amount adsorbed, and it can be seen that porous Vycor glass has an energetically heterogeneous surface.

Surface Migration without Capillary Condensation

The permeability of surface self-diffusion P_s^* and the permeability of surface flow P_s for sulfur dioxide at 30°C are shown in Figure 3. The surface self-diffusion coefficient D_s^* and the surface flow coefficient D_s are given in Figure 4. The surface migration in the absence of the gradient of the amount adsorbed or the surface self-diffusion and the surface flow in the presence of this gradient are equal to each other, and D_s^* and D_s increase with the amount adsorbed. If the mechanism of surface migration is described based on viscous flow caused by a driving force, such as the spreading pressure gradient, D_s^* and D_s should be different from each other. Therefore, the above experimental results show that the mechanism of surface flow obeys a diffusional mechanism rather than a viscous flow mechanism.

A model for surface flow has been proposed by the authors (Okazaki et al., 1981). This model can be applied in the range of monolayer to multilayer adsorption. According to the proposed model, the correlating equation of the surface flow coefficient for the heterogeneous surface is given as follows when adsorption equilibria obey the B.E.T. equation.

$$D_s = D_{s0}F = \frac{D_{s0}(1-x)\int_{E_{a0}^0}^{E_{a0}} ((e^{-aE/RT} - e^{-E/RT})/\{(1-e^{-E/RT})\ [1-(1-x)\theta(1-\tau_1/\tau_0)]\})g(E)dE}{\int_{E_{a0}^0}^{E_{a0}} g(E)dE} \tag{7}$$

where

$$\tau_1/\tau_0 = (e^{-aE/RT} - e^{-E/RT})\ (1 - e^{-Ea1/RT})/\{(e^{-Es1/RT} - e^{-Ea1/RT})\ (1 - e^{-E/RT})\} \tag{8}$$

The variables, except a and D_{s0}, in Eq. 7 can be evaluated from the adsorption isotherms and the viscosity of adsorbate in the liquid state at various temperatures (Okazaki et al., 1981). This equation contains two parameters a and D_{s0} and explains the dependence of the surface flow coefficient on the amount adsorbed. The coefficients at 30°C calculated by Eq. 7 are shown in Figure 4, where $a = 0.38$ and $D_{s0} = 2.16 \times 10^{-3}$. It is seen that D_s^*, as well as D_s, can be correlated by Eq. 7.

Migration of Adsorbate with Capillary Condensation

The permeabilities of surface self-diffusion and surface flow at −10°C are shown in Figure 3. The surface self-diffusion coefficient and the surface flow coefficient in the presence of capillary condensation are named the apparent surface self-diffusion coefficient D_{sapp}^* and the apparent surface flow coefficient D_{sapp}, and are given in Figure 4. D_{sapp} and D_{sapp}^* show a large difference at −10°C; that is, D_{sapp} increases with the amount adsorbed while D_{sapp}^* decreases. This difference is attributed to the flow of the capillary condensate. Therefore, we should take into account the capillary flow as well as the hopping of the adsorbed molecules.

Apparent Surface Flow. When capillary condensation coexists at −10°C as shown in Figure 2, the adsorption region might be divided into gas-phase adsorption and capillary condensation. For the flow of the adsorbate, a transport model has been proposed by the authors (Tamon et al., 1981). The permeability in the adsorbed phase P_d is

$$P_d = (D_{s0}F\rho_{\mathrm{app}})\ (dq_{BET}/dp)\ \{(S_T - S_C)/S_T\} \tag{9}$$

The permeability of the capillary condensate P_c becomes as follows using the Kozeny-Carman equation and the Kelvin equation.

$$P_c = (S_T/S_C)^2(V_C/V_T)^3(p_s/\bar{p})P_c^o \tag{10}$$

where

$$P_c^o = \rho_L^2\epsilon_T^3RT/(\mu_LK_CS_T^2\rho_{\mathrm{app}}^2M^2p_s) \tag{11}$$

The apparent surface flow coefficient D_{sapp} containing the terms of surface flow and capillary flow is given by

$$D_{sapp} = (P_c + P_d)/\{(dq/dp)\rho_{\mathrm{app}}\} \tag{12}$$

Refer to the previous paper (Tamon et al., 1981) for the procedure to calculate D_{sapp} using Eqs. 9, 10, 11 and 12. The calculated results are given in Figure 4, where $a = 0.38$, $D_{s0} = 2.16 \times 10^{-3}$ and $P_c^o = 66.9 \times 10^{-8}$ were used. These results agree with the experimental data.

Apparent Surface Self-Diffusion. When the concentrations of sulfur dioxide on both sides of Vycor glass are equal, it is considered from the Kelvin equation that the gradient of capillary force is not formed across Vycor glass and capillary flow does not occur. The transport rate in the capillary condensed phase may be neglected because the self-diffusion in the liquid phase is ordinarily small. Hence, only the surface self-diffusion in the adsorbed phase controls the apparent surface self-diffusion. The apparent surface self-diffusion coefficient D_{sapp}^* is

$$D^*_{sapp} = (D_{s0}F)\,(dq_{BET}/dp)\,(dp/dq)\,\{(S_T - S_C)/S_T\} \qquad (13)$$

The results calculated by Eq. 13 are shown in Figure 4. The calculated results nearly agree with the experimental ones. This indicates that the method previously proposed by the authors is useful, giving the transport rate in the adsorbed phase for the case where capillary condensation coexists.

CONCLUSIONS

The surface self-diffusion and the surface flow of sulfur dioxide on porous Vycor glass at −10°C and 30°C were measured by the radioisotope tracer method.

Surface Migration without Capillary Condensation. The experimental surface self-diffusion coefficient was equal to the surface flow coefficient in the range of monolayer to multilayer adsorption. Also, the dependence of both coefficients on the amount adsorbed was well described by the hopping model previously proposed by the authors (Okazaki et al., 1981). This indicates that the mechanism of surface flow can be explained based on the hopping model rather than the hydrodynamic model.

Migration of Adsorbate with Capillary Condensation. The apparent surface self-diffusion coefficient and the apparent surface flow coefficient differed when capillary condensation occurred. This difference was attributed to the flow of the capillary condensate. Applying the proposed transport model (Tamon et al., 1981) to the experimental results from this standpoint, the calculated coefficients agreed with the observed coefficients for both cases of surface self-diffusion and surface flow.

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NOTATION

A = cross-sectional area of sample, cm^2
a = constant defined in Eq. 7
D_s = surface flow coefficient, cm^2/s
D_{sapp} = apparent surface flow coefficient, cm^2/s
D_{s0} = constant defined in Eq. 7, cm^2/s
D^*_s = surface self-diffusion coefficient, cm^2/s
D^*_{sapp} = apparent surface self-diffusion coefficient, cm^2/s
E = adsorption energy, kJ/mol
E_{a0} = differential heat of adsorption, kJ/mol
E_{a1} = heat of vaporization, kJ/mol
E_{s1} = activation energy for migration in all layers above the first layer, kJ/mol
F = function defined in Eq. 7
$g(E)$ = number of molecules adsorbed which have the heat of adsorption between E and $(E + dE)$
I = counting rate, s^{-1}
K_C = Kozeny constant
L = flow rate of gas, mmol/s
l' = thickness of sample, cm
M = molecular weight, kg/kmol
N_T = total flow rate, mmol/s
N^*_T = total flow rate including surface self-diffusion, mmol/s
P_c = permeability of capillary condensate, mmol · m^{-1} · s^{-1} · Pa^{-1}
P_d = permeability of surface flow in adsorbed phase, mmol · m^{-1} · s^{-1} · Pa^{-1}
P'_g = gas-phase permeability, mmol · m^{-1} · s^{-1} · Pa^{-1}
P_s = permeability of surface flow, mmol · m^{-1} · s^{-1} · Pa^{-1}
P^o_c = permeability in the case that all pores are filled with capillary condensate, mmol · m^{-1} · s^{-1} · Pa^{-1}
P^*_s = permeability of surface self-diffusion, mmol · m^{-1} · s^{-1} · Pa^{-1}
P^*_T = total permeability including surface self-diffusion, mmol · m^{-1} · s^{-1} · Pa^{-1}
p = partial pressure, kPa
$\bar{p}$ = average value of partial pressure on both sides of sample, kPa
p_s = saturated vapor pressure, kPa
q = amount adsorbed, mol/kg
q_{BET} = amount adsorbed calculated by B.E.T. equation, mol/kg
R = gas constant, J · K^{-1} · mol^{-1}
S_C = specific surface area of capillary condensed phase, m^2/kg
S_T = specific surface area, m^2/kg
T = temperature, K
V_C = volume of capillary condensed phase, cm^3/kg
V_T = total pore volume, cm^3/kg
x = relative pressure $(=p/p_s)$
y = mole fraction

Greek Letters

ϵ_T = porosity of sample
θ = surface coverage
μ_L = viscosity in liquid state, Pa · s
ρ_{app} = apparent density of sample, kg/cm^3
ρ_L = density in liquid state, kg/cm^3

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